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DEVELOPMENT OF REFRIGERANTS: A BRIEF REVIEW

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ABSTRACT

Refrigeration and air-conditioning play a vital role in domestic and industrial applications. They have great impact on our day-to-day life. They have also contributed to the world's major environmental issues like ozone layer depletion and global warming. The development of the refrigeration systems and the refrigerants used in them, from the days when refrigeration was not known to the present day is very interesting. The development of different refrigerants over time took place based on safety, durability and environmental impact issues. In this paper, the different generations of refrigerants beginning with those refrigerants used before the development of mechanical refrigeration system to the possible next generation refrigerants which are environmental friendly and can replace the conventional refrigerants have been discussed. The low GWP refrigerants like hydro-fluoro-olefins and natural refrigerants like ammonia and carbon dioxide are considered as environmental friendly next generation refrigerants.

KEYWORDS: Air-conditioning, GWP, Hydro-fluoro-olefins, Natural Refrigerants, Refrigeration.

Refrigeration is an old technology that started a long time ago. Refrigeration is the process of removing heat from an enclosed space or from a substance in order to maintain a lower temperature than the surroundings. Before 1830, food preservation methods like salting, spicing, smoking, pickling and drying existed. Evaporative cooling was practised in India and Egypt. It was discovered that adding chemicals like sodium nitrate or potassium nitrate to water caused the temperature to fall. Before mechanical refrigeration systems were introduced, people cooled their food with ice transported from the mountains, and ice was stored by using snow cellars, pits that were dug into the ground and insulated with wood and straw.

REFRIGERANTS

Refrigerants are the working medium used in refrigerating systems which evaporates by taking the heat from the space that is to be cooled, thus producing the cooling effect. Refrigerant development throughout the history, took place due to different reasons, such as safety, stability, durability, economic or environmental issues, thus giving rise to new research and equipment improvement in terms of safety and efficiency. The refrigerants can be classified into different generations which are discussed below. Different generations of refrigerants and their behaviours have been shown in Fig. 1 [Calm and Hourahan, 2001].

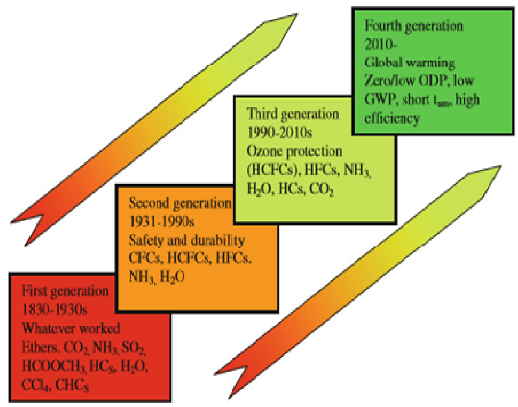

Fig 1: Different Generations of Refrigerants

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First Generation Refrigerants

Beginnings of mechanical refrigeration, starting from early 19th century were characterized by use of natural refrigerants. Refrigerators that were built in the late 1800s to 1929 used the first generation refrigerants like methyl chloride, ammonia and sulphur dioxide. The common refrigerants for the first hundred years included whatever worked and whatever was available. Nearly all the first generation refrigerants were flammable, toxic or both and some were also highly reactive. The characteristics of some of the first generation refrigerants are discussed below.

Water is one of the oldest refrigerants being used for refrigeration applications down to about the freezing of water. When water is coupled with protective solutions to prevent freezing (i.e. propylene or ethylene glycol), it can be used well below water's normal

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freezing point in applications such as ice slurries. Water is easily available and has excellent thermodynamic and chemical properties. Besides these advantages, there are technical challenges that result from its high specific volume at low temperatures. These challenges include high pressure ratio across the compressor and high compressor outlet temperatures.

