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Is HFO the last generation of synthetical refrigerants?

Kenneth Hoffmann[a], Jan Gerritsen[a], Armin Hafner[b]

[a]GEA Refrigeration, De Beverspijken 7c, 5221 EE `s-Hertogenbosch, Netherlands
[b]NTNU, Trondheim, Norway

Abstract

Since 1920 many different synthetical refrigerant have been introduced onto the market. The latest so-called 4th generation synthetical refrigerant is the unsaturated HFC or HFO (Hydrofluoroolefins). They introduced to combat an environmental issue, i.a. the global warming potential of HFC refrigerant, however, they are creating a new challenge. Recent research has shown that there is a build-up of fluoride substances as Trifluoroacetic acid (TFA) in drinking water globally. Some of the HFO molecule are breaking down 100% into trifluoroacetic acid, which can lead to large health cost in the future, due to this environmental pollution. Whereas the heat pump industry working with natural refrigerant are focusing on low charge and no leakages solutions, due to the flammability and toxicity of some of the natural refrigerant, there is very little effort by the industry working with synthetical refrigerant to create similar safe and low charge solutions. Research have shown that all current HFO based system solutions could be replaced by units applying natural refrigerants without significant cost implication.

Keywords: HFO; R1234yf; TFA; global warming; heat pumps; toxicity; natural refrigerant.

1. Introduction

The market of refrigeration and heat pump is growing each year, however, also the concern for the global environment and humans' impact on Earth's climate. We all want to keep the Earth healthy for the next generations to come. This paper has collected some of the recent research into the effect of introducing HFO as a refrigerant in large scale. Most of the research have been made on R-1234yf which is the main refrigerant discussed in this paper, although many other HFO refrigerants with similar properties have been introduced into the marked lately.

2. The history of refrigerants

Humans learned already from the primitive times that keeping food cold helped to extend their shelf life. In Egypt and Greek time there where, widespread use of storage pits to keep products cool. In the 1740's the first scientific results of creating cold by creating pressure change was proven by William Cullen. It took however another 60 years before Thomas Moore invented commercial refrigeration by taking energy from an ice storage into a dairy plant. This was the start of refrigeration as we know it today. Up through the 19th hundred mechanical compression refrigeration was introduced using CO_2, Ammonia or SO_4 as refrigerants. Due to lack of knowledge, training and material quality there where several accidents with these first refrigeration system, with several of them being fatal. By 1930 the first synthetical refrigerants, chlorofluorocarbons also known as CFC's, where commercialised by Thomas Midgley[1]. The CFC's where introduced as safe refrigerants as they are not flammable. This led to a large increase in use of refrigeration, in new areas where the end user's knowledge of refrigeration was limited like home appliances, supermarket- and HVAC units.

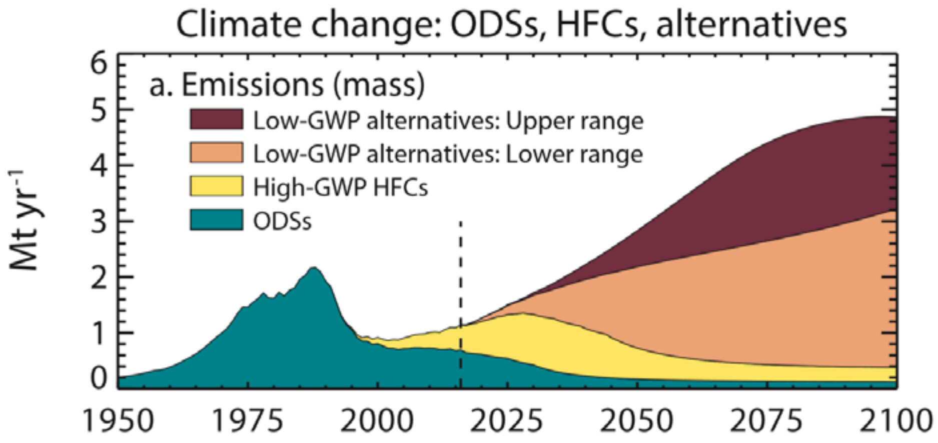


Figure 1: The figure shows the emission of refrigerant gas in Mt per year[4]. After 2016 it is a forecast based on current global development and legislation. By 2040 the release of low GWP refrigerants (HFOs) will exceed the peak release of ODS refrigerants (CFCs).

