

Refrigerant Evolution over a Hundred Years: Part 2

By K Raghavan

In Part 1 of this article published in the July-August 2022 issue of the Journal, we saw how the refrigerant and ACR industry evolved over many decades during the 20th century. Refrigerants like R11, R12, R22 and R502 remained dominant till the 1980s and 1990s in specific applications in the ACR industry and set a benchmark for comparison for any potential future refrigerants. In Part 2 of this 3-part article, we will get an overview of the refrigerant journey during the 1990s until somewhere close to 2020.

New Findings and Changed Scenario in 1990s

The period from 1990s to 2020 has been very eventful and fast-paced with new technologies evolving not only in HVACR but on a vast horizon especially IT, software, telecom, data center, automobiles, etc. and with greater vigor from the global community to address the greenhouse gas (GHG) emissions.

The key turning point for the industry as a whole and HVACR in particular has been the findings of scientists on the thinning of the ozone layer and effects of global warming, which brought the limelight back on refrigerants.

Ozone Depletion and Global Warming

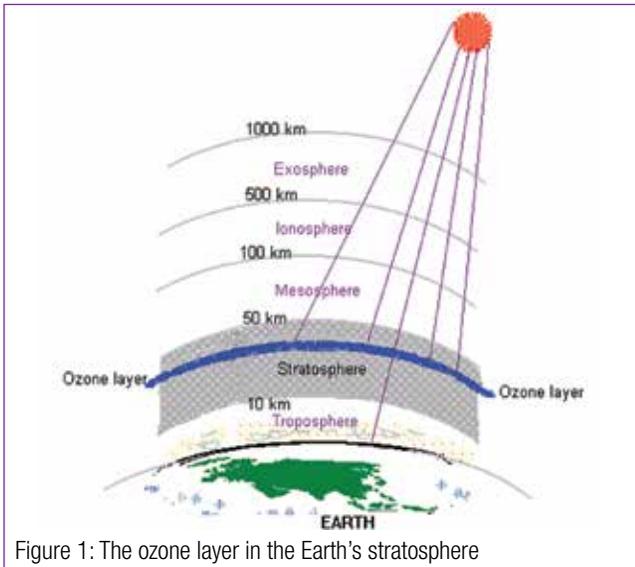


Figure 1: The ozone layer in the Earth's stratosphere

About the Author

K Raghavan is a mechanical engineer with 34 years' experience in HVACR field. The views expressed in this article are his own, drawing from his experience. He was a member of ISHRAE Refrigerants Committee, which came out with a Position Paper on Alternate Refrigerants in 2015-16. He was a HIDECOR trainer over 2002-06 to train SMEs on implementing CFC transition in the field. He also contributed to updating the Refrigerant chapter of the text book by Shri P N Ananthanarayanan, revised and published by ISHRAE in 2014.

Ozone is present in the Earth's atmosphere (as shown in *Figure 1*) filtering out harmful UV-B and UV-C rays from reaching earth and affecting humans and other forms of life. In the mid-1980s, scientists discovered a hole (severe depletion) in the ozone layer of earth's atmosphere above Antarctica. Man-made chemicals containing halogens (chlorine, bromine) were determined to be the main cause of ozone loss. These chemicals are collectively known as ozone-depleting substances (ODS). One chlorine atom can destroy up to 1,00,000 ozone molecules, a rate of destruction far higher than the creation of new ozone molecules in nature, leading to thinning of the layer.

Table 1: ODS classification (groups emerged over a period of time)

Class I ODS		ODP
Group 1	CFC11, 12, 113, 114, 115	1.0 to 0.6
Group 2	Halon 1301, 2402, 1211 (Bromine compounds)	10.0 to 3.0
Group 3	CFC of methane, ethane and propane base (e.g., R13)	1.0
Group 4	Carbon Tetra Chloride	1.1
Group 5	Methyl Chloroform	0.1
Group 6	Methyl Bromide	0.7
Group 7	Many other bromine compounds	1.0 to 0.1
Group 8	Chloro bromo methane	0.12
Class II ODS	HCFC platform: R22, R121, R141b, etc.	0.1 to 0.009

The ODS are divided into class I and class II categories as shown in *Table 1*. Chlorofluorocarbon (CFCs) were one of the prominent ODS in class I category, requiring immediate attention for phase-out and HCFCs are present in class II with their ODP being in fractions of that of class I refrigerants, but still requiring attention. The term ODP reflects the ozone-depletion potential of a substance, on a mass per kilogram basis as compared to CFC-11, which is taken as the base for

comparison. The ODP number is based on the substance's atmospheric lifetime, the molecular weight of bromine and chlorine, and the substance's ability to be photolytically disassociated.

In the 1980s, the global community decided to do something about ozone depletion. In response, the Vienna Convention for the Protection of the Ozone Layer was adopted in 1985 followed by the Montreal Protocol on Substances that Deplete the Ozone Layer in 1987. They are the first international environmental treaties to be universally endorsed by 198 nations of the world and they inspired similar actions on climate change in later years.

The Montreal Protocol was a comprehensive document and global agreement signed by all countries and consisted of many sections (referred as Articles) focusing on all the finer details of implementing the protocol and phasing out the ODS. Article 5 of this document focused on the situation of developing countries and allowed them a delay of up to ten years in implementing the ODS phase-out in comparison with developed countries. A criterion of less than 0.3 kilograms per capita of ODS consumption was set for qualifying any country under Article-5.

