

## Review of Environment Eco-Friendly Refrigerants Used in Vapor Compression Refrigeration and Air-Conditioning System

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### Abstract

Refrigeration may be a method to remove temperature from the substance for cool along with freeze designed for maintains the heat of environment for perpetuation purpose- einsteinium and luxury. Refrigerants area unit the equipment to utilize in space-conditioning and cooling. This piece of writing illustrate the enlargement and narration of the 1<sup>st</sup>-, 2<sup>nd</sup>-, 3<sup>rd</sup>- and 4<sup>th</sup>-invention refrigerants. In addition, to the main center of attention is on a 4<sup>th</sup>- invention refrigerant, viz. HFO-1234yf (R-1234yf), HFO1234ze having nil gas diminution latent as well as really little warm latent. Mixture formula, chemistry, purpose and utilization standard of R-1234yf area unit explicated.

Keywords: Air-conditioning and refrigeration, 4<sup>th</sup>- invention refrigerants, heating latent, Gas diminish latent

### 1. Introduction

REFRIGERATION and air-conditioning give several benefits to society by maintaining the temperature for living areas, preservation of food and temperature management of business processes<sup>(1)</sup>. With technological and economical developments, cooling system is gaining abundant attention everywhere the planet. Refrigeration and air-conditioning applications have an effect on the setting in terms of gas depletion and heating caused by the emission of refrigerants. Regulation agencies

area unit engaged on harmful refrigerants by phasing out and commutation them with environment friendly alternatives of refrigerants. In some countries the main focus is on reducing emissions by choosing appropriate refrigerants, instrumentation style maintenance and scrutiny processes, etc<sup>(2)</sup>. Choice of acceptable Refrigerant alternatives has been a vital issue for each HVAC (heating, ventilation and air-conditioning) and automobile industries. The worldwide warming potential (GWP) of most of hydro fluorocarbons

(HFCs) is terribly high. It's thus necessary to seek out AN eco-friendly alternate for refrigerants so as to safeguard the setting. It ought to even be safe and economical in term of the present system, style and installation procedure and cut back gas (GHG) emissions and shield the gas layer.<sup>(3)</sup> Hydrofluoroolefins (HFOs) area unit thought-about as an acceptable various with low heating potential (GWP)-4. The Montreal Protocol and different such treaties helped within the transition of NH<sub>3</sub>, CO<sub>2</sub>, etc. (first-generation refrigerants) to HFO-1234yf (fourth-generation refrigerant). Though CO<sub>2</sub> is taken into account as non-toxic and non-flammable, it's some drawbacks like high in operation pressure and poor performance/efficiency underneath extreme climates. A CO<sub>2</sub>-based mobile air-conditioning system operates at superior in operation pressure to all or any different conventional refrigerants creating it very troublesome to forestall escape. CO<sub>2</sub> being a hard-hitting system with a awfully low condensation temperature, encompasses a reduced efficiency at warmth. it should still be costlier than different alternatives at industrial scale<sup>(4)</sup>. The second-generation refrigerants were supported low toxicity and flammability, whereas the main focus of third-generation refrigerants was to safeguard the ozonosphere. The fourth generation refrigerants specialize in zero gas diminution latent, little Global warming potential, non toxicity as well as. Recently, HFOs with low heating potential are

introduced as fourth-generation no flammability refrigerants. This text highlights the history of refrigerants, their categories and provides a short discussion concerning the fourth generation refrigerant, HFO-1234yf.

## 2. Narration of refrigerant

The narration of refrigerants will be divided into four generations of fabric supported the definition of choice criteria

### 2.1. I<sup>st</sup> generation refrigerants (1830–1930)

In the fundamental quantity between 1830 and 1930 once the cooling was evolving, ammonia; dioxide, pollutant, ethers, hydrocarbons and air were used as refrigerants. These were classified as first- generation refrigerants. The choice of refrigerants within the first-generation was supported accessibility and whatever work. These refrigerants had high flammability, toxicity and reactivity.

