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Letter to the Editor

Refrigerants: There is still no vision for sustainable solutions

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ABSTRACT

The history of refrigerants is elaborated and the international agreements concerning protection of the ozone layer and climate change are presented. We have to learn from mistakes in the past. There are countries with successful policies.

The most used natural refrigerants are presented: ammonia, CO2 and hydrocarbons. Their advantages and disadvantages are described and their applications. The fourth generation of fluorine-based gases is elaborated: hydrofluoroolefins. The most used are R1234yf and R1234ze(E), and their blends with HFCs.

A vision for the future with environmental refrigerants is described. Innovations such as new types of components, new concepts of low charge ammonia systems and their expansion in many applications. There are improvements of CO2 systems installing parallel compressors, ejectors as an expansion device and usage of evaporative condenser. There is a big potential of R290 to be a refrigerant no. 1 for split air conditioning units. Finally, a new approach is recommended.

1. Introduction

In 1974 scientists Rowland and Molina published information on the depletion of the ozone layer in the stratosphere from CFC gases and recommended a complete ban on the future release of CFCs to the environment.

In the same year, the author of this paper has graduated at the Faculty of Mechanical Engineering and 43 years after working in refrigeration he has retired in 2017. So almost in all his working life he was/is under "pressure" and dilemma with the refrigerants. The choice of refrigerant (and technology) has become a very complicated issue. In the RAC industry, confusion and uncertainties related to working fluids in many applications are still continuing and will continue in the future. In addition, there are many groups with diverse interests: chemical companies, manufacturers of equipment, distributors, contractors, end users, environmental organizations, politicians and the public.

So far, there are no universal solutions for the refrigerants if you take into consideration all relevant aspects: size of cooling capacity, temperature regime, type of application, cost, available service, energy efficiency, ambient air, safety, regulations, environment etc.

2. History of refrigerants

Fig. 1 shows the history of refrigerants since the first mechanical production of cooling in 1834 where Ethyl-Ether was used. After that, several natural refrigerants were applied such as ammonia, CO2, hydro-carbons etc.

Since 1930 there is a big expansion of CFC refrigerants called Freons. And later HCFC refrigerants were introduced mostly in the air conditioning sector. The CFC gases are excellent refrigerants, very stable and friendly to the human body. Furthermore, CFCs were used in inhalers; it means direct entry in the human organism.

However, CFCs are ozone depletion substances (ODS) and this was a reason for phasing them out with the international agreement called Montreal Protocol since 1987. Furthermore, CFCs have a very high global warming potential (GWP).

In the Montreal Protocol (1987) the HCFC gases were not included because they have a very low Ozone Depletion Potential (ODP). For example, the most applied refrigerant in the air conditioning (HCFC-22) has ODP = 0.034. A number of companies which were more conscientious started with replacement of CFCs to R22 or blends with HCFCs. However, in 1992 with the Copenhagen amendment, the HCFCs were included in a group with a little longer period for phase-out. In fact, the companies which already had made conversions from CFCs to HCFCs were cheated in a way.

In 1990 the Norwegian scientist Gustav Lorentzen stated that solutions can be found with natural working fluids which are ozone friendly refrigerants. Not only a scientist, but he was an experienced engineer and had worked previously with ammonia and CO2. It means these were already proven refrigerants. It was necessary to work on further development of CO2 systems in order to improve their energy efficiency in transcritical working conditions.

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Nomenclature

AHRI	Air conditioning, heating and refrigeration institute
CDM	Clean development mechanism
CER	Certified emission reduction
CFC	Chlorofluorocarbon
CO2	Carbon dioxide
COP	Coefficient of performance
GWP	Global warming potential
HC	Hydrocarbon
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
HFO	Hydrofluoroolefin
IIR	International institute for refrigeration
MAC	Mobile air conditioning
ODP	Ozone depletion potential
ODS	Ozone depleting substance
PHE	Plate heat exchangers
RAC	Refrigeration and air conditioning
RTOC	Refrigeration, AC and heat pumps technical options committee
TEAP	Technology and economic assessment panel
TEWI	Total equivalent warming impact
UNEP	United Nations Environment Programme
UNFCCC	United Nations Framework Convention on Climate Change

HFCs are compatible with the CFC equipment excepting small changes such as the oil type. With a retrofit procedure many existing CFC systems were converted in HFC systems. Therefore, without changing the production lines, processes and skills of workers, most manufacturers switched to HFCs. From economical and technological aspect this was expected because there were no regulations for restriction on F-gases at that time. Thus we could say that the HFCs appeared on the market because of the Montreal Protocol. **In fact, the HFCs are products of the Montreal Protocol**.

According to the Montreal Protocol and its amendments, the phase-out process of CFC refrigerants is finished in 2010 including the developing countries.

