Regulation on fluorinated refrigerants for high-temperature heat-pumps: reasons for a time-limited derogation to ensure a smooth energy transition

Paul-M. Bever, Cordin Arpagaus, Stefan Bertsch

Ostschweizer Fachhochschule, Institut für Energiesysteme

Zusammenfassung

Hochtemperatur-Wärmepumpen für den industriellen Einsatz erfordern Kältemittel mit einem anspruchsvollen Leistungsprofil:

- Die Wärmeversorgung sollte vorzugsweise unter subkritischen Bedingungen erfolgen, was eine hohe kritische Temperatur des Kältemittels erfordert.
- Die Füllmenge des Kältemittels ist höher, was bedeutet, dass Entflammbarkeit und Toxizität für das Sicherheitsmanagement an Bedeutung gewinnen.

Im Hinblick auf ihre thermodynamischen Eigenschaften eignen sich mehrere Kohlenwasserstoffe (natürliche" Kältemittel) einerseits und teilhalogenierte Fluorolefine (HFO) oder teilhalogenierte Fluorolefine (HCFO) andererseits für den Einsatz in industriellen Wärmepumpen und können sich gegenseitig ersetzen.

Die Nachteile fluorierter Kältemittel hinsichtlich ihres Treibhauspotenzials sind mit der Markteinführung von HFOs und HCFOs entweder irrelevant geworden oder werden durch die Vermeidung der CO_2-Emissionen aus der Verbrennung fossiler Brennstoffe bei weitem überkompensiert. Die Freisetzung von HFOs und HCFOs kann jedoch zur Bildung und Anreicherung von Abbauprodukten in der Atmosphäre führen, was die EU-Kommission zu einem Vermarktungsverbot in der EU veranlasst. Daher gerät die Verwendung von fluorierten Gasen als Kältemittel für die industrielle Energieerzeugung derzeit zweifach unter regulatorischen Druck: durch die Überarbeitung der F-Gas-Verordnung und eine weitreichende Beschränkung der fluorierten Stoffe im Rahmen von REACH.

Aber auch Kohlenwasserstoffen und Ammoniak als mögliche Substitute weisen deutliche Nachteile auf, insbesondere ihre Entflammbarkeit und Toxizität. Einige Kohlenwasserstoffe können aufgrund ihrer Kanzerogenität als "besonders besorgniserregende Stoffe" eingestuft werden, d. h. Ersatzstoffe können selbst Gegenstand der Substitution werden. So könnte z. B. eine anstehende Überarbeitung der REACH-Verordnung weitere Beschränkungen für Kohlenwasserstoff-Kältemittel vorsehen.

Generell sollte ein Vermarktungsverbot von Kältemitteln für den Einsatz in Hochtemperatur-Wärmepumpen im industriellen Bereich allein aufgrund von Gefahrstoffmerkmalen kritisch geprüft werden. Bei diesen Verwendungen sind die Risiken sowohl für natürliche Kältemittel als auch für HFOs/HCFOs beherrschbar, indem diffuse Emissionen durch sorgfältige Überwachung und Wartung von Wärmepumpen vermieden werden.

Die schnelle und nachhaltige Einführung von Hochtemperatur Wärmepumpen in bestehende industrielle Produktion erfordert Verlässlichkeit und Designfreiheit. Daher muss bei einem Vermarktungsverbot eine ausreichende Übergangszeit vorgesehen werden, um die laufende Energiewende in der industriellen Produktion nicht auszubremsen. Die geplante REACH Beschränkung sollte mindestens eine fünfjährige Ausnahmeregelung für HFOs und HCFOs als Kältemittel in Hochtemperaturwärmepumpen vorsehen.

Abstract

High-temperature heat pumps for industrial use require refrigerants with an advanced performance profile for the following reasons:

- heat should preferably be supplied under sub-critical conditions, which requires a high critical temperature of the refrigerant,
- the refrigerant charge is higher than in domestic or automotive heat pumps or air conditioning systems, so flammability and toxicity are more relevant for safety management.

Considering their thermodynamic properties, several hydrocarbons ("natural" refrigerants) on the one side and hydrofluoroolefins (HFOs) or hydrochlorofluoroolefins (HCFOs) on the other side are suitable for use in industrial heat pumps and can mutually replace each other.

The disadvantages of fluorinated refrigerants regarding their greenhouse warming potential either have become irrelevant with the market introduction of HFOs and HCFOs or are outbalanced by far by avoiding current CO_2 emissions from the incineration of fossil fuels. However, the release of HFOs and HCFOs may lead to the formation and accumulation of degradation products in the atmosphere and drives the attempt to phase them out in the EU. Moreover, regulatory pressure from two sides threatens the use of fluorinated gases as refrigerants for industrial energy production: the revision of the F-gas regulation and a broad restriction of fluorinated substances under REACH.

Flammability and toxicity are distinct disadvantages of hydrocarbons and ammonia. Therefore, some hydrocarbons may qualify as "substances of very high concern," i.e., substitutes may become subject to substitution. For example, a pending revision of REACH may add further restrictions for hydrocarbon refrigerants.

In industrial high-temperature heat pumps, risks for natural refrigerants and HFOs/HCFOs can be mitigated by avoiding diffuse emissions through diligent monitoring and maintenance of heat pumps.

Retaining design flexibility will be critical to introducing heat pump technology into industrial production. Therefore, any phase-out must allow sufficient transition time to continuously foster energy efficiency in the industrial heat supply. The REACH restriction should therefore grant a 5-year derogation period for HFOs and HCFOs as refrigerants in high-temperature heat pumps.

1 Introduction

While cooling machines and heat pumps for the building sector are well-established technologies operating in similar temperature ranges, industrial heat pumps operate at significantly higher temperatures and require more design flexibility since they have to be integrated into existing production environments (Figure 1). Bless et al. (2022)[i] and Arpagaus et al. (2022)[ii] have identified uncertainties and the costs of integration as major challenges for establishing heat pump technology in the industry.

