

Fourth-generation refrigerant: HFO 1234yf

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Refrigeration is a process to transfer heat from the objects for cooling and freezing for maintaining the temperature of surroundings for preservation purposes and comfort. Refrigerants are the materials to use in air-conditioning and refrigeration system. This article describes the developments and history of the first-, second-, third- and fourth-generation refrigerants. Moreover, the focus is on a fourth-generation refrigerant, viz. HFO-1234yf having zero ozone depletion potential and very low global warming potential. Synthesis procedure, chemistry, applications and consumption norms of HFO-1234yf are explained.

Keywords: Air-conditioning and refrigeration, fourth-generation refrigerants, global warming potential, ozone depleting potential.

REFRIGERATION and air-conditioning provide many benefits to society by maintaining the temperature for living spaces, preservation of food and temperature control of industrial processes¹. With technological and economical developments, refrigeration system is gaining much attention all over the world. Refrigeration and air-conditioning applications affect the environment in terms of ozone depletion and global warming caused by the emission of refrigerants. Regulation agencies are working on harmful refrigerants by phasing out and replacing them with environment friendly alternatives of refrigerants. In some countries the focus is on reducing emissions by selecting suitable refrigerants, equipment design maintenance and inspection processes, etc.². Selection of appropriate refrigerant alternatives has been an important issue for both HVAC (heating, ventilation and air-conditioning) and automobile industries. The global warming potential (GWP) of most of hydrofluorocarbons (HFCs) is very high. It is therefore necessary to find an eco-friendly alternative for refrigerants in order to protect the environment. It should also be safe and economical in term of the existing system, design and installation procedure and reduce greenhouse gas (GHG) emissions and protect the ozone layer³. Hydrofluoroolefins (HFOs) are considered as a suitable alternative with low global warming potential (GWP)-4. The Montreal Protocol and other such treaties helped in the transition of NH₃, CO₂, etc. (first-generation refrigerants) to HFO-1234yf (fourth-generation refrigerant). Although CO₂ is considered as non-toxic and non-

flammable, it has some drawbacks such as high operating pressure and poor performance/efficiency under extreme climates. A CO₂-based mobile air-conditioning system operates at superior operating pressure to all other conventional refrigerants making it extremely difficult to prevent leakage. CO₂ being a high-pressure system with a very low condensation temperature, has a reduced efficiency at high temperature. It may still be more expensive than other alternatives at industrial scale⁴. The second-generation refrigerants were based on low toxicity and flammability, whereas the focus of third-generation refrigerants was to protect the ozone layer. The fourth generation refrigerants focus on zero Ozone Depletion Potential (ODP), low GWP, non toxicity and non-flammability. Recently, HFOs with low global warming potential have been introduced as fourth-generation refrigerants. This article highlights the history of refrigerants, their classes and provides a brief discussion about the fourth-generation refrigerant, HFO-1234yf.

History of refrigerant

The history of refrigerants can be divided into four generations of material based on the definition of selection criteria.

First-generation refrigerants (1830–1930)

In the time period between 1830 and 1930 when the refrigeration system was evolving, ammonia, carbon dioxide, sulphur dioxide, ethers, hydrocarbons and air were used as refrigerants. These were classified as first-generation refrigerants. The selection of refrigerants in the first-generation was based on availability and whatever work. These refrigerants had high flammability, toxicity and reactivity.

Second-generation refrigerants (1931–1990)

In 1930, a safer class of refrigerants became available with chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) being classified as second-generation of refrigerants. The focus of these refrigerants was on reduced toxicity and flammability. Due to their special characteristics, such as stability, inflammability, non-toxicity and good material compatibility, CFCs and HCFCs were produced and consumed on a large scale, particularly in developed countries. Some other refrigerants of this

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generation were NH_3 , hydrocarbons (HCs), H_2O , etc. In 1987, the Montreal Protocol was designed as a framework to protect the ozone layer by phasing out the refrigerants which are responsible for ozone depletion.