In the past eight decades CFC gases with very high GWP values have been emitted in the atmosphere, and what is even worse is that they have a long lifetime. For example, the most used refrigerant R12 has GWP = 10,300 and a lifetime of 102 years (UNEP, 2014). This and other CFC gases are all around us and I am not sure what the current amount in the atmosphere is. But it is strange that in many reports today there is no information how much is the share of CFC gases in the total effect on global warming. In 1990 it was believed that the share was approximately 15%, but taking into account their chemical stability, still plays a major role, certainly higher than HFC gases. And it is a fact that even though it is forbidden, CFC gases are still released into the atmosphere in some developing countries.

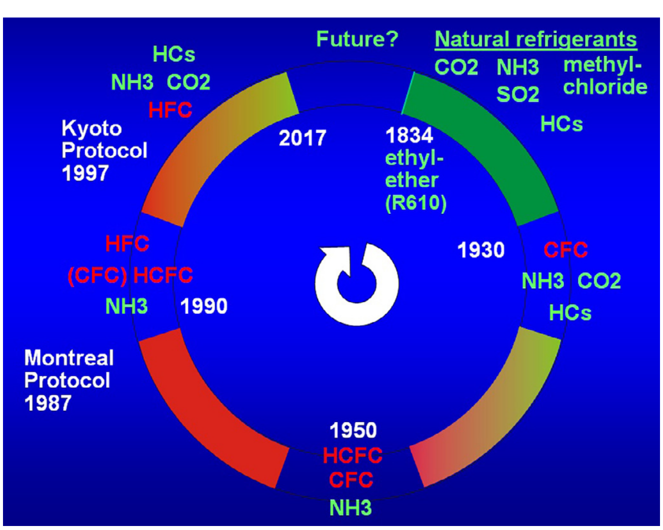

Fig. 1. History of refrigerants.

The phase-out process of HCFC gases started later, and it will last until 2040 in the developing countries. It is known that the most widely used HCFC is R22 having GWP = 1780, and its lifetime is 12 years. What is the common share of CFC and HCFC gases to the total greenhouse effect today?

3. We have to learn from mistakes in the past

In order to perceive mistakes from the work in the past regarding phasing-out of ODS, below is a list of specific agreements by years.

1987:	Montreal Protocol
1992:	UNFCCC (United Nations Framework Convention on Climate Change); Introduction of HFCs
1997:	Kyoto Protocol (HFCs under control)
2007:	Acceleration of HCFC phase-out (Montreal Protocol) Climate friendly technologies to take into account;
2015:	Paris agreement on climate change
2016:	Kigali amendment to the Montreal Protocol – HFCs phase-down Introduction of HFOs (unsaturated HFCs)

It can be noted that the use of HFC refrigerants as alternatives to CFCs started almost at the same time as the Convention for climate change (UNFCCC) which has been introduced in 1992. In the Kyoto Protocol (1997) HFC fluids (F-gases) are placed in the basket of controlled greenhouse gases because they have a high global warming potential (GWP). At the same time, an expansion of the HFC applications was carried out. It could be said that this was an "intentional mistake" at a global level. To a large extent, this situation could have been mitigated by natural refrigerants (ammonia, hydro-carbons and CO2), but the international community did not respond with an adequate way to the lobby of chemical and other companies involved in HFCs. Of course, there were other factors as well, such as the compatibility of refrigeration technologies of CFCs and HFCs, cost, practices, etc. But the big mistake was that the bodies of the Montreal Protocol and the implementation agencies (UNEP, UNIDO, UNDP, World Bank) generally ignored the aspect of climate change. This was an obvious "intentional" mistake.

In 1990, starting with the economy transition in Eastern Europe (including Former Yugoslavia), started a period of phase-down of ammonia which was a traditional refrigerant in this region. In many cold stores ammonia systems were replaced with new systems with CFC, HCFC and later with HFC refrigerants. There are many reasons listed and explained in more details in (Ciconkov, 2010). Furthermore, many manufacturers for ammonia systems were closed and the human resources involved in ammonia refrigeration technology are lost. There was one big factory in the Republic of Macedonia for refrigeration equipment, including ammonia plants, where the well known scientist Gustav Lorentzen has worked as a young expert around 1960. In 2000 this factory was closed. This was also one of the reasons why the author of this paper initiated to organize the IIR Conference on ammonia refrigeration technology, which is biannually held in Ohrid since 2005.

In almost all projects in A5 countries funded under the Montreal Protocol in the past, CFCs and HCFCs were replaced

