Refrigerants for Low GWP HVAC&R

Prof.S.SRINIVASA MURTHY
Renewable & Clean Energy Technologies
Interdisciplinary Center for Energy Research
INDIAN INSTITUTE OF SCIENCE
BANGALORE-560012 (INDIA)

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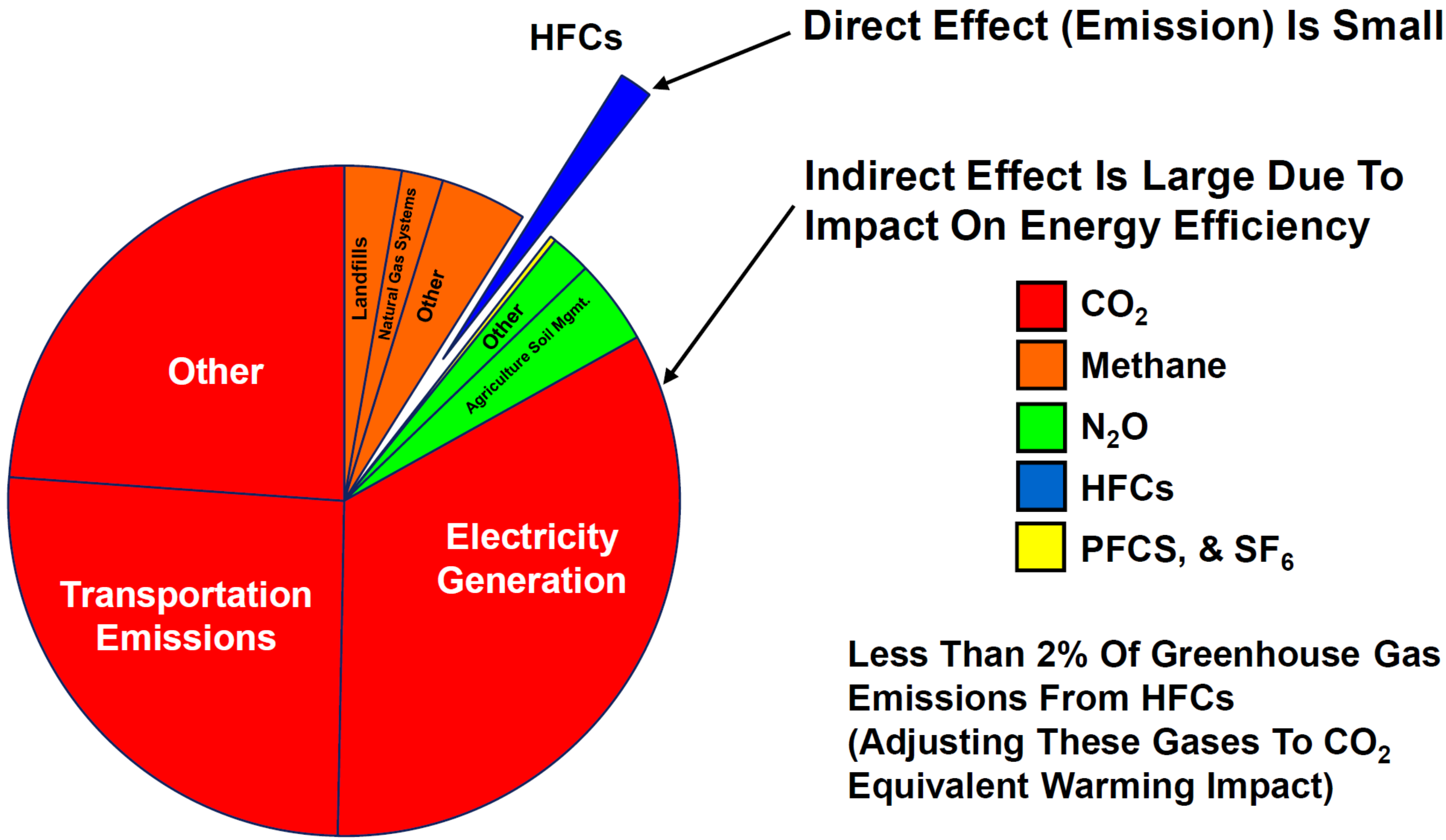
THE GLOBAL WARMING EFFECT

- **Briefly, two types of global warming effects are envisaged with reference to HVAC&R systems:-**
  - **First is the direct GWP that is due to the emission / leakage of refrigerants. Type and charge quantity.**
  - **Second is indirect GWP resulting from the equivalent CO2 emission due to the energy consumption by the HVAC&R equipment during its life-time. (May also includes energy for manufacturing). TEWI.**

- **Efforts should be made to reduce both these interrelated components of GWP.**

- **It is important to note that in a typical HVAC&R plant, about 90% of GWP contribution can come from the energy use.**

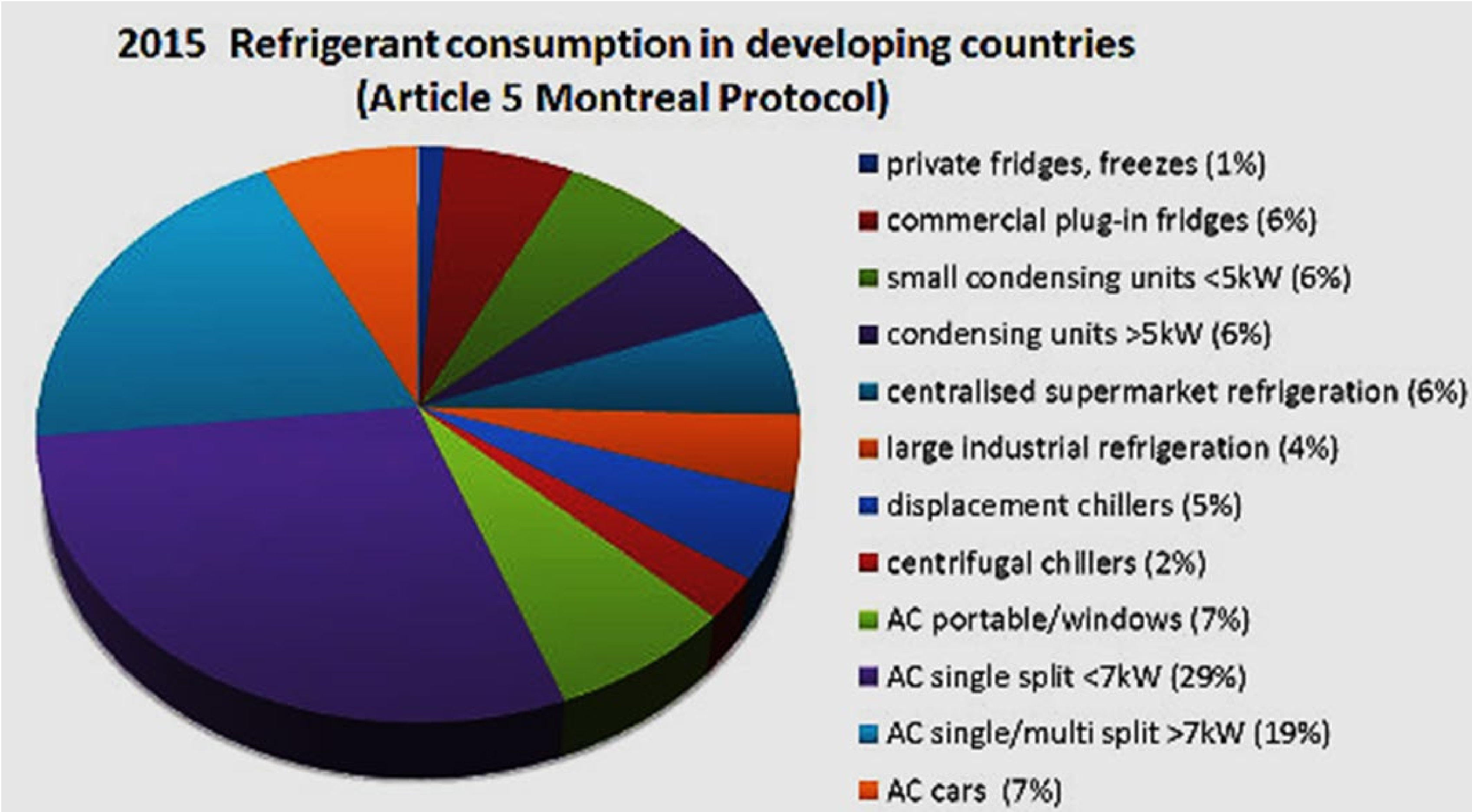


Less Than 2% Of Greenhouse Gas Emissions From HFCs (Adjusting These Gases To CO_2 Equivalent Warming Impact)