Table 2: CFC phase-out schedule for developed and developing countries

Chlorofluorocarbons (applicable to production and consumption)			
Non-Article 5 parties		Article 5 parties	
Baseline	1986	Baseline	Average of 1995-1997
Freeze	July 1, 1989	Freeze	July 1, 1999
75 per cent reduction	January 1, 1994	50 per cent reduction	January 1, 2005
100 per cent reduction	January 1, 1996 (with possible essential use exemptions)	85 per cent reduction	January 1, 2007
		100 per cent reduction	January 1, 2010 (with possible essential use exemptions)

Please note that as per Ozone Cell, MoEF, GoI notification, manufacturing of new appliances using CFC refrigerants was banned from 1-1-2003 in India.

India is one of the many developing countries classified under Article-5 and this group is referred as A-5 countries. 'Non-A5' term denotes the developed countries. A multi-lateral fund was set-up to assist the A5 countries to implement

the Montreal Protocol. Table 2 gives the CFC phase-out schedules agreed by the developed countries (non-A5) and the developing countries (A5 countries).

Global Warming

The Kyoto Protocol came into force in 1997, inspired by the global cooperation and commitment on Montreal Protocol. This operationalizes the United Nation Framework Convention on Climate Convention (UNFCCC) by committing developed countries to limit and reduce GHG emission as per individual set targets. The objective was to stabilize the greenhouse gases concentration in atmosphere at a level that would prevent interference with the climate system.

Table 3: Greenhouse gases resulting in global warming

1	Carbon dioxide – CO ₂
2	Methane – CH ₄
3	Nitrous Oxide – N ₂ O
4	Hydrofluoro Carbons – HFC
5	Perfluoro carbon – PFC
6	Sulphur Hexafluoride – SF ₆

Figure 2 explains how the GHGs in the lower atmosphere stop the reflected infrared waves from earth, resulting in increased temperature of earth. Table 3 lists the major GHGs that contribute to global warming. The HCFC gases and the Hydro Fluoro Carbon (HFC) refrigerants, which were emerging as the alternatives for replacing the high ODP CFC refrigerants are one of the major GHGs, which are supposed to be contained and phased out in the future.

CO₂ was taken as the base against which all the other GHGs were compared with respect to their Global Warming Potential (GWP). The GWP numbers of different substances are continuously evaluated by an Intergovernmental Panel on Climate Change (IPCC) scientific research team by analyzing the last few years data and predicting the likely effect over 100 years period. These reports are referred to as Assessment Reports (AR). AR5 released in 2014 is the latest. It is normal to see some slight changes in published GWP values of fluids. It is now a normal practice to indicate the AR-X number while mentioning a GWP value.

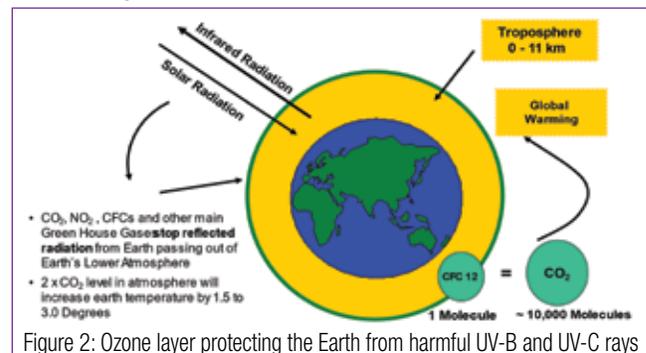


Figure 2: Ozone layer protecting the Earth from harmful UV-B and UV-C rays

Alternate Refrigerant Scenario

Table 4: HCFC phase-down schedule for developed and developing countries

HCFCs (Applicable to consumption)			
Non-Article 5 parties		Article 5 parties	
Baseline	1989 HCFC consumption +2.8per cent of 1989 CFC consumption	Baseline	Average of 2009-2010
Freeze	1996	Freeze	January 1, 2013
35 per cent reduction	January 1, 2004	10 per cent reduction	January 1, 2015
75 per cent reduction	January 1, 2010	35 per cent reduction	January 1, 2020
90 per cent reduction	January 1, 2015	67.5 per cent reduction	January 1, 2025
100 per cent reduction	January 1, 2020 and thereafter - allowance of 0.5 per cent of baseline consumption until January 1, 2030 for the uses defined in Article 2F Paragraph 6(a) and - possible essential us exemptions	100 per cent reduction	January 1, 2030 and thereafter - allowance of 2.5 per cent of baseline consumption when average over ten years 2030-2040 until January 1, 2040 for the uses defined in Article 5 paragraph 8 ter (e) (i) and - possible essential us exemptions

The above brief discussion on Montreal Protocol and Kyoto Protocol explains how the alternate refrigerant scenario started becoming complex. The CFC phase out in new appliances in India was to happen on 1-1-2003 and the HCFC phase down approximately 10 to 12 years later as shown in Table 4. Let us now review how the scenario emerged.

AHRI sponsored Alternate Refrigerant Evaluation Program (AREP) involved intense research by refrigerant manufacturers, including evaluating the already known fluids like R134a and doing a lot of collaborative work with compressor manufacturers and appliance manufacturers. This resulted in the development of a range of alternative HFC and HC fluids for the existing CFC refrigerants. All the existing CFC refrigerants like R11 and R12 belonged to A1 safety classification (non-toxic and non-flammable) category. The alternate HFC refrigerants have A1 designation whereas the hydrocarbons (HC) belong to A3 (non-toxic; but highly flammable) category.