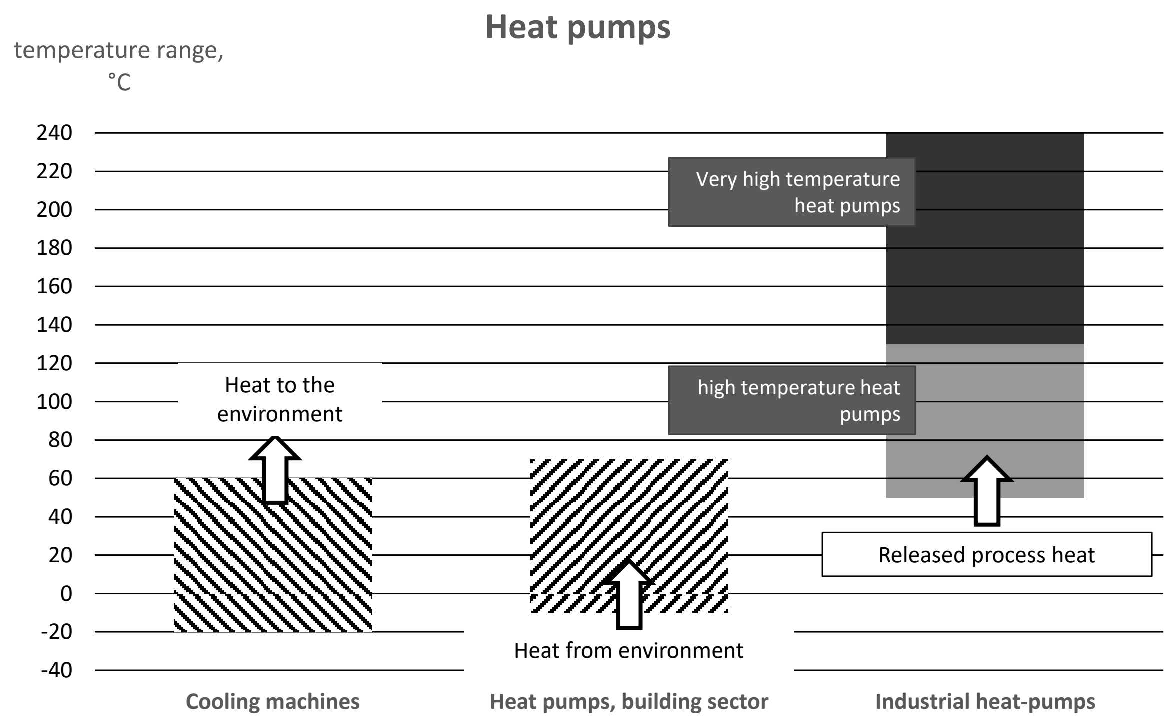

Figure 1: Typical temperature ranges of cooling machines, heat pumps for the building sector, and industrial heat pumps.

Usually, industrial heat pumps use waste energy rather than ambient heat (air or brine). They may generate low-pressure steam, which can transform mechanical vapor recompression into very high-temperature steam. In the "medium" temperature range of 50°C to 130°C, a number of refrigerants are thermodynamically suitable. Nevertheless, the state of technology still requires substantial development work. The reasons are:

- a larger variety of process conditions, like temperatures of heat source and sink,
- large amounts of heat at high-temperature levels and larger quantities of refrigerants,
- space and infrastructure constraints in existing production environments.

Arpagaus (2023)[iii] published an overview of 33 commercially available high-temperature heat pumps, see Table 7. Seventeen of these heat pumps are at a technical readiness level (TRL) of 9 (out of 10)[1], many of them in the very high-temperature range. Out of these 17 heat pump systems, 7 are operated with water or water/ammonia, while 7 others contain fluorinated refrigerants. Heat pump systems with hydrocarbons are still at TRLs below 9.

[1] The author cautions that the information in this overview has been provided by the suppliers without third-party validation and was provided as an indicative basis and may be different in final installations depending on application-specific parameters.

This demonstrates the importance fluorinated refrigerants still have for establishing heat pump technology in energy production for industrial use.

Regulatory pressure from two sides is increasing, threatening the use of fluorinated refrigerants for industrial energy production, i.e., the medium temperature range: the revision of the F-gas regulation and a very broad restriction under REACH covering the entire substance family of PFAS (per- and polyfluoroalkyl substances).

The current paper looks at the consequences of a ban on these refrigerants, i.e., the availability and viability of substitution products.

The objective is to offer information for increasingly complex regulatory decision taking. These decisions must consider both, a timely energy transition and environmental protection.

2 Background

2.1 Refrigerants considered in this paper

The focus is on refrigerants, which allow heat pump operation in a temperature range between 60 °C (heat source) and 130 °C (heat sink) (see the blue bar in Figure 2). This diagram shows the vapor pressure curves for the refrigerants in Table 1. Due to their low critical temperatures, the chosen temperature range leads to the deselection of propane (R290) and some of the HFOs, which are frequently used for residential heat pumps. Water was deselected for its vapor pressure below 1 bar at temperatures below 100 °C. However, the diagram demonstrates the attractiveness and uniqueness of water as a refrigerant for very high temperatures.