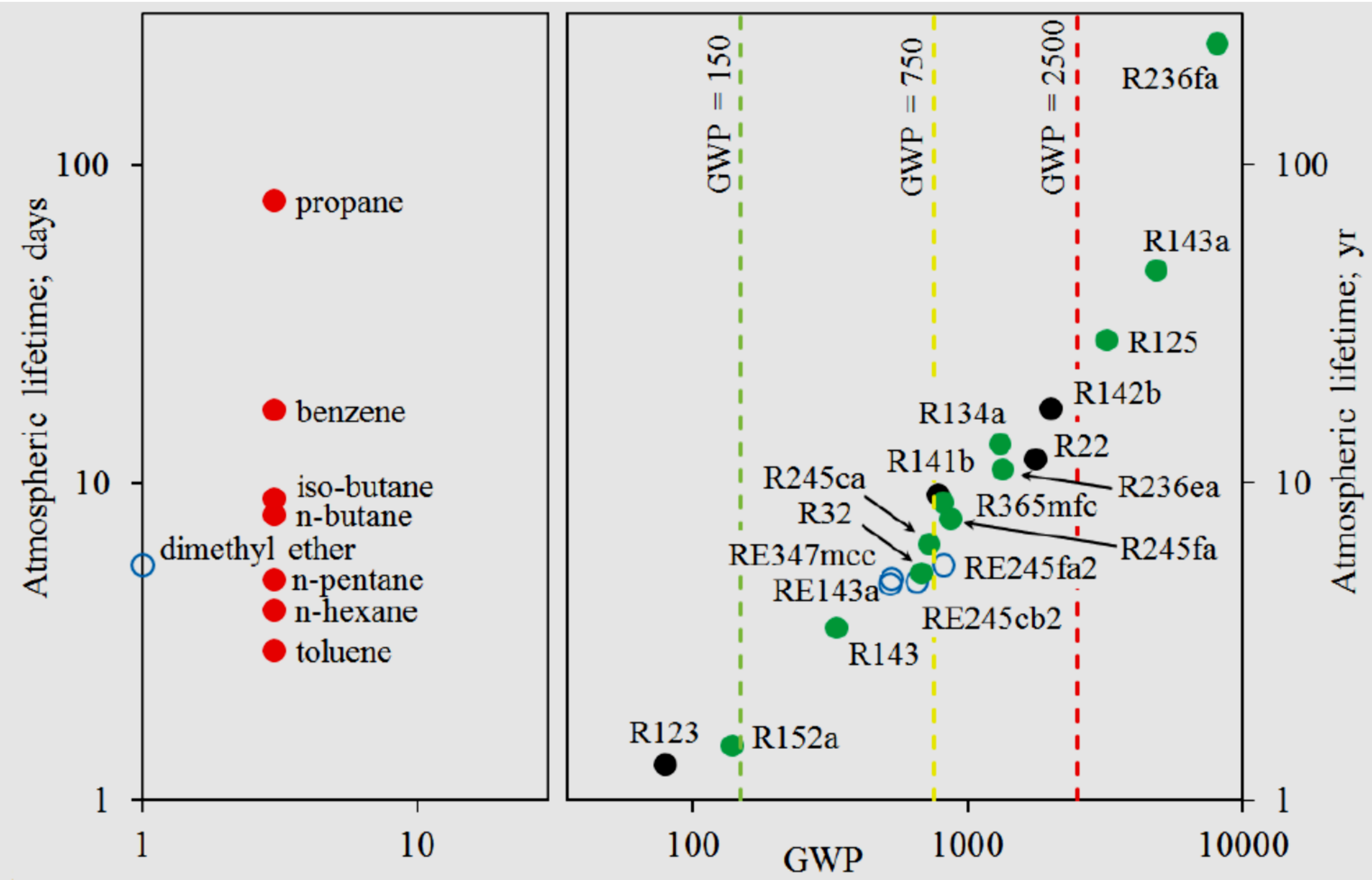
Source: Environmental Protection Agency, U.S. Greenhouse Gas Emissions & Sinks: 1990-2002

10% Of Global Carbon Emissions (And Energy Use) Due To Refrigeration, A/C And Heat Pumps

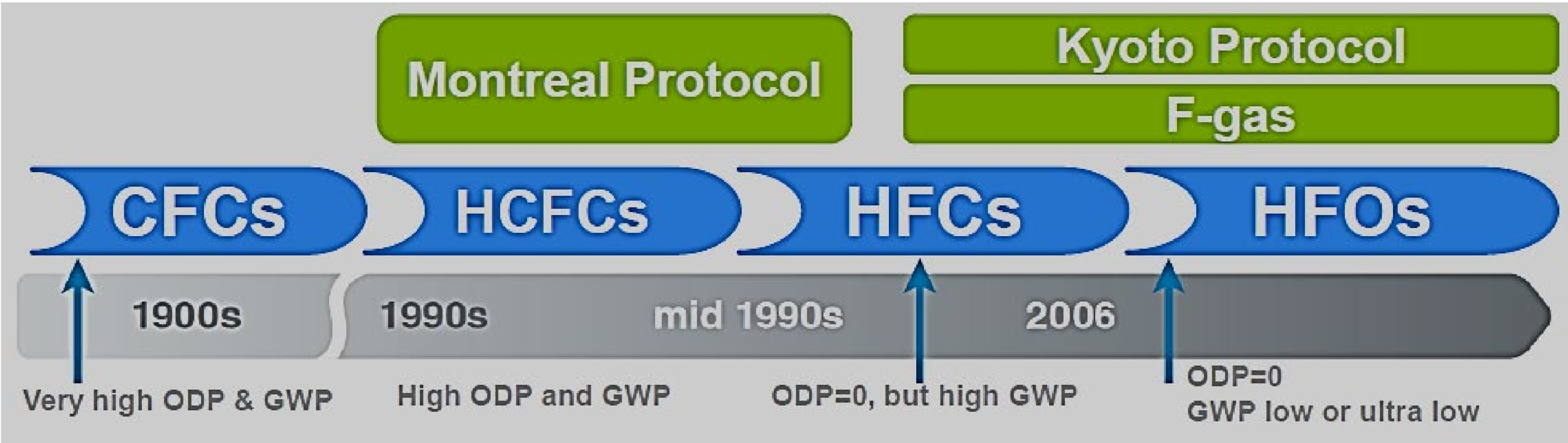
Effect Of HFCs On Global Warming



Today most of the HFCs are used in refrigeration and air conditioning equipment. In Article 5 countries under the Montreal Protocol, R22 (an HCFC) is still being used in this sector. Demand for refrigerants is expected to increase significantly in the short to medium term, especially to satisfy expected growth in the use of AC and supermarket refrigeration.