Third-generation refrigerants (1990–2010)

The initial step of the Montreal Protocol was to switch over to CFCs to HCFCs due to ODP of HCFCs. Subsequently, a range of HFCs and their derivatives or blends was developed to meet the specifications of refrigeration applications. Attention was given on reduced service and emissions of refrigerants during service and disposal⁵. This class of refrigerants was considered as third generation. In 1994, under the United Nations Framework Convention on Climate Change (UNFCCC), the Kyoto Protocol was designed as a concrete implementing tool to control GHG emissions. Both developed and developing countries are making efforts to reduce the use of ozone-depleting agents as well as strengthening controls outlined in the Protocol.

Presently, HCFCs and HFCs contribute only about 2% of the total global warming, therefore, these are on a schedule to be phased out by 2030.

Fourth-generation refrigerants (2010 onwards)

The fourth-generation refrigerants include fluorinated propene (propylene) isomers with low GWP. At present, the most likely replacement is another new class of fluorocarbon refrigerants, viz. HFOs. They have very low GWP and are expected to replace HFCs in many applications⁶. A representative of this class is HFO-1234yf. Figure 1 depicts the history of refrigerants.

Classes of refrigerants

On the basis of chemistry and chemical structure, refrigerants may be divided into the following three classes.

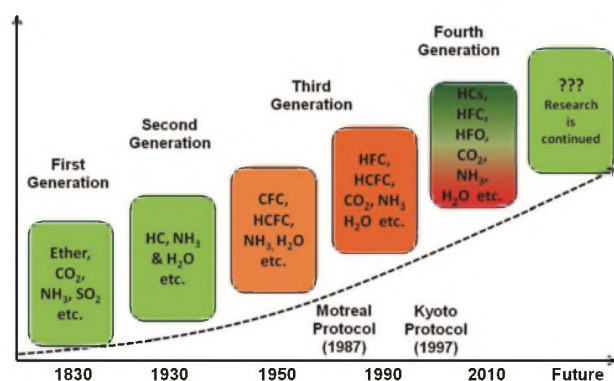


Figure 1. History of refrigerants.

Hydrocarbons and inorganics

This class of refrigerants includes ammonia, CO_2 , water and hydrocarbons; they are often known as 'natural refrigerants' with zero ODP, low GWP and low toxicity. These refrigerants are not suitable for small cooling applications⁷. The refrigerants of this class are ethane, propane, butane, isobutene, etc. The drawback of these refrigerants is their high flammability which makes them unsuitable for use in refrigeration systems.

Halocarbons

The refrigerants of this class are CFCs, HCFCs, HFCs, etc. The most common ones are CFC-11, CFC-12, HCFC-22 and HFC-134a. CFCs were phased out due to their high ozone depletion potential which affected the stratospheric ozone.

Hydrofluoroolefins

HFOs are unsaturated organic molecules having carbon, hydrogen and fluorine. They are unstable molecules with low GWP and small atmospheric lifetime due to the presence of double bond. HFOs differ from traditional HFCs by being derivatives of alkenes rather than alkanes. There are two types of refrigerants in this class: HFO-1234yf (2,3,3,3-tetrafluoropropene) and HFO-1234ze (trans 1,3,3,3-tetrafluoropropene) HFOs, HFO-1234yf and HFO-1234ze are now considered as the most promising fourth-generation refrigerants^{8,9}.

HFO-1234yf

HFO-1234yf (2,3,3,3-tetrafluoropropene) is a fourth-generation refrigerant with zero ODP and very low GWP (4). Figure 2 shows the chemical structure of HFO-1234yf.

Properties of HFO-1234yf (2,3,3,3-tetrafluoropropene)

Table 1 lists the important properties of HFO-1234yf.

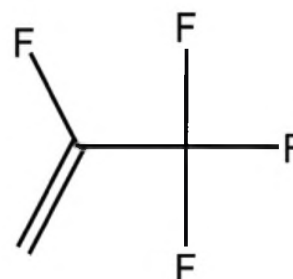


Figure 2. Chemical structure of HFO-1234yf.