Though HFCs with A1 designation should have been an automatic choice for CFC substitution, the below points made the HVACR manufacturers to evaluate all available options:

1. HFCs necessitated the use of polyol ester (PoE) oil in compressors in place of the conventional mineral oil and this called for associated changes in the manufacturing or service process.

2. Impending low-GWP refrigerant use within the next 10 to 20 years, which called for a long-term plan at the manufacturers' end.

HC refrigerants being natural refrigerants (refer Part-1 of this article) offered solutions both for ODP and GWP; but being highly flammable, it required process changes and investments on the design, manufacturing and servicing fronts. Simply put, either alternative be it HFC or HC, needed investments, on the existing CFC manufacturing and service set-up.

Let us now understand in detail the design characteristics of HFC and HC refrigerants to be able to appreciate the subsequent directions taken by different manufacturers.

HFC Refrigerants

HFC fluids do not have chlorine atom and have zero ODP. The GWP for the alternate HFCs ranges from moderate to relatively high levels (650 to 4,000). One critical change from CFC to HFC design involved switching from mineral oil to POE oil. HFC refrigerants' oil miscibility and solubility with standard mineral oils, which were used in CFC or HCFC systems for many decades till then, is very poor. The oil-refrigerant miscibility and solubility properties affect the lubrication oil return to compressors and the heat transfer effectiveness in the heat exchanger coils.

Table 5: Lubrication oil compatibility with moisture and impurities

Properties	Mineral Oil	POEs
Elements	C and H ₂ , i.e., Hydrocarbons	Organic: Alcohols and Acids
Water solubility at 25°C	53 ppm	1500 ppm
Stability at high temperature	Good	Good
System impurities	Dissolve in CFC	Insoluble in R134a, polymerize in POE

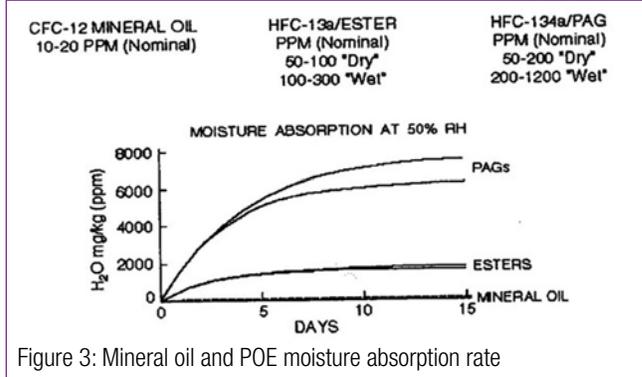


Figure 3: Mineral oil and POE moisture absorption rate

POE oil has very high affinity for moisture. Figure 3 and Table 5 indicate that it is 30 times higher than CFC at 25°C temperature. Higher moisture absorption rate affects the system reliability, due to 'hydrolysis' (chemical reactions within system, resulting in acids, corrosion etc.). Table 6 gives the lubricating oil and refrigerant compatibility relationship

with other elements in a refrigeration system. POE (along with HFC) is an excellent solvent compared to CFC-mineral oil combination, and whatever residues are washed-off the inner surface of the system components are not kept in solution by HFC-POE solution, leading to a very high chance of blockage of expansion device or capillary tube in system.

Table 6: Refrigerant lubrication oil characteristics

Lubricant	CFC12 synthetic	HC natural	HFC synthetic
Mineral oil (natural)	Miscible at all temperatures	Same as for CFC	Immiscible
POE oils (Synthetic)	Miscible	Miscible	Miscible
Lubricity	Good, as presence of chlorine assists	Same as CFC12 – but more soluble	Not so good; may need additives
Material compatibility	Taken as base for comparison (with mineral oil)	Same as for CFC12	Changes in motor, polymers and elastomers
Cleaning properties	Good, with mineral oil	Same as CFC/MO	Very good with POE
Impurities, contaminant solubility	Dissolve in CFC12 and mineral oil	Same as CFC and mineral oil	Do not dissolve; cause capillary (expansion device) chokes
Effect of moisture	Limited solubility	Less harmful	High solubility; very harmful

The hygroscopic POE oil and the inability of POE-HFC to keep residues in solution required key process changes on the manufacturing lines, component suppliers' manufacturing line evaluation for the solvents they were using and modifications in service practices in field etc. The Indian HVACR industry could prepare and adapt themselves well with necessary training and technical inputs from the government and other organizations associated with the task. We will touch upon this point soon.

The product design approach till that time with CFC/HFCs has been to standardize refrigerants and lubrication oils in such a way to limit proliferation of too many variants, which make the field servicing that much more difficult to manage.

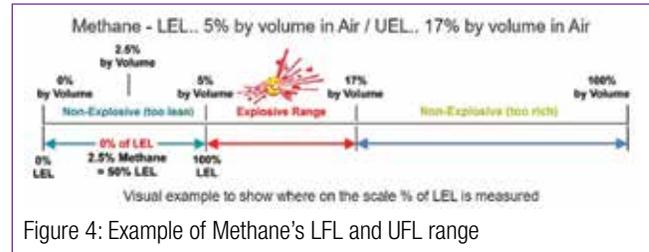
HC Refrigerants

In Part 1 of this article, we reviewed how the natural refrigerants were dominant in the refrigeration industry till the 1940s and gave way to halocarbons in the 1950s and only ammonia among the natural refrigerants survived in the industrial refrigeration segment. All the natural refrigerants have zero ODP and almost zero GWP. The Kyoto Protocol and other global legislations for environment protection brought the limelight back on hydrocarbons, which were well known to the industry. They would have been an automatic choice, but for the safety concerns related to their flammability. Remember most of them are either flammable or toxic. This was the very reason they lost out to the highly safe (non-toxic and non-flammable) and A1 category CFCs and HCFCs in the 1950s.