Atmospheric lifetime; days
Atmospheric lifetime; yr
GWP
GWP = 150
GWP = 750
GWP = 2500
100
10
1
10000
propane
benzene
iso-butane
n-butane
dimethyl ether
n-pentane
n-hexane
toluene
R236fa
R143a
R125
R142b
R134a
R22
R141b
R236ea
R245ca
R365mfc
R32
R245fa
RE347mcc
RE245fa2
RE143a
RE245cb2
R143
R123
R152a



Today, hydro-fluorocarbon (HFC) refrigerants such as R134A, R410A, R407C with zero ODP have been the leading replacement for CFC and HCFC refrigerants in HVAC&R systems.

HOWEVER, INTERNATIONAL CONCERN OVER HIGH GWPS OF HFCS HAS NECESSITATED TO PHASE THEM OUT.

Hydro-Fluoro-Olefins (HFOs) are relatively unstable, have a small atmospheric lifetime and therefore a small GWP.

R1234yf and R1234ze are two recent HFOs.

R1234yf has been widely accepted for use in cars by the automobile industry because of its very low GWP of 4. It is expected to replace R134a, which is currently being widely used in air-conditioning plants, automobile air conditioners, domestic refrigerators, etc……

In spite of some differences in energy parameters, several HFOs and their mixtures such as R1234yf, L40, DR-5 and R444B can be good alternatives to R134a, R404A, R410A and R22, respectively.

- **Hydrocarbons (HC) are the refrigerants favoured in many European countries.**
- **Propane (R290), n-butane (R600) and iso-butane (R600a) and their mixtures are the leading candidates.**
- **At the height of implementation of Montreal Protocol, several HC based domestic refrigerators came in to the Indian Market.**
- **There is need to extend HCs in to unitary refrigeration, airconditioning and heat pump systems replacing HFCs.**

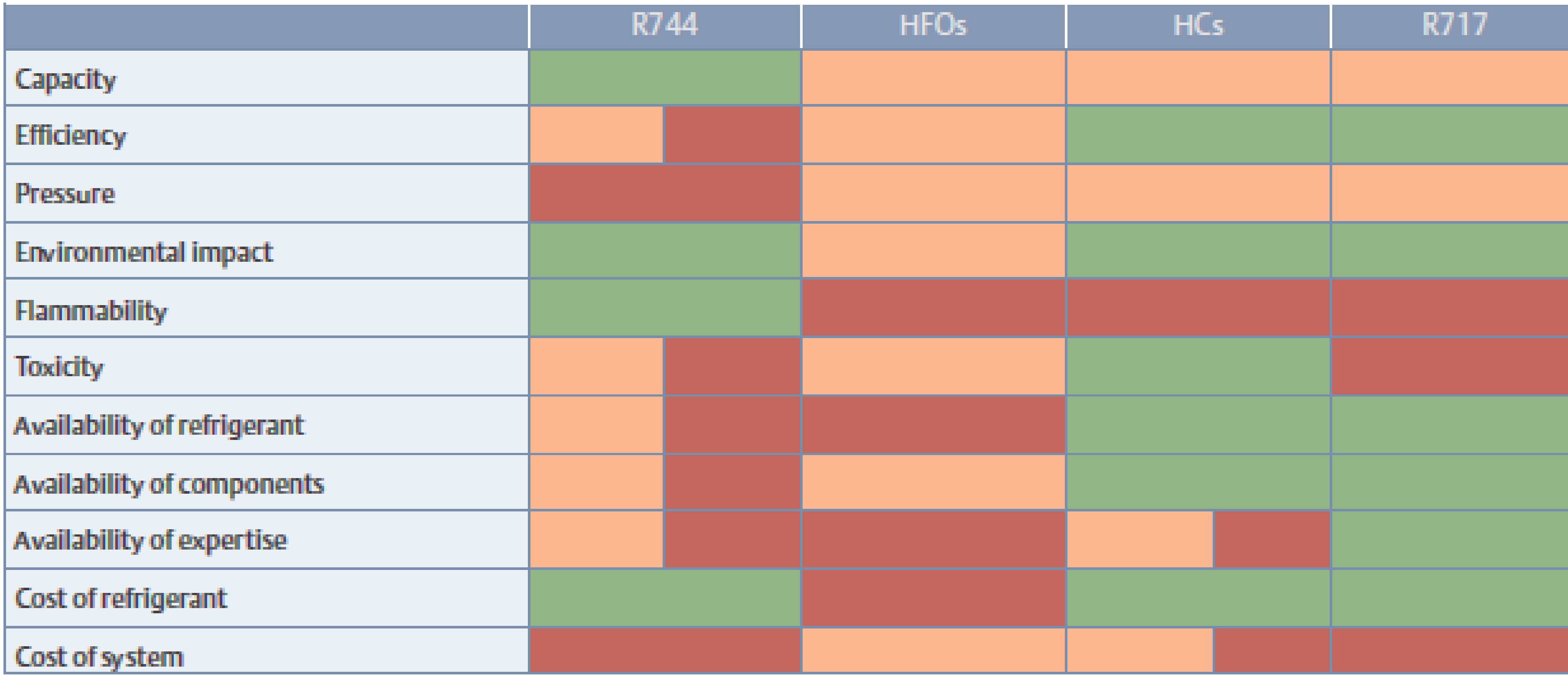
- **Ammonia** based systems, well known for 120 years need widespread application; including airconditioning through district cooling route.
- While toxicity (beyond 2500 ppm) is an issue, noticeable smell even at 5 ppm can cause panic.

- **Carbon dioxide** as a refrigerant is feasible as it is nontoxic, nonflammable and cheap.
- High operating pressure of CO_2 systems is an issue.
- Trans-critical systems in cascade mode need to be developed.

The most commonly used alternatives to HFCs and HCFCs and their characteristics are listed in the table below.

Alternative	Global Warming Potential (GWP)	Properties to be addressed	Commercial availability
Hydrocarbons	3-5	Flammable	Immediate
CO_2 (R744)	1	High pressure	Immediate
Ammonia (NH3, R717)	1	Toxic	Immediate
Water (R718)	1	No risks	Immediate
R32 (an HFC)	675	Mildly flammable	Immediate
HFOs	4-9	Mildly flammable	Immediate/ Short-term
R32-HFO blends	200-400	Mildly flammable	Mid-term

When seeking alternatives to HFCs and HCFCs in specific applications, it is the total greenhouse gas emissions linked to the use that counts. Hence, suitable climate-friendly alternatives must show sufficiently high energy efficiency so that the reduction in direct emissions from the alternatives to HFCs and HCFCs is not offset by higher indirect emissions from energy use.



Refrigerant is similar to HFCs;

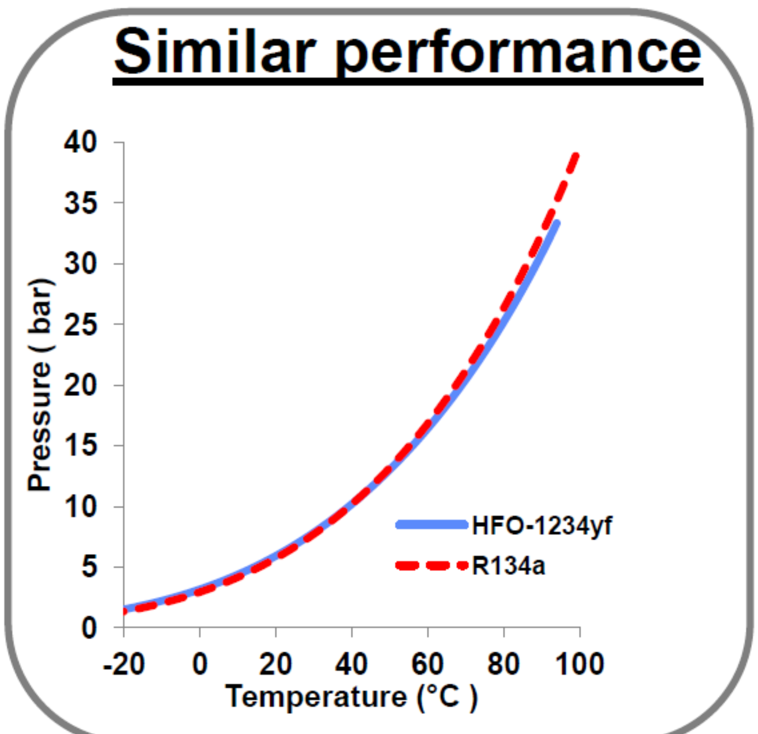
Aspect of the refrigerant is worse than HFCs;