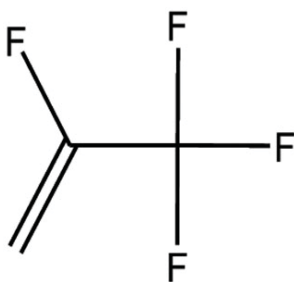
### 2.2. II<sup>nd</sup> -generation refrigerants (1931–1990)

In 1930, a safer category of refrigerants became offered with CFCs and HCFCs being classified like second-generation of refrigerants. the main focus of those refrigerants was on reduced toxicity and flammability. thanks to their special characteristics, like stability, inflammability, non-toxicity and smart material compatibility, CFCs and HCFCs were produced and consumed on an oversized scale, particularly in developed countries. Some other refrigerants of this generation were NH<sub>3</sub>, hydrocarbons (HCs), H<sub>2</sub>O, etc. In 1987, the

urban center Protocol was designed as a frame work to shield the ozonosphere by phasing out the refrigerants that are chargeable for gas depletion.

### 2.3. III<sup>rd</sup>-generation refrigerants (1990–2010)

The initial step of the city Protocol was to change over to CFCs to HCFCs because of ODP of HCFCs. afterward, a variety of HFCs and their derived or mingle was developed to fulfill the specifications of refrigeration applications. Attention was given on concentrated examine along with emissions of refrigerants throughout examine and removal <sup>(5)</sup>. This category of refrigerants was thought-about as third generation. In 1994, underneath the global organization Framework Convention on temperature change (UNFCCC), the metropolis Protocol was designed as a concrete implementing tool to regulate GHG emissions. Each developed and developing countries square measure creating efforts to scale back the



employment of ozone- depleting agents further as strengthening controls outlined within the Protocol. Presently, HCFCs and HFCs contribute solely concerning two percentage of the whole heating, therefore, this square measure on a schedule to be phased out by 2030.

### 2.4. IV<sup>th</sup>-generation refrigerants (2010 beyond)

The fourth-generation refrigerants embody fluorinated gas (propylene) isomers with low GWP. At present, the foremost probably replacement is another new category of halocarbon refrigerants, viz. HFOs. They need terribly low GWP and square measure expected to exchange HFCs in several applications <sup>(6)</sup>. A representative of this category is HFO-1234yf.

## 3. Classes of refrigerants

On the premise of chemistry and chemical structure, refrigerants could also be divided into the subsequent 3 categories

### 3.1. Hydrocarbons and in organics

This category of refrigerants includes ammonia, CO<sub>2</sub>, water and hydrocarbons; they're usually called 'natural refrigerants' with zero ODP, low GWP and low toxicity. These refrigerants aren't appropriate for tiny cooling applications <sup>(7)</sup>. The refrigerants of this category are C<sub>2</sub>H<sub>6</sub>, propane, butane, isobutene, etc. the disadvantage of those refrigerants is their high flammability that makes them unsuitable to be used in refrigeration systems.

**Figure 1.** Chemical structure of HFO-1234yf

### 3.2. Halocarbons

The refrigerants of this category are CFCs, HCFCs, HFCs, etc. the foremost common ones are R-11, R-12, R-22 and R-134a. CFCs were phased

out thanks to their high gas depletion potential that affected the stratospheric gas.

### 3.3. Hydrofluoroolefins

HFOs square measure unsaturated organic molecules having carbon, H<sub>2</sub> and Fluorine. They're unstable molecules with low GWP and tiny part period thanks to the presence of covalent bond. HFOs take issue from ancient HFCs by being derivatives of alkenes instead of alkenes'. There square measure 2 sorts of refrigerants during this class: R-1234yf and R-1234ze HFOs, HFO-1234yf and HFO-1234ze square measure currently thought of because the majority capable 4<sup>th</sup>-invention refrigerants<sup>(8,9)</sup>.

### 3.4. HFO-1234yf

HFO-1234yf could be a 4<sup>th</sup>- invention refrigerant with nil Ozone layer diminution potential and really little Global warming potential.