Ammonia is denoted as R717 and is also a very old refrigerant used in vapour compression and absorption refrigeration systems. The advantages of R717 are that they have a lower molecular weight, wide range of working temperature because of its high critical point, high latent heat of vapourization and easy leak detection. However, R717 also has some disadvantages. It is highly toxic, highly irritating and flammable. Ammonia has high affinity to water, thus it is difficult to keep ammonia dry.

Table I: Properties of Refrigerants

Substance	R Number	M (kg/ kmol)	NBP (^{o}C)	ODP	GWP
Carbon dioxide	R-744	44.01	-55.6	0	1
Ammonia	R-717	17.03	-33.3	0	0
Sulphur dioxide	R-764	64.06	-10.0	0	0
Ethyl ether	R-610	74.12	35	0	0
Dimethyl ether	R-170	46.07	-25	0	0
Methyl chloride	R-40	50.49	-24.2	0.02	16

When it contains water it is corrosive to copper and most copper alloys. At high discharge temperatures generated by ammonia, it has the tendency to dissociate giving nitrogen and hydrogen. When these gases enter condenser their pressures are added to the condensing pressure thereby increasing total pressure head and power consumption.

Sulphur dioxide is one of the most used refrigerants in 1920's and 1930's, having been replaced first by methyl chloride and later by more desirable fluorocarbon refrigerants. It is highly toxic but non-explosive and non-flammable. It is non-corrosive in pure state but when it combines with moisture it forms sulphurous acids and sulphuric acids which are highly corrosive.

Methyl chloride was first used in 1878. Methyl chloride is a colourless extremely flammable gas with a mildly sweet odour. Methyl chloride is a halocarbon of the methane series and it has many of the properties desirable in a refrigerant, which accounts for its wide use in the past in both domestic and commercial applications. Methyl chloride is corrosive to aluminium, zinc, magnesium and the compounds formed in combinations with these materials. In the presence of moisture, methyl chloride forms a weak hydrochloric acid, which is corrosive to both ferrous and non-ferrous metals. It is also explosive. There were numerous fatal accidents that occurred in the 1920s when methyl chloride leaked out of refrigerators. This has lead to the discovery of the next generation refrigerants. Few first generation refrigerant and their properties have been shown in table I.

Second Generation Refrigerants

The second generation refrigerants were distinguished by a shift to chlorofluoro chemicals for safety and durability. Thomas Midgley and his associates studied the property tables of elements of periodic table. They disregarded compounds that are unstable, toxic, yielding insufficient volatility and inert gases based on their low boiling point. In 1928, Midgley and his colleagues made critical observations regarding flammability and toxicity of compounds containing elements like carbon, nitrogen, oxygen, sulphur, hydrogen, fluorine, chlorine and bromine. Their first publication was on fluorochloro refrigerants and it showed how the variation of chlorination and fluorination of hydrocarbons influences boiling point, flammability and toxicity of the refrigerants. Thus CFC refrigerants made the second generation of refrigerants. CFC is a non-toxic, non-flammable gas with relatively high mass. It is a good refrigerant because it can be compressed easily to liquid and carries away lots of heat when it evaporates. It is very stable that only UV rays can break it down In fact, it's well suited to a variety of applications because it doesn't react with anything; it works well as a solvent, a blowing agent, a fire extinguishing agent and an aerosol propellant. Because it is a single molecule, not a mixture, it doesn't separate out at different pressures or temperatures. Some of the refrigerants of this generation are presented here along with their thermodynamic properties and applications.

R-11 is considered to be safe refrigerant as it is non-flammable and non-explosive. It is used in the applications like air conditioning of small buildings, factories, departmental stores, theatres etc. It can be used in the applications where the refrigeration load ranges from 150 to 2000 tons along with the centrifugal compressor. R-11 refrigerant is also used as the solvent and the secondary refrigerant. The problems that have restricted the use of this refrigerant are low operating pressures and high potential to deplete ozone layer. Since R11 has highest potential to cause the depletion of ozone layer, as per the Montreal Protocol, its use and production had to be stopped completely. R-11 is now being replaced by other environment friendly refrigerants, of which the most common is R-123.