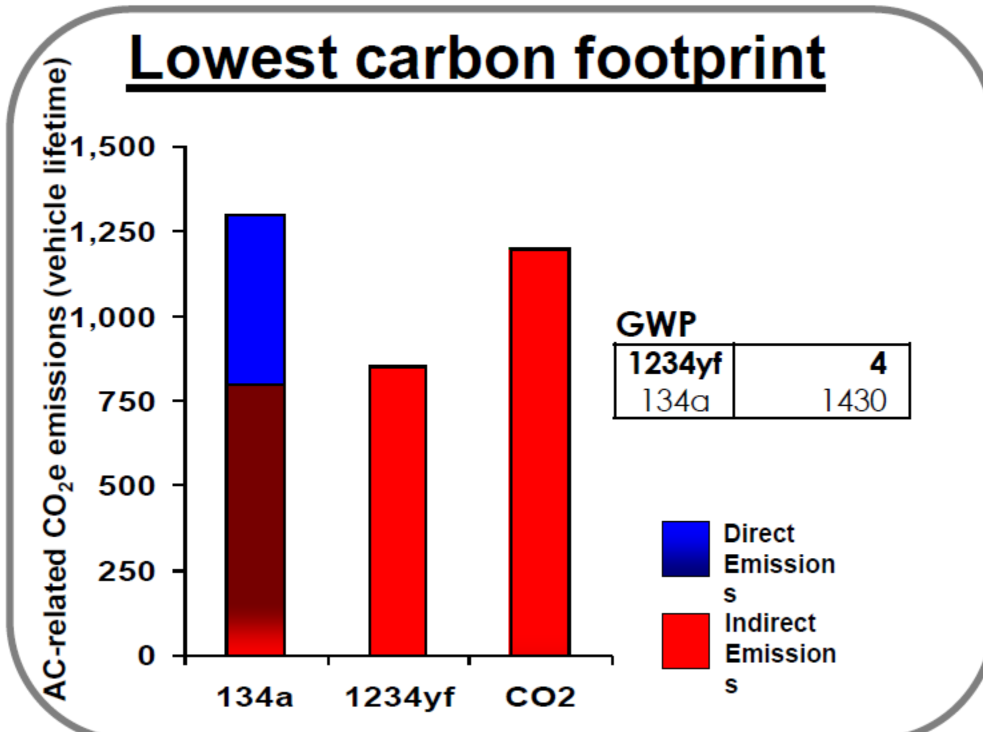
Aspect of the refrigerant is better than HFCs.

HFO: Hydro Fluoro Olefin, e.g., R1234yf
HC: Hydro Carbon, e.g., R290
R717: Ammonia

Flammability	Safety code	
	Lower toxicity	Higher toxicity
higher flammability	A2	B2
lower flammability	A2L	B2L
no flame propagation	A1	B1

Property	R1234yf	R134a
Chemical formula	$CF_3CF{=}CH_2$	$C_2H_2F_4$
Boiling point, t_{0n} [°C]	−29	−26
Critical temperature t_{cr} [°C]	95	102
Liquid density, ρ_l at 25 °C [kg m^3]	1094	1207
Vapour density, ρ_v at 25 °C [kg m^3]	37.6	32.4
ODP	0	0
GWP	4	1300





The future lies with REFRIGERANT MIXTURES having low environmental impacts with high energy efficiency.

HFO mixtures:

This represents a very promising research and development area and may hold a solution for selection of alternative refrigerants in the future.

There are attempts to find mixtures of R1234yf and other HFCs such as R32 for use in other applications such as domestic air conditioners since mixtures containing R1234yf will have low GWP, typically less than 1000.

***Carbon dioxide-based mixtures*:**

Major drawbacks of CO2 are its high critical pressure with lower critical temperature and lower cycle efficiency.

Owing to its lower critical temperature, CO2 can be operated with trans-critical cycle.

To overcome the drawbacks, CO2 can be blended with other refrigerants to improve the performances.

Cascade refrigerating systems working with blends of CO2 and HFC mixtures such as R744/RR41, R744/R32, R744/R23 and R744/R125 as working fluids in low temperature circuit are possible.

Ammonia-based mixtures:

NH3-based azeotropic mixture (R717/R170) has been reported to have lower compressor discharge temperature, which favours system reliability and improves the cycle efficiency.

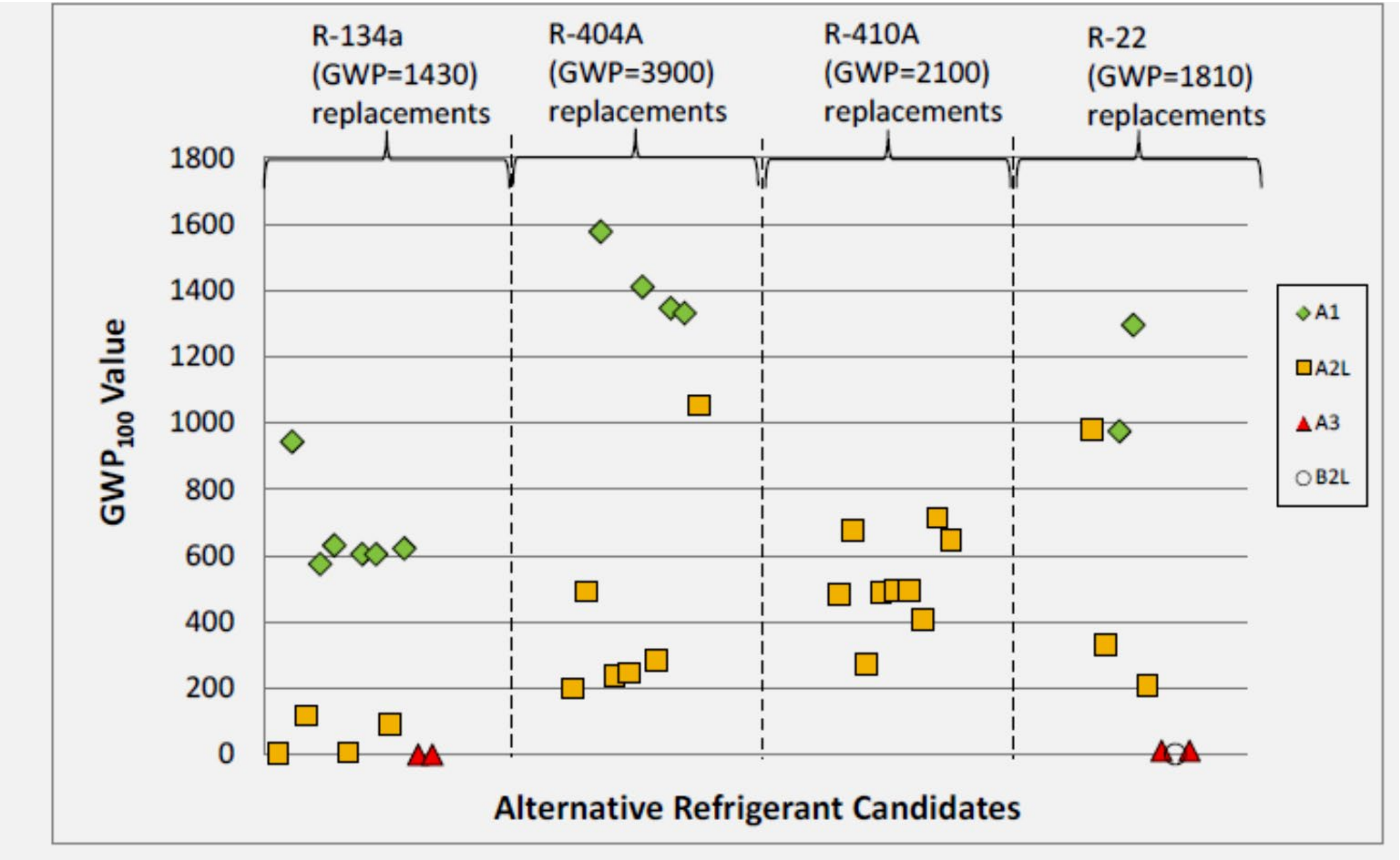
The mixture has good miscibility with mineral oil, thereby reducing the usage of highly hygroscopic synthetic oils.

