Vonsild Consulting

Online morgenkaffemøde: Kølemidler – sikkerhed, klimagevinster og forbud

20. marts 2024, 8.30 - 09.15

Introduktion af Asbjørn

Asbjørn Vonsild
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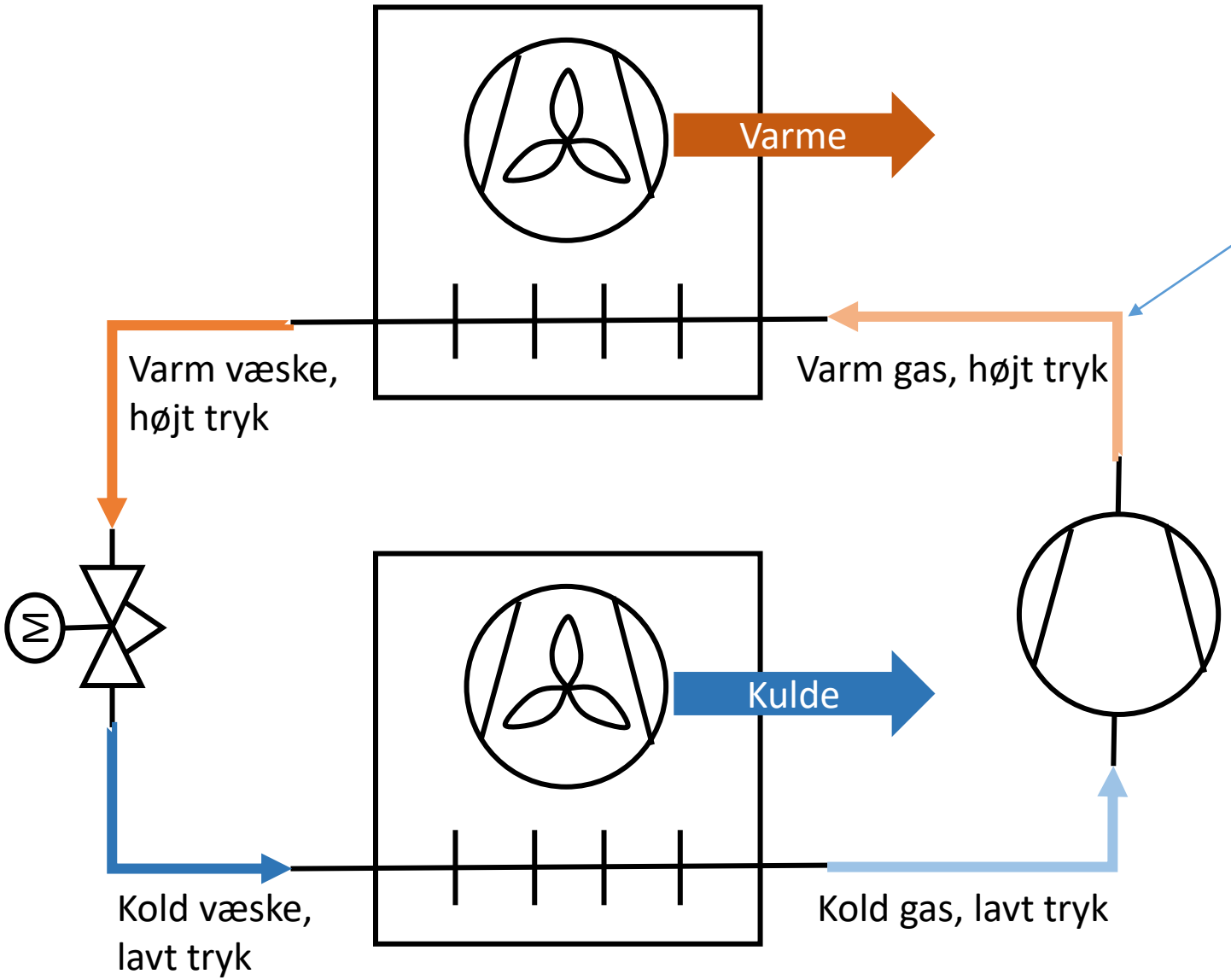
Speciale:

- Standarder og lovgivning indenfor køle-, klima- og varmepumpeanlæg.
- Brandbare kølemidler.

Eksterne roller:

- Formand for IEC/TC61D/SC61D, styregruppen for **IEC 60335-2-40**.
- Medlem af CEN/TC182/WG6 og CEN/TC182, arbejdsgruppen og styregruppen for **EN 378**.
- Medlem af ISO/TC86/SC1/WG1 og ISO/TC86/SC1, arbejdsgruppen og styregruppen for **ISO 5149**.
- Formand for den danske spejlkomite for standarder til store kølesystemer (s251).
- Medlem af den danske spejlkomite for standarder til elektrisk apparater herunder mindre kølesystemer (s561).
- Medlem af RTOC (Refrigerant Technical Options Committee), teknisk rådgivningsgruppe for Montreal Protokollen, og hovedforfatter på kapitlet om kølemiddelegenskaber.

Hvad er et kølemiddel?



Et kølemiddel er det medie der cirkulere inde i rørene i en varmepumpe eller et kølesystem