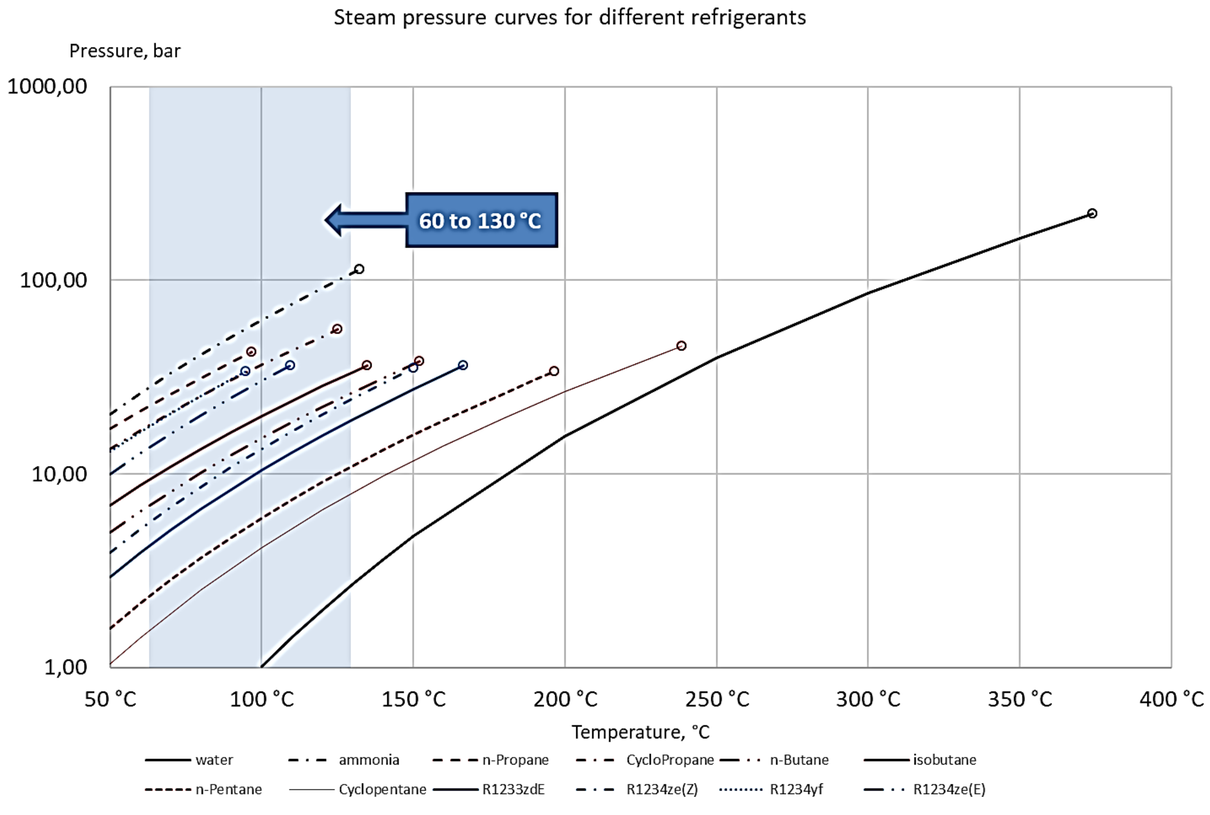

Figure 2: Comparison of thermodynamic data for various refrigerants (Data source: REFPROP).

Table 1: Refrigerants considered in this paper.

Substance	Chemical name	Molecular formula	T_{crit}, °C	P_{crit}, bar
inorganic refrigerants				
R717	ammonia	NH3	132,4	114
hydrocarbons				
R290	propane	C3H8	96,7	43
R600	n-butane	C4H10	152,0	38
R600a	isobutane	C4H10	134,7	36
R601	n-pentane	C5H12	196,6	34
	cyclo-pentane	C5H10	238,6	46
HFO				
R 1234yf	2,3,3,3-tetrafluoropropene	CF3CF=CH2	94,7	34
R 1234ze(Z)	(1E)-1,3,3,3-tetrafluoropropene	trans-CF3CH=CHF	150,1	35
R 1336mzz(Z)	(2Z)-1,1,1,4,4,4-hexafluorobutene	cis-CF3CH=CHCF3	171,4	29
HCFO				
R 1224yd(Z)	cis-1-chloro-2,3,3,3-tetrafluoropropene	cis-CF3CF=CHCl	155,5	33
R 1233zd(E)	(E)-1-chloro-3,3,3-trifluoropropene	trans-CF3CH=CHCl	166,5	36
HFC				
R 245fa	1,1,2,2,3-pentafluoropropane	CHF2-CF2-CHF-CH2	153,9	37

Most of the refrigerants in Table 1 are already contained in a review comparison of refrigerants regarding their process performance, published by Arpagaus et al. (2018). [iv]

2.2 Driver for upcoming regulation: persistence in the environment

The EU chemical law REACH regulates the manufacture, placing on the market or use of chemical substances in the EU.

A prerequisite for a restriction under REACH is that a substance poses an unacceptable risk to human health or the environment[v]. A restriction forbids the production, placing on the market or using a substance on its own, in mixtures or in articles (e.g., in heat pumps). Risk means that a substance has a hazardous property and either man or the environment is exposed to this hazard. In the case of the PFAS family PFAS (per- and polyfluoroalkyl substances), the hazard common to all family members is their own persistency or the persistency of their final degradation products. Persistency has been considered to be a hazard category of “very high concern” only in the combination with toxicity and bioaccumulation, but not by itself. Other hazard properties, like endocrine disruption, are only attributable to some members of the PFAS substance family.

The German Environment Agency UBA has published a comprehensive review of the environmental effects which emissions of unsaturated F-gases and TFA formation may have in the atmosphere as well as in soil and water bodies after precipitation[vi]. Critique or support of this assessment is beyond the scope of this paper. Publications of the European Association for Fluro Chemical Producers, EFCTC.[vii, viii] put forward a different perspective with fewer concerns regarding TFA formation.

The UBA report projects a rise in emissions and TFA formation by 2050 as the result of the replacement of fluor hydrocarbons by HFOs and an unintentional release of these chemicals during operation. Currently, the main source of these emissions is mobile air conditioning systems, mostly for cars. This is important to note because stationary heat pumps for industrial applications, which are the focus of the current comparison, can be designed, operated and maintained with much lower leakage rates of refrigerants. EFCTC disputes a risk of TFA accumulation in the atmosphere presenting evidence that several HFOs and HCFOs decompose into TFA at a low rate compared to HFOs.

2.3 Revision of the F-gas regulation[ix] (2022/0099(COD))

The F-gas regulation in its current form distinguishes between fluorinated greenhouse gases and "other fluorinated greenhouse gases subject to reporting", see Figure 3. For HFOs and HCFOs, the regulation only requires reporting on production, import, export, feedstock use and destruction.

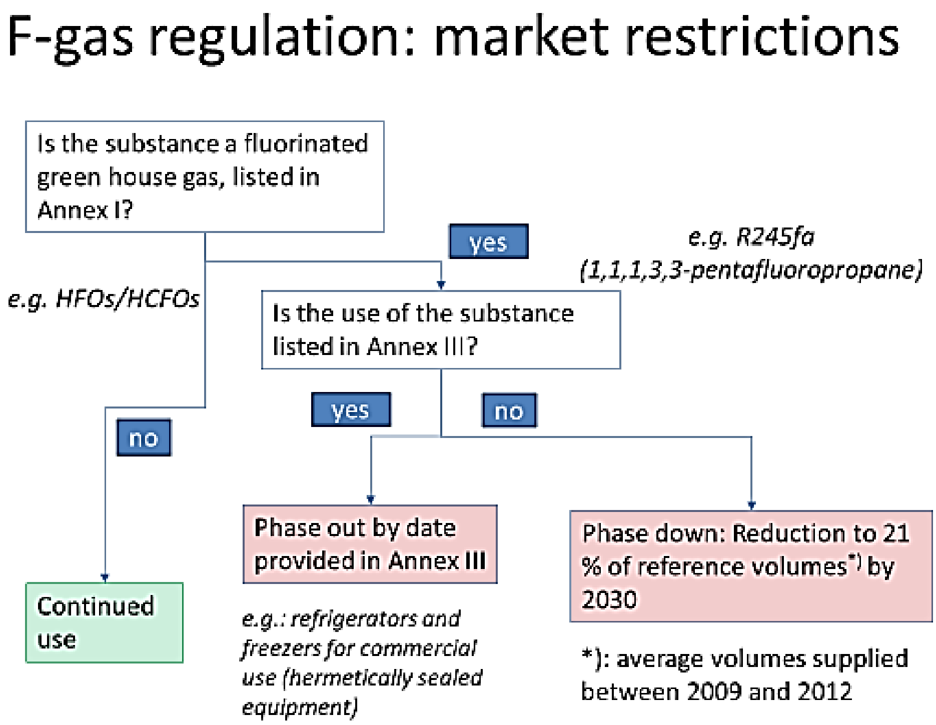

Figure 3: Market restrictions under the F-gas regulation.