Baseline	Refrigerant	Composition	(Mass%)	Classification	GWP_{100}
R22	ARM-32a	R-32/R-125/R-134a/R-1234yf	(25/30/25/20)	A1*	1577
	LTR4X	R-32/R-125/R-134a/R-1234ze(E)	(28/25/16/31)	A1*	1295
	N20	R-32/R-125/R-134a/R-1234yf/R-1234ze(E)	(12.5/12.5/31.5/13.5/30)	A1*	975
	D52Y	R-32/R-125/R-1234yf	(15/25/60)	A2L*	979
	L20	R-32/R-152a/R-1234ze(E)	(45/20/35)	A2L*	331
	LTR6A	R-32/R-744/R-1234ze(E)	(30/7/63)	A2L*	206
	R290	R290	100	A3	<20
	R1270	R1270	100	A3	<20
	R717	R717	100	B2L	<1

Baseline	Refrigerant	Composition	(Mass%)	Classification	GWP_{100}
R-134a	AC5X	R-32/R-134a/R-1234ze(E)	(7/40/53)	A1*	622
	ARM-41a	R-32/R-134a/R-1234yf	(6/63/31)	A1*	943
	D-4Y	R-134a/R-1234yf	(40/60)	A1*	574
	N13a	R-134a/R-1234yf/R-1234ze(E)	(42/18/40)	A1*	604
	N13b	R-134a/R-1234ze(E)	(42/58)	A1*	604
	XP-10	R-134a/R-1234yf	(44/56)	A1*	631
	AC5	R-32/R-152a/R-1234ze(E)	(12/5/83)	A2L*	92
	ARM-42a	R-134a/R-152a/R-1234yf	(7/11/82)	A2L*	117
	R1234yf	R1234yf	100	A2L	4
	R1234ze	R1234ze	100	A2L	6
	R600a	R600a	100	A3	<20
	R290/R600a	R290/R600a	(40/60)	A3*	<20

Baseline	Refrigerant	Composition	(Mass%)	Classification	GWP_{100}
R404A	ARM-32a	R-32/R-125/R-134a/R-1234yf	(25/30/25/20)	A1*	1577
	DR-33	R-32/R-125/R-134a/R-1234yf	(24/25/26/25)	A1*	1410
	N40a	R-32/R-125/R-134a/R-1234yf/R-1234ze(E)	(25/25/21/9/20)	A1*	1346
	N40b	R-32/R-125/R-134a/R-1234yf	(25/25/20/30)	A1*	1331
	R744	R-744	100	A1	1
	ARM-30a	R-32/R-1234yf	(29/71)	A2L*	199
	ARM-31a	R-32/R-134a/R-1234yf	(28/21/51)	A2L*	491
	D2Y65	R-32/R-1234yf	(35/65)	A2L*	239
	DR-7	R-32/R-1234yf	(36/64)	A2L*	246
	L40	R-32/R-152a/R-1234yf/R-1234ze(E)	(40/10/20/30)	A2L*	285
	R-32	R-32	100	A2L	675
	R-32/R-134a	R-32/R-134a	(50/50)	A2L*	1053
	R290	R-290	100	A3	<20

Baseline	Refrigerant	Composition	(Mass%)	Classification	GWP_{100}
R410A	R-744	R-744	100	A1	1
	ARM-70a	R-32/R-134a/R-1234yf	(50/10/40)	A2L*	482
	D2Y60	R-32/R-1234yf	(40/60)	A2L*	272
	DR-5	R-32/R-1234yf	(72.5/27.5)	A2L*	490
	HPR1D	R-32/R-744/R-1234ze(E)	(60/6/34)	A2L*	407
	L41a	R-32/R-1234yf/R-1234ze(E)	(73/15/12)	A2L*	494
	L41b	R-32/R-1234ze(E)	(73/27)	A2L*	494
	R32	R32	100	A2L	675
	R32/R134a	R-32/R-134a	(95/5)	A2L*	713
	R32/R152a	R-32/R-152a	(95/5)	A2L*	647



Low-GWP Alternative Refrigerant Candidates

2014 study for the European Commission (https://ec.europa.eu/clima/index_en)

Suitable alternatives under high ambient temperatures generally faced in Article 5 Countries.

Icon	Description
	Energy efficiency too low or cost too high compared to other alternatives
	Energy efficient. Safe. But costly and no short term availability
	Energy efficiency high. No or acceptable additional cost. Short term availability

Domestic refrigeration

Hydrocarbon refrigerants have been used for many years in domestic refrigerators and freezers. Over 90% of new appliances nowadays contain hydrocarbon refrigerants. These appliances are very efficient also under high-ambient temperatures.

Global Situation	HC (direct)	HFO	R32	R32 -HFO blends
GWP	3	4	675	200 -400
Domestic Refrigeration				

Commercial refrigeration

Plug-in equipment used in small stores and supermarkets such as vending machines that rely on hydrocarbons and CO_2 have been available for some years throughout the world. In large supermarkets refrigeration ("centralized systems"), CO_2 cascade systems are an alternative to common HFC systems in cold and moderate climates. Hydrocarbons also have proven to be highly efficient alternatives in most applications under high-ambient temperatures, except for larger condensing units.

High-ambient temperatures	HC (DX or cascade)	HFO (DX or cascade)	R32-HFO blends
GWP	< 6	< 8	200-400
Stand-alone eq.	🟢	🟡	🔴
Cond. Units < 5kW	🟢	🔴	🟡
Cond. Units > 5kW	🔴	🟢	🟢
Centralised systems	🟢	🟢	🟡

Stationary air conditioning

Hydrocarbons are safely used in room air conditioning systems in several countries. For larger systems, pure R32 with a medium-high GWP can be employed. In chillers, the use of hydrocarbons and ammonia are safe and energy-efficient alternatives, both under moderate and high-ambient temperature conditions. Hydrofluoroolefins (HFOs) are already commercially available for use in very large (centrifugal) chillers.

	HC (direct)	HC (indirect)	HFO	R32	R32-HFO blends
GWP	3	3	< 10	675	200-400
Portable/Windows	🟢	🔴	🔴	🔴	🟡
Single Split < 7kW	🟢	🔴	🔴	🔴	🟡
Split/Multi. > 7kW	🔴	🔴	🔴	🟢	🟡

	HC	NH3	HFO	R32	R32-HFO blends
GWP	3	0	< 8	675	200-400
Chiller < 150kW	🟢	🔴	🔴	🔴	🟢
Chiller > 150 kW	🟢	🟢	🔴	🔴	🟢
Centrifugal	🔴	🔴	🟢	🔴	🔴

Industrial refrigeration

In industrial refrigeration such as large cooling facility for food processing, ammonia systems have been used for many years. High-ambient temperatures do not result in lower energy-efficiency of ammonia systems.