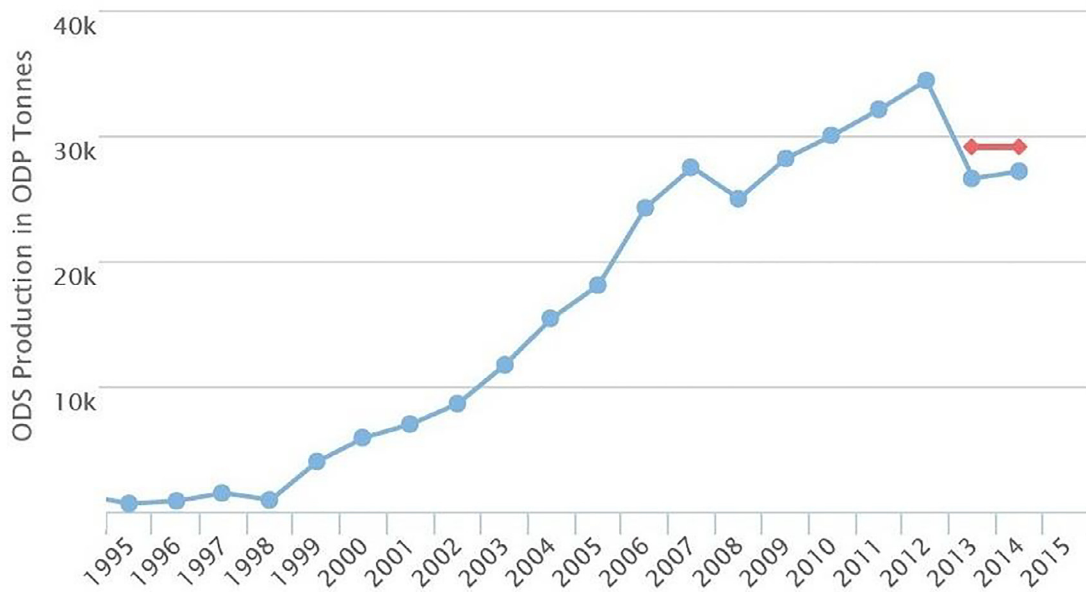

Fig. 2. Production trend of HCFCs in China, (UNEP, 2016a).

with HFCs, with minor exceptions at domestic refrigerators (Ciconkov, 2010). The main reason preferring HFC systems was the lower first cost (named as cost effectiveness) which is not a correct approach instead what should be taken into account is the life cycle cost, small TEWI value and other environmental benefits.

With the transition from CFCs to HFCs, the equivalent greenhouse gas emissions were reduced, but this was not a sustainable solution. For this reason a Kigali's amendment to the Montreal protocol was introduced in 2016; we have to work for the next several decades on phasing-down of HFCs.

3.1. HCFC-22, HFC-23 and the Kyoto protocol

The Clean Development Mechanism (CDM) is one of the Flexible Mechanisms defined in the Kyoto Protocol that supports GHG emissions reduction projects which generate Certified Emission Reduction units (CERs) which may be traded in emissions trading schemes. In 2008–2010 prices for CERS were 10–20 USD/ton. By September 2012, prices for CERS had collapsed to below 5 USD, and now (2017) are below 1 USD.

HFC-23 is a by-product during production of HCFC-22. HFC-23 has GWP = 12,400 and it was very attractive for registration of CDM projects for destruction of HFC-23. In fact, CDM provided perverse incentives to generate more HFC-23 (more money). After several years, the trading with CERs generated from HFC-23 was prevented. The production of HCFCs increased drastically in China since 1998; see the production trend in Fig. 2. The GWP of HCFC-22 is 1780.

4. Policies as successful examples

The typical example that a country policy can have a successful influence on the elimination of harmful refrigerants is Denmark. In 2001 and 2002, Denmark introduced national regulation on F-gases (EPA Denmark, 2011). The aim was to reduce the consumption and emission applying a number of instruments. They comprised a ban on the use of F-gases for certain purposes, F-gas taxation and support for research and development of alternative technologies. It was decided to phase-out HFC refrigerants in most sectors since 2006. Today Denmark is the most advanced country regarding ozone and climate friendly refrigerating technologies. Later, several European countries introduced F-gas taxation.

As a successful policy to reduce the use of HFC refrigerants is the EU regulation 519/2014 which came into force on January 2015 with the following package of measures (Eurammon, 2017):

- Phase-down: the F-gases will be gradually reduced 79% below 1990 levels by 2030.
- Restrictions on use: F-gases with high GWP, such as R404A from 2020.
- Quota system: F-gas quotas will be allocated in order to control the actual consumption of F-gases.
- Leak tests: to avoid leakages, stricter regulations will apply in the future.
- Operator obligations on: installation, maintenance, servicing, repairs or decommissioning. It must be performed only by certified personnel.

The German Government gives subsidies for building systems with natural refrigerants. Today, the biggest number of supermarkets with transcritical refrigerating systems with CO2 refrigerant is in Germany. The Japan Government gives subsidies to users to buy heat pumps for domestic hot water with CO2 refrigerant named as Eco-cute. During the last years several millions such heat pumps are sold.

Today businesses in Europe can receive grants or tax relief for investing in natural refrigerant systems. This is one reason that the EU is most advanced using natural refrigerants compared to other parts of the world. On the other side, some global companies (supermarket chains etc.) build supermarkets in developing countries where refrigeration systems use HFC (R404A). The main explanation: there are no trained personnel for CO2 and ammonia systems in these countries.

5. Natural refrigerants

The most used natural refrigerants are ammonia (R717), CO2 (R744) and hydro-carbons such as isobutane (R600a) and propane (R290). These are known refrigerants used since 19th century.