R-12 is a highly versatile refrigerant that is used for wide range of refrigeration and air conditioning applications. Refrigerant R12 is used in domestic refrigerators and freezers, liquid chillers, dehumidifiers, ice makers, water coolers, water fountains and transport refrigeration. R12 is nontoxic, non-flammable, and non-explosive. This makes it highly popular for the domestic as well as the commercial applications. R12 is highly stable CFC and it does not disintegrate even under the extreme operating conditions. Unfortunately, it is the CFC and it has unusually high potential to cause the depletion of the ozone layer. R12 is being replaced by other refrigerants and some of the suggested replacements for R12 are: R-134a, R-401a, R- 401b.

In the 1970s, after decades of dumping about a million tons of the stuff into the air each year, scientists learned that CFC isn't harmless after all. In 1973 Prof. James Lovelock discovered Freon to be harmful to the ozone layer. The CFC molecules are destroyed by the sun's ultraviolet rays in the stratosphere the chlorine atoms drift free.

Table II: Properties of Second Refrigerants

Substance	R No.	M Kg/ kmol	NBP (^oC)	ODP	GWP
Trichloro fluoro methane	R-11	137.4	23.71	1	4000
Dichloro difluoro methane	R-12	120.91	-29.75	1	8500
Chloro trifluoro mthane	R-13	104.5	-81.3	1	11700
Chloro difluoro methane	R-22	86.47	-40.8	0.05 5	1700
R-22/R115	R-502	111.6	-45.3	0.33	5600

They break unstable ozone molecules (O3) into oxygen molecules (O2). The chlorine is not consumed in the reaction, so it continues ruining ozone for years. This is a big deal, because stratospheric ozone is the shield that protects all living things on the planet from the Sun's ultraviolet radiation. In 1987, the Montreal Protocol limits the production and consumption of CFCs. January 2010 marked the end of global production of CFCs under the Protocol. In 2009 the Montreal Protocol was universally ratified by 196 nations. Few second generation refrigerant and their properties has been shown in table II.

Third Generation Refrigerants

They were mostly low ozone depletion potential refrigerants. Properties of different third generation refrigerants are listed in table III. Another new class of fluorocarbon refrigerants called hydrofluoro-olefin (HFO) with potential for reduced GWP have been developed. Their primary advantage, other than their low GWP, is that they can be used with existing refrigeration system designs. This is good for the industry and their customers, but it is still a fluorinated gas. There is growing political pressure to regulate it out of production and force the industry to develop an even lower-impact refrigeration technology. So the search continues. Figure 2 represents GWP values of some third generation refrigerants [Pavkovic, 2013].

Natural Refrigerants

Natural refrigerants are easily available, and long experience exists with their application dating far into the beginning of mechanical refrigeration. Many new refrigerants have come into picture to overcome the disadvantages of using natural refrigerants but the "circle" is now somehow closed as we already returned to natural refrigerants, but now with new technologies and with a lot of experience behind us. Natural refrigerants divide conveniently into hydrocarbons, ammonia and CO2 and have been discussed here.

The dominant characteristic of the hydrocarbon refrigerants is their high flammability. Provided precautions are taken to mitigate the consequences of their flammability, hydrocarbons make excellent refrigerants in practice. They are miscible with mineral oils and have relatively high critical temperatures.