Table 1. Properties of HFO-1234yf

Chemical name	2,3,3,3-tetrafluoro prop-1-ene
Molecular formula	C ₃ H ₂ F ₄
Molecular mass	114 g/mol
Physical state	Colourless gas
Density (@25°C)	1.1 g/cm ³
Boiling point	-30°C
Solubility in water (@25°C)	198.2 mg/l
CAS no.	754-12-1

Synthesis of HFO-1234yf

In the literature, different methods of synthesis of HFO-1234yf starting with different raw materials are described. Nappa *et al.*^{10,11} described a process for the synthesis of HFO-1234yf by conversion of 1,1,1,2-tetrafluoro-2-chloropropane in the presence of chromium (III) oxide catalyst and 1% alkali metal. Bektsev *et al.*¹² synthesized HFO-1234yf by dehydro-halogenation of tetrafluorochloropropane and pentafluoropropane (HCFC-244bb and HFC-245cb) in the presence of caustic solution. Wang and Tung¹³ described a process for the synthesis of HFO-1234yf through dehydrochlorination of 2-chloro-1,1,1,2-tetrafluoropropane (HCHC-244bb). It was found that the presence of HF decreases selective conversion of HCFC-244bb to HFO-1234yf. Accordingly, a method of removing hydrogen fluoride (HF) from such material was developed to improve the overall conversion efficiency process^{14,15}.

A method for the synthesis of HFO-1234yf has been described by fluorination and dehydro-chlorination of 1,1,1,2-tetrachloro-2-fluoropropane (HCFC-241bb) with or without a catalyst^{16,17}. The synthesis of HFO-1234yf was carried out by dehydro-halogenation of pentafluoropropane (CH₃CF₂CF₃) in the presence of a base and a catalyst chromium oxyfluoride¹⁸⁻²¹. HFO-1234yf was synthesized by the reaction of HCFO-1233xf (2-chloro-3,3,3-trifluoropropene) with HF in the presence of catalyst²²⁻²⁵. Bektsev *et al.*²⁶ described a method in which 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) was obtained by the fluorination of 1,1,2,3-tetrachloropropane (HCFO-1230xa) and then hydrogenation to form HFO-1234yf. This is a relatively low-yielding process and a very large percentage of the organic starting material is converted to unwanted and/or unimportant by-products, including a sizeable amount of carbon black which tends to deactivate the catalyst used in the process. A process was also developed for producing HFO-1234yf by fluorination of tetrafluoropropene to produce HCFO-1233xf; and reaction of HCFO-1233xf with HF to produce HCFC-244bb; followed by dehydrochlorination of HCFC-244bb to produce HFO-1234yf (ref. 27). Nose and Komatsu²⁸ described a simple and economical method suitable for implementation on an industrial scale, for preparing 2,3,3,3-tetrafluoropropene, by 1,1,1,2,3-penta-

chloropropane (HCC-240) by reacting with HF in the presence of chromium-based catalyst.

A process was described for the preparation of HFO-1234yf by the reaction of chlorotrifluoroethylene (CTFE) with methyl halide to form an intermediate product and of intermediate product stream with HF to produce HFO-1234yf (ref. 29). A process for the manufacture of HFO-1234yf from 1,1,2,3-tetrachloropropane (TCP) was described in three integrated steps that include: (i) R-1 hydrofluorination of TCP to form 1233xf; (ii) hydrofluorination of 1233xf to form 244bb and (iii) dehydrochlorination of 244bb to form HFO-1234yf (ref. 30).

HFO-1234yf was also synthesized using a simple and economical method that is suitable for implementation on an industrial scale. In this method HFO-1234yf was synthesized by the reaction of 1,1,1,2,3-pentachloropropane (HCC-240db) with hydrogen fluoride³¹. A process was also developed to produce HFO-1234yf by the reaction of 1-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235cb) with hydrogen gas in the presence of catalyst³². Devic *et al.*³³ developed a method to synthesize HFO-1234yf by hydrogenation followed by dehydrofluorination of hexafluoropropylene. A simple and economical process was developed to produce 1,1-dichloro-2,3,3,3-tetrafluoropropene (CFO-1214ya) from 1,1-dichloro-2,2,3,3,3-pentafluoropropane (HCFC-225ca) as well as 2,3,3,3-tetrafluoropropene (HFO-1234yf) from 1-chloro-2,3,3,3-tetrafluoropropane (HCFC-244eb). A composition of HCFC-244eb and HCFC-225, including HCFC-225ca was made to react with an alkali solution in the presence of catalyst (phase transfer) to produce HFO-1214ya from HCFC-225ca as well as to produce HFO-1234yf from HCFC-244eb. This is a simple and economical process for producing HFO-1234yf without requiring purification of the raw material component³⁴. The synthesis of HFO-1234yf was also carried out by dehydrofluorination of HCFC-225ca in the presence of dehydrofluorination catalyst, followed by hydrogenation in the presence of palladium³⁵⁻³⁷.