5.1. Ammonia (R717)

Ammonia is an excellent refrigerant which is in use in the past 140 years mostly for larger cooling capacities in refrigerating systems in industries. Its advantages are (Pearson, 2008):

- Environmental: ODP = 0, GWP < 1;
- High energy efficiency including at high condensing temperatures;
- Excellent thermodynamic properties: high critical temperature (132 °C), large latent heat, large vapour density and excellent for heat transfer coefficients;
- The compression discharge temperatures offer excellent possibilities for waste heat recovery;
- In vapour condition it is lighter than air;
- Easy detection due to pungent smell; hence self-alarming;
- Low price.

Disadvantages of ammonia:

- It is toxic.
- Moderately flammable in concentration in the air from 16 to 28%.
- It is not compatible with copper.
- The discharge temperature is higher compared to other refrigerants. This is due to the larger adiabatic exponent.

Ammonia is difficult to ignite, it is flammable only at high concentrations and under extremely limited conditions and with an uninterrupted external flame source.

The Threshold Limit Value (TLV) of ammonia is 25 ppm. The toxicity is the only real disadvantage of ammonia. However, concentration of 5 ppm can be smelled and the pungent odour worries humans to the point that it forces them to leave the premises.

Ammonia refrigerating systems are liable to legal regulations and standards because of the safety issues; however, these exist for other refrigerants as well. If these regulations and standards are strictly enforced along with a good training routine for the personnel, the level of risk can be minimized at a level as at other refrigerants.

The ammonia refrigeration systems are the best solutions for cold stores and many industrial applications such as food and drink processing, breweries, dairies and heat pumps for hot water up to 90 °C. Ammonia liquid chillers with indirect cooling are used in applications such as central air conditioning of buildings (airports, hospitals, administration buildings …), supermarkets etc. With the future development of low charge technology, expansion of ammonia system in commercial refrigeration is expected.

5.2. Carbon-dioxide (R744)

CO2 has a long history since the middle of 19th century, but it was completely re-moved from appliance after 1950 making way to refrigerants which were more efficient at that time. Today, CO2 has a successful comeback in refrigeration in various applications. R744 is very different than other most used refrigerants. Its advantages are (Pearson, 2014):

- Environmental: ODP = 0, GWP = 1;
- Non toxic and non flammable;
- High volumetric cooling capacity = > smaller compression volume in the compressor
- Excellent thermophysical properties = > heat transfer advantages;
- Lesser sensitivity to pressure drop = > easier for design of heat exchangers;
- Smaller dimensions (diameter) of suction pipeline;
- Excellent potential for charge reduction (microchannel heat exchangers);
- Possibilities for heat recovery for hot water;
- Compatible with most of materials (non corrosive);
- Low price.

Disadvantages of CO2:

- Low critical temperature: 31 °C;
- High pressure (120 bar and more): high design pressure of equipment;
- Excessive pressures at standstill (need for additional equipment to avoid it).

The refrigeration cycle which occurs above the critical temperature is called a transcritical cycle, and compared with the conventional one it is energetically less efficient at conventional configuration of the system. This was the reason that the CO2 systems were used firstly in regions with cold and moderate climate (Northern Europe) where subcritical operation is dominant.

In the last several years, the R&D on CO2 systems contributed to significant improvement of their energy efficiency. The transcritical operation can be improved with the following modifications (Minetto et al., 2014; Hafner and Hemmingsen, 2015; Ciconkov, 2016):

- to install a parallel compressor(s);
- to build an internal heat exchanger;
- to install an external subcooler;
- to install ejectors as an expansion device;

The subcritical operation of CO2 systems is very efficient and it can be achieved using an evaporative condenser even in locations with hot climate (Visser, 2017). The subcritical operation can also be achieved at an air-cooled condenser combined with a water spray or / and with a wet pad (using evaporative effect).

The compression discharge temperatures offer excellent possibilities for waste heat recovery. In this way, the overall energy efficiency of the refrigerating system is improved.

Today, the CO2 refrigerant is the first option for the commercial refrigeration systems which is very important as replacement for R404A which has GWP = 4200. Furthermore, the annual leakage rate at the central systems in the supermarkets in the past was about 30% in the developed countries and much more in the developing countries. During the last several years, the CO2 refrigerant expands its use in many applications faster than expected which is described in a further section of this paper.

5.3. Hydro-carbons

Hydro-carbons were also used as refrigerants in the past, but later were excluded with the introduction of CFC refrigerants which are safer, remaining in some industrial complexes as the refineries. Today, they are mostly used as refrigerants: isobutane (R600a), propane (R290), propylene (R1270) and some blends. HC refrigerants are a great substitute for CFCs, so units which use CFC can work with HC without big modifications because HCs are compatible with copper and they are miscible with mineral oils.

Their negative side is that they are very easily flammable in the air, and that is the only obstacle towards wide appliance.

5.4. Isobutane (R600a)

Isobutane is an excellent alternative for R12 in domestic refrigerators and small commercial units. Mass production of domestic refrigerators with R600a started in Germany in 1995, and then spread in the whole world except in the USA where due to strict safety regulations this type of production is not allowed.