HC alternate fluids for CFC and HCFC offer excellent thermodynamic characteristics can work with already known conventional mineral oils and could keep the system residues in solution. Their only demerit is their flammability. To better illustrate the flammability issue, the LPG we use at home is a hydrocarbon, a mixture of propane and butane. The LPG is not in a pure form and it also has a pungent smelling agent added to it, to caution people around, in case of leak. This additive cannot be added to the refrigerant quality pure HC as it is harmful to the motor insulation.

For any chemical to catch fire, it requires

- 1) A fuel of sufficient % concentration in the given room or space air volume,
- 2) A spark to ignite the air-fuel mixture or a sufficiently high temperature to start and sustain a fire and
- 3) presence of oxygen.



To sustain burning, the % of fuel concentration, in a given room volume, needs to be between Lower Explosive or Flammable Limit (LEL or LFL) and Upper Explosive or Flammable Limit (UEL or UFL). Below the LFL, the mixture does not have enough fuel to catch fire and sustain. Above the UFL, the mixture is fuel-rich without enough air and will not be able to sustain combustion. Figure 4 illustrates the limits of methane for example.

The safety classification of refrigerants is governed by ASHRAE standard 34, ISO-817 and EN378 (generic safety) and EN60335 for specific appliances prescribing charge limit. These standards evaluate specific refrigerant's LFL, burning velocity and burning energy (heat of combustion) and classify them as A1 or A3, etc.

(Note: In India, the safe use of hydrocarbons is regulated by the Petroleum Act, 1934 and Petroleum Rules, 1976, which relate to handling of a variety of petroleum products. The latter also specifies licensing requirements for handling hydrocarbons. The Gas Cylinder Rules, 1981, addresses filling, possession, import and transport of cylinders.)

From the HVAC appliance or equipment design point of view, the design engineers could easily find engineering solutions to avoid or conceal all electrical points that could create a spark. To the maximum extent possible, low charge equipment could be designed to limit the possibility of creating a flammable fuel concentration in a given room size.

However, the safety classifications are governed by local municipal, State and Central Government Safety Codes and regulations and have been a constraining factor in the

promotion of non-A1 refrigerant equipment. Europe with more environment awareness among the public, industries, EU state authorities, experience of more natural refrigerant use (airports in many EU cities are thermal conditioned by Ammonia for many decades now) and their F-gas regulation is more forward looking in adopting low-GWP alternates, which are non-A1 refrigerants. In comparison, USA has adopted a very measured and cautious approach with respect to adopting HC fluids due to their government safety regulations.

In this type of emerging scenario of HFC Vs HC scenario, which was seriously scrutinized and debated by the industry, the key extract seemed to be

HFC

Hygroscopic POE and HFC fluids needed appropriate design changes in components or appliance or equipment, process changes across supply chain and education, associated cost increase and investments. It is an interim solution for ODP only. In the near future (~15 years), will have to adopt another low-GWP fluid.

HC

Existing CFC design and mineral oil are good enough, non-hygroscopic and to that extent no design or process changes were necessary. But to address flammability concerns, critical design changes to avoid gas leakage and spark protection from all electrical components were needed along with necessary safety process change on the manufacturing and testing lines, storage warehouse and service set-up. This needed investments over existing CFC line set-up. A big advantage of HC is the final long-term fluid with zero ODP and almost zero GWP.

The environmental concerns related to existing gases and the emerging new alternates, prompted many to prefix the chemical name with the refrigerant number, for example, HCFC22 instead of R22 and HFC134a instead of R134a. This is not mandatory by any code; but helps to the end-users on environment concerns.

India Phase-out Schedules

In *Table 2*, we observed that the CFC was to be phased out in new appliances from 1st January, 2003 in India (A5 countries schedule) with continuous CFC production cuts at gas manufacturers' end and strict ban on imports as per the Government of India schedule. Service sector was allowed to use limited capacity of CFC till 2009 and from 2010 it was to be completely stopped.

USA and European Union being developed countries (non-A5 countries) had switched to CFC-alternates in the 1990s (ten years ahead of A5) and this experience of adoption, technology and education helped manufacturers in the developing countries including India to tread the chosen or proven path.

Domestic Refrigerator

The very high volumes of domestic refrigerator made this a key segment of focus to phase down the CFC notwithstanding the very small amount of gas charge like around 100-130 grams

in a 165 liter conventional refrigerator, which was the highest selling model in India during the 1980s and 90s. Interestingly, more than CFC12 substitution in the refrigerator, equally important was switching out of CFC11, which was used as a blowing agent in the PUF insulation. In 165 liter model refrigerator, this was around 400 to 500 grams.¹

Table 7: Insulation blowing agent comparison

	CFC-11	HFC 141b	Cyclopentane
ODP	1.0	0.11	0
GWP (AR-5)	4,660	782	5
Atmospheric life	45 years	11 years	Few days
Phase-out schedule	1 st group to be phased out; 2003 onwards in India	Completed in India in 2020	N.A

CFC11 was replaced by HCFC141b (or) cyclopentane as the blowing agent for PUF insulation as mentioned in *Table 7*. This new non-ODS manufacturing line set-up also involved significant investment from the manufacturers.