Global situation	HC	NH3	HFO	R32-HFO blends
GWP	< 6	0	< 8	200-400
Large industrial	🔴	🟢	🔴	🔴

Mobile air conditioning

The refrigerant HFC-134a used so far in air conditioning of cars is being substituted in new car models. Alternative refrigerant options include CO_2 and the HFO refrigerant R1234yf

Global	CO_2	HC (direct)	HFO	R32	R32-HFO blends
GWP	1	3	4	675	200-400
MAC	🟢	🔴	🟢	🔴	🔴

Limited options for low-global-warming-potential refrigerants

Screening based on various criteria with special attention to Unitary ACs

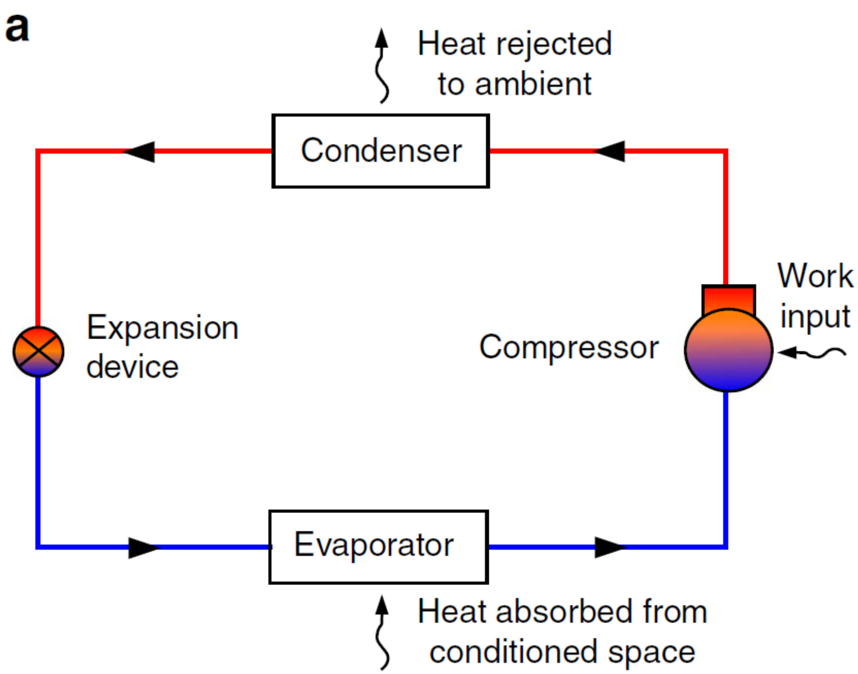
IUPAC name	Structure	ASHRAE designation	GWP_{100}
Hydrocarbons and dimethylether			
Ethane	CH_3-CH_3	R-170	6†
Propene (propylene)	CH_2=CH-CH_3	R-1270	2†
Propane	CH_3-CH_2-CH_3	R-290	3†
Methoxymethane (dimethylether)	CH_3-O-CH_3	R-E170	1†
Cyclopropane	-CH_2-CH_2-CH_2-	R-C270	86
Fluorinated alkanes (HFCs)			
Fluoromethane	CH_3F	R-41	116†
Difluoromethane	CH_2F_2	R-32	677†
Fluoroethane	CH_2F-CH_3	R-161	4†
1,1-Difluoroethane	CHF_2-CH_3	R-152a	138†
1,1,2,2-Tetrafluoroethane	CHF_2-CHF_2	R-134	1120†

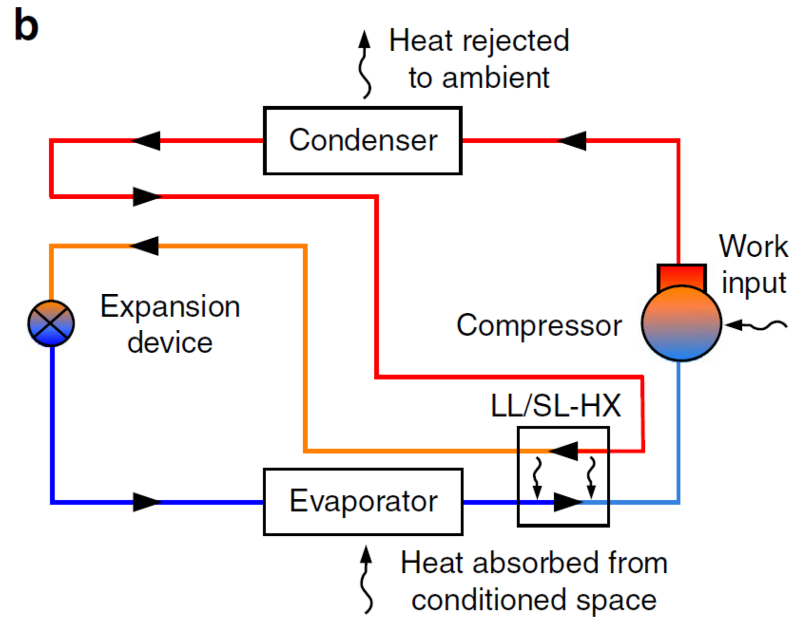
International Union of Pure and Applied Chemistry (IUPAC)

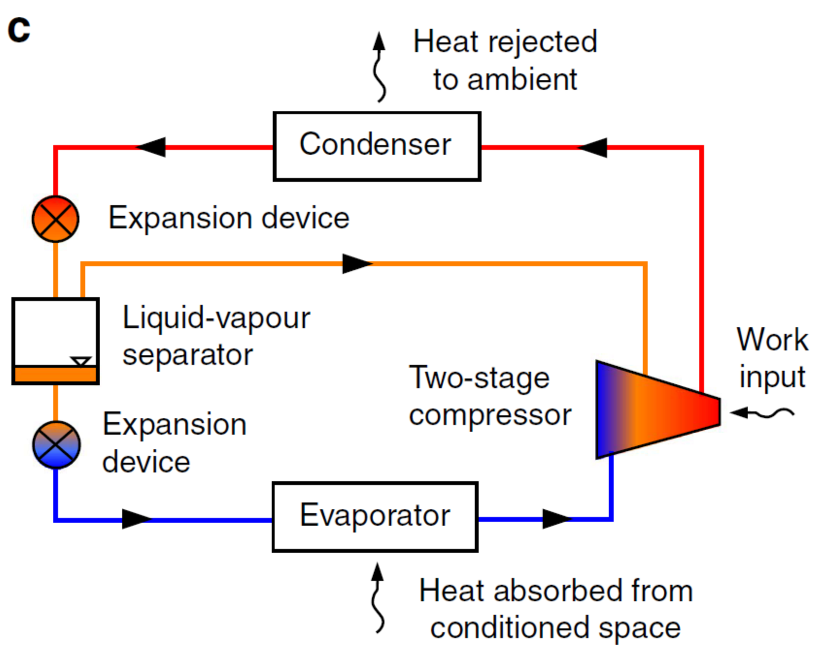
McLinden, Domanski et al; Nature Communications; 17 February 2017; DOI: 10.1038/ncomms14476

IUPAC name	Structure	ASHRAE designation	GWP_{100}
Fluorinated alkenes (HFOs) and alkynes			
Fluoroethene	$CHF{=}CH_2$	R-1141	<1†
1,1,2-Trifluoroethene	$CF_2{=}CHF$	R-1123	3
3,3,3-Trifluoroprop-1-yne	$CF_3\text{-}C{\equiv}CH$	NA	1.4
2,3,3,3-Tetrafluoroprop-1-ene	$CH_2{=}CF\text{-}CF_3$	R-1234yf	<1†
(E)-1,2-difluoroethene	$CHF{=}CHF$	R-1132(E)	1
3,3,3-Trifluoroprop-1-ene	$CH_2{=}CH\text{-}CF_3$	R-1243zf	<1†
1,2-Difluoroprop-1-ene§	$CHF{=}CF\text{-}CH_3$	R-1252ye§	2
(E)-1,3,3,3-tetrafluoroprop-1-ene	$CHF{=}CH\text{-}CF_3$	R-1234ze(E)	<1†
(Z)-1,2,3,3,3-pentafluoro-prop-1-ene	$CHF{=}CF\text{-}CF_3$	R-1225ye(Z)	<1†
1-Fluoroprop-1-ene§	$CHF{=}CH\text{-}CH_3$	R-1261ze§	1

The COP determines the energy efficiency of an AC system, and Qvol has a large influence on the physical size of the equipment, with larger values of Qvol corresponding to more compact systems.