A revision of the F-gas regulation is in progress and may tighten the phase-down schedule as well as the rules for HCFOs and HFOs: in an amendment to the Commission proposal, the European Parliament (EP) has suggested also covering HFOs/HCFOs by bans with a phase-out date 1 January 2028. The Council position at the start of trilogue negotiations proposes a phase-out date only for refrigerants with GWP > 150, which would not include HFOs/HCFOs.

Whether the EP proposed phase-out dates will find their way into the finally adopted text will be subject to negotiations between Commission, Parliament, and Council. If the three institutions find an agreement within the first reading, the revised F-gas regulation may enter into force as early as 2024.

2.4 Restriction for PFAS under REACH

The EU plans a restriction under REACH to ban PFAS, i.e., a group of several thousand substances, which are chemically similar and have comparable hazard properties. The European Chemical Agency ECHA published the draft proposal on February 7, 2023[x]. ECHA initiated a public consultation on 22 March 2023, which will last until September 2023. After adoption by the European Parliament and Council, a restriction may become effective within the next three years (minimum 18 months after entering into force). The following summary is based on the proposal, which may still change during consultation.

HFCs, HFOs or HCFOs fall into the scope of the restriction.

The restriction proposal[xi] covers a very broad scope: "the manufacture, placing on the market, as well as the use of PFASs as such and as constituents in … articles ..."

Regarding uses, the proposal states: "All uses of PFASs are covered by this restriction proposal, … unless a specific derogation has been formulated." The Commission is considering two restriction options (RO):

- RO 1: a full ban with no derogations and an 18-month transition time.
- RO 2 (favored by dossier submitters): a full ban with use-specific time-limited derogations (18-month transition period plus either a five- or 12-year derogation period).

Suggested criteria for time-limited derogations:

Table 2: Duration of time-limited derogations under the PFAS restriction, option 2[x]

18-month transition period	**5 years after the transition period ends**	**12 years after the transition period ends**
Default case	Currently, no technically and economically feasible alternatives on the market, but possible alternatives to PFAS use are still in the development phase	No technically and economically feasible alternatives on the market and will likely not become available in the near future, or
	known alternatives are currently not available **in sufficient quantities** on the market or cannot be implemented before the transition period ends.	certification or regulatory approval of PFAS-free alternatives cannot be achieved within a five-year derogation period.

So far, under RO 2, a number of derogations for HVACR equipment (Heating, Ventilation, Air Conditioning and Refrigeration) have been proposed. The one relevant for high-temperature heat pumps in industrial applications refers to existing plants and would allow the 12-year transition time:

i. maintenance and refilling of existing HVACR equipment … and for which no drop-in alternative exists until 13.5 years after EiF;

The availability of alternatives is a prerequisite for REACH restrictions. The registration dossier considers butane, pentane, and heptane as suitable alternatives[2], but acknowledges uncertainties regarding industrial heat pumps[3].

Considering the criteria in Table 2 and a lack of maturity for alternative heat-pump refrigerants, see. Chapter 1, we believe that a derogation period of 5 years is appropriate.

[2] *"Heat pumps will have to produce steam at a temperature of about 160 °C or higher if fossil steam boilers are to be phased out as this is a kind of standard in current steam systems. Even 250 °C is used in some drying processes where dry saturated steam is needed because of its hygroscopicity. No universal non-PFAS refrigerant is suitable for all applications up to about 230 °C. However, the hydrocarbons butane (R600), iso-butane (R600a), pentane (R601) and heptane (R603) are applicable solutions. For temperatures in the range 230 to 250 °C, steam (R718) is an option."*

[3] *"For the industrial market particularly, there appear to be specific niches where alternatives are unable to provide the conditions required for some processes."*

2.5 Planned revision of REACH: phase out of "substances of very high concern" (SVHC)

An aspect relating to hydrocarbons as potential substitutes may result from a pending revision of REACH. Currently, no formal revision proposal has been submitted by the Commission. Therefore, the following considerations are based on legislative concepts, which may still change even before the proposal enters the legislative process.

The Commission plans to introduce the concept of a "generic approach to risk management" (GARM), i.e., automated market ban for substances, which fit into the category of "substance of very high concern". This category will likely include carcinogens and mutagens and may be extended to other hazard categories. This mechanism could lead to an overall broadening of market restrictions for refrigerants, see Figure 4.

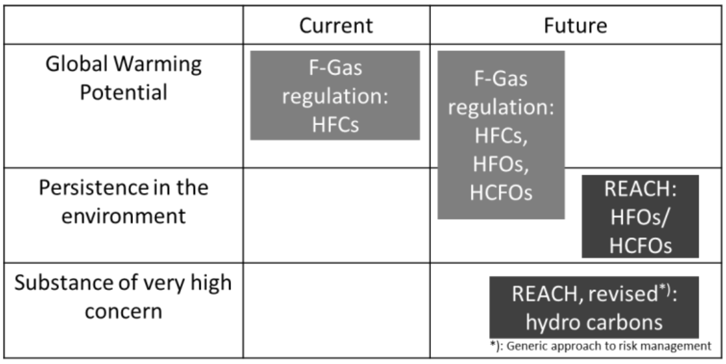

Figure 4: Current and future regulatory pressure on refrigerants

3 Heat pump performance and cost

We compared the system performance, i.e., the energy efficiency (coefficient of performance, COP) and the volumetric heat capacity (VOC) as an indicator for the size of the compressor and system (closely related to the investment cost), for the refrigerants in Table 1.