IPCC AR6 Synthesis Report,
20. marts 2023

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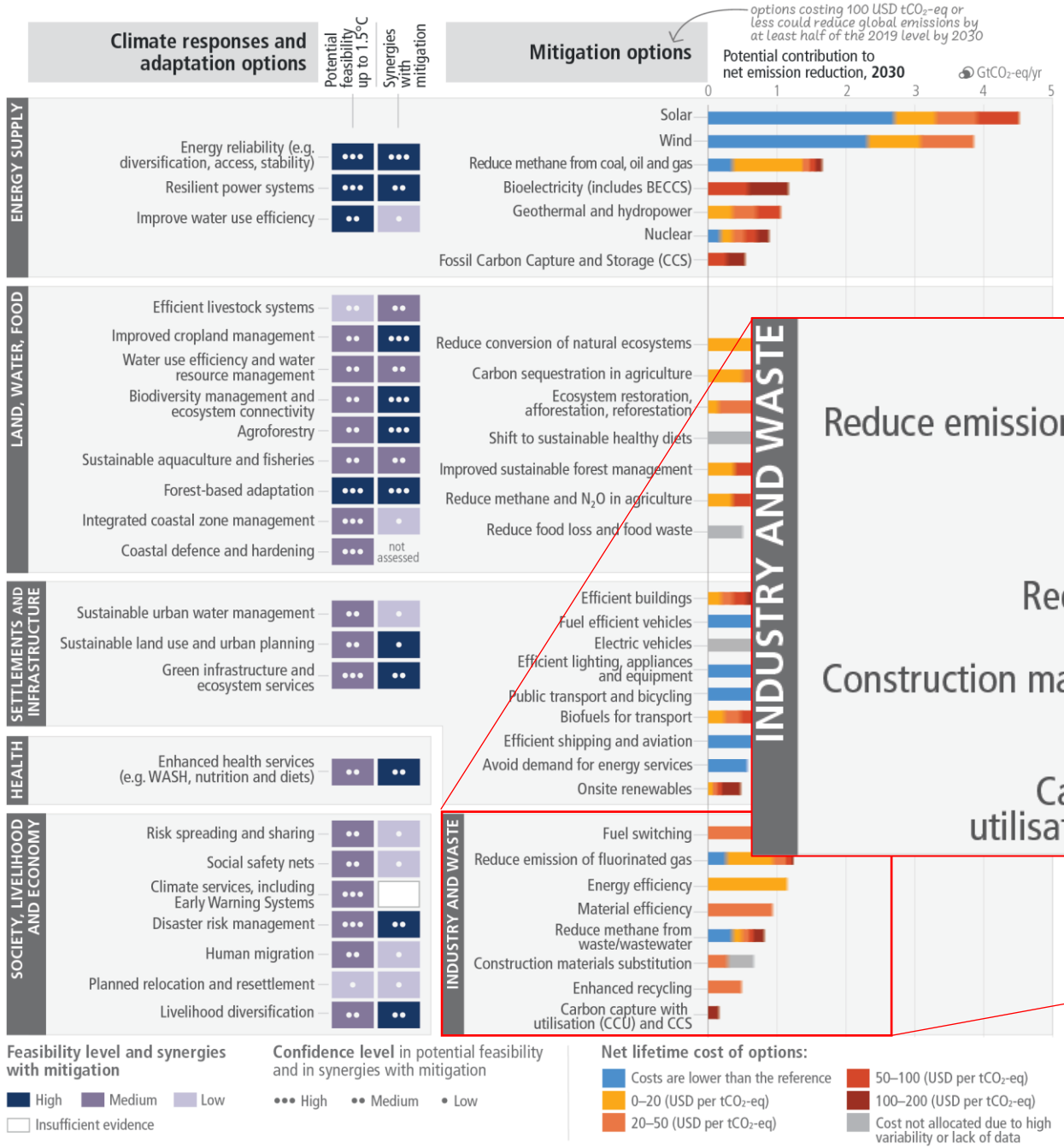
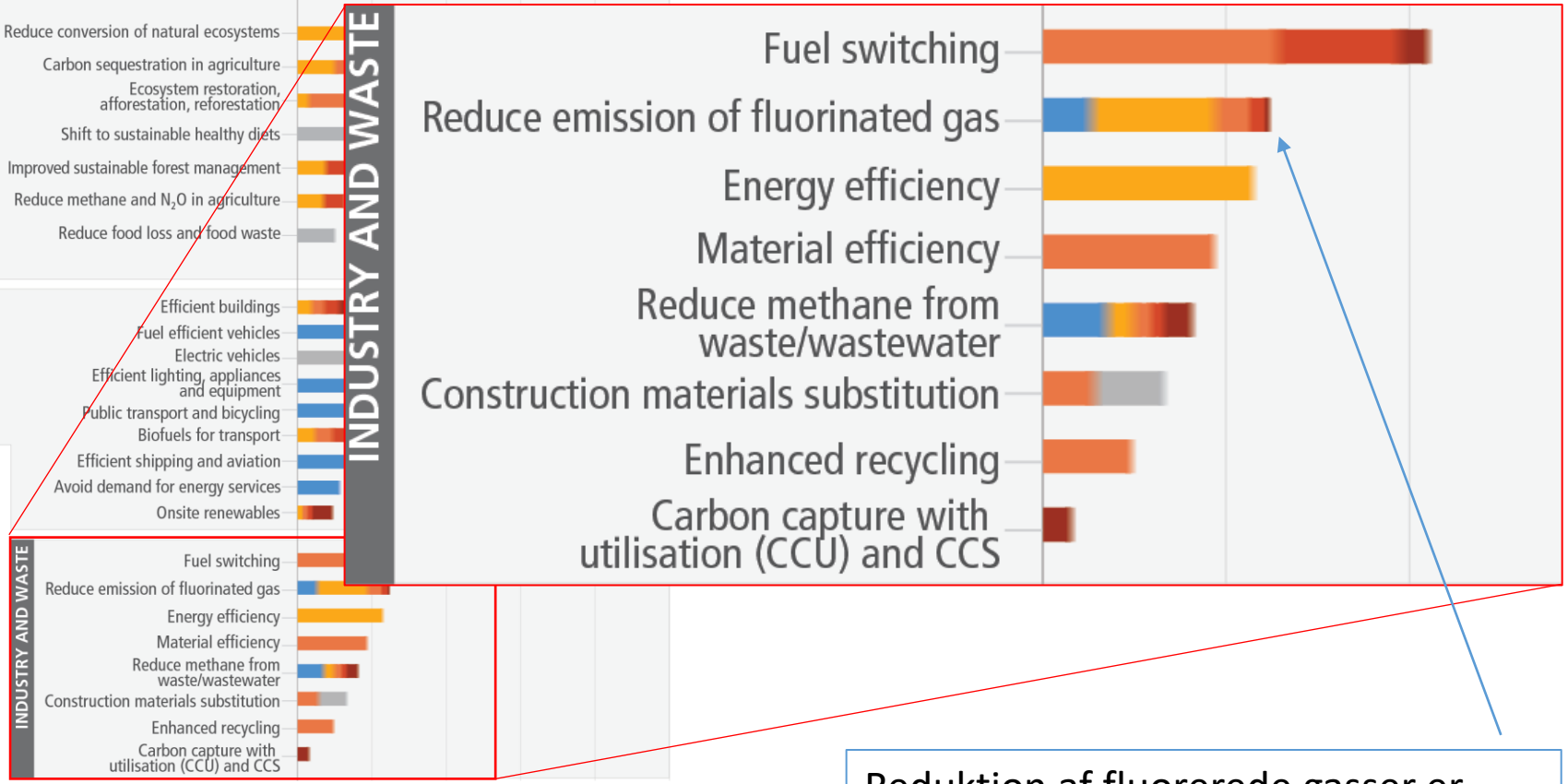
There are multiple opportunities for scaling up climate action

a) **Feasibility of climate responses and adaptation, and potential of mitigation options in the near-term**





Reduktion af fluorerede gasser er vigtigere end f.eks. el-biler og A-kraft!

Kølemiddel historie

Historie:

- **1830-1930** – alt der virkede, CO2, kulbrinter, NH3, vand, SO2, æter, myresyre, tetraklor, ...
- **1931-1990** – sikkerhedskølemidler, CFC (R11, R12, …) og HCFC (R22, R123, …)
- **1989-2010** – undgå ozonnedbrydning, HFC (R134a, R404A, R407C, R410A, …)
- **2010-i dag** – undgå klimapåvirkning, HFO/HCFO (R1234yf, R1234ze(E), 1233zd(E)…), HFC/HFO blandinger (R448A, R449A, R454C, R513), "naturlige kølemidler" (CO2, kulbrinter, NH3, vand…)

Hvad nu?

- **2024-????** – accelerere den grønne omstilling. Undgå PFAS? HFO/HCFO? "naturlige kølemidler" (CO2, kulbrinter, NH3, vand…)

Hvad er et godt kølemiddel?

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Ønskelisten er lang:

- Kogepunktet under arbejdstemperaturen
- Ikke brandbart
- Ikke giftigt
- Ikke ozon nedbrydende
- Ikke klima skadeligt
- Høj energieffektiviteten
- Komponenter tilgængelige på markedet
- God materiale kompabilitet
- Høj kemisk stabilitet
- Højt kritisk punkt
- Gode varmeovergangstal
- Osv.

Kølemiddel sikkerhedsklasser

Høj brandbarhed	**A3:** Kulbrinter	**B3:** Ingen kølemidler
Brændbar	**A2:** R152	**B2:** Sjældent brugt
Lav brandbarhed	**A2L:** De fleste HFO's, R32	**B2L:** Ammoniak
Ingen flamme-udbredelse	**A1:** CFC, HCFC, fleste HFC'ere	**B1:** R123
	Lav giftighed	**Høj giftighed**

Brandbarhed

Giftighed

Trade-off

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- Den vigtigste parameter for klimaeffekten/GWP er molekylets levetid i atmosfæren
- For at nedbringe GWP, skal molekylet være mere ustabilt!
- Det øger brandbarheden og potentielt giftigheden og den kemiske kompleksitet