The energy efficiency is very good, and according some information it is better compared with R134a. The advantage is low refrigerant charge (around 70 g), and the price of the isobutane is much lower. Because of lower working pressures there is smooth operation resulting with low noise. Regarding safety, reports are positive and the assumption is that the number of manufactured domestic refrigerators with isobutane surpasses the number of refrigerators with R134a.

5.5. Propane (R290)

The thermodynamic properties of propane are similar with the ones of R22, which means this is its corresponding substitute. In the past years propane's appliance has increased, but only in special cases because of the safety reasons and state regulations. Highest usage is now in small commercial units (refrigerated display cabinets) where it has small charging up to 150 g.

There are initiatives for use of propane in room air conditioning units which are factory sealed and with adapted electrical elements. There are already production lines in China and India.

Propane is an excellent refrigerant for vehicle air conditioning, but here also the obstacle is safety of the passengers. Unofficially there are thousands of vehicles with propane in their air conditioning units in Australia, and there are still no negative reports of their appliance.

6. HFO refrigerants

HFOs (hydro-fluoro-olefins) are unsaturated HFCs and they are the fourth generation of fluorine-based gases. These synthetical refrigerants are categorized as: ODP = 0, with low GWP (Bitzer GmbH, 2016) and as A2L gases (mildly flammable).

The ban on the use of R134a in mobile air-conditioning (MAC) systems within the EU has triggered a series of research projects. DuPont and Honeywell jointly developed the first HFO, it is R1234yf. This is a low GWP replacement for R134a for use in MAC systems with similar thermodynamic properties as R134a.

R1234ze(E) is sometimes called an R134a substitute, but its volumetric refrigerating capacity is more than 20% below that of R134a or R1234yf (Bitzer GmbH, 2016). Moreover, the boiling point (−19 °C) considerably limits its use for lower evaporation temperatures. Therefore, it is preferably used in liquid chillers and for high temperature applications.

R1234yf and R1234ze(E) are also used as base components in HFO/HFC blends.

New HFO/HFC blends:

In view of the EU F-Gas Regulation and later the Kigali amendment, these blends are developed as "Low GWP" alternatives to R134a, R404A, R507A, R22, R407C and R410A. Some of these refrigerants have already been tested with regard to refrigerating capacity and efficiency as parts of the "Alternative Refrigerants Evaluation Program" (AREP) initiated by AHRI and have also been used in real systems (AHRI, 2012–2016).

Those having the lowest GWPs also tend to be flammable which may limit their applicability and further work is needed before they become a real viable option.

In Table 1 there are HFOs and HFO/HFC blends as alternatives to HFC refrigerants with a high GWP.

6.1. Prices of HFO refrigerants

An unfavourable side of the HFO refrigerants is their very high price. The retail price for a 5 kg bottle of R1234yf was £462 (www.boconlineshop.com, visited on July 2017), which means 120 USD/kg. Visiting several websites, it was found that this price was between 110 and 150 USD/kg. The retail price of the refrigerant R1234ze(E) was three times lower compared to R1234zf, it means from 35 to 50 USD/kg, and this price is very high too. If we add that there are currently only two manufacturers of HFOs in the world, then the situation with new alternative HFO refrigerants is even more unfavourable.

6.2. Is there a risk using HFOs?

R1234yf is mildly flammable and usage in MAC systems could be a potential risk. Some investigations made by Daimler-Benz in their own laboratory show an increased risk. This is why various manufacturers have again intensified the development of alternative technologies. On the other hand, in extensive test series, it has been shown that a potentially increased risk of the refrigerant flammability in MAC systems can be avoided by implementing suitable constructive measures.

In case of fire, thermal decomposition products of HFO-1234yf are: hydrogen fluoride (HF) and carbonyl fluoride (COF2) which are extremely toxic. Also, in case of leakage in the atmosphere, HFOs break down into trifluoroacetic acid (TFA), which has a potential to accumulate and adversely affect ecosystems by increasing their acidity (Hoffmann and Plehn, 2010). Are we starting with a new long term experiment on the environment with new synthetical refrigerants?

7. Wrong approach

The direct climate impact of the refrigerants can be expressed with their Global Warming Potential (GWP). In the UNEP publication RTOC 2014 Assessment Report there is a classification of GWP with a 100 years horizon. This is presented in the Table 2.

This classification is based on the past when refrigerants with high GWP prevailed. Looking at the future in the context of sustainable development, this classification is not appropriate, especially not from an environmental point of view. For example, refrigerants with GWP = 300 to 1000 cannot be placed in the category of "medium".

So far, 2016 was the hottest year in the history. In this context, there is a question whether the refrigerant with GWP = 704 (as R32) is a good alternative for R410A?! And since 2015, millions of AC units with R32 are sold on the market.

It is very important to leapfrog from HFC refrigerants with high GWP directly to final refrigerants with low GWP. It is significantly less expensive to avoid a slow and costly progression from high-GWP to medium-GWP and later to lower-GWP HFCs. There is an example happening now with conversion: from R410A (GWP = 2088) to R32 (GWP = 704), and in the near future to refrigerant with a low GWP should be expected?!