We looked at a simple heat-pump cycle for the following refrigerants, see also:

- synthetic hydrofluorocarbon olefins (HFOs) and HFOs containing Chlorine (HFCOs). We have chosen these refrigerants because they are suited for high temperatures and have a relatively low global warming potential (GWP) and ozone depletion potential (ODP); another aspect was the availability of thermodynamic property data; the established hydrofluorocarbon (HFC) R245fa was added as a reference, although it is being phased down and hence no viable alternative,
- natural refrigerants, i.e., hydrocarbons with suitable thermodynamic properties and ammonia. We left out propane because its critical temperature is too low for the chosen boundary conditions.

Boundary conditions for this calculation:

- evaporation temperature: 60°C, condensation temperature: 130 °C
- subcooling in the condenser and superheating in the evaporator: 5 K

- isentropic efficiency of the compressor: 0.7 (no assumptions made regarding the dependence on pressure levels)

For results, see Table 8. For more details on the methodology compare with Arpagaus et al. (2018)[iv]

Figure 5, displays a benchmarking of the volumetric heat capacity of the heat pump and the coefficient of performance.

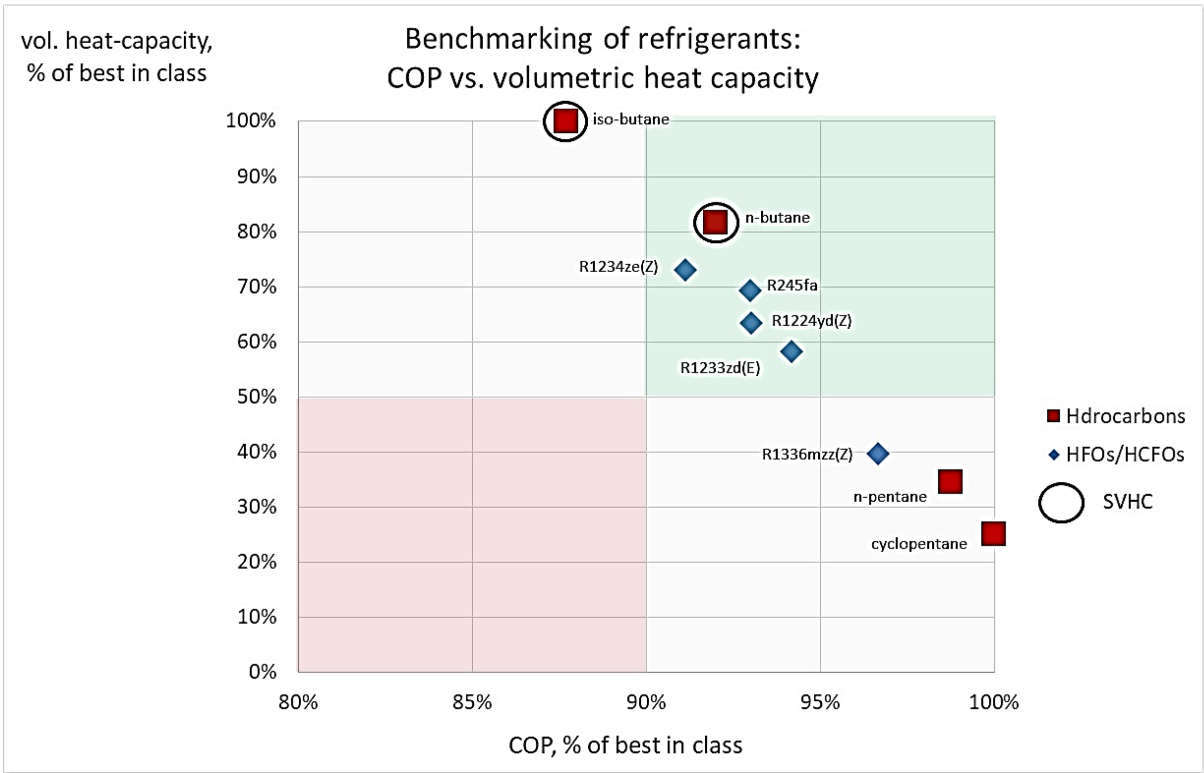

Figure 5: Benchmarking of various refrigerants, evaporation temperature 60°C, condensation temperature 90°C

- The hydrocarbons cover a broad range: The two butanes perform well regarding the volumetric heat-capacity, but less so regarding the COP. The reverse is the case for the pentanes: they show a low volumetric heat capacity which would result in large and expensive equipment. At the same time, cyclopentane is best in class regarding the COP value. The HFOs and HCFOs are "in between".
- The differences between the refrigerants regarding the COP are smaller than the variations regarding the volumetric heat capacity.
- For the sake of comparison, we assumed that the compressor efficiency of 0.7 is the same for all refrigerants included in the benchmarking. Own experimental data obtained with a piston compressor suggest that this value correlates with the density at the inlet of the compressor and should therefore be generally lower for refrigerants with high normal boiling points and critical temperatures. However, application-specific compressor designs may overcome this disadvantage.
- Inorganic refrigerants like ammonia, CO_2 or water have not been included in the diagram. CO_2 is supercritical at temperatures above 31 °C, which is a disadvantage to producing steam. Water exhibits a vacuum pressure (0.2 bar, absolute) at the evaporator temperature and would require a large compressor. Ammonia`s critical temperature yields a low COP at the

condensation temperature of 130 °C. The VHC of Ammonia and the COP of water are much higher than the values for the other fluids and therefore are shown separately in Table 3.

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Table 3: Results for water and ammonia, percentage range of the benchmark.

	Ammonia	**Water**	
Vol. heat-capacity	>500%	12%	Very low density and pressure of water at compressor inlet.
COP	76%	138%	Ammonia in condenser close to the critical point

- A use of ammonia and water in a two-stage heat pump (ammonia at temperature up to 110°C, water at pressure level above ambient pressure) would provide an energy-efficient, but complex "functional" alternative to the operation of a 1-stage heat pump with a fluorinated refrigerant, see also Table 7.

4 Other features of the refrigerant comparison

4.1 Process safety: toxicity and flammability

The overview in Table 4 taken from Arpagaus et al. (2018)[iv] and adapted for this paper, classifies natural and synthetic refrigerants according to their flammability and acute toxicity. The scheme shows that in the preferred class A1 (low toxicity, no flame propagation) apart from water and CO_2, only HFOs and HCFOs are available.

For visualization, butane and pentane were added to the ASHRAE B3 classification. Butane and pentane are very hazardous substances according to the legally binding ("harmonized") EU classification with respect to carcinogenicity, mutagenicity and aspirational toxicity.