EU F-Gas Forordningen er opdateret

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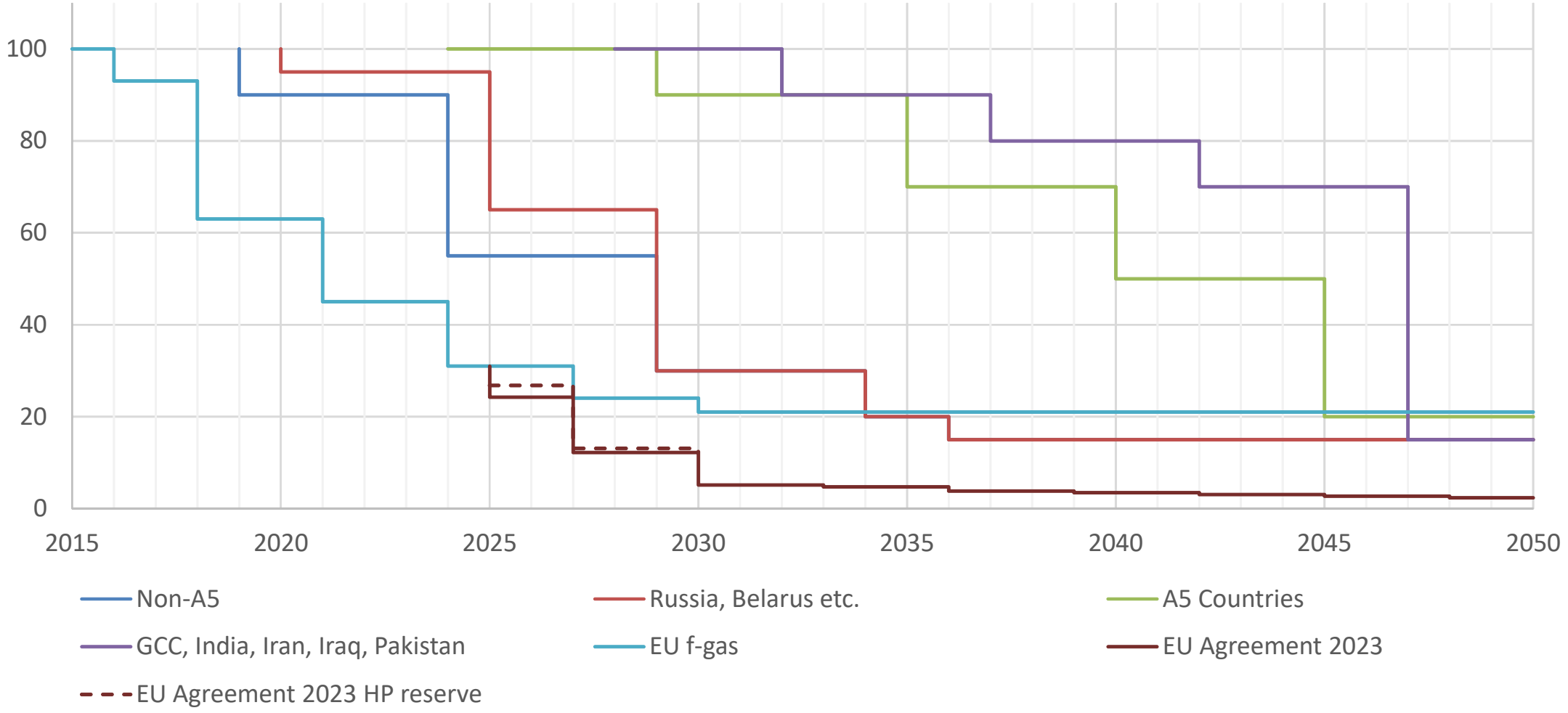
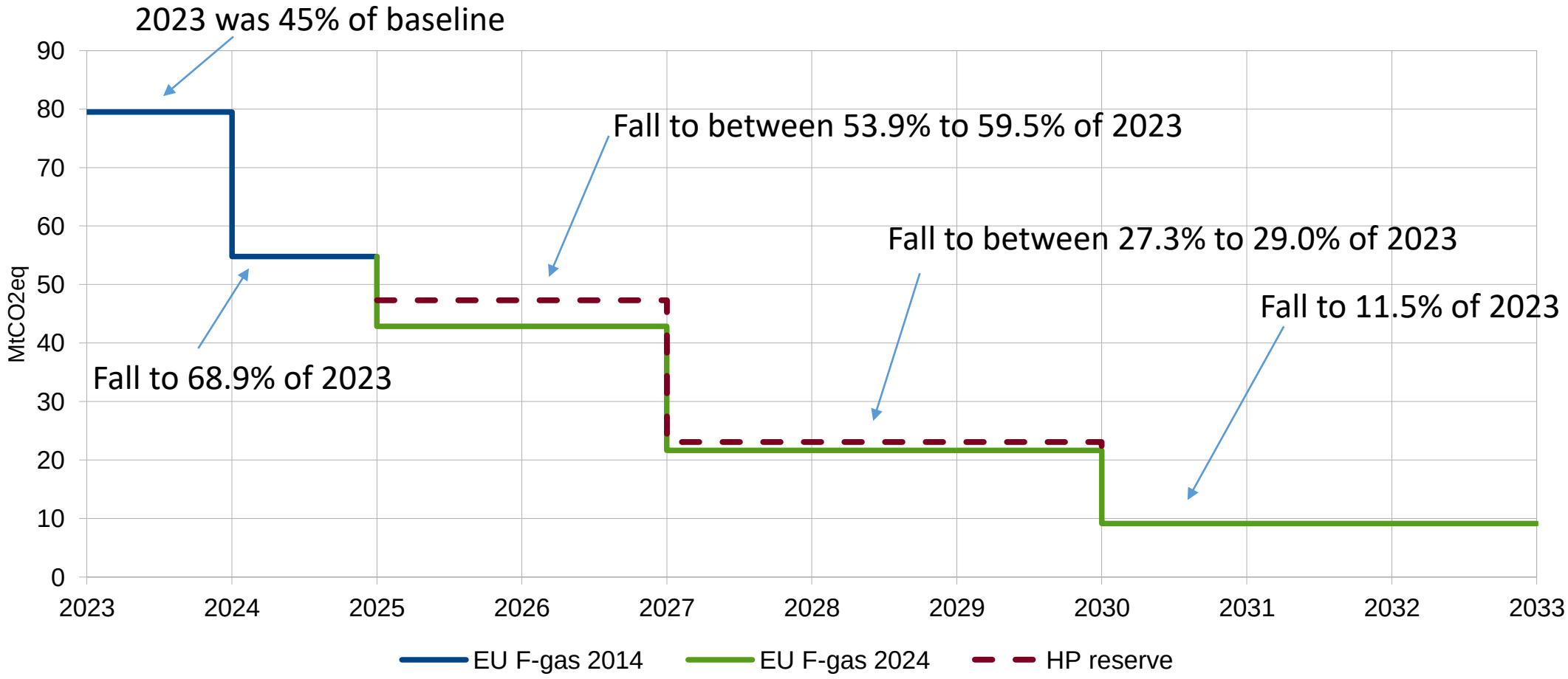
- Den nye EU F-Gas Forordning trådte i kraft 11. marts 2024

- Tidsline:
  - De fleste nye krav træder i kraft 1. januar 2025.
  - 12. marts 2025 bliver det forbudt at eksportere systemer der er forbudt at sælge i EU.
  - De følgende år kommer flere nye forbud og nedskæringer i mængden af HFC der kan sælges i EU.

European and Global phase down of HFC



Zooming in…



NOTES:

- HFC containting equipment can be imported based on authorisations from previous years.
- HP reserve will be released if the commission finds it necessary.

Nedfasning er i CO_2 ækvivalenter

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GWP: Klimapåvirkning per kg kølemiddel:

- F.eks 1 kg 410A svare til 2087,5 kg CO2, dvs. GWP = 2087,5

Eksempel:

Med 1000 tCO_2e (ton CO_2 ækvivalenter) kvoter kan man:

- R-410A har GWP 2087,5. Man kan importere 1000/2087,5 = 0,479 ton.
- R-32 har GWP 675. Man, kan importere 1000/675 = 1,481 ton.

Antallet af kvoter

- Antal kvoter i 2015 var 183.1 millioner tCO_2e
- Antal kvoter i 2023 er ca. 82 millioner tCO_2e
- I 2025-26 bliver der 42.9 millioner tCO_2e (muligvis med 4.4 millioner tCO_2e extra)

EU F-gas regulation bans - Current

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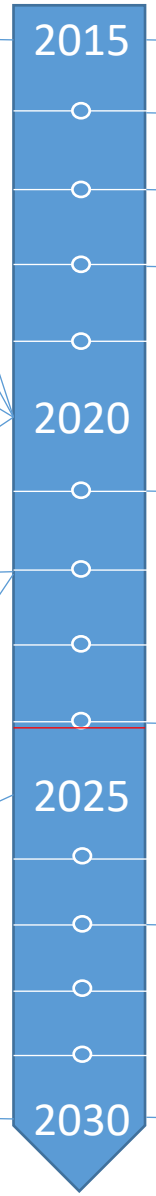
Bans

- Domestic refrigerators and freezers, ban GWP < 150 (all current HFC)
- Ban on service using new refrigerant with GWP >2500 (R507A) except for evap. <-50C or charge > 40 tCO_2eq
- Hermetic commercial refrigerators and freezers, ban GWP >2500 (R507A)
- Stationary refrigeration with GWP >2500 (R507A) except for evap. <-50C
- Hermetic movable room A/C, ban GWP >150
- Hermetic commercial refrigerators and freezers, ban GWP >150
- Multipack systems for commercial use with >40kW capacity, ban GWP >150 (GWP up to 1500 allowed for primary circuit in cascade systems)
- Split A/C systems with <3kg charge, ban GWP >750
- Ban on service using GWP >2500 (R507A) except evap. <-50C or charge > 40 tCO_2eq



Phase down

- 2015: Phase down starts with 100%
- 2015: Phase down to 93%
- 2015: Pre-charged equipment included in phase down
- 2015: Phase down to 63%
- 2020: Phase down to 45%
- 2025: Phase down to 31%
- 2025: Phase down to 24%
- 2030: Phase down to 21%

The EU regulation uses a quota system to phase down HFC production and import.