There is a dilemma: natural or synthetical refrigerants (see the Fig. 3)? After several conversions of several refrigerant types (including their blends): CFCs -> HCFCs -> HFCs -> HFOs (?) we must learn the lesson from the past and nowadays. We have to avoid entering into uncertain future of the ecosystems.

8. Vision for the future with environmental refrigerants

8.1. Ammonia refrigeration systems

As the safety reason is the main barrier, new concepts of ammonia systems are developed where the refrigerant charge is reduced. It can be achieved mostly using new types of heat exchangers and new scheme avoiding receivers and pump system. The following solutions can be used:

- Dry expansion (DX) evaporators where the refrigerant charge is lower. The refrigerant evaporates in tubes, but this requires miscible oil, so new developed oils are already applied.
- Plate heat exchangers (PHEs) are introduced in ammonia systems too, as evaporators and condensers. The traditional brazing materials are not compatible with ammonia, so new types

Table 1
HFO and HFO/HFC blends as alternatives to HFCs.

Designation	To replace	Composition	HFO or HFO/HFC blend	GWP	Safety class
R-444A	R-134a	R-32/152a/1234ze(E)	blend	93	A2L
R-448A	R-404A	R-32/125/134a/1234yf//1234ze(E)	blend	1400	A1
R-449A	R-404A	R-32/125/1234yf/134a	blend	1400	A1
R-450A	R-134a	R-134a/1234ze(E)	blend	570	A1
R-452A	R-404A	R-32/R125/1234yf	blend	2140	A1
R-452B	R-410A	R-32/R125/1234yf	blend	675	A2L
R-454A	R-404A	R-1234yf/32	blend	250	A2L
R-454B	R-410A	R-32/1234yf	blend	490	A2L
R-454C	R-404A	R-1234yf/32	blend	150	A2L
R-513A	R-134a	R-1234yf/134a	blend	600	A1
R-1234yf	R-134a	–	HFO	<1	A2L
R-1234ze(E)	R-134a	–	HFO	<1	A2L

Sources: UNEP 2016b; www.chemours.com.

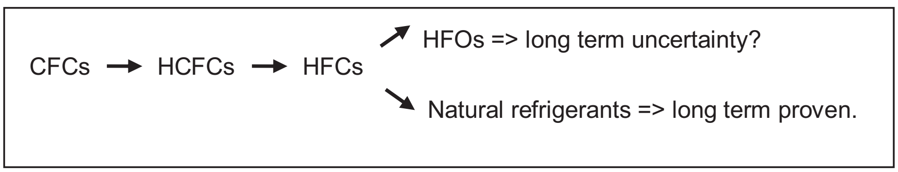

Fig. 3. Conversions and dilemma.

Table 2
Classification of 100 year GWP levels.

GWP 100 years	Classification
<30	Ultra-low or negligible
<100	Very low
<300	Low
300–1000	Medium
>1000	High
>3000	Very high
>10,000	Ultra-high

Source: UNEP, RTOC 2014 Assessment Report.

are developed with stainless steel welded modules and nickel brazed exchangers. The PHE evaporator is also implemented with dry expansion which requires small ammonia charge, an electronic expansion valves and miscible oil too. The PHEs have higher energy efficiency and smaller dimensions.
- Shell-and-plate heat exchangers are new type, in fact these ones are combined of a shell-and-tube and PHE. They are very compact and with a small refrigerant charge. In the market there are liquid chillers with relatively small ammonia charge where shell-and-plate heat exchangers are used. These liquid chillers are compact, assembled and tested in a factory. A chiller with about 50 kg ammonia charge can give 1000 kW cooling capacity.
- The microchannel heat exchangers are excellent possibilities for ammonia and CO2. New designs in microchannel heat exchangers allow much smaller refrigerant charges than in conventional heat exchangers. Aluminium is very suitable for manufacturing of these types of heat exchangers, compatible with ammonia.

Although ammonia is most used in the industrial refrigeration since the 19 century, a new concept is developed in this sector a few years ago: all components incorporated in a container, similar to rooftop air conditioning units. These units are preassembled in a factory and one manufacturer (Evapco, 2017) states the following advantages: lower ammonia charge, lower regulatory burden, lower energy consumption, eliminated central machine room, faster installation and startup, competitive cost and single source design and manufacturing. It is more attractive compared to a field erected system.

Ammonia is not compatible with copper and this is a reason that ammonia is not used for hermetic and semi-hermetic compressors where the electro-motors are made with copper windings. However, liquid chillers with ammonia semi-hermetic compressors on the market recently appeared where the electro-motors are made with aluminium windings. The first cost of ammonia chillers is higher compared with fluorinated chillers, but the life cycle cost is lower because of higher energy efficiency. In case of mass production of ammonia semi-hermetic compressors, the first cost of ammonia systems will decrease. Obviously the incentives are necessary in this initial phase.