Table 4: Safety group classification of refrigerants[ii], according to DIN EN 378-1 and ASHRAE, A: lower toxicity, B: higher toxicity, 1: no flame propagation, 2: lower flammability (2L: "mildly flammable"), 3: higher flammability

Flammability					
	higher	**A3**	R290	**„B3$_{extended}$"** *)	(R600, R600a, R601)
	lower	**A2**		**B2**	
		A2L	R1234ze(E), R1234yf	**B2L**	R717
	no flame propa-gation	**A1**	R1336mzz(Z), R1336mzz(E), R1233zd(E), R1224yd(Z), R718, R744	**B1**	R245fa
		lower		higher	
		Toxicity			

*): Substances are included in A3, rather than in the established category B3; a category B3extended has not been defined under ASHRAE.
The substances are added here to visualize the severity of the EU harmonized classification.

Table 5: Harmonized classification of potential hydrocarbon refrigerants, taken from the ECHA data base[xii] (3 Apr. 2023)

Substance		**EU harmonized classification (only cat. 1) ECHA inventory (explanation in footnote)**
name	CAS number	
n-propane	74-98-6	
cyclo propane	75-19-4	
n-butane	106-97-8	CMR, pot SVHC
iso butane	75-28-5	CMR, pot SVHC
n-pentane	109-66-0	asp. toxicity
iso pentane	78-78-4	asp. toxicity
cyclo pentane	287-92-3	
hexane	110-54-3	asp. toxicity
cyclo hexane	110-82-7	asp. toxicity, aquatic toxicity (acute and chronic)

For a definition of toxicological endpoints and explanations of acronyms see foot-note[4] or the regulation itself.

[4] *CMR: includes carcinogenicity, germ cell mutagenicity or reproduction toxicity. Each of these three hazard features contain categories 1A, 1B and 2, with 1A and 1 B being the most severe levels. Criteria:*
for carcinogenicity: substances known (1A) or presumed (1B) to have carcinogenic potential for humans, classification is largely based on human evidence (1A) or animal tests (1B)

4.2 Greenhouse gas emissions

SMARDT OPK[5] proposed an indicative estimate of the greenhouse gas emission associated to the operation of a heat-pumps operated with a particular refrigerant (TEWI: Total Equivalent Warming Impact). The method quantifies greenhouse gas emissions during the life cycle of the heat-pump. The TEWI value is composed of three contributions:

TEWI =
Leakage during operation (1 % of the charge per year)
+ recovery loss
+ secondary GHG emissions based on the local power-mix.

The latter term allows to differentiate based on the efficiency of the actual refrigerant and constitutes the largest contribution to TEWI, see Table 6 and Figure 6. The required electric power for a fictious heat-pump cycle delivering 1 MW heat has been taken from the simulation results in Table 8.

Table 6: Results of TEWI Benchmarking

			TEWI contributions, kg CO2eq./a			
	GWP	Electric energy demand, kW	Leakage,	recovery loss	secondary contribution	total
ammonia	0	340,1	0	0	1.142.883	1142883
isobutane	3	288,3	3	3	968.545	968551
n-Butane	4	274,8	4	4	923.306	923314
n-Pentane	5	256,0	5	5	860.326	860336
Cyclopentane	5	252,8	5	5	849.553	849563
R1233zd(E)	1	268,5	1	1	902.094	902096
R1234ze(Z)	<1	277,5	*1*	1	932.235	932235
R1336mzz(Z)	2	261,6	2	2	879.000	879004
R1224yd(Z)	<1	271,8	*1*	1	913.384	913384
R245fa	858	271,9	858	858	913.520	915236
electric heater ("COP" = 1)		1000,0			3.360.000	

for germ cell mutagenicity 1A/1B: substances known to induce heritable mutations or to be regarded as if they induce heritable mutations in the germ cells of humans.
Aspirational toxicity: Substances known to cause human aspiration toxicity hazards or to be regarded as if they cause human aspiration toxicity hazard.
Aquatic toxicity: short (acute) and long term (chronic) toxicity for aquatic life.
Potential SVHC: very hazardous chemicals are identified as substances of very high concern in a formal process. Substances with CMR properties, cat. 1A or 1B, are prioritized for this process. The legal consequence is of a SVHC identification is a phase out.

[5] https://www.opk.de/information/was-ist-tewi

GWP	Greenhouse Warming Potential		
L	annual leakage rate	1%	of charge per year,
n	life time of heat pump	10	years
t	operating time of heat pump	8000	h/a
m	refrigerant charge	100	kg
$1-\alpha_{recovery}$	recycling loss	0,1	
E_{annual}	annual electric energy demand resulting from simulation assuming 1 MW heat supply		kWh
β	CO_2 emissions per kWh	0,42	kg/kWh

$$TEWI = (GWP * L * m) + (GWP * m * [1-\alpha_{recovery}]/n) + (E_{annual} * \beta)$$