In the 1980's it was realised that the CFC refrigerants was causing a hole in the ozone layer in the stratosphere, which protects the Earth from UV radiation[2] . Although the CFC's were deemed safe, this was partly on a local level, on a global level, they had the potential to eradicate the human population if no action was taken and the ozone layer would have disappeared completely. To avoid this, it was decided in 1987 (Montreal protocol [3]) to curb the use of CFC with the goal to stop using all CFC's within 26 years (Last legal production of CFC in Article 5 countries where in 2003[3]). As alternative to the CFC's the refrigerant industry developed the HCFC, which had 10 times less ozone depleting effect compared to the CFC's, these where accepted as an intermediate refrigerant until a better solution was found. The HCFC will be fully phased out by 2040 in Article 5 countries. Since followed the developments of the hydrofluorocarbons - HFC's which have no ozone depleting effect. This was great news for the ozone layer and in recent years there has been some restoring of the ozone layer in the stratosphere [4].

Table 1: Article 5 country phase-out schedule for HCFC production and consumption [3]

Schedule	Year
Baseline	Average of 2009 and 2010
Freeze	2013
90% (reduction of 10%)	2015
65% (reduction of 35%)	2020
32.5% (reduction of 67.5%)	2025
Annual average of 2.5%	2030 to 2040
0% (reduction of 100%)	2040

The HFC's unfortunately raise another potential issue as they have a significant high global warming potential. With increasing temperatures on earth, due to the excessive usage of fossil fuels over the last 100 years it seems not logical to apply such harmful refrigerants. With increased water level and more severe weather phenomena's, there are potentially many deaths in the future related to global warming. This is especially the case if the human population does not manage to keep the goals from the Paris agreement of "keeping global average temperature to well below 2 °C above pre-industrial levels and pursuing efforts to limit the temperature increase to 1.5 °C" [5]. The Paris agreement have been ratified by 185 of the 197 participating countries. It has been followed up by the Kigali amendment [6] in 2016, declaring that all high GWP refrigerants will be phased out by 2047 globally, this will avoid 0.4˚C global warming. The lessons learned is that if it was only the refrigeration industry polluting the world the effect on the global climate would be limited. However, as there are many other sources which effect the global climate, we must be very vigilant regarding the exposure to the global climate as there is only one Planet Earth.

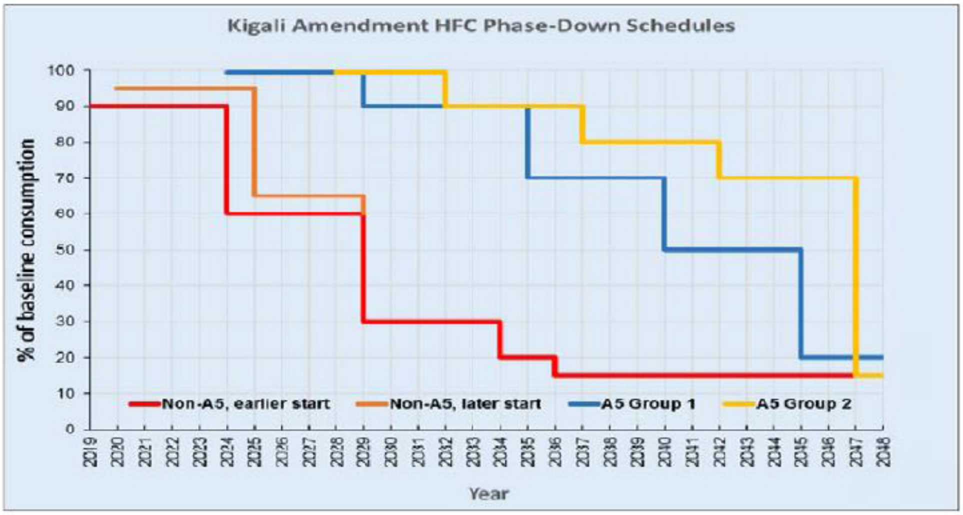


Figure 2: Global phasedown schedule for HFC production and consumption [3].