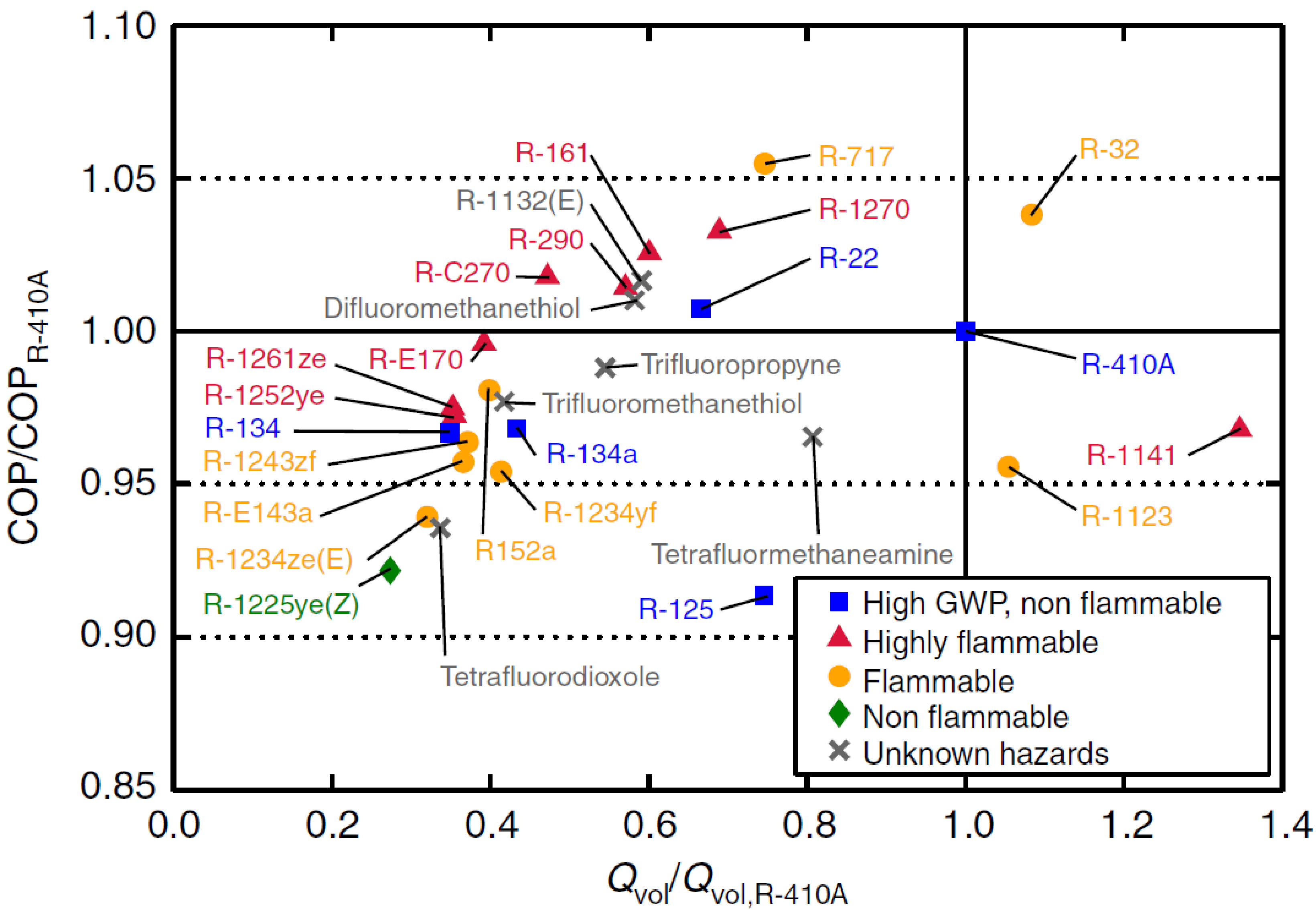




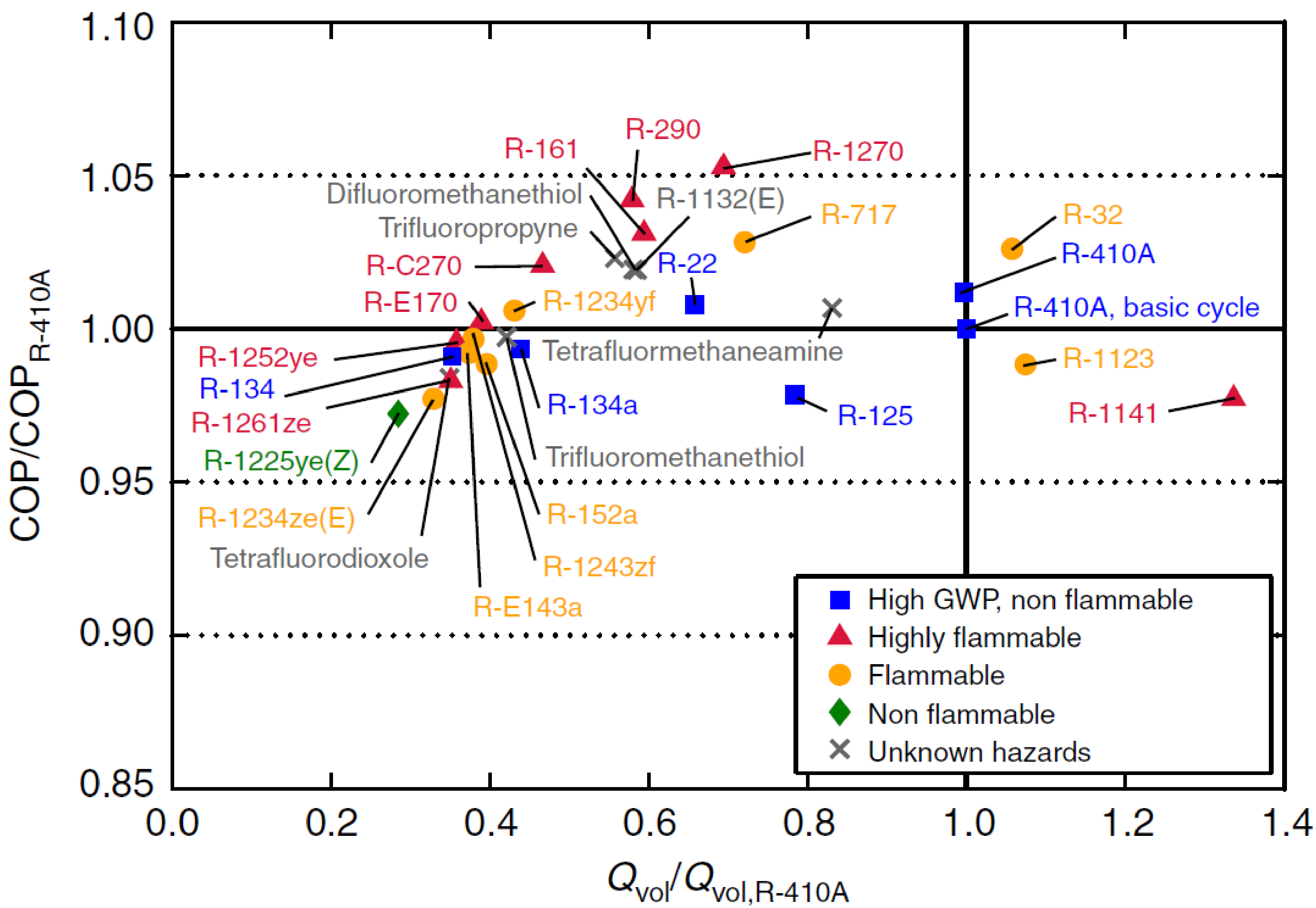


(a) Basic vapour compression cycle;
(b) Cycle with LL/SL-HX;
(c) Two-stage flash economizer cycle.