$$E_{annual} = P_{el} * t = 1\ MW / COP * t$$

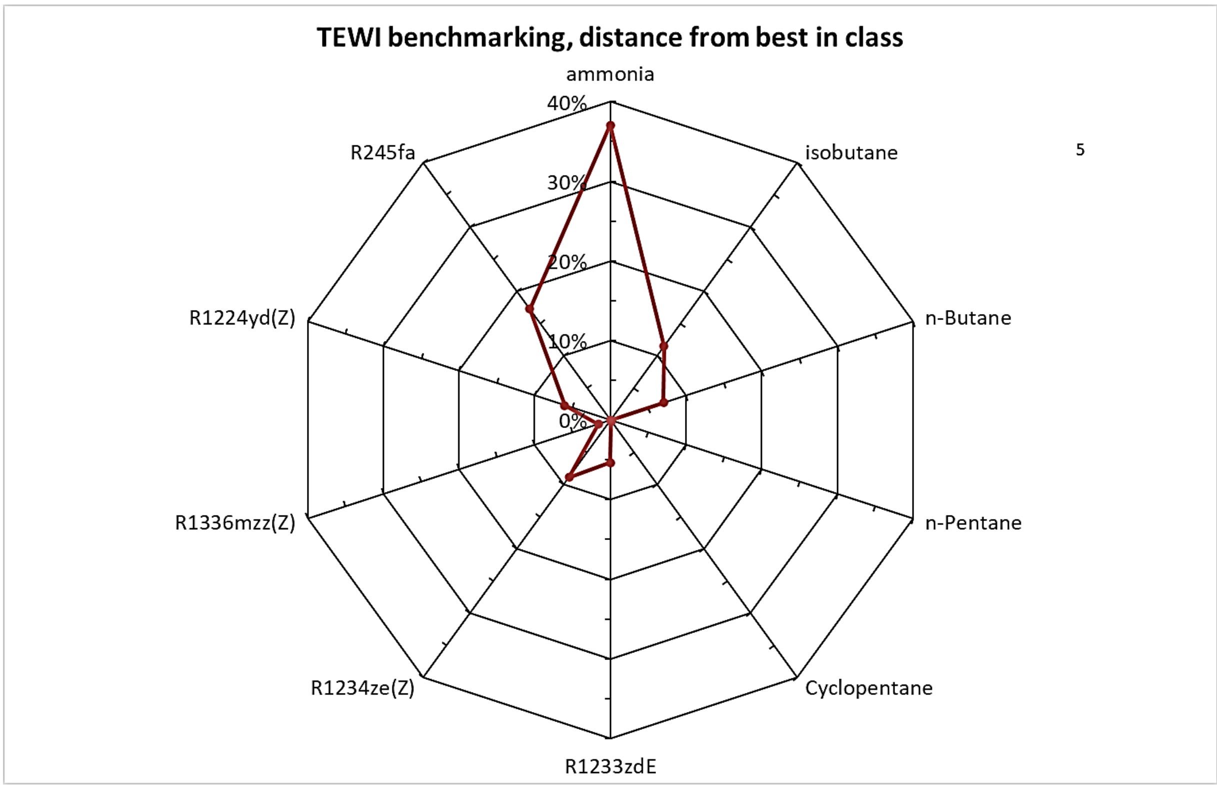

Figure 6: Result of TEWI benchmarking.

The largest contribution to the TEWI value comes from the secondary emissions, i.e. the production of the electric energy for the compressor. Note, that a German energy mix has been assumed, with 420 g CO_2 emissions per kWh[xiii]. All other contributions are negligible (< 1%) even for the HFC R245fa. Disregarding ammonia, the differences are the same within a band-width of ±5%. Ironically, ammonia, which has a GWP = 0 but a relatively high energy consumption during operation, performs worst. Due to its efficient performance, cyclopentane is “best in class”.

However, when the power mix for electricity supply would be carbon neutral, recovery and diffusion losses have more influence. In this case, ammonia would be superior while the HFC becomes disadvantageous due to its high global warming potential. HFOs and HCFOs remain favourable.

Note, that an electric heated boiler would result in the highest TEWI value, by far; see bottom line of Table 6.

5 Summary and Conclusion

Considering their thermodynamic properties, fluorinated refrigerants can be replaced by natural refrigerants considering the mounting regulatory pressure and the risk that they will not be available on the EU market in the near future. It is both, a business decision, and a matter of pending regulation, how fast this substitution happens. Predictability and the relatively low degree of maturity should guide the regulatory decisions.

There are some natural refrigerants, notably the pentanes, which “on paper” show a superior efficiency as refrigerants for a high-temperature heat-pump. Their downside is that due to their lower volumetric heat capacity they require larger equipment, notably compressors and heat exchangers, due to their lower volumetric heat capacity. This causes higher investment cost and thus slows down the motivation of companies to engage in a sustainable energy transition. They also show higher flammability and toxicity.

The remaining global warming potential of the HFOs and HCFOs is irrelevant:

- The GWP is strongly reduced and less than the one for the hydrocarbons.
- The contribution to global warming resulting from well-sealed industrial plants (losses of 1 % of the hold-up) is small compared to the CO_2-emission saving from the heat pump and with the current power-mix even marginal compared to the differences of the resulting energy efficiencies. (This generally puts the proportionality of a F-gas ban in question.)

As the ecotoxicological concern “persistency”, which drives the REACH restriction on HFOs and HCFOs, relates to products of degradation under atmospheric conditions, it seems disproportionate to ban substances (for use in high-temperature heat pumps) which are handled under strictly controlled conditions in closed apparatuses; even more so, considering risks of explosions and the chemical hazard properties of the substitution products.

In summary, if minimization of leakage to the extent possible in industrial applications becomes mandatory, neither the safety properties nor the remaining impact of the refrigerants and their degradation products is a relevant concern.

If the Commission chooses to regulate the use of fluorinated refrigerants in industrial high-temperature heat pumps by a restriction under REACH, a time-limited derogation of at least 5 years seems appropriate given that some of the non-PFAS refrigerants have limitations, the technology is still in the developing phase and considering the high urgency to establish the heat-pump technology in industrial production and thus contribute to the energy transition towards climate neutrality.

Acronyms

COP	coefficient of performance
GWP	Global warming potential
HC	Hydro-Carbon
HCFO	Hydro-Chloro-Fluoro-Olefins
HFC	Hydro-Fluoro-Carbon
HFO	Hydro-Fluoro-Olefins
ODP	Ozone depleting potential
TFA	trifluoroacetic acid
UBA	Umweltbundesamt, German Environment Agency
VHC	volumetric heat capacity, MW/m^3

Table 7: New Developments and Products for Supply Temperatures above 100 °C, Arpagaus (2023)[iii]