Applications of HFO-1234yf

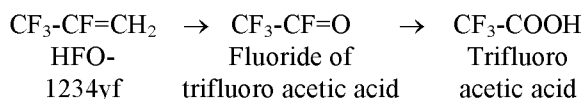
Due to its low GWP, HFO-1234yf has been used in refrigerants, heat transfer applications, foaming agents, propellants, blowing agents, carrier fluids, drying agents, buffing abrasion agents, expansion agents, gaseous dielectrics, sterilant carrier, particulate removal fluid, power cycle working fluid in liquid or gaseous form^{38,39}. HFO-1234yf is also a monomer or co-polymer starting material for the synthesis of thermally stable and highly flexible rubber material, having good market potential⁴⁰.

Hazardous nature of by-product

The by-products formed during the synthesis and use of HFO-1234yf are described below.

During synthesis: The by-products which are formed during the synthesis of HFO-1234yf are HF, HCl, unreacted hydrogen, other starting materials and intermediates such as HFO-1214ya. In the reduction reaction, reduction reactor contains the product HFO 1234yf, unreacted raw material CFO-1214ya, intermediate product 1-chloro-2,3,3,3-tetrafluoropropene (HCFO 1224yd) and by-products such as 1-chloro-2,3,3,3 tetrafluoropropane (HCFC-244eb), etc. Here, the unreacted raw material CFO-1214ya and the intermediate product HCFO-1224yd can be effectively utilized by recycling them to the reduction reactor after separating them by distillation from the desired product HFO-1234yf. However, the by-product HCFC-244eb has a boiling point close to HCFO-1224yd and CFO-1214ya, and can be separated by distillation from these compounds. HCFC-244eb is returned to the reduction reactor together with CFO-1214ya and HCFO-1224yd. HCFC-244eb is an inactive compound in the reduction reaction, and as the operation of returning it to the reduction reactor is repeated, its concentration increases in the reduction reactor thereby lowering the production efficiency of HFO-1234yf (ref. 34).

Atmospheric oxidation: Atmospheric oxidation of HFO-1234yf gives trifluoroacetic acid (CF_3COOH) which is corrosive in nature, but it does not consider as the hazardous material because the carbon–fluorine bond is stable. Due to the short life cycle of HFO-1234yf in the atmosphere (approximately 11 days), it degrades very fast resulting in low GWP. HFO-1234yf is decomposed in two stages to form trifluoroacetic acid (TFA)⁴¹



TFA is not very toxic and is a ubiquitous natural component of the hydrosphere^{42–46}. It is biodegradable⁴⁷ and does not accumulate in animal species⁴⁸. It has been concluded^{42–48} that there is no significant risk from TFA formed by atmospheric degradation of HFOs.

HFO-1234yf: replacement of HFC-134a

Due to similarity in properties, HFO-1234yf (GWP of 4 compared to CO_2 (ref. 49)) can be used as ‘near drop-in replacement’ for HFC-134a, which means that automobile manufacturers need not do many alterations in the design of the system to adopt HFO-1234yf as an alternative refrigerant due to the suitability of HFO-1234yf with existing refrigeration system design. As soon as its commercial availability is ensured, HFO-1234yf would replace HFC-134a, which is currently used in air-conditioning systems in automobiles and other refrigera-

tion systems. Attempts have also been made to use blends of HFO-1234yf with other HFCs such as R-32 in applications such as air-conditioners for domestic purposes and other refrigeration systems, since HFO-1234yf and its blends have low GWP.