With growing global demand and sales of refrigerants of more than 15 bn US dollar, the refrigerant manufactures have a huge interest in replacing HFC's and they launched the first alternatives in 2008 [8]. Shortly after, the first articles appeared about the properties of unsaturated HFC's (HFO) refrigerants, which have a very short life in the atmosphere (a few days only). The issue is that HFOs are not safe refrigerant as previous synthetical refrigerants, however, they are flammable and toxic when combusting.

3. How do HFO differ from HFC?

HFC are created of stable molecules bonds, which are difficult to break down. This makes them good refrigerants, but it also gives them high global warming effect, as these stable fluids stay in the atmosphere for a very long time while absorbing radiation. HFO-1234yf is an unstable molecule with a double bond that breaks up quickly in the atmosphere, the degradation produces a 100% molar yield of trifluoroacetic acid (TFA) within days of release. Although TFA is naturally occurring on the oceans there is significant evidence that all TFA found in freshwaters, is human made. R134a does also break down to TFA, but only 20% of the molecules break down to TFA and it's over a much longer period.

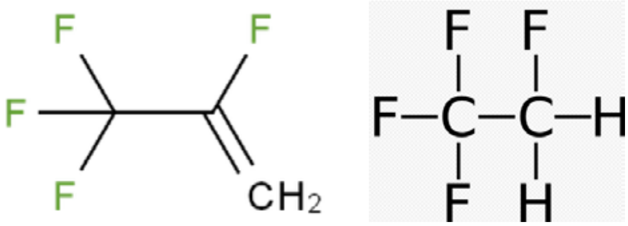


Figure 3: The molecule the left is the unsaturated HFO-1234yf 2,3,3,3-tetrafluoroprop-1-ene, C3H2F4; CF3CF=CH2 with an unstable double bound that breaks down within 10 days[4] in atmosphere. To the right is an HFC-134a 1,1,1,2-Tétrafluoroéthane, $C_2H_2F_4$ molecule, which has a stable structure that stays in the atmosphere for 10 years[4].

Table 2: Table showing the mass amount of TFA created from the refrigerant when decomposed in atmosphere

Molar yields of TFA from degradation of HFO's and HFC's	
HFOs	
R1234ze	<10% (as cited by WMO, 2010)
R1234yf	100% (as cited by WMO, 2010)
HFCs	
R134a	21% (as cited by WMO, 2010)
R227ea	100% (as cited by WMO, 2010)
R245fa	<10% (as cited by WMO, 2010)
R365mfc	<10% (as cited by WMO, 2010)
R236fa	<10% (as cited by WMO, 2010)

4. Toxicity of combustion products from HFO

HFO refrigerants are most commonly categorised as A2L refrigerants as they are so-called mildly flammable. This is a major change from the commonly applied R134a, which is and A1 refrigerant and classified as non-flammable. Although most refrigeration engineers in Europe have been trained since 2007 according to the F-gas regulations a new set of training of the personnel is required to keep themselves and the environment safe when handling HFO refrigerant.

Table 3: Flammability comparison of HFO with other commonly used refrigerants. LFL (lower flammability limit), UFL (upper flammability limit) [8].

Property	R290	R152a	R32	R717	R1234yf
Flame limits (ASTM E681-04) @ 21°C					
Lower Flammability Level (vol% in air)	2.2	3.9	14.4	15.0	6.2
Upper Flammability Level (vol% in air)	10.0	16.9	29.3	28.0	12.3
Delta UFL – LFL	7.8	13.0	14.9	13.0	5.8
Minimum Ignition energy (mJ)	0.25	0.38	30 – 100	100 – 300	5.000 – 10.000
Burning velocity (cm/s)	46	23	6.7	7.2	1.5

The new refrigerants also require new standard from the equipment suppliers. They need to thoroughly assess the component used to ensure enough effort is made to make the system leak tight. Unfortunately, a lot of global economy is driven by lowest capital cost and not life cycle cost. With most heat pump installation being used where there is a continued heat demand for more than 20 years, there should be a greater focus on durability than only fit for purpose throughout the warranty period. With the heat pump industry mainly using flammable refrigerant it could backfire on the industry not focusing on quality if there is an increase in fatal failures.