HTHP supplier (High-Temperature Heat Pump)	Country	Compressor type	Working fluid (Refrigerant)	Max. heating capacity (MW)	Max. supply temp (°C)	TRL (Technology Readiness Level)	Spec. invest. cost (EUR/kW)
Spilling	DE	Piston (MVR)	R718 (water)	15	280	9	100 to 400
Enerin	NO	Piston	R704 (helium)	10	250	6	600 to 800
Qpinch	BE	Chemical heat transformer	R718, H_3PO_4 and derivatives	2	230	9	1000 to 2000
Piller	DE	Turbo (MVR)	R718	70	212	8 to 9	850
Olvondo	NO	Piston (double acting)	R704	5	200	9	1200
Turboden	IT	Turbo	Application specific	30	200	7 to 9	300 to 700
ToCircle	NO	Rotary vane	R717 (ammonia), R718	5	188	6 to 7	250 to 430
Kobelco MSRC160	JP	Twin -screw (MVR)	R718	0.8	175	9	n.a.
Kobelco SGH165	JP	Twin-screw (MVR)	R245fa/R134a (mixture), R718	0.62	175	9	n.a.
Heaten	NO	Reciprocating, custom design	HFOs (hydrofluorolefins)	6	165	7 to 9	250 to 350
SPH	DE	Piston	HFOs (hydrofluorolefins)	5	165	6 to 8	150 to 1000
SRM	SE	Screw (MVR)	R718	2	165	5	n.a.
Siemens Energy	DE	Turbo (geared or single-shaft)	R1233zd(E), R1234ze(E)	70	160	9 (to 90 °C)	250 to 800
Enertime	FR	1- or 2-stage centrifugal	R1336mzz(Z), R1224yd(Z), R1233zd(E)	10	160	4 to 8	300 to 400
Weel & Sandvig	DK	Turbo (MVR)	R718	5	160	4 to 9	150 to 250
Rank	ES	Screw	R245fa, R1336mzz(Z), R1233zd(E)	2	160	7	200 to 400
MAN	DE	Centrifugal turbo with expander	R744 (CO_2)	50	150	7 to 8	300 to 500
Epcon	NO	Centrifugal fan / Blower	R718	30	150	9	200 to 400
Ohmia Industry	NO	Piston, Centrifugal fan (MVR)	R717, R718	10	150	7 to 8	n.a.
ecop	AT	Rotational heat pump	ecop fluid 1 (He, Kr, Ar)	0.7	150	6 to 7	700
Mayekawa FC Comp	BE	Screw	R601 (n-pentane)	1	145	5	720
GEA Refrigeration	NL	Semi-hermetic piston	R744	1.2	130	8	200 to 300
Mitsubishi Heavy Ind.	JP	Two-stage centrifugal	R134a	0.6	130	9	n.a.
Hybrid Energy	NO	Piston/screw	R717/R718 mixture	5	120	9	200 to 600
Johnson Controls	DK	Reciprocating	R717, R600 (n-butane) (cascade)	5	120	7 to 8	n.a.
Fenagy	DK	Reciprocating	R744	1.8	120	5 to 6	250 to 425
Mayekawa HS Comp	BE	Piston	R600 (n-butane)	0.75	120	7	450
Kobelco SGH120	JP	2-stage twin-screw	R245fa	0.37	120	9	n.a.
Mayekawa EcoCircuit	JP	Reciprocating	R1234ze(Z)	0.1	120	9	n.a.
Fuji Electric	JP	Reciprocating	R245fa	0.03	120	9	n.a.
Emerson	US	Scroll and EVI scroll	R245fa, R410a, R718	0.03	120	6	n.a.
Skala Fabrikk	NO	Piston (semihermetic)	R290 (propane), R600 (cascade)	0.3	115	7	500 to 700
Mayekawa EcoSirocco	JP	Reciprocating	R744 (CO2)	0.1	100	8 to 9	n.a.

Table 8: System performance with different refrigerants, simulation results

Evaporation temperature	60	°C
Condensation temperature	130	°C
delta T IHX	5	K
Subcooling	5	K
Superheating	5	
efficiency compressor	0,7	
heat flow condensor	1	MW

			Entrance compressor		Exit compres		Mass Flow	el. Power	COP	vol. Heat-Ca	pressure rati
	Tcrit	pcrit	pressure	Dens1	pressure	temp.					
	°C	bar	bar	m³/kg	bar	°C	t/h	MW	-	kW/m³	-
ammonia	132,4	113,6	26,1	12,1	108,9	401,7	2,4	0,3	2,95	18099	4,2
isobutane	134,7	36,3	8,7	15,5	33,6	209,3	9,3	0,3	3,62	5987	3,9
n-Butane	152,0	38,0	6,4	11,3	26,3	207,6	8,4	0,3	3,77	4850	4,1
n-Pentane	196,6	33,7	2,1	4,6	11,0	197,2	8,2	0,2	4,04	2040	5,1
Cyclopentane	238,6	45,8	1,4	2,9	8,0	214,2	7,2	0,2	4,03	1463	5,6
R1233zdE	166,5	36,2	3,9	15,2	19,1	220,2	15,9	0,3	3,83	3435	4,9
R1234ze(Z)	150,1	35,3	5,2	17,6	24,5	226,7	14,7	0,3	3,71	4305	4,7
R1336mzz(Z)	171,4	29,0	2,4	12,0	13,5	201,9	18,2	0,3	3,98	2368	5,5
R1224yd(Z)	155,5	33,4	4,4	19,6	21,1	216,4	18,7	0,3	3,81	3767	4,8
R245fa	153,9	36,5	4,6	18,4	23,5	214,7	16,1	0,3	3,81	4110	5,1

References

[i] Bless, F. , Arpagaus, C. , Speich, M., Bertsch, S.: "Electrification of Heat Generation in Industry: State of Technologies, Integration Examples, and Integration Barriers", Young Energy Researchers Conference 2022

[ii] Arpagaus, C., Bless F., Bertsch S.: "Techno-economic analysis of steam generating heat pumps for integration into distillation processes". 15th IIR-Gustav Lorentzen conference on Natural Refrigerants, June 13-15 2022, Trondheim, Norway

[iii] Arpagaus, C.: High-Temperature Heat Pumps for Industrial Applications – New Developments and Products for Supply Temperatures above 100 °C, Australian Alliance for Energy Productivity (A2PH) Webinar, 22 February 2023

[iv] Arpagaus, C., Bless F., Uhlmann M., Schiffmann J., Bertsch S.: "High temperature heat pumps: Market overview, state of the art, research status, refrigerants, and application potentials". Energy, Vol. 152 (2018), pp. 985 – 1010.

[v] Regulation (EC) No 1907/2006, Title VIII

[vi] David Behringer et al.:"Persistent degradation products of halogenated refrigerants and blowing agents in the environment: type, environmental concentrations, and fate with particular regard to new halogenated substitutes with low global warming potential.", Report No. FB000452/ENG, September 2020

[vii] European Fluorcarbons Technical Committee (EFCTC): "LEARN ABOUT HCFOs, HBFOs, Stratospheric Ozone and Climate Change", 01/2018, rev. 01/2020.

[viii] "Published evidence supports very low yield of TFA from most HFOs and HCFOs", EFCTC Position Paper, August 2021.

[ix] REGULATION (EU) No 517/2014 of the European Parliament and of the Council on fluorinated greenhouse gases, 16 April 2014.

[x] ECHA, ANNEX XV Restriction Report, Proposal for a restriction of per- and polyfluoroalkyl substances (PFASs), 7 Feb. 2023, Version 1. The proposal was drafted by the following D, NL, S and DK, as well as Norway

[xi] Annex XV Restriction Report: Proposal for a restriction, Substance Names: Per- and polyfluoroalkyl substances (PFASs); Publication 7 Feb. 2023, Version 1. https://echa.europa.eu/restrictions-under-consideration/-/substance-rev/69104/term

[xii] https://echa.europa.eu/information-on-chemicals/cl-inventory-database

[xiii] UBA: https://www.umweltbundesamt.de/themen/co2-emissionen-pro-kilowattstunde-strom-steigen