Brown⁵⁰ studied the feasibility of HFOs as alternative refrigerants. There are also studies focusing on the thermodynamic properties of HFO-1234yf available in the literature^{51–55}. Reaser *et al.*⁵⁶ compared the thermophysical properties of HFO-1234yf with HFC-134a and R-410a to determine the drop-in replacement potential of the former, and concluded that the properties were comparable with HFC-134a and not with R-410a. Zhang *et al.*⁵⁷ evaluated non-azeotropic mixtures of HFO as a replacement for HFC-134a and CFC-114 in air-conditioning applications and high-temperature systems. It has been experimentally analysed HFO-1234yf can be used as a replacement for HFC-134a in a vapour compression system with the 9% lower cooling capacity of HFO-1234yf as compare to HFC-134a, which diminishes with the use of internal heat exchanger⁵⁸. Jung *et al.*⁵⁹ studied HFO-1234yf and HFO-1234yf/HFC-134a blends in three compositions and found that coefficient of performance (COP), discharge temperature and capacity of HFO-1234yf and its blends are similar to HFC-134a, with decrease in flammability as the content of HFC-134a increases.

Figures 3 and 4 show a comparison of pressure–enthalpy and temperature–entropy diagrams of HFO-1234yf and HFC-134a respectively.

As can be seen from Figure 3, the specific cooling capacity of HFC-134a is significantly higher than HFO-1234yf while the specific compression work is slightly lower. The lower value of compression work of HFC-134a causes improvement in coefficient of performance (COP) of refrigeration system⁶⁰. Table 2 lists the thermodynamic properties of HFO-1234yf compared with R-134a (ref. 61).

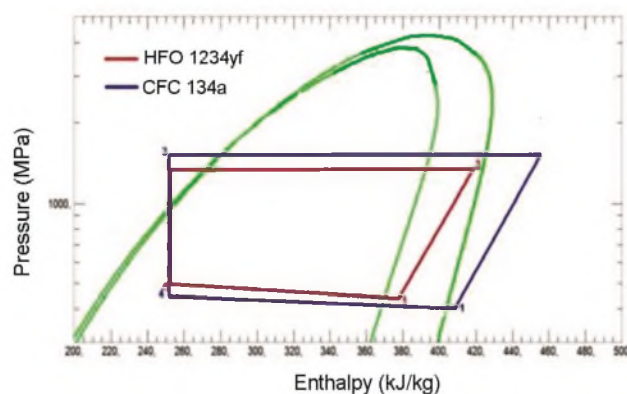


Figure 3. Comparison of pressure–enthalpy diagrams of HFO-1234yf and HFC-134a.

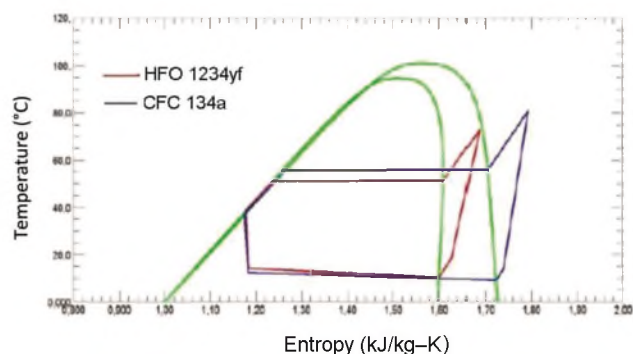


Figure 4. Comparison of temperature–entropy diagrams of HFO-1234yf and HFC-134a.

Table 2. Comparison of thermodynamic properties of HFO-1234yf and HFC-134a

Property	HFO-1234yf	HFC-134a
Boiling point (°C)	–29	–26
Critical point (°C)	95	102
Vapour pressure (MPa; at 25°C)	0.677	0.665
Vapour pressure (MPa; at 80°C)	2.44	2.63
Liquid density (kg/m ³ ; at 25°C)	1094	1207
Vapor density, (kg/m ³ ; at 25°C)	37.6	32.4
Volumetric capacity (kJ/m ³)	1577	1643
Coefficient of performance (COP)	2.77	2.87
COP relative to HFC-134a (%)	97	100