The phase down is combined with sectorial bans to guide the industry, and limit the black market.

EU F-gas regulation bans – New in orange

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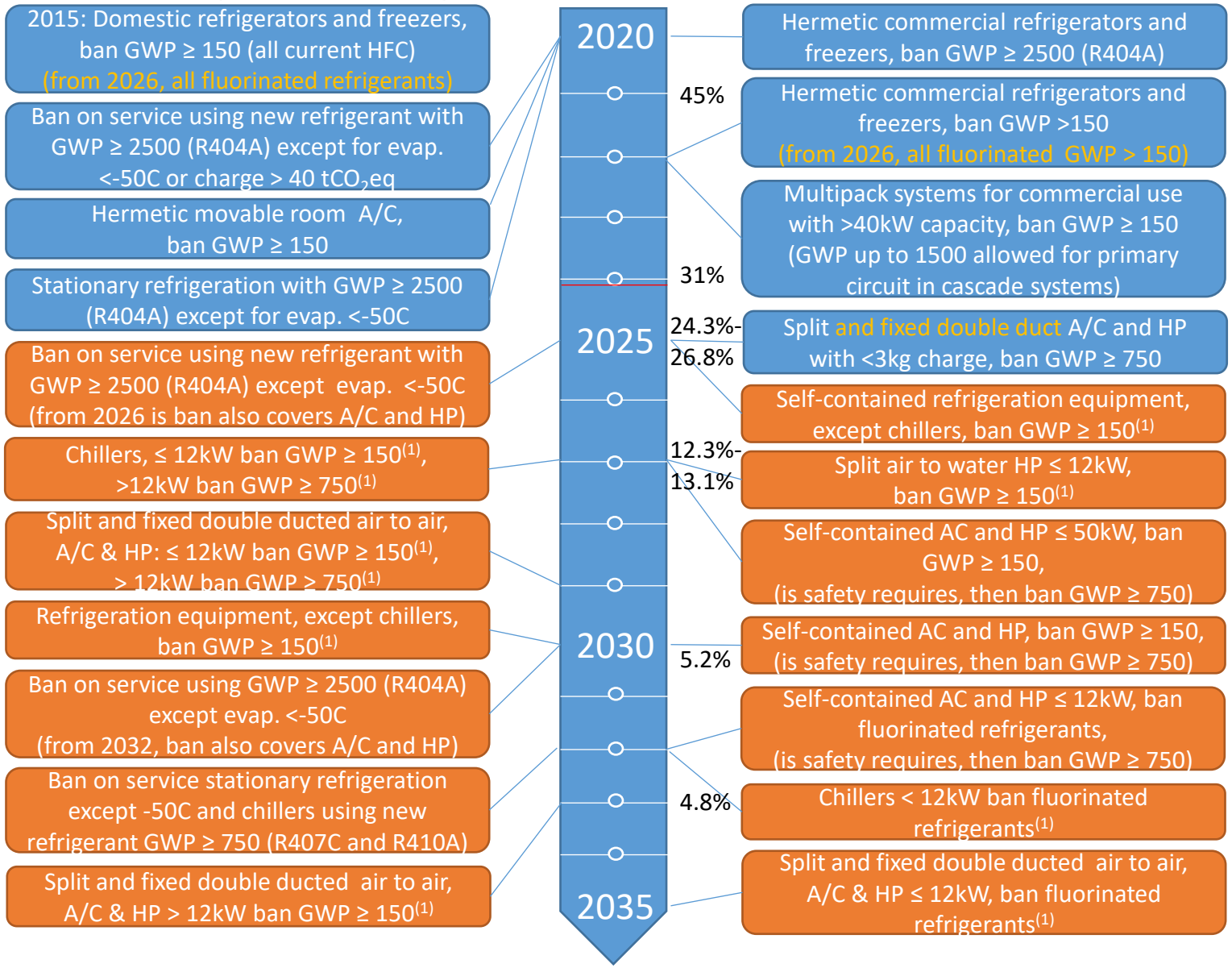
Bans



Bans in the current regulation are marked in blue, with changes in yellow and new bans in orange.

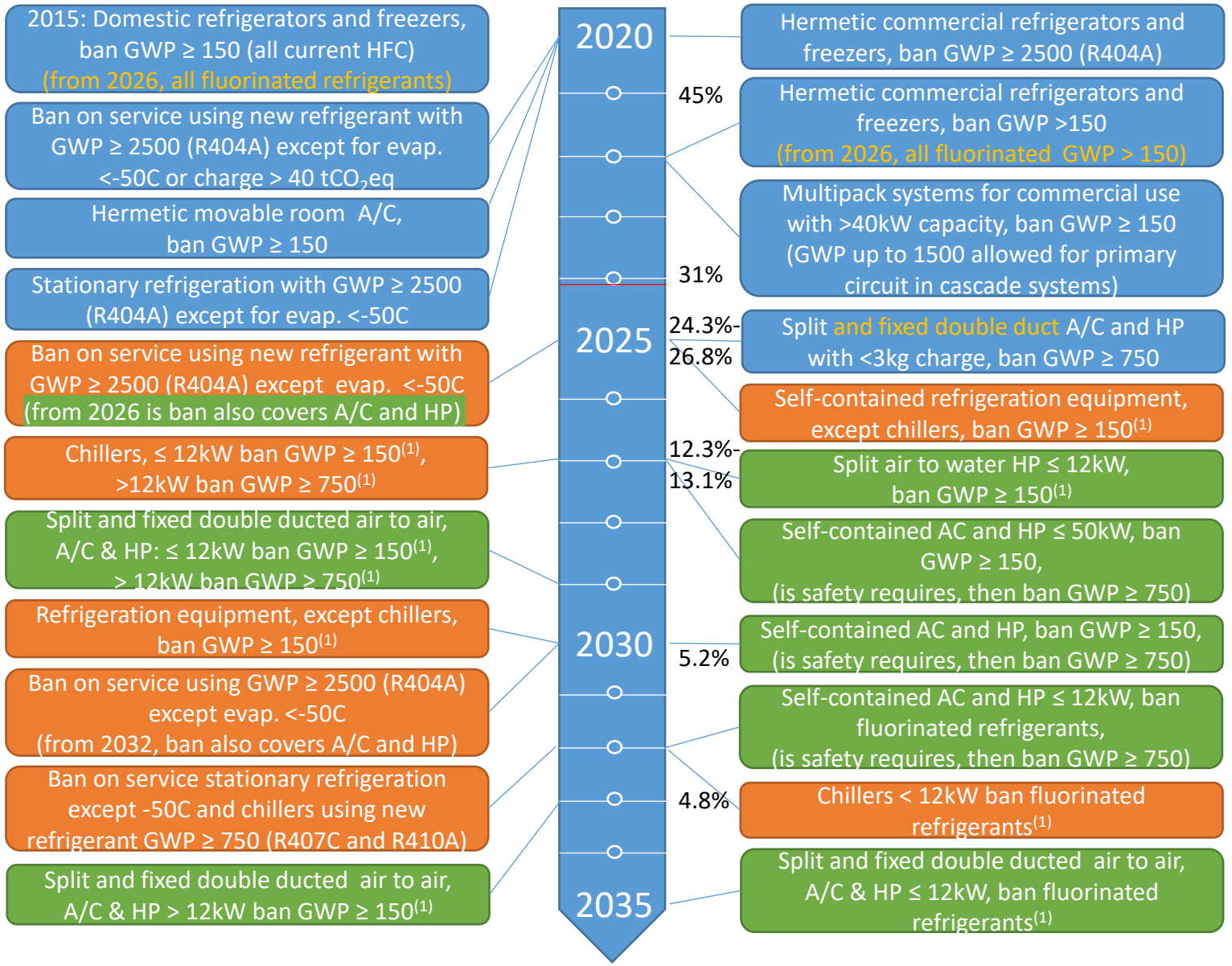
Dispensations are possible

Chillers are defined as having cooling as the primary function as opposed to heat pumps.