Based on test made by Umaa University in 2016 the following findings are reported when investigating the products from combustion of HFO-1234yf "Amongst the detected chemicals with relatively high emission factors, COF_2, HF and CO are of greatest health concern. COF_2 (which is about three times as potent as chemical warfare agent phosgene used in World War I) reacts immediately with water to form HF. This will take place in the airways upon contact with the lung lining fluid; mucus and surfactants. HF is highly toxic and corrosive. HF may induce pulmonary edema upon inhalation and may cause severe burns following skin exposure. It can be adsorbed and penetrate tissues, and by binding to calcium HF may cause hypocalcemia. CO binds to haemoglobin and forms carboxyhaemoglobin which inhibits the transport of oxygen in the body resulting in hypoxia in many tissues of organs." [10]

$$CF_3CFCH_2 + 2.5(O_2 + 3.76N_2) \Rightarrow 2CO_2 + 2HF + COF_2 + 9.4N_2 \quad (1)$$

Formula 1: This is the chemical process that takes place when combusting HFO-1234yf

Due to the slow burning of HFO-1234yf it is difficult to create conditions where you get 100% combustion of the refrigerants. Most of the by-product are unburned HFO-1234yf (220-480 mg/g), but there is also a significant amount of carbonyl difluoride (170-360 mg/g), carbon dioxide (120-320 mg/g) and hydrogen fluoride (70-240 mg/g) which all can cause a health risk in very small quantities.

Table 4 [11]: There are three categories of Protective Action Criteria (PACs) representing concentrations at or above which the general population may experience health effect based on 60 minute exposure. PAC-1: Mild, transient health effect, PAC-2: Irreversible or other serious health effect that could impair the ability to take protective action, PAC-3: Life-threatening health effects [12].

	PAC-1 (mg/m^3)	PAC-2 (mg/m^3)	PAC-3 (mg/m^3)
HFO-1234yf; 2,3,3,3-Tetrafluoropropene	10,000	11,000	66,000
Carbonyl difluoride (COF_2)	0.069	0.76	2.2
Hydrogen fluoride (HF)	0.82	20	36

In case of a fire in a car with (typically around 700g refrigerant) HFO-1234yf within a tunnel (cross section area 10 x 5 m), there is a potential health risk to anyone within 154 m (based on HF, PAC-2 level).

$$\frac{220\frac{mg}{g}HF \times 700\ g\ of\ R1234yf}{(10 \times 5\ m^2) \times 20\frac{mg}{m^3}} = 154\ m \qquad (2)$$

Formula 2: Calculation of the distance the air will contain more than 20 mg/m^3 HF, based on Umaa University's combustion test.

If this is transferred to industrial refrigeration where centrifugal chillers can contain up to 10,000 kg of refrigerant the health risk of the HFO-1234yf becomes very apparent. HFO refrigerants should not be treated as safe refrigerant as they are flammable and the combustion products are highly toxic.

5. Environmental impact of fluorinated gasses

Nordic Council of Ministers [13] highlighted in their report that almost all people have fluorinated substances in their bodies today. It is estimated that this leads to an annual health-related costs to 52 – 84 billion EUR for all EEA countries. Exposure occurs primarily through contamination of drinking water. Most of this pollution is not from refrigerant releases, however, as for the global warming gasses and ozone depletion gasses it is part of the puzzle and we need to take responsibility.

HFO refrigerants breaks down to trifluoroacetic acid (TFA) within days in the atmosphere, which is toxic in larger amount to humans and can affect the reproduction [14]. Although TFA is naturally occurring in the oceans it has only become detectable in fresh water in Europe within the last 10 years.