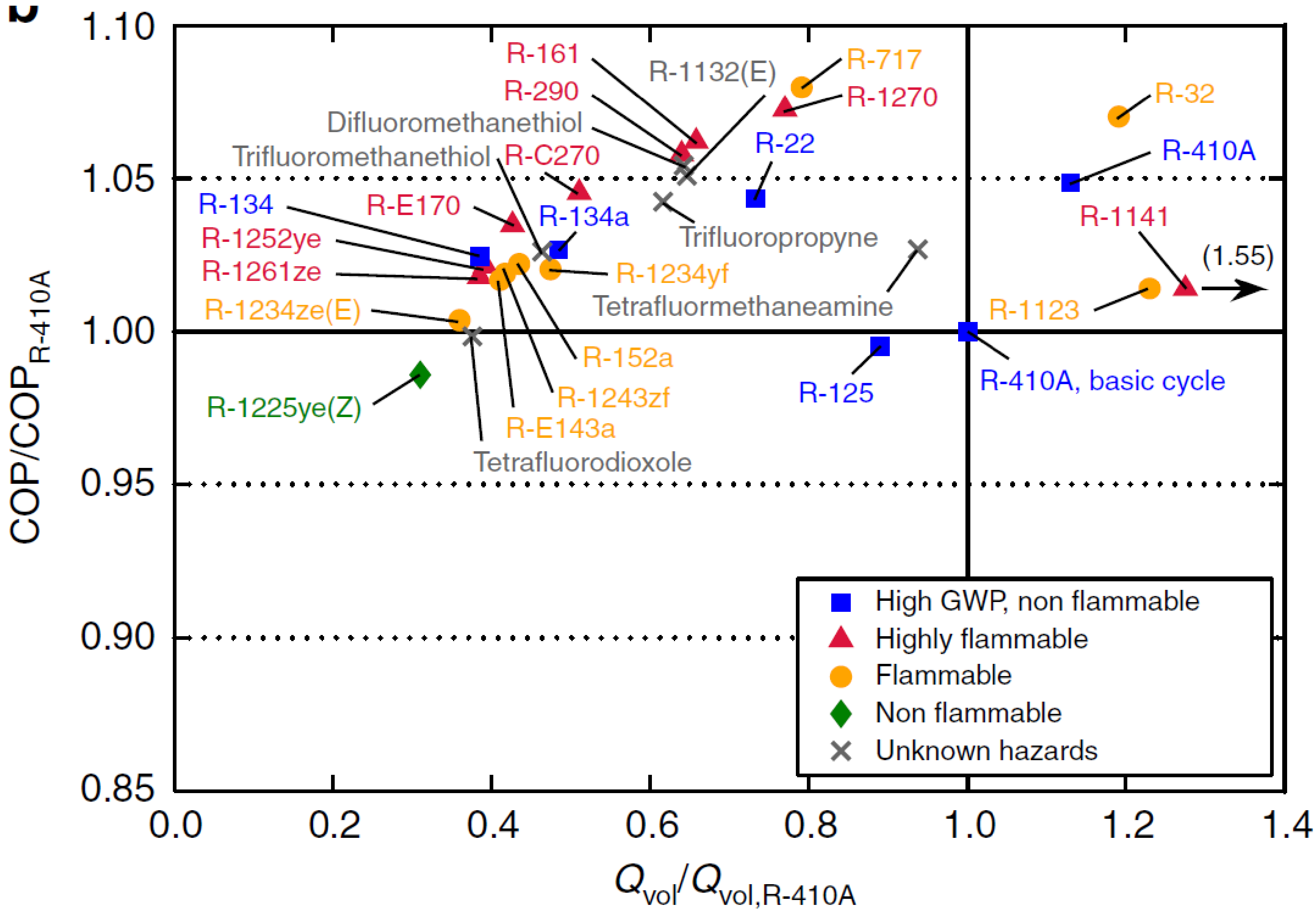
Evaporator temperature 10 C
Condensing temperature40 C



Coefficient of performance and volumetric capacity of selected low-global-warming-potential fluids. Results are shown for the basic vapour compression cycle; values are relative to those for R-410A



Coefficient of performance versus volumetric capacity for the liquid-line/suction-line heat exchanger cycle. Values plotted are relative to those for R-410A in the basic cycle ($COP_{R\text{-}410ª}$ 5.35 and $Q_{vol,R\text{-}410ª}$ 6.93 MJ m_3)



Coefficient of performance versus volumetric capacity for the two-stage flash economizer cycle. Values plotted are relative to those for R-410A in the basic cycle (COP$_{R\text{-}410a}$ 5.35 and Q$_{vol,R\text{-}410a}$ 6.93 MJ m$_{3}$)

- **Major conclusion is that the viable candidates for single component low-GWP alternatives for small AC systems are very limited, especially for refrigerants with volumetric capacities similar to R-410A.**
- **Fluids with good COP and low toxicity are available, but all are at least slightly flammable.**
- **Nonflammable candidates exist among the fluids with low volumetric capacity, but use of such fluids in small AC systems would require extensive redesign and may result in lower COP.**
- **Blends offer additional possibilities, and the refrigeration industry is actively investigating blends of HFCs and HFOs with the intent of reducing or eliminating flammability with the trade-off of increased GWP.**
- **Although this study focused on unitary AC systems (that is, residential and small commercial single-package and split systems), the general conclusions would apply also to room AC units and to refrigeration and heat-pumping systems currently using R-410A or R-22.**

The suitability of new refrigerants and their mixtures in the HVAC&R systems requires further RESEARCH AND DEVELOPMENT in the following main areas:

- **Identification of HFOs, HCs, Natural Refrigerants, and their mixtures for specific applications (domestic, commercial and industrial sectors) with India specific operating conditions (especially high condensing temperatures).**
- **The environmental properties, flammability, toxicity and safety issues of new refrigerants and their mixtures.**

- **Adaptation of existing compressor technologies to new refrigerants. Performance and Reliability of refrigerant compressors working with new environment-friendly alternatives.**
- **Development of a new lubricants to replace the existing synthetic lubricants; heat transfer, oil solubility and oil return issues.**
- **Development of a new heat exchanger designs to accommodate the non-linear temperature variations of new refrigerant mixtures during phase change.**
- **Novel compact heat exchanger designs to improve efficiency and reduce the total refrigerant charge.**

- **Optimization of complete vapour compression refrigeration plant working with new refrigerants.**
- **Development of reversible unitary systems for year round operation in regions of extreme summer-winter (example Delhi) using new refrigerants.**
- **Material related issues, especially in valves, seals and bearings.**
- **Not-in-kind sorption based unitary cooling systems with refrigerants like water and ammonia operating on low grade heat sources (renewable / waste heat) for low carbon footprints.**

Thank You Very Much