Footnote (1): Except where safety requires higher GWP , but unclear how to prove this.

EU F-gas regulation bans - HP

Bans



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Dispensations are possible

Chillers are defined as having cooling as the primary function as opposed to heat pumps.

Footnote (1): Except where safety requires higher GWP , but unclear how to prove this.

Export bans

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- From spring 2025 (one year after coming into force) systems cannot be exported if they are covered by a ban in EU.
- Could have significant impact on export to countries with strong legislation.
- Can spark EU producers to move some production out of EU

New GWP values

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- The GWP values for natural refrigerants and HFO/HCFO’s have been lowered, and more fluids added.
- This impacts blends containing HFO’s
- Example, R454B: Current GWP is 466.3, new GWP is 465.2

Impact:

- Effect is too small to impact bans or amount of quota on the market
- Labels on new equipment needs to be updated from Jan 1st 2025. There is no official transition period, but it is probably better to be a bit too late than too early, since the new GWP values are lower.

Quota is based on CO_2 equivalents

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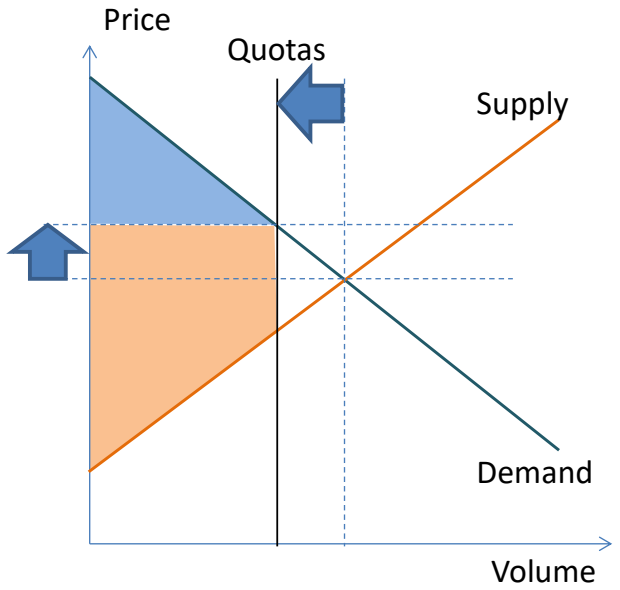
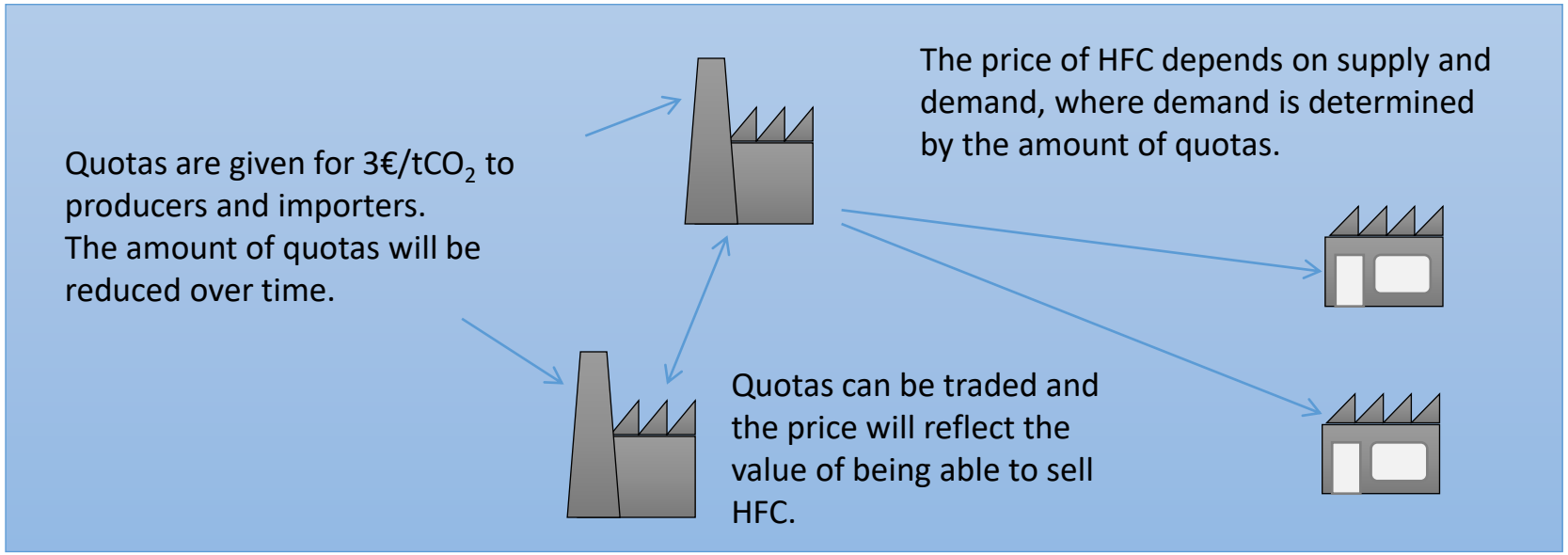
- With 1000 tCO2eq quota, you can e.g. chose between importing:
  - 479 kg of R-410A (GWP 2087.5)
  - 563 kg of R-407C (GWP 1773.9)
  - 699 kg of R-134a (GWP 1430)
  - 1481 kg of R-32 (GWP 675)
  - 6798 kg og R-479A (GWP 147,1)

Quota System -> Price Increases on HFC

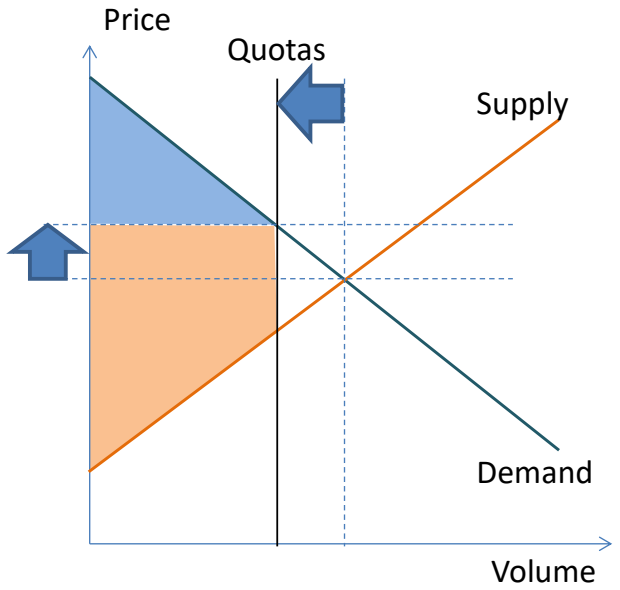
- Phase-down is controlled by a quota system
- The quota system gives falling supply of HFC
- Unless demand falls equally rapidly (and why would it) the price will go up