**Table 1.** Properties of R-1234yf

compound name	2,3,3,3-tetrafluoro propylene
Molecular prescription	C <sub>3</sub> H <sub>2</sub> F <sub>4</sub>
Molecular mass	114 g/mol
Physical state	pale gas

solidity (@25°C)	1.1 g/cm <sup>3</sup>
Boiling point	-30° C
Solubility in water (@25°C)	198.2 mg/l
CAS no( Chemical Abstracts Service)	754-12-1

### 4. Synthesis of HFO-1234yf

In the literature, totally {different|completely different} ways of synthesis of HFO- 1234yf beginning with different raw materials are delineate. Nappa *et al.*<sup>(10,11)</sup> delineate a method for the synthesis of HFO-1234yf by conversion of one,1,1,2,tetra- fluoro-2-chloropropane within the presence of metal (III) chemical compound catalyst and 1 Chronicles metal. Bektesevic *et al.*<sup>(12)</sup> synthesized HFO-1234yf by dehydro-halogenation of tetrafluorochloropropane and pentafluoropropane (HCFC- 244bb and HFC-245cb) within the presence of caustic solution. Wang and Tung<sup>(13)</sup> delineate a method for the mixture of R-1234yf through de hydro chlorination of 2-chloro-1,1,1,2-tetrafluoropropane (HCHC-244bb). it absolutely was establish to facilitate the presence of HF diminish discriminating renovation of R-244bb to R-1234yf. Consequently, a way of eradicate fluoride (HF) from such substance was developed

in the direction of enhance the general conversion potency process<sup>(14,15)</sup>.

A method for the synthesis of HFO-1234yf has been delineated by fluorination and dehydrochlorination of one,1,1,2-tetrachloro-2-fluoropropane (HCFC-241bb) with or while not a catalyst<sup>(16,17)</sup>. The synthesis of HFO-1234yf was applied by dehydro-halogenation of pentafluoro gas ( $\text{CH}_3\text{CF}_2\text{CF}_3$ ) within the occurrence of a base and a medium Cr ox fluoride<sup>(18-21)</sup>. HFO-1234yf was synthesized by the reaction of HCFO-1233xf (2-chloro- trifluoropropene) with HF within the occurrence of medium<sup>(22-25)</sup>. Bektsevic *et al.*<sup>(26)</sup> delineated a technique during which 2-chloro-trifluoropropene (HCFO-1233xf) was obtained by means of the fluorination of one,1,2,3-tetrachloropropene (HCFO-1230xa) so chemical process to make HFO- 1234yf. this is often a comparatively low-yielding method and a really massive share of the natural beginning substance is reborn to redundant and /or insignificant by-products, together with a sizeable quantity of soot that tends to deactivate the catalyst utilized in the method. A method was conjointly developed for manufacturing HFO-1234yf by fluorination of tetrafluoropropene to provide HCFO-1233xf; and reaction of HCFO-1233xf with HF to provide HCFC-244bb; followed by dehydrochlorination of HCFC-244bb to provide HFO-1234yf<sup>(27)</sup>. Nose Associate in Nursingd Komatsu<sup>(28)</sup> delineated an easy and economical methodology appropriate for

implementation on an industrial scale, for making ready a pair of,3,3,3-tetrafluoropropene, by 1,1,1,2,3-penta-chloropropane (HCC-240) by retort by means of HF within the existence of chromium-based medium.

A method was delineate for the preparation of HFO- 1234yf by the reaction of chlorotrifluoroethylene (CTFE) with alkyl radical salt to make an transitional creation and of intermediate product stream with HF to provide HFO- 1234yf<sup>(29)</sup>. A method for the produce of HFO- 1234yf from -tetrachloropropene (TCP) was delineate into 3 incorporated steps that include: (i) R-1 hydro fluorination of protocol to make 123xf; (ii) hydro fluorination of 1233xf to make 244bb and (iii) dehydro- chlorination of 244bb to make HFO-1234yf<sup>(30)</sup>.

HFO-1234yf was conjointly synthesized employing a straightforward associate degreed economical methodology that's appropriate for implementation on an industrial scale. During this methodology HFO-1234yf was synthesized by the reaction of one, 1,1,2,3-pentachloropropane (HCC-240db) by means of gas fluoride<sup>(31)</sup>. A method was conjointly developed to supply HFO-1234yf by the effect of 1-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235cb) with gas within the presence of catalyst<sup>(32)</sup>. Devic *et al.*<sup>(33)</sup> developed a way to synthesize HFO-1234yf by chemical process followed by dehydrofluorination of hexa-