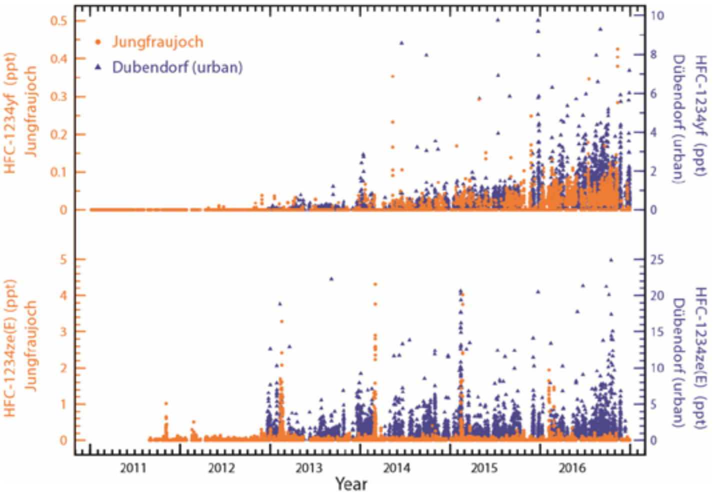


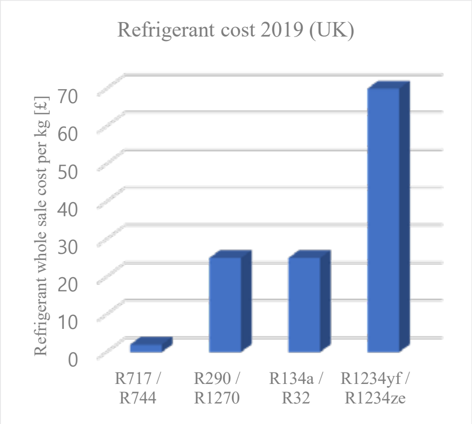
Figure 3: The table shows the increase amount of HFO found in the atmosphere at 2 European sites, The Mountaintop site Jungfraujoch (3,580 meteres above sea level) and urban Dubendorf site. The different colours indicate results from different sites. By mid-2016, 1 – 4 ppt of R1234yf and ~1 ppt of R1234ze(E) were regularly observed at Dubendorf, with pollution events containing up to 20 ppt of R1234ze(E), suggesting that it is more prevalent used in this region.

Several studies of the increased level of TFA in our drinking water due to refrigerant gas releases have shown that at the current amount of release there is very limited concerns. However, with the projected rise in release over coming years (See figure 1), in 20 years' time when the release to atmosphere is at the same level as at the peak of Ozone depletion substances a review will be needed. This is under the assumption that only refrigeration will add to the TFA pollution, however, we need to realise that many other processes are adding to the fluoride acid pollution and we need to act. The Norwegian Environment Agency recommend in their report from 2017[14] "phasing out HFOs (and consequently TFA), or emission reduction strategies along with best practise measures that help ensure efficient capturing of HFO/TFA during recycling operations"

After 90 years of different type of synthetical refrigerants it is time to realise that there is not such a thing as "safe refrigerant". Some refrigerant poses a local risk if not handled with due care and others pose a global risk. HFO poses both a local and global risk if not handled safely and kept inside the refrigeration system until disposed. All refrigerants should be handled with due care. Refrigerant charge should be minimised in all systems. Systems should be made "leak tight" and everyone handling refrigerants should have proper training. In IEA Annex 54[18] "Heat pump systems with low GWP refrigerants" more investigation has been made into handling refrigerant with due diligence.

6. The economic dilemma

The global market for synthetical refrigerant gasses exceeds $15 bn US dollars per year[7] and it is forecasted to continue to grow in the coming years. Every time a new generation of synthetical refrigerants have entered the marked the specific price per kg have increased. The 4th generation of refrigerant is priced at around £70 per kg which is almost 50 times more than = the most commonly used natural refrigerants.



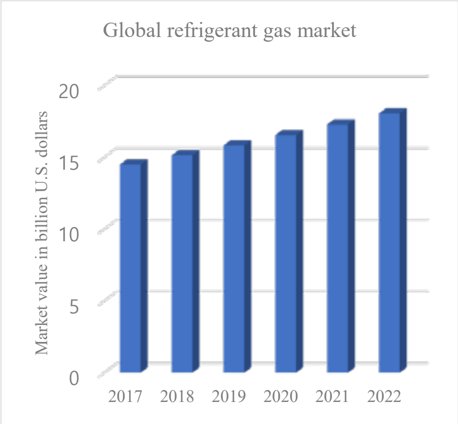


Figure 4: On the graph to the left is the retail cost of refrigerant in the UK 2019 (Source: BOC/Wolseley), to the right is a forecast of the global value of refrigerant sales in billion US dollars [7]

If the refrigeration and heat pump industry hypothetically would stop all production of synthetical refrigerants it would have a huge impact on the turnover for the companies producing and selling refrigerant gasses globally. The main question is whether the global and local consequences of increased releases of HFO are acceptable for the society, since only a few companies are benefitting economically. The next generation will have to tackle the consequences, in the same way as we have had to pay the price for replacing the ozone depletion substances (CFC's) in the first place and global warming fluids (HFC's) lately. Is it worth the risk and is it fair?