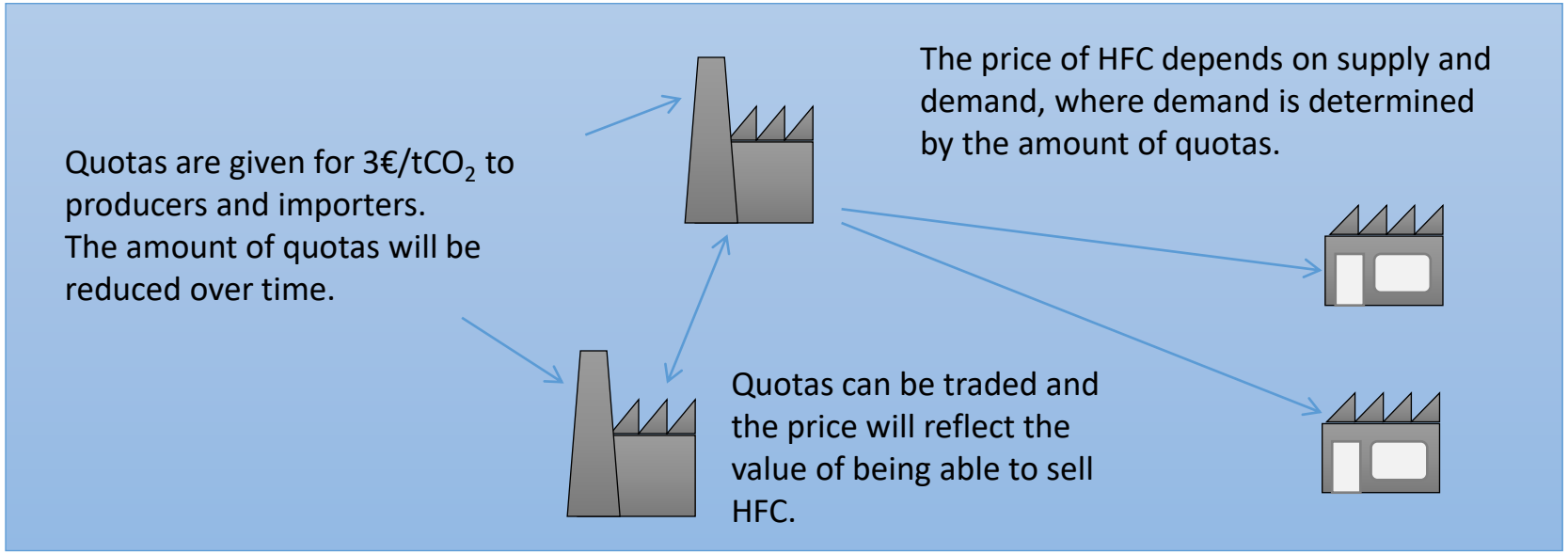




Quota System

- Quota is only for importing of bulk HFC containing refrigerant
  - Not systems containing HFCs
  - Not PFC's or HFO's
- Quota are specific for a given calendar year
- Unused quota is lost at the end of the year





Regular leak checks, I

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Currently:

- Leak check required for more than 5 tCO_2eq
- Hermetic systems: 10 tCO_2eq

New F-Gas:

- Leak check required for
  - more than 5 tCO_2eq, or
  - more than 1 kg of HFO/HCFO
- Hermetic systems:
  - more than 10 tCO_2eq, or
  - more than 2 kg of HFO/HCFO
  - except residential < 3 kg
- Also applicable for mobile applications

Frequency:

- 5 tCO_2eq or 1 kg HFO → every 12 months
- 50 tCO_2eq or 10 kg HFO → every 6 months
- 500 tCO_2eq or 100 kg HFO → every 3 months
- Leak detection system → double interval

National regulations can place additional requirements

Regular leak checks, II

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The limit to kg of HFO's complicates requirements:

Refrigerant	Composition	Boiling point	F-Gas GWP	Limit in kg for regular systems		Limit in kg for hermetic systems	
				1 kg HFO	5 tCO_2eq	2 kg HFO	10 tCO_2eq
134a, A1	CH2FCF3	–26	1430		3,5		7
404A, A1	R-125/143a/134a (44.0/52.0/4.0)	–46,6/–45,8	3921,6		1,27		2,5
407C, A1	R-32/125/134a (23.0/25.0/52.0)	–43,8/–36,7	1773,9		2,82		5,6
410A, A1	R-32/125 (50.0/50.0)	–51,6/–51,5	2087,5		2,4		4,8
448A, A1	R-32/125/1234yf/134a/1234ze(E) (26.0/26.0/20.0/21.0/7.0)	–45,9/–39,8	1386	3,7	3,61	7,4	7,2
449A, A1	R-32/125/1234yf/134a (24.3/24.7/25.3/25.7)	–46,0/–39,9	1396,2	3,95	3,58	7,9	7,2
452A, A1	R-32/125/1234yf (11,0/59,0/30,0)	–47,0/–43,2	2139,4	3,33	2,34	6,7	4,7
452B, A2L	R-32/125/1234yf (67.0/7.0/26.0)	–51,0/–50,3	697,4	3,85	7,17	7,7	14,3
454A, A2L	R-32/1234yf (35.0/65.0)	–48,4/–41,6	236,6	1,54	21,1	3,1	42,3
454C, A2L	R-32/1234yf (21.5/78.5)	–46,0/–37,8	145,5	1,27	34,4	2,5	68,7
455A, A2L	R-744/32/1234yf (3.0/21.5/75.5)	–51,6/–39,1	145,5	1,32	34,4	2,6	68,7
507A, A1	R-125/143a (50.0/50.0)	–47,1/–47,1	3985		1,25		2,51
513A, A1	R-1234yf/134a (56/44)	–29,2/–29,1	629,5	1,79	7,9	3,6	15,9

PFAS proposal

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Denmark, Norway, Sweden, Germany, and Netherlands have proposed a ban on all PFAS, including refrigerants. E.g.:

- PFAS in this proposal is defined as:

  CF3-X or X-CF2-X', without any H/Cl/Br/I attached to it

  EXCEPT where X = -OR or -NRR' and X' = methyl (-CH3), methylene (-CH2-), an aromatic group, a carbonyl group (-C(O)-), -OR'', -SR'' or –NR''R''', and where R/R'/R''/R''' is a hydrogen (-H), methyl (-CH3), methylene (-CH2-), an aromatic group or a carbonyl group (-C(O)-).
- Including R125, R143a, R134a: Components of R404A, R407C, R410A etc.
- Including R1234yf, R1234ze(E), R1224yd(Z), R1233zd(E), R1336mzz(Z): Components of all the new A2L refrigerants.
- Not including R-23, R-32, R-11xx series.

Exception from ban:

- refrigerants in HVACR-equipment in buildings where national safety standards and building codes prohibit the use of alternatives.
- 1.5 year postponement of ban for service of existing equipment, or 13.5 year if no drop-in refrigerant exists.
- 6.5 year postponement of ban for < -50 °C.
- 13.5 year postponement of ban for laboratory equipment

This is still only a proposal.

- Expect large changes to the proposal, and at least a couple of years before a final law is in place.
- 40 documents approx. 80 pages each with comments from industry is available on the EU web-site (consultation ends on 25th of September)
- Expect restrictions of refrigerants to be at least a couple of years later

https://echa.europa.eu/it/registry-of-restriction-intentions/-/dislist/details/0b0236e18663449b