Table 3. Flammability parameters of HFO-1234yf

Property	Value
Lower flammability limit (LFL)	6.5
Upper flammability limit (UFL)	12.3
Delta UFL – LFL	5.8
Minimum ignition energy (mJ)	5000–10000
Burning velocity (cm/s)	1.5

Low GWP and zero ODP of HFO-1234yf were compared with HFC-134a as a possible alternative refrigerant in automotive air-conditioning and stationary refrigeration applications. Ansari *et al.*⁶² compared GWP and ODP of HFO-1234yf with HFC-134a and concluded that the performance parameters of the former are smaller compared to the latter. Due to the small difference in values and its environmental-friendly properties, HFO-1234yf can be a better alternative to HFC-134a. Thus, HFOs are the most viable emerging alternative refrigerants and their performance is closely similar to HFC-134a. HFO-1234yf has been widely accepted for future motor vehicle air-conditioning (MVAC) systems.

Compatibility

Several studies on the compatibility and stability of HFO-1234yf with other lubricants and polymers were carried

out. The refrigerants were tested with three lubricants, viz. mixed acid polyester (POE), branched acid polyester and poly vinyl ether (PVE) oil. No degradation of the HFO-1234yf refrigerant–oil blend was observed. Similarly, compatibility studies of HFO-1234yf with plastics and elastomers (including electric motor winding insulation in hermetic or semihermetic compressors) have shown high stability in the presence of POE or PVE lubricants with similar behaviour to HFC-134a (ref. 63).

Flammability

HFO-1234yf was considered to be flammable on studying the flammability parameters such as lower flammability limit (LFL) and upper flammability limits (UFL) according to the standard ASTM-E681-04. However, the results showed mild flammability while comparing the LFL of HFO-1234yf with other refrigerants^{61,64}. HFO-1234yf has relatively high minimum ignition energy from 5000 to 10,000 mJ, which indicates very low potential ignition source in a vehicle. HFO-1234yf also has a very low burning velocity (1.5 cm/s), indicating very low potential for ignition⁶⁵. Table 3 provides the flammability parameters of HFO-1234yf.

SAE International has already issued a press release stating that HFO-1234yf could be used safely worldwide as a refrigerant for vehicle air-conditioning systems⁶⁶. HFO-1234yf has been accepted outside the US for use in future MVAC systems⁶⁷. A survey by the German Association of the Automotive Industry (VDA) of international manufacturers revealed that they are in favour of using HFO-1234yf. Thus HFO-1234yf is the candidate for standardized, worldwide introduction of a new refrigerant with a low GWP⁶⁶.

Conclusion

Thus we have provided a brief discussion on the history of refrigerants. These have been classified on the basis of their chemistry such as hydrocarbons and inorganic compounds, halocarbons such as CFCs, HCFCs and HFCs and HFOs. Focusing on fourth-generation refrigerants, the properties, synthesis procedure and applications of HFO-1234yf have been reviewed in detail.

HFO-1234yf is environment-friendly refrigerant with zero ODP and very low GWP for use in mobile air-conditioning (MAC) systems. The chemistry of HFO-1234yf is well-defined as $\text{CF}_3\text{CF}=\text{CH}_2$. It is synthesized by different chemical routes using HCFC-241bb, HFC-245, HCFC-244, HCFO-1233xf, HFO-1214ya and HCFC-225.

HFO-1234yf is a good alternative for HFC-134a in MAC systems in the automotive industry. HFO-1234yf has a very low GWP compared to HFC-134a. It has some issues related to mild flammability, but due to low

burning velocity and high minimum ignition energy, HFO-1234yf can be safely used for mobile air-conditioning. It is compatible with plastics and elastomers (including electric motor winding insulation in hermetic or semihermetic compressors). It has good miscibility with POE and PVE lubricants and shows good thermal stability. Atmospheric oxidation of HFO-1234yf gives TFA in a molar yield of essentially 100%; however, no significant environmental impact of TFA is expected. Thus it can be concluded that HFO-1234yf can be safely used in refrigeration and air-conditioning applications in mobile as well as stationary systems and without much change in vehicle design, engineering and manufacture.

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