fluoropropylene. A straightforward and economical method was developed to supply one,1-dichloro-2,3,3,3-tetrafluoropropene (CFO-121ya) from one,1-dichloro-2,3,3,3-penta-fluoropropane (HCFC-225ca) still as a pair of,3,3,3-tetrafluoropropene (R-1234yf) from 1-chloro-2,3,3,3-tetrafluoropropane (HCFC-244eb). A composition of HCFC-244eb and HCFC-225, together with HCFC-225ca was created to react with associate degree alkali resolution within the presence of catalyst (phase transfer) turn out to supply to provide} HFO-1214ya from HCFC-225ca still on produce HFO-1234yf from HCFC-244eb. This is often a straightforward and economical method for manufacturing HFO-1234yf while not requiring purification of the material component <sup>(34)</sup>. The synthesis of HFO- 1234yf was conjointly dispensed by dehydrofluorination of HCFC-225ca within the presence of dehydrofluorination catalyst, followed by chemical process within the presence of palladium <sup>(35-37)</sup>.

### 5. Applications of HFO-1234yf

Due to its low GWP, HFO-1234yf has been employed in refrigerants, heat transfer applications, foaming agents, propellants, processing agent, transporter fluid, aeration agent, polish graze agent, growth agent, foamy dielectrics, sterility carrier, particulate removal fluid, power cycle operating fluid in liquid or foamy form<sup>(38,39)</sup>. HFO-1234yf is additionally a compound or co-polymer beginning

material for the synthesis of thermally stable and extremely versatile rubber material, having sensible market potential<sup>(40)</sup>

### 6. Hazardous nature of by-product

The by-products shaped throughout the synthesis and use of HFO-1234yf area unit delineate below.

During synthesis: The by-products that area unit shaped throughout the synthesis of HFO-1234yf area unit HF, HCl, un- reacted atomic number 1, different beginning materials and intermediates like HFO-1214ya. Within the reduction reaction, reduction reactor contains the merchandise HFO 1234yf, un- reacted stuff CFO-1214ya, intermediary creation 1-chloro-2,3,3,3-tetrafluoropropene (HCFO 1224yd) and by-products like 1-chloro-2,3,3,3 tetrafluoropropane (HCFC-244eb), etc. At this juncture, the unreached stuff CFO-1214ya and therefore the intermediary creation HCFO-1224yd will be efficiently used through exercise them to the diminution reactor when separating them by distillation from the required product HFO-1234yf. However, the by-product HCFC-244eb includes a boiling purpose on the point of HCFO-1224yd and CFO-1214ya, and might be separated by distillation from these compounds. HCFC-244eb is came back to the reduction reactor in conjunction with CFO-1214ya and HCFO- 1224yd. HCFC-244eb is an stationary complex within the diminution effect, and because

the function of recurring it to the diminution reactor is recurrent, its concentration increases within the reduction reactor thereby lowering the assembly potency of HFO-1234yf<sup>(34)</sup>. Atmospheric oxidation: region oxidation of HFO-1234yf offers trifluoroacetic acid (CF<sub>3</sub>COOH) that is corrosive in nature, however it doesn't take into account because the risky material as a result of the carbon-fluorine bond is stable. Thanks to the short life cycle of HFO-1234yf within the atmosphere (approximately eleven days), it degrades in no time leading to low GWP.

HFO-1234yf is rotten in 2 states to create trifluoroacetic acid (TFA)<sup>(41)</sup>



TFA isn't terribly noxious and could be a present natural component of the hydrosphere<sup>(42-46)</sup>. It's biodegradable<sup>(47)</sup> and doesn't accumulate in animal species<sup>(48)</sup>. It's been concluded<sup>(42-48)</sup> that there's no vital risk from TFA shaped by region degradation of HFOs. HFO-1234yf: replacement of HFC-134a

Due to similarity in properties, HFO-1234yf (GWP of four compared to greenhouse emission<sup>(49)</sup>) may be worn as 'close to crash-in substitution' for HFC-134a, which suggests so as to vehicle makers needn't do several alterations within the style of the system to adopt HFO-1234yf as associate alternative refrigerant thanks