REACH Process for PFAS proposal

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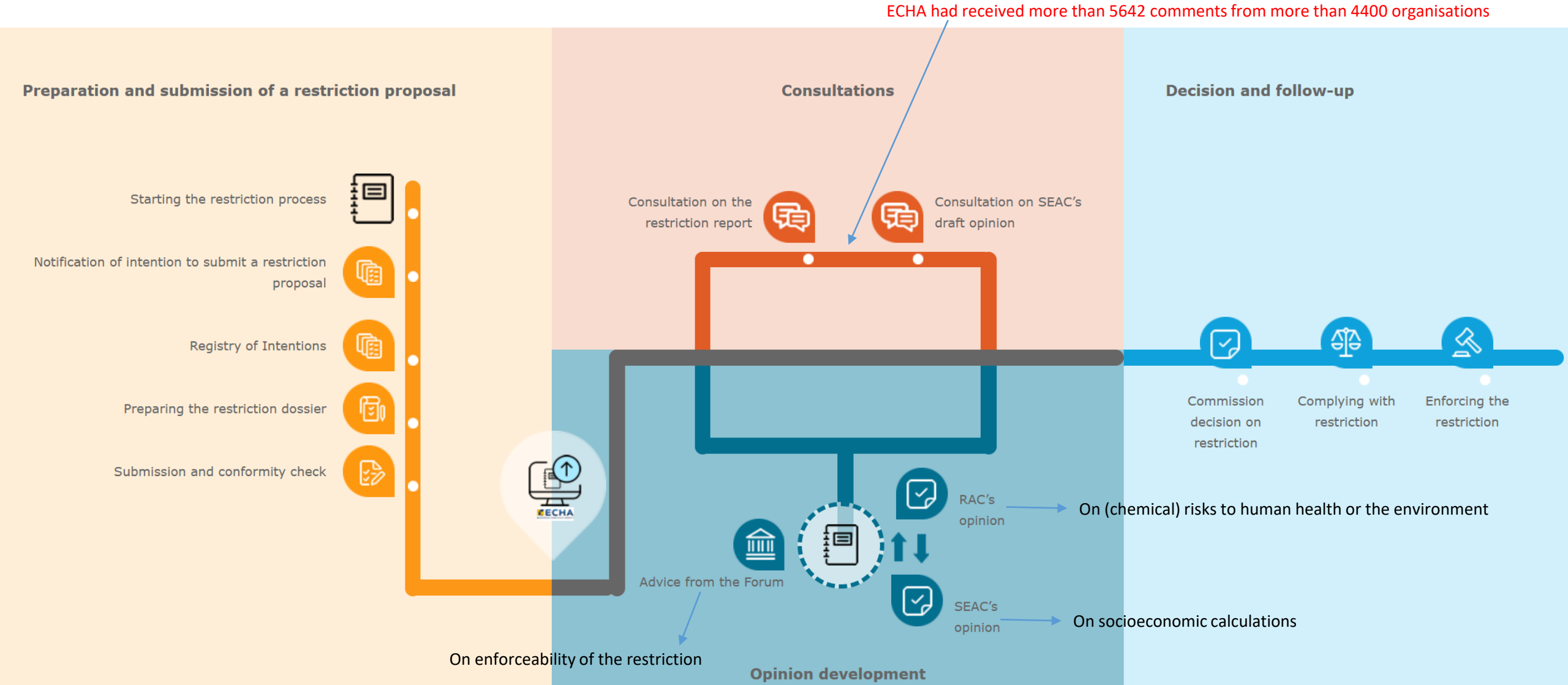

New refrigerants

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Year	Refrigerant
2009	**1234yf**, 433B, 433C, 438A.
2010	407F, 417B.
2011	439A, 440A, 441A, **1234ze(E)**, 511A.
2012	512A, 442A, 443A.
2013	**444A**, 417C, **445A**, 419B, 422E.
2014	**1233zd(E)**, **446A**, **447A**, **448A**, **449A**, **450A**, **444B**.
2015	**451A**, **451B**, **513A**, **452A**, 453A, **1336mzz(Z)**, **449B**, **454A**, **454B**.
2016	407G, **455A**, **513B**, **454C**, **449C**, **1130(E)**, **514A**, **515A**, **447B**, **452B**, **456A**, **457A**, **452C**, 458A.
2017	**459A**, **459B**, **460A**, **460B**, 407H, 461A, **516A**, **1224yd(Z)**, 462A, **1132a**.
2018	**463A**, **460C**, **464A**, 407I, **465A**, 436C.
2019	**1336mzz(E)**, 13I1, 427B, 466A, 467A, **468A**, 469A, **470A**, **515B**.
2020	470B, **471A**, 472A, **457B**.
2021	**473A**, **448B**, 427C, **475A**, 472B, **468B**, **468C**.
2022	**457C**, **474A**, **476A**, 477A, 477B.
2023	**455B**, **457D**, **474B**, **478A**, **479A**, **480A**, **481A**, **482A**, 483A, 484A, **485A**, **486A**, 487A, **488A**, 489A
2024	**454C**, **455C**. Expected soon: **475B**, 490A, **491A**, **492A**

Key:
A1 **B1**
A2L
A2 **B2**
A3

TFA - Trifluoroacetic acid

Most synthetic low GWP refrigerants contain R-1234yf

R-404A is 52% R-143a

- TFA is causing concern as a break down product of several refrigerants (and insecticides), especially HFO-1234yf
- TFA is a very strong acid, highly soluble in water, but with relatively low toxicity
- There are no known break-down processes of TFA in nature
- TFA can accumulate in soil, plants, and fresh water, and has been found in ground water (e.g. Denmark & Germany)
- TFA is occurring naturally in the oceans, but not in fresh water
- TFA is generated locally from HFO's
- TFA from refrigerants is **not currently** considered to be a problem…

Refrigerant	Fraction that becomes TFA	Source of data
R-134a	21%	Solomon K, Velders G, Wilson S, Madronich S, Longstreth J, Aucamp P, Bornman J., "Sources, fates, toxicity, and risks of trifluoroacetic acid and its salts: Relevance to substances regulated under the Montreal and Kyoto protocols". Journal of Toxicology and Environmental Health B, 2016.
R-143a	100%	
R-1234yf	100%	
R-1234ze(E)	Less than 10%	Javadi MS, Søndergaard R, Nielsen OJ, Hurley M, Wallington T., "Atmospheric chemistry of trans-$CF_3CH=CHF$: Products and mechanisms of hydroxyl radical and chlorine atom initiated oxidation. Atmos Chem Phys 8:3141-3147", 2008.
	0%	T.J. Wallington, M.P. Sulbaek Andersen, O.J. Nielsen, "Atmospheric chemistry of short-chain haloolefins: Photochemical ozone creation potentials (POCPs), global warming potentials (GWPs), and ozone depletion potentials (ODPs)", Chemosphere 129 (2015) 135–141, 2015 *
R-1233zd(E)	0%	
R-1233zd(Z)	0%	
R-32	0%	Due to chemical composition

*TFA production is not the primary topic of the Wallington, 2015 paper, and it gives no references or arguments as to where this data comes from.

TFA from commonly used refrigerants

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Refrigerant	Composition	Boiling point	F-Gas GWP	TFA w/w
134a, A1	CH2FCF3	–26	1430	0,22
404A, A1	R-125/143a/134a (44.0/52.0/4.0)	–46,6/–45,8	3921,6	0,03
407C, A1	R-32/125/134a (23.0/25.0/52.0)	–43,8/–36,7	1773,9	0,12
410A, A1	R-32/125 (50.0/50.0)	–51,6/–51,5	2087,5	0,01
448A, A1	R-32/125/1234yf/134a/1234ze(E) (26.0/26.0/20.0/21.0/7.0)	–45,9/–39,8	1386	0,25
449A, A1	R-32/125/1234yf/134a (24.3/24.7/25.3/25.7)	–46,0/–39,9	1396,2	0,32
452A, A1	R-32/125/1234yf (11,0/59,0/30,0)	–47,0/–43,2	2139,4	0,31
452B, A2L	R-32/125/1234yf (67.0/7.0/26.0)	–51,0/–50,3	697,4	0,26
454A, A2L	R-32/1234yf (35.0/65.0)	–48,4/–41,6	236,6	0,65
454C, A2L	R-32/1234yf (21.5/78.5)	–46,0/–37,8	145,5	0,78
455A, A2L	R-744/32/1234yf (3.0/21.5/75.5)	–51,6/–39,1	145,5	0,75
507A, A1	R-125/143a (50.0/50.0)	–47,1/–47,1	3985	0,02
513A, A1	R-1234yf/134a (56/44)	–29,2/–29,1	629,5	0,66

Source for TFA yield: https://ozone.unep.org/system/files/documents/EEAP-2022-Assessment-Report-May2023.pdf