If semi-hermetic compressors are used in ammonia systems, this means the road is open to produce ammonia hermetic compressors. The hermetic and semi-hermetic ammonia compressors are a big challenge. Such products will enable use of ammonia in small and medium commercial systems with low ammonia charge that should not be dangerous for people in most cases. If to these new technical circumstances we add a real possibility for the application of aluminium microchannel heat exchangers, then the small and medium ammonia systems can make a revolution in commercial refrigeration and air conditioning. There are no real technical difficulties to start production of small and medium ammonia systems. So far the main problems are the prices of the components. This can be overcome with incentives in the beginning in order to achieve mass production.

Hrnjak (2017) describes in more details the low charge ammonia systems including Table 3 with some commercially available ammonia chillers.

Lamb (2016) describes a packaged system, with an air cooled condenser, pumpless overfeed to aluminium evaporators where the ammonia charge is less than 0.5 kg/kW.

The concept of the compressor rack at CO2 systems can be applied in the ammonia systems too, but because of another reason: to make the ammonia system with two or more circuits. The air cooled condenser can be in one piece with correspondent number of circuits. The number of circuits at the evaporator(s) will depends on the application. This way, the ammonia charge is divided in two or more independent parts (circuits) and in case of failure the quantity of leakage will be smaller. With this concept the safety is improved, reducing the ammonia charge divided in more circuits with lower refrigerant charges.

Table 3
Incomplete list of some commercially available ammonia chillers (Hrnjak, 2017).

Air cooled chillers	Capacity (kW)	Charge (g/kW)	Water cooled chillers	Capacity (kW)	Charge (g/kW)
Hrnjak and Litch	13	18	Palm, KTH—Sherpa	9	11
CTS - AMCHIL 5	20	22	ILKA MAFA 100.2	108	23
Cecchinato and others	120	84	ABB (York) BXA	108	157–43
Refcomp VKA16-14	16	125	Gram (York) LC	38–228	228–37
York YSLC F4F00UW	220	129	Sabroe (York) PAC	57–1074	172–36
N.R. Koeling LK 25	25	159	Mycom	270	370
Mycom	35	250	Evapco	100–200	400
Evapco	100–200	400			

8.2. CO2 refrigeration systems

The revival of CO2 as refrigerant was initiated by Gustav Lorentzen in 1992. The CO2 systems really came back at about 2010, mostly in northern Europe because the transcritical systems with a conventional configuration are less efficient in hot climate. Until recently (up to 2014), there was a so called “CO2 equator” where the CO2 systems below it were less efficient and not recommended. However, the new technological innovations are crossing the CO2 equator and the CO2 systems are efficient for regions with warm climates as well.

According to Ona et al. (2017) the number of supermarkets with transcritical CO2 systems in Europe in 2017 is 9000. It is estimated that this number will be 25,000 in 2020, and 55,000 in 2025. If CO2 systems for smaller stores become simpler and cheaper, these systems are expected to become more competitive compared to HFCs systems.

The CO2 is very convenient to use in heat pumps for sanitary hot water, they are very efficient. There are millions of such heat pumps (under the name Eco-Cute) in Japan because the government supports their use by giving subventions.

Usually the end users (as supermarkets) need refrigeration at various temperature levels (cabinets and cold rooms), heating and air conditioning of occupied area and sanitary hot water. The CO2 systems are open for many possibilities. Integrated CO2 systems can simultaneously provide refrigeration as low as −50 °C, air conditioning, space heating and sanitary hot water (Hafner, 2017). Such concept outperforms all other HFC systems regarding energy efficiency.

In the last several years, the transcritical CO2 systems are also becoming interesting in industrial refrigeration applications with big cooling capacities. There are numerous examples from Europe which indicate that CO2 is becoming increasingly competitive for this segment too (Ona, 2017).

Several countries announced that they will reduce fuel engine cars and will support electric cars. It is expected that the use of electric cars will expand faster and it seems that in near future they will take over the market compared to fuel engine cars. The space heating in electric cars is a big problem because a resist heater spends electrical energy which is very precious to drive the car. More suitable solution is a reversible heat pump (cooling and heating). This is a big chance for CO2 air conditioning units which are more efficient in a heating mode than the HFO heat pumps.

It seems that CO2 will become a refrigerant no. 1 in the near future.

8.3. HC refrigeration systems

HC-600a is the primary refrigerant option for production of new domestic refrigerators. It is projected that about 75% of new refrigerator production will use HC-600a by 2020 (UNEP-2, 2016b) at a global level.

In commercial refrigeration self-contained systems are increasingly replacing R404A and R22 to R290 with refrigerant charges of up to 150 g. Charge limits continue to limit the size of the equipment with the HC refrigerant. Several manufactures reported better energy efficiency (about 10%) for R290 units than for comparable R404A units (IIR, 2016).

Table 4
Technical data of AC units with R290; projects in China and India (Wypior, 2014).

Project in	Cooling capacity (kW)	COP (EER)	Charge (g)
China	2.70	3.55	265
China	3.50	3.52	330
India	3.34	3.70*	300

* SEER = 5.2 for the inverter model.