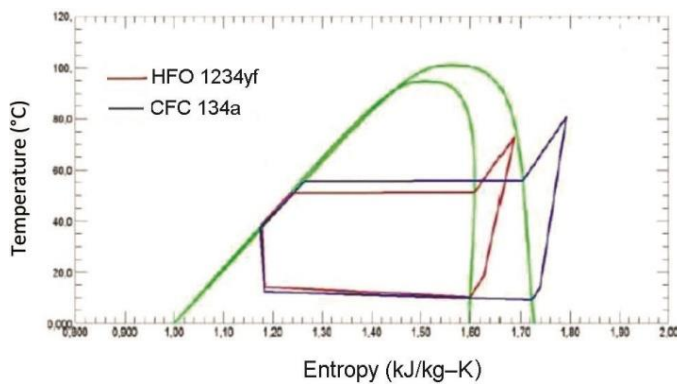
to the suitability of HFO-1234yf with existing cooling style. As before long as its industrial convenience is ensured, HFO-1234yf would replace HFC-134a that is presently utilized in air-acquisition systems in vehicles and alternative refrigeration systems. makes an attempt have conjointly been created to use blends of HFO-1234yf with alternative HFCs like R-32 in applications like air conditioners for domestic functions and alternative refrigeration systems, since HFO-1234yf and its blends have low GWP. Brown<sup>(50)</sup> studied the practicableness of HFOs as different refrigerants. There also are studies specializing in the natural philosophy properties of HFO-1234yf offered within the literature<sup>51-55</sup>. Reaser *et al.*<sup>(56)</sup> compared the thermo physical belongings of R-1234yf with R-134a and R-410a to work out the crash-in substitution latent of the farmer, and ended that the belongings be comparable HFC-134a and not with R-410a. Zhang *et al.*<sup>(57)</sup> evaluated non-azeotropic mixtures of HFO as a alternate for R-134a and CFC-114 in air-conditioning applications and elevated-temperature method. it's been by experimentation analyzed HFO-1234yf may be used as a substitute for R-134a during a vapour density arrangement with the 9% lower cold capability of R-1234yf as compare to R-134a, that moderates by means of the utilization of domestic warm exchanger<sup>(58)</sup>. Jung *et al.*<sup>(59)</sup> studied R-1234yf and R-1234yf/R-134a blends in 3 composition and located that

coefficient of performance ,discharge temperature and capability of HFO- 1234yf and its blends square measure the same as R-134a, with decrease in flammability because the substance of R-134a will increase.

Figures 2 and 3 show a comparison of pressure– enthalpy and temperature–entropy diagrams of HFO- 1234yf and HFC-134a respectively.

As may be seen from Figure two, the particular cooling capacity of HFC-134a is considerably on top of HFO1234yf whereas the particular compression work is slightly lower. The lower price of compression work of HFC-134a causes improvement in constant of performance (COP) of refrigeration system<sup>(60)</sup>. Table. 2 lists the thermodynamic property of R-1234yf measure up to with R- 134a <sup>(61)</sup>.

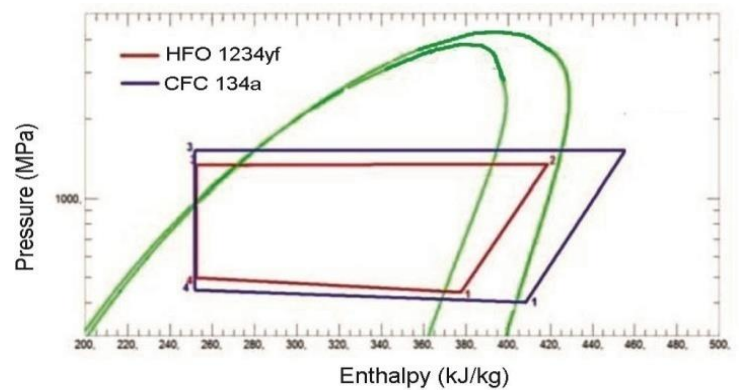
**Fig. 2.** Comparison of pressure–enthalpy diagrams of R-1234yf and R-134a.