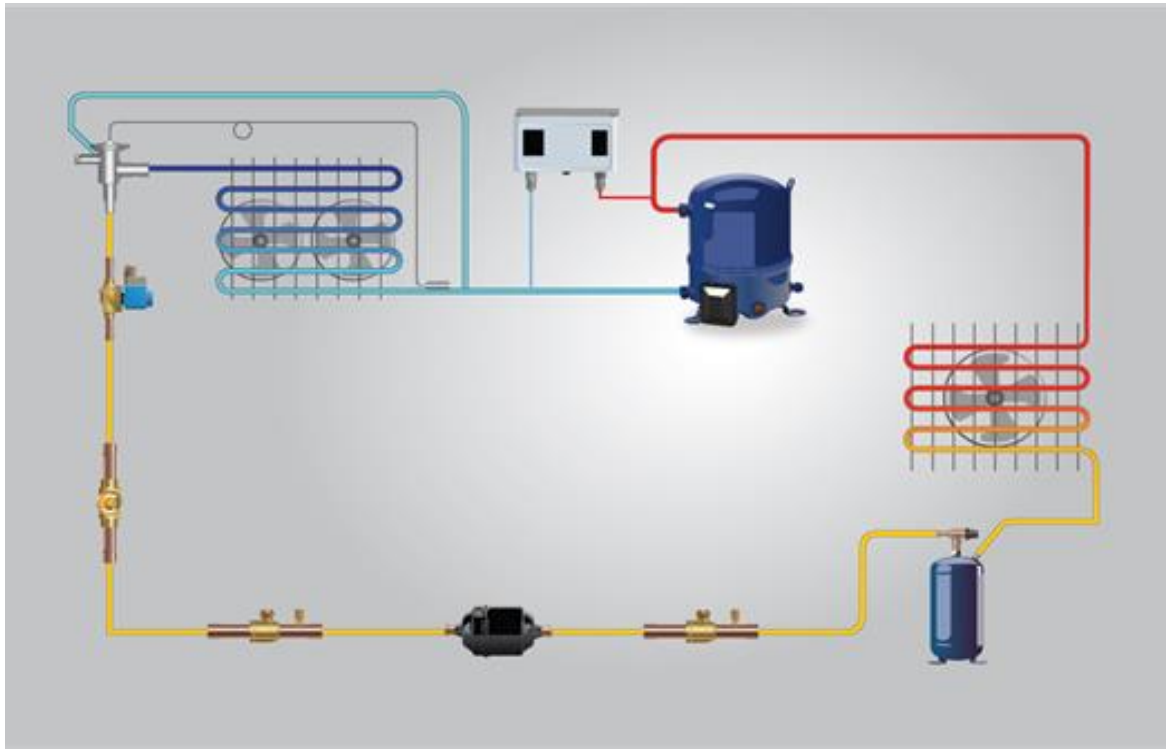
TFA from halogenated refrigerants with GWP < 150

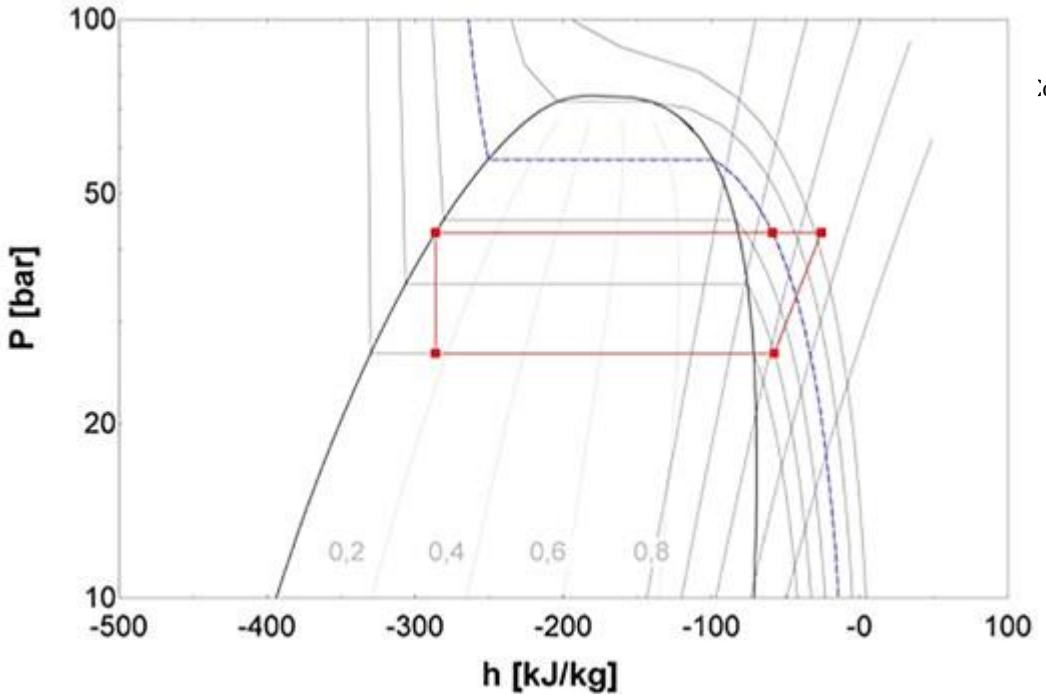
Refrigerant	Composition	Boiling point	F-Gas GWP	TFA w/w
(HFO-1123, A2L)	CHF=CF2	–59		0
HFO-1234yf, A2L	CF3CF=CH2	–29.4	0,501	1,00
HFO-1234ze(E), A2L	CF3CH=CHF	–19.0	1,37	0,02
R-444A, A2L	R-32/152a/1234ze(E) (12.0/5.0/83.0)	–34.3/–24.3	88,3	0,02
R-445A, A2L	R-744/134a/1234ze(E) (6.0/9.0/85.0)	–50.3/–23.5	129,9	0,04
R-451A, A2L	R-1234yf/134a (89.8/10.2)	–30.8/–30.5	146,3	0,92
R-454C, A2L	R-32/1234yf (21.5/78.5)	–46.0/–37.8	145,5	0,78
R-455A, A2L	R-744/32/1234yf (3.0/21.5/75.5)	–51.6/–39.1	145,5	0,75
R-457A, A2L	R-32/1234yf/152a (18.0/70.0/12.0)	–42.7/–35.5	136,7	0,70
R-457C, A2L	R-32/1234yf/152a (7.5/78.0/14.5)	–37.3/–32.1	69,0	0,78
R-457D, A2L	R-32/1234yf/152a (4.0/82.0/14.0)	–34.5/–31.0	44,8	0,82
R-459B, A2L	R-32/1234yf/1234ze(E) (21.0/69.0/10.0)	–44.0/–36.1	142,2	0,69
R-465A, A2	R-32/290/1234yf (21.0/7.9/71.1)	–51,8/–40,0	142,1	0,71
R-468A, A2L	R-1132a/32/1234yf (3.5/21.5/75.0)	–51.3/–39.0	145,5	0,75
R-468B, A2L	R-1132a/32/1234yf (6.0/13.0/81.0)	–52.4/–36.8	88,2	0,81
R-471A, **A1**	R-1234ze(E)/227ea/1336mzz(E) (78.7/4.3/17.0)	–16,9/–13,8	142,6	0,04
R-474A, A2L	R-1132(E)/1234yf (23.0/77.0)	–43.1/–36.4	0,6	0,77
R-474B , A2L	R-1132(E)/1234yf (31.5/68.5)	–45.8/–38.4	0,7	0,68
(R-475B, A2L)	R-1234yf/134a/1234ze(E) (35.4/10.1/54.5)	–26.3/–25.5	145,4	0,39
R-476A, **A1**	R-134a/1234ze(E)/1336mzz(E) (10.0/78.0/12.0)	–19,1/–16,1	146,2	0,04
R-479A, A2L	R-32/1132(E)/1234yf (21.5/28.0/50.5)	–50.4/–44.7	145,7	0,50
R-482A, **A1**	R-134a/1234ze(E)/1224yd(Z) (10.0/83.5/6.5)	–19.6/–17.0	144,1	0,04
R-485A, **A1**/A2L	R-1132a/744/32 (10.0/69.0/21.0)	–81.6/–71.4	141,8	0
R-486A , **A1**	R-1234yf/134a/13I1/1234ze(E) (21.9/6.3/38.0/33.8)	–25.7/–24.9	90,7	0,24
R-488A , A2L	R-32/1234yf/152a/1234ze(E) (6.0/50.0/3.0/41.0)	–35.1/–28.0	45,0	0,51
(R-492A, A2/A2L)	R-1132a/32/152a/1234ze(E) (12.0/18.0/14.0/56.0)	–58.1/–31.1	139,6	0,01
R-516A, A2L	R-1234yf/134a/152a (77.5/8.5/14.0)	–29.4	142	0,79
(A2L)	R-1123/1234yf (32.0/68.0)	–46.3/–37.3	0,3	0,68
(A2L)	R-1123/R-32/R-1234yf (40.0/21.5/38.5)	–55.1/–47.6	145,3	0,38

Toxic refrigerants and refrigerants with boiling point above 0° C not included.

Minimise design changes

Picture from Danfoss





To minimize design changes when changing refrigerants, it is preferable if the new refrigerant has the same:

- Pressure at relevant temperatures
- Evaporation energy at relevant temperatures

A quick screening technique is to look at the boiling point.

Vonsild Consulting