There is a big expansion of room air conditioners (split systems), especially in developing countries using HCFC-22 and HFC-410A. China produces 100 million air-conditioning units per year, 40% of which are exported to other countries (Hydrocarbons21.com, 2017). Within the project for HCFC phase-out in China and India, several new production lines for AC units on R290 are built and certified with support of GIZ—Proklima. Some technical data are presented in Table 4.

The benefits of using R290 as a refrigerant in AC units: higher energy efficiency, very low GWP (=3), higher cooling capacity and coefficient of performance and cheaper refrigerant. Challenges faced are flammability and limited charge sizes (in correlation with room area) due to standards and building codes. It is necessary to introduce more flexible safety requirements to improve the safety level in order to facilitate the market, including training for installation and servicing. Until 2016, 250,000 split AC units with R290 were sold in India, and this year (2017) it is expected 100,000 units to be delivered on the market in China (Denzinger, 2016).

Xu et al (2016) proposed and investigated experimentally a novel low charge microchannel condenser in a split AC unit. The cooling capacity was increased at 3.2 kW and the optimum charge of R290 was reduced to 190 g. If other components (like compressor) are improved, the system charge may be reduced to 150 g, so as to meet IEC safety charge requirement.

For bigger cooling capacity (e.g. 7 kW) maybe the R290 AC unit could be performed in two refrigeration circuits (two compressors in the condensing unit). This design will be more expensive, but all things should be taken into consideration when compared with a conventional HFC system.

8.4. Notice

The water (R718) and the air (R729) as refrigerants are not included in this review. They belong to the group of natural refrigerants and especially R718 could be very attractive in near perspective. Further research and improvements are necessary in order to be competitive to other conventional refrigeration technologies.

8.5. NIK technologies

Not-in-kind (NIK) refrigeration technologies are not discussed in this paper. However, absorption and adsorption machines, magneto-caloric units and other NIK technologies are open as future sustainable options to research and to find economically viable solutions. Absorption machines are competitive in some specific applications using waste heat, in combined production of electricity, heat and cold (trigeneration), future perspective of using in solar air conditioning, etc.

9. Discussion and conclusions

It is announced that the Montreal Protocol is the most successful agreement in the world achieving complete phase-out of CFCs in 2010; however there are facts that say something different. The bodies of the Montreal Protocol ignored the climate change issue and mentioned it for the first time in their document in 2007, without further mechanism of activities in this regard. In fact, the Montreal Protocol opened the door for HFC refrigerants. What hypocrisy, the Kigali amendment to the Montreal Protocol is introduced (in 2016) for phase-down of HFCs (UNEP-3, 2017)! This process will last until 2036 for developed countries and until 2047 for developing countries in order to achieve a plateau of 85% reduction of HFCs. It means, the overall process (1987 to 2047) of the Montreal Protocol will last 60 years?! Or maybe longer if HFO refrigerants are applied more and later if a harmful impact on the environment will be found? And how many thousands of people in international and national administrations have to work on collecting data for export/import and allowed F-gas quotas expressed in CO2-eq, permissions, custom control, quantities of leakage, etc? How many thousands of people will be directly or indirectly involved, such as end users, service technicians, engineers, manufacturers of RAC equipment etc?

The natural refrigerants, such as ammonia, CO2 and hydrocarbons, are the best alternatives for HFCs, but there are some limitations: toxicity, flammability and poor material compatibility. These can usually be addressed through suitable product design and proper maintenance of equipment. Safety levels should be maintained and risks minimized, but standards, codes and legislation should be adapted to technological progress and allow the use of more climate-friendly alternatives (European Commission, 2016).

The initial cost of the equipment with natural refrigerants is often higher in certain sectors compared to HFC based systems (e.g. ammonia liquid chillers). However, the cost of equipment decreases with growing production capacities and when more suppliers enter the market; this is a basic economic principle. Furthermore, the life cycle cost is more relevant than the first cost. The environmental aspect should be taken into account as well.

Refrigeration, including air conditioning and heat pumping, represents more than 17% of the world electricity consumption (Coulomb, 2016). The use of refrigeration will continue to grow steadily in the future, particularly in developing countries where there is 81% of world population. Ciconkov (2010) elaborated the problems and barriers for using natural refrigerants in the developing countries and proposed some suggestions.

Even in the developed countries, there are not enough people trained in refrigeration technologies with natural refrigerants, especially with CO2. It is necessary to establish a fund for supporting and organization of trainings on using natural refrigerants in the developing countries. The Multilateral Fund of the Montreal Protocol and its existing ozone networks should be included to overcome this barrier. Such activity could be a direct contribution to the phase-out of HCFCs and phase-down of HFCs, why wait?

For over 30 years we talk about phase-out of CFCs and now phase-down of HFCs, there are many discussions and lost time, spent money, transition refrigerants and trainings.

Instead to be occupied with a phase-down of HFC gases, drop-in refrigerants, retrofit of systems, environmental taxes, data collecting, restrictions etc., let's start with **a new approach: PHASE-IN OF NATURAL REFRIGERANTS such as ammonia, CO2 and hydrocarbons. These are ozone and climate friendly refrigerants; it means long term and sustainable solutions.**

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