Table 8: Properties of CFC12 alternates

	CFC12	HFC134a	HC600a	HC600a-HC290 blend (Care30)
Boiling point at atmospheric pressure	(-)29.8°C	(-)26.8°C	(-)11.7°C	(-)31°C
Chemical name	Dichlorodifluoro methane	1-1-1-2 Tetrafluoro ethane	Isobutane	Blend of propane and isobutane
Molecule origin	Methane	Ethane	Isobutane	Propane and isobutane
Chemical formula	CCl ₂ F ₂	C ₂ H ₂ F ₄	C ₄ H ₁₀	C ₄ H ₁₀ -C ₃ H ₈
Saturation pressure at -23.3°C	4.5 psig	2 psig	Vacuum: 11" of mercury	5.5 psig
Evaporating Temperature #				
Saturation pressure at 55°C condensing temperature	180 psig	198 psig	98 psig	174 psig
ODP	1.0	0	0	0
GWP (AR5)	10,200	1,300	3	3
Safety classification	A1	A1	A3	A3
Flammability % volume in air (LFL-HFL)	N.A	N.A	1.85% - 8.5%	1.95% - 9.1%
Atmospheric life	102 years	14.6 years	-	-

Suction pressure is given at low temperature application rating condition of compressor. The evaporating temperature in a conventional refrigerator will be around -15°C

Table 9: Refrigeration system design changes for CFC12 alternates (in comparison with CFC12)

	HFC134a	HCR600a	HC600a-HC290 50:50 blend (Care30)
Compressor	(1) ~3-5% displacement increase to achieve same capacity (2) Oil change from mineral to POE (3) Motor insulation material change	~70% higher displacement; other elements same as that of CFC12	No change
Liquid line drier	Higher molecular sieve desiccant grade is required (XH7/9) than R12 (XH5/6)	No change	No change
Gas charge quantity	95% of R12	40% of R12	40% of R12
Nature of decision	Short-term; need another low-GWP alternate in 15 – 20 years	Long-term	Long-term
System efficiency	~ 2-3% lower	Same as R12	~ 10 – 15% higher
Sound level	~ 1 dBA higher	~ 2-3 dBA lower	Almost same as R12

(The above performance comparison was done by retrofitting CFC12 Refrigerator under Indo-Swiss-German collaborative program by a few OEMs in India during 2000-01.)

CFC12 had dominated the domestic refrigerator market for so long in the 20th century and now HFC134a, HC600a and a HC blend of R290-R600a (with a brand name of CARE30) were evaluated by India manufacturers. Table 8 gives a comparison of technical characteristics of these fluids. Table 9 gives a comparison of these alternate HFC and HC options in domestic refrigerators vis-à-vis CFC12. Each refrigerant offered its own benefits as explained above on a short-term and long-term perspective. The HC fluids require only 40% gas charge quantity i.e. ~40 grams in a 165 liter refrigerator against ~100 grams of CFC12.

Considering the LFL % of HC the above referred safety standards have allowed the use of HC refrigerants up to 150 grams in domestic refrigerator. With further heat exchanger redesign and other optimization possibilities to minimize the gas charge further, 150 grams HC charge limit paves way for a long-term solution of alternate refrigerant in domestic refrigerators segment.

The position on A3 fluids by USA and its associates and the already proven track record of HFC134a for about 10 years in those countries, made many refrigerator manufacturers to opt for HFC134a. Only one Indian OEM decided to go with HC refrigerants in refrigerator - CARE30 to start with and then HC600a.

Commercial Refrigeration Appliances

During the late 1990s, the Indian commercial refrigeration appliances segment had presence of many small and medium scale manufacturers across India other than a few large OEMs. The appliances covered under this segment are chest freezers, chest coolers, visi coolers (vertical cabinets with front glass),

drinking water coolers, etc. The large-scale presence of SMEs made the alternative refrigerant scenario that much more challenging in terms of ODS education and sticking to the phase-out schedule.

HFC134a, HC600a and CARE30 HC blend were the alternates to CFC12 in commercial refrigeration. HFC134a was predominantly adopted in many appliances for reasons already discussed. The SMEs opted mostly for R141b for insulation foaming rather than cyclopentane. (This was the initial scenario in the early 2000s. The fluid has been phased out currently in India).

The Indian Refrigeration Industry had its own share of initial hiccups in getting the supply chain (suppliers who were manufacturing and supplying the refrigeration components) recalibrate themselves for the stringent process requirements for POE oil and HFC134a combination. All the commercial appliances used capillary tubes for expansion. Any let-up at suppliers’ side or on manufacturing line led to capillary tube chokes either at the beginning of the capillaries (due to washed-off residues from components) or towards the tail-end portion (due to excess moisture presence).

HC600a and CARE30 offered viable alternates on a long-term basis. The approved HC gas charge limit for commercial refrigeration was also pegged at 150 grams, which is an adequate amount for the majority of chest freezers, visi coolers etc.

(Note: In 2022, some developed countries started discussing about increasing the HC gas charge in commercial refrigeration up to 500 grams. We will review this scenario in the concluding Part-3 of this series).



Figure 5: Commercial refrigeration visi coolers and chest freezers using natural refrigerants

In India, though OEMs opted for HFC134a in commercial refrigeration to begin with the demand for equipment using climate-friendly HC refrigerant from a few MNCs with a corporate goal and achievement targets on environment protection, helped entry of HC gas in commercial refrigeration cabinets in India around 2010-11 as shown in Figure 5. A few of them have tried CO₂ also in commercial appliances subsequently.