**Fig. 3.** Relationship of temperature–entropy diagrams of R- 1234yf and R-134a

**Table 2.** Relationship of thermodynamic belongings of R-1234yf and R-134a

Property	R-1234yf	R-134a
swelting point (°C)	-29	26
decisive point (°C)	95	102
steam pressure (MPa; at 25°C)	0.677	0.665
Vapor pressure (MPa; at 80°C)	2.44	2.63
Liquid density (kg/m <sup>3</sup> ; at 25°C)	1094	1207
Vapor density, (kg/m <sup>3</sup> ; at 25°C)	37.6	32.4
Volumetric capacity (kJ/m <sup>3</sup> )	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
Lesser flammability limit	6.5
Higher flammability limit	12.3
Change in HFL – LFL	5.8
Minimum ignition energy (mJ)	5000–10000
Burning velocity (cm/s)	1.5

Low GWP and nil ODP of HFO-1234yf were compared with R-134a as a doable various refrigerant in automotive air-conditioning and stationary refrigeration applications. Ansari *et al.*<sup>(62)</sup> compared GWP and ODP of HFO-1234yf with HFC-134a and ended that the performance parameters of the former are unit smaller compared to the latter. Because of the tiny distinction in values and its environmental-friendly properties, HFO-1234yf may be a stronger various to HFC-134a. Thus, HFOs are unit the foremost viable rising various refrigerants and their performance is closely almost like HFC-134a. HFO-1234yf has been widely accepted for future motorcar air-conditioning (MVAC) systems.

## 7. Compatibility

Several studies on the compatibility and stability of HFO-1234yf with alternative lubricants and polymers were done out. The refrigerants were tested with 3 lubricants, viz. assorted acidic polyester, pronged acidic polyester in addition to poly vinyl etheroil. No degradation of the HFO-1234yf refrigerant–oil mix was ascertained. Similarly, compatibility studies of HFO-1234yf with plastics and elastomers (including motor winding insulation in tight or semi hermetic compressors) have shown high stability within the presence of POE or PVE lubricants with similar behavior to HFC-134a<sup>(63)</sup>.

## 8. Flammability

HFO-1234yf was thought-about to be combustible on learning the flammability parameters like lesser flammability boundary and higher flammability limits according to the quality ASTM-E681-04. However, the results showed delicate flammability whereas scrutiny the LFL of HFO-1234yf with alternative refrigerants<sup>(61,64)</sup>. R-1234yf has relatively elevated least explosion power beginning 5000 to 10,000 mJ, that specify terribly low potential ignition supply during a vehicle. HFO-1234yf conjointly encompasses a terribly low burning rate (1.5 cm/s), representing terribly low down latent for ignition<sup>(65)</sup>. Table

three provides the flammability parameters of HFO-1234yf.

SAE International has already issued a release stating that HFO-1234yf can be used safely worldwide since a refrigerant on behalf of vehicle air-conditioning systems <sup>(66)</sup>. HFO-1234yf has been accepted outside the U.S. For use in future MVAC systems <sup>(67)</sup>. A survey by the German Association of the Automotive trade (VDA) of international makers disclosed that they're in favor of mistreatment HFO-1234yf. So HFO-1234yf is the candidate for standardized, worldwide introduction of a brand new refrigerant with a low GWP <sup>(66)</sup>.

## 9. Conclusion

Thus we've provided a short discussion on the history of refrigerants. These are classified on the premise of their chemistry like hydrocarbons and inorganic compounds, halocarbons like CFCs, HCFCs and HFCs and HFOs. That specialize in fourth-generation refrigerants, the properties, synthesis procedure and applications of HFO-1234yf are reviewed very well.

HFO-1234yf is environment-friendly refrigerant with nil Ozone layer depletion and really little Global warming potential to be worn in portable air-conditioning (PAC) system. The chemistry of HFO-1234yf is well-defined since  $\text{CF}_3\text{CF}=\text{CH}_2$ . it's synthesized by totally different chemical routes victimization HCFC-241bb, HFC-245,

HCFC-244, HCFO-1233xf, HFO-1214ya and HCFC-225.

HFO-1234yf may be a smart various for HFC-134a in raincoat systems within the automotive trade. HFO-1234yf encompasses a terribly low GWP compared to HFC-134a. It's some problems associated with gentle flammability, however because of low down flaming rate as well as elevated least explosion power, HFO-1234yf is safely used for mobile air acquisition. It's compatible with plastics and elastomers (including motor winding insulation in her alien or semi hermetic compressors). It smart miscibility with Edgar Allen Poe and PVE lubricants and shows smart thermal stability. Part reaction of HFO-1234yf offers TFA during a molar yield of primarily 100 percent.

However, no important environmental impact of TFA is expected. therefore it is terminated that HFO-1234yf is safely employed in refrigeration and air-conditioning applications in mobile still as stationary systems and while not a lot of modification in vehicle style, engineering and manufacture.

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