Many end-users have been forced to change their refrigeration / heat pump installation before the end of service life due to phase-out of previous generation of synthetical refrigerants. We saw a large replacement of industrial refrigeration system before 2015 in Europe due to the phase-out of HCFC-22. The same is now happening in commercial refrigeration with the phase-out of R404A in 2020 in EU. This will also happen in the rest of the World as they get closer to their deadline for phase out of these refrigerants. This is an added cost to the end-user, which was not communicated at the time of sales. There is no guarantee from the current sales people of refrigerant that this will not happen again in the near future with the HFO's. Does the refrigeration industry need this detour?

7. What are the alternatives?

The fake argument is often used that there is no alternative to HFO and that the alternatives are too costly. But is this true? As HFO are classified as A2L refrigerants they are not "safe" refrigerants so the quality of the components and assembly of heat pumps using HFO should be the same as used for natural refrigerants like CO_2, Ammonia or propane. If HFO heat pumps units are only build as "fit for purpose" throughout the warranty period then there is high risk to the end-user of the system, as small leaks can go undetected for a while until the ignition limit is reached with risk of fire and the toxic by-products from this.

For hydrocarbon refrigerants like R1270, R290 and R600a which all are classed A3 refrigerants, there are additional ATEX requirement to the electrical installation. However, this has been proven by many suppliers to have a very small impact on the cost and is outweighed by the significant lower cost of the refrigerant compared to HFO refrigerants.

For industrial heat pumps where customers do not only evaluate the equipment based on purchase price but also consider the service and operation costs as part of a total life cycle cost analysis, ammonia heat pumps do have significant advantages.

Table 5: Comparison for natural refrigerant (ammonia) industrial heat pump with an industrial heat pump using R1234ze refrigerant. Whereas the ammonia heat pump has a refrigerant charge of 41 kg, there is 140kg of R1234ze refrigerant on the synthetical refrigerant option. This is based on the industry standard for these type of heat pumps. Carrier have informed that they would have 210kg of R1234ze on a 1200 kW heat pump.

Example	RedGenium 1100 heat pump (source: GEA)	HFO Heat pump (Source: Oilon)
Chilled water inlet:	15˚C	15˚C
Chilled water outlet:	10˚C	10˚C
Cooling duty:	557 kW	494 kW
Heating water in:	45˚C	45˚C
Heating water out:	65˚C	65˚C
Heating duty:	716 kW	701 kW
Heating COP:	4.06	3.31
Refrigerant charge	41 kg	140 kg
Capital cost:	£177,000	£120,000
Refrigerant cost:	£80	£10,000
Service cost (20 year):	£125,000	£145,000
Running cost (20 years, £0.1 per kWh, 5000 h per year):	£1,724,137	£2,114,803
Total life cycle cost:	**£2,026,217**	**£2,389,803**

When taking into consideration that for large industrial heat pumps where the refrigerant charge can be up to 10,000 kg, there is also a considered financial risk. In case of a catastrophic failure where the entire charge of the plant is lost the customer would need to spend £700,000 on new refrigerant.

Currently there is a lot of research ongoing in developing high temperature (>100˚C) heat pumps. Where some HFO refrigerant can be used due to their relatively low saturated pressure at high temperature. However similar results can be achieved which R600a and R600, which has been proven by experimental investigations at NTNU / Sintef in Norway[17].
For car AC units many of the manufactures have now introduced alternatives to HFO. Fiat have launched a model with propane and both Daimler and Volkswagen [15] have introduced car models with CO_2 as refrigerant, so there certainly are alternatives to HFO. CO_2 air conditioning and heat pumps have also been proven to be very efficient in electric busses where Valeo[16] has demonstrated that the CO_2 heat pump can add up to 30% extra kilometres in temperatures as low as -20˚C.

For domestic heat pumps many manufacturers also have models with hydrocarbon. For ground source heat pumps there are manufacturer like Heliotherm, and Kensa who has introduced hydrocarbon heat pumps and for airsource heat pumps Nibe and Innotec have introduced a range of airsource heat pumps with hydrocarbons.

For split units air-conditioning and heat pumps there is also many suppliers globally, although some of the main suppliers have been reluctant to include hydrocarbon refrigerant models in their portfolio as they claim that there is added risk of using these refrigerants. Fact is that there is a larger risk by installing a leaking HFO system than a tight hydrocarbon split unit.

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