Refrigerant Evolution over a Hundred Years: Part 2

The continuous training programs conducted across India in various cities on how to handle the 'Alternative Refrigerants' by Ozone Cell and HIDECOR helped the SMEs in a big way to maneuver the situation.

Role of Ozone Cell, MoEF&CC*

The Ozone Depleting Substances (Regulation and Control) Rules, 2000, and its amendments, have been published by the Central Government in the Gazette of India under Environment (Protection) Act, 1986. The mandate of Ozone Cell, Ministry of Environment and Forest and

Climate Change, Government of India (GoI) is to manage and coordinate all activities related to implementing the Montreal Protocol commitments in the country. (#The department was initially known as MoEF, and CC (Climate Change) got added at a later date).

With the Ozone Cell's key role, the government exempted the customs and central excise duties on capital goods imported under the multilateral fund. This was further extended for all ODS phase-out projects and investment in non-ODS technology.

Table 10: Key characteristics of HCFC22 alternates for air conditioning

	HFC410A	HFC407C	HFC134a	HC290
Flammability	Nonflammable	Nonflammable	Nonflammable	Flammable
Glide °F	0.2	9.7	0.0	0.0
GWP	2,088	1,774	1,430	< 20
Pressure at 130°F, psia	494	328	214	274
Compressor Energy Efficiency Ratio (%R22)	102 – 105%	95 – 101%	95 – 97%	97 – 99%
Capacity (%R22)	149 – 155%	98 – 105%	65%	85%
Heat Transfer	Higher	Lower	Lower	Same
Pressure Drop	Lower	Same	Higher	Lower
Tubing Size	Smaller	Same	Larger	Same
System Performance (%R22)	98 – 105%	95 – 100%	97 – 98%	100-103%
Redesign Required	Significant	Minor	Significant	Significant*

*To address safety issues of flammable refrigerant

Table 11: HFC alternates Impact on AC system design

	HFC134a	HFC407C	HFC410A
Description	Single Substance CH2FCF3	Blend Of HFC32/125/134a (23/25/52% by weight)	Blend Of HFC32/125 (50/50% by weight)
Boiling Point	-26.5°C	-43.5°C	-51.5°C
Operating Pressure	68%	101%	159%
Temperature Glide	0K	6K	0.2K
Evaporator Heat Transfer	90%	90%	135%
Condenser Heat Transfer	95%	95%	105%
Pressure Drop	128%	100%	72%
Tubing Size	Larger	Same	Smaller
Refrigerant Charge	100%	95%	70%
Re-design Required	Significant	Minor	Significant
System COP	95 – 100%	95 – 100%	98 – 106%
System Cost	Slightly higher	Same	Lower

Source: Copeland Corporation

The Ozone Cell conducted a lot of educational and awareness creation workshops across the country and also facilitated more focused training programs for the service sector, which is key to making the ODS phase-out program a success. They also partnered with likeminded organizations. The training program under Indo-Swiss-German collaboration focusing on SME sector and service technicians conducted across many cities and small towns is worth mentioning here. It was highly effective in educating the target audience.

Other Refrigeration Segments

In supermarket refrigeration units, CFC502 was phased out and HFC404A was adopted. Prior to ODS phase-out, CFC502 use was very sparse in India, but HFC404A started becoming popular in India in commercial refrigeration and supermarket refrigeration from 2003 onwards.

In Europe and USA, CO₂ use in supermarket refrigeration in stand-alone or cascade mode has begun. This could become a future solution for low GWP fluids.

In low-temperature cascade units, HCFC23 became a short-term alternative for CFC13 and CFC503. At a later stage, HFC508B an azeotropic blend became the low-side refrigerant.

Air Conditioning Segment

In India, CFC phase-out was completed in the first decade of 21st century. For service purpose though the CFC12 was allowed till 2010, the industry was able to completely phase-out CFC12 and CFC11 and move to alternatives for refrigerant use and foam blowing agent use in refrigeration appliances, a little ahead of the deadline.

Industry deliberations with the Ozone Cell on HCFC phase-down for air-conditioning use, especially HCFC22, had started in the first decade but really picked speed around 2009-10. Non-A5 countries had shifted to HFC407C and HFC410A from HCFC22 and Europe had tried HC290 in small AC within the allowed gas charge limit. HFC32 (refer Part-1 article; it was known to the industry long time ago) with many patents held by a Japanese brand was also a strong contender as viable alternate.

With reference to India and A5 countries phase-down schedule as mentioned in *Table-4* HCFC phase-down (% reduction in consumption) had started in year 2015. Let us now briefly discuss the refrigerant properties of these alternative contenders. *Table 10* and *Table 11* give a comparison of all the alternatives against HCFC22.

HFC Alternatives for AC Segment

HFC407C is a near to HCFC22 alternative. It has similar pressures like HCFC22. HFC407C was easily adopted as zero ODP solution in commercial AC segment. The initial concerns on hygroscopic POE oil use and 407C being a zeotrope with a noticeable glide, were overcome with more field experience.

HFC410A is a high pressure refrigerant significantly higher than HCFC22 and HFC407C. This necessitated a different design compressor with increased thickness of shell, compression elements, internal accessories and motor design. The heat exchangers and refrigeration system accessories like drier, receiver, accumulator etc. also needed design revamp to withstand higher pressures and deliver optimum performance. The system efficiency was higher by ~5% compared to HCFC22, but the overall cost for HFC410A system was much higher and was an impediment in large scale use in ducted AC and packaged AC.

HC290

HC290 scores high on all other required properties except on the A3 (highly flammable) classification. The gas charge limit of 150 grams restricted on safety LFL value restricts use in higher capacity appliances. A few European countries are evaluating the possibility of enhancing the gas charge quantity to 300 grams.

HFC32

We discussed in Part-1 of this article that R134a and R32 were known refrigerants for a long time. Many manufacturing patents for HFC32 were with a Japanese brand that released many of the patent rights and collaborated with many governments and regional brands, promoting HFC32 as a viable moderate- GWP alternative for future.

The HFC32 is a high pressure and high discharge gas temperature fluid. The compressor manufacturers and system designers take appropriate cognizance of these properties.

Room Air conditioners

Alongside alternative refrigerants, a major turning point of room AC segment in India was the energy labeling (star labeling) program announced and implemented by the Bureau of Energy Efficiency from 2009-10 onwards. Energy labeling of appliances and energy efficiency improvement programs are key strategies for every country to be able to meet the carbon emission goals from the global warming or climate control commitment point of view. As per BEE schedule, the efficiency of AC was required to be increased every two years, which was a challenging task. This became an additional qualifying criterion along with zero ODP and low GWP needs while assessing alternates to replace HCFC22.

As it happened in the domestic refrigerator segment, only one Indian manufacturer adopted HC290 in window AC and split AC and the other OEMs opted for HFC410A or HFC32. HFC407C was never in the race in room AC segment, especially with the COP performance in more focus.

Commercial Air Conditioning

Till the HCFC phase-down schedule kicked-in, HCFC22 continued to be the most used refrigerant in commercial AC. Interest shown in non-ODS equipment by climate-conscious

corporates right from 2007 onwards enabled Indian OEMs to start offering HFC407C in ducted AC, packaged AC and data center precision AC, offering close to HCFC22 performance at affordable cost and optimum engineering investments. Subsequently, HFC410A units were also announced.

VRF segment, trend-set by Japanese, Korean and Chinese brands in India, was predominantly with HFC410A (barring initial few years with HCFC22) for the major part of the two decades in 21st century. HFC32 has become a strong contender for the coming years with moderate GWP level. We will discuss about the emerging scenario in detail in the concluding part-3 of this article.

Chillers

Strong market forces driving for energy efficiency and climate protection in the commercial building sector along with active push for ratings for buildings by Indian Green Building Council (IGBC), The Energy Research Institute (TERI), and BEE demanded high efficiency chillers. The Indian chiller market has large presence of American and European chiller brands along with equally competent and competitive Indian brands. Similar to VRF scenario in commercial AC segment, best-in-class and high efficiency products were offered in the chiller segment.

HFC410A in scroll chillers and HFC134a in screw and centrifugal chillers were the most commonly used fluids till 2020. One USA brand offered HCFC123 (B1 classification) in centrifugal. HCFC123 GWP (AR5) is 79 and ODP is 0.012. This could be an interesting futuristic question for the industry while trying out different HFO low-GWP fluids:

Can we accept real low-GWP alternatives with very negligible (in fraction) ODP? We will discuss this in detail in Part-3 of this article.

Ozone-friendly HFC is not Climate-friendly

It is interesting to note that many a time, either due to over exuberance (or) the marketing team not being fully sensitized about the technical details, we see technically wrong claims of HFC equipment being environment friendly in advertisements or presentations or in other forms of marketing collaterals of quite a few organizations around us. Products being ozone-friendly do not necessarily mean they are environment friendly as well, especially with fluids having higher or moderate GWP. Unless the GWP is also very low (zero or near to zero) like natural refrigerants, such claims could be challenged.

In Australia, around 2002-03, a well-known brand advertised their HFC HVACR equipment as environment-friendly and the firm was taken to the court by environment group activists, resulting in a very heavy fine for the firm and negative publicity. One needs to pay attention to the environmental-benefit claims being technically correct.

Discussion on being technically correct brings up one more such topic like the correct model designation of refrigerants.

Correct Model Designation of Refrigerants

Without any exception almost everyone – all the major brands, consultants, corporates – incorrectly write the model designation of HFC refrigerants on websites, handbooks, tender specs, catalogues, presentations etc. We see in their descriptions, refrigerant designations like R134A, R600, R600A, R404a, R410a, etc. These are technically wrong and do not follow the standard for refrigerant designation established by ASHRAE or ISO.

- One should not delete a suffix letter; it is there for a reason.
- One should not capitalize the suffix letter (or) turn a capital letter into small one.

The refrigerants are chemicals derived for refrigeration use having specific properties. The chemical compounds have more than one element, blended in certain proportion and with specific molecular bond structure. Omitting a letter or capitalizing a small letter etc., actually will mean a different chemical compound. A few examples are given below:

Example-1: R600a

Table 12: HC600 and HC600a nomenclature comparison

Refrigerant	R600	R600a
Chemical name	Butane	Isobutane
Chemical formula	CH ₃ CH ₂ CH ₂ CH ₃	CH(CH ₃) ₂ CH ₃
Molecular mass	58.1 g/mol	58.1 g/mol
Boiling point at Atm. Pressure	(-)0.5°C / 31°F	(-)11.7°C / 11°F

In reference to *Table 12*, R600a is different from R600. Though the molecular weight and number of hydrogen and carbon atoms present in both fluids are equal, the chemical formula itself is written in a different manner to indicate that the bond structure is different. The bond structure is built differently by scientists after a lot of research to derive the required property necessary for refrigeration application, which in this case is the lower boiling of R600a in comparison to R600.

Example-2: R134a

Table 13: HFC134 and HFC134a nomenclature comparison

Refrigerant	R134	R134a
Chemical name	Tetrafluoro ethane	1-1-1-2 Tetrafluoro ethane
Chemical formula	C ₂ H ₂ F ₄	CH ₂ FCF ₃
Molecular mass	58.1 g/mol	58.1 g/mol
Boiling point at Atm. Pressure	-19°C/-2.2°F	-26.8°C/-16.2°F

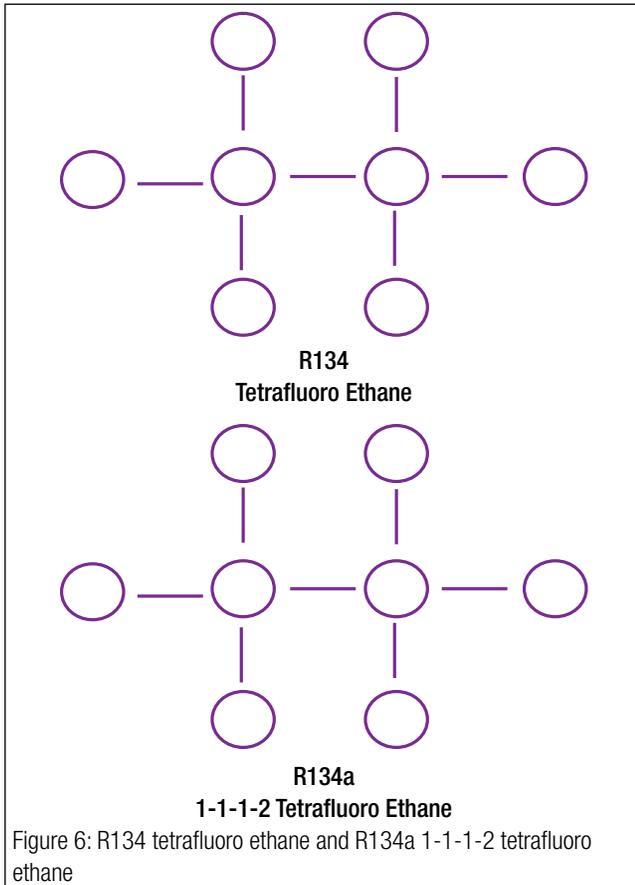


Figure 6: R134 tetrafluoro ethane and R134a 1-1-1-2 tetrafluoro ethane

As shown in Table 13 and Figure 6, a separate fluid with R134 designation does exist with a different boiling temperature. Figure 6 explains how for the isomer 134a, the bond structure is different.

(Note: suffix 'a', 'b', 'c', etc., in small letter indicates that it is an isomer with a different bond structure.)

Example-3: R407C

Table 14: HFC407 zeotropic blend ratios and model nomenclature change

	Blend ratio of R32 : R125 : R134a	Bubble point	Dew point
R407A	20 : 40 : 40	-45.2°C	-38.7°C
R407B	10 : 70 : 20	-46.8°C	-42.2°C
R407C	23 : 25 : 52	-43.8°C	-36.7°C
R407D	15 : 15 : 70	-39.4°C	-32.7°C
R407E	25 : 15 : 60	-42.8°C	-35.6°C
R407F	30 : 30 : 40	-46.1°C	-39.7°C

As explained in part-1 of this series, the R400 series are HFC refrigerant blends. The suffix letter will always be in capital. The blends are mixed in different ratios and each ratio indicated by a different suffix capital letter. It arbitrarily started from 'A' and subsequent different % mixture is given next letter in the alphabet as shown in Table 14. HFC407 series refrigerant is available as of now in six different ratios from R407A to R407F. R407C is well known in AC application.

Important Re-classification of Refrigerants

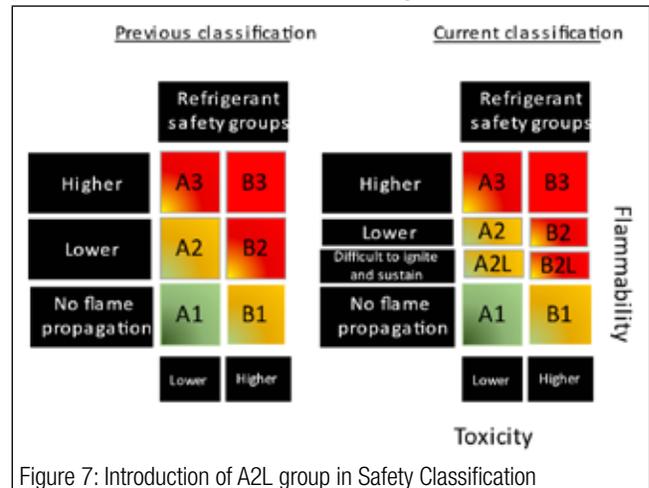


Figure 7: Introduction of A2L group in Safety Classification

Throughout the 20th century, we had only three classifications for refrigerants related to their flammability 1, 2 and 3 as shown in Figure 7. A major review and critical re-classification for refrigerants over the last 20 years has been the introduction of a new category i.e. 2L. Ammonia is now B2L and HFC32 is A2L.

The next decade for the HVACR industry is anticipated to be very challenging with HCFC phase-out and HFC high-GWP fluids' phase-down approaching fast and the difficulty in finding A1-classified, low-GWP alternate refrigerants for different applications. The industry faces many questions like, will there be a large proliferation of alternate refrigerants across applications and segments, how do we manage the safety aspects, how efficient and safe are the new HFO alternatives, etc. We will review these aspects in the next concluding part of this article.

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