Table III: Properties of Third Generation Refrigerants

R number	M Kg/kmol	NBP (^oC)	GWP
R-32	-52.02	-51.65	580
R-134A	102.03	-26.07	1300
R-404A	97.6	-46.6	3800
R-407C	86.2	-43.8	1600
R-410A	72.59	-51.6	1900
R-507	98.86	-47.1	4000
R-508A	100.1	-87.4	13000

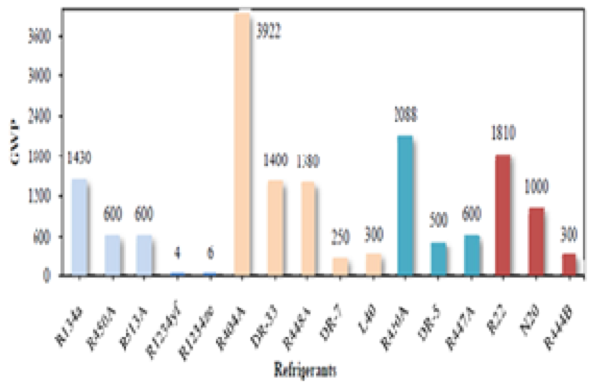

Figure 2: Representation of GWP for various refrigerants

Propane (R290) and propylene (R1270) have normal boiling points below –40°C and are therefore suitable for general refrigeration applications. Butane (R600) and isobutane (R600a) have much higher boiling points but they also have high critical temperatures, which tends to make them very efficient in operation. The greatest success of hydrocarbons has been in the application of R600a to domestic refrigerators.

Propane and blends containing propane could safely be used in window air conditioners provided appropriate precautions were taken and provided they were used in fully sealed systems. Propane could also be used, with an acceptable degree of risk, for car air conditioning, again provided that appropriate precautions were taken. R1270 is a refrigerant similar in performance to propane but much more expensive and therefore unlikely to find general favour. Hydrocarbons would not appear attractive for large-scale air conditioning applications but they will certainly appear as a refrigerant for window air conditioners of low charge.

Carbon dioxide is present in the atmosphere and it is non-flammable and non-toxic. Despite the high pressures associated with its use, carbon dioxide has been used as a refrigerant since 1862. It is odourless, non-toxic, non-flammable, non-explosive and non-corrosive. Carbon dioxide continued to be in use in marine refrigeration as a non-toxic alternative to ammonia and to methyl chloride. However, the advent of halocarbons in the 1930s led to the abandonment of the much less efficient carbon dioxide, which finally went out of use in the 1950s. The reason for poor efficiencies obtained when using carbon dioxide as a refrigerant is that it has a low critical temperature. There are several ways in which this defect can be overcome. As a result of modern methods and developments, carbon dioxide is coming back into use as a refrigerant in systems which have efficiencies at least as great as the efficiencies of halocarbon and ammonia systems. It is an ideal refrigerant. If properly applied it is very efficient to use.

DESIRABLE PROPERTIES OF NEW REFRIGERANTS

Selection of refrigerant has significant impacts on the safety, reliability and energy consumption of the system.

Thermodynamics Properties: The thermodynamic characteristics most importantly normal boiling point, critical temperature and heat capacity must match the application for the system to operate efficiently.

Chemical Stability: A refrigeration system is expected to operate many years, and all other properties would be meaningless if the refrigerant decomposes or reacts to form something else.

Safety and Impact on Health and Environment: The ideal refrigerant should have low toxicity and be non-flammable at the same time should have zero ODP and lowest GWP.

Thermo-physical Properties: Favourable transport properties like low viscosity and high thermal conductivity have an impact on the size of the heat exchangers and thus cost of the overall system. A final set of practical criteria relate to materials and impact the long-term reliability of a system. The refrigerant must be compatible with common materials of construction, including metals and seals.

NEXT GENERATION REFRIGERANTS

The alternative refrigerants have been categorized as transitional refrigerant or HCFC/HFC partly chlorinated refrigerants and into medium and long term refrigerants (Fig.3). HCFC/HFC (partly chlorinated refrigerants) such as R22 and R134a are on the way to phase-out due to environmental concern. Under medium and long term refrigerants like HFC chlorine free and their blend, low GWP refrigerant (R1234yf,1234ze) and halogen free refrigerant (natural refrigerant) are at present looking as the viable options for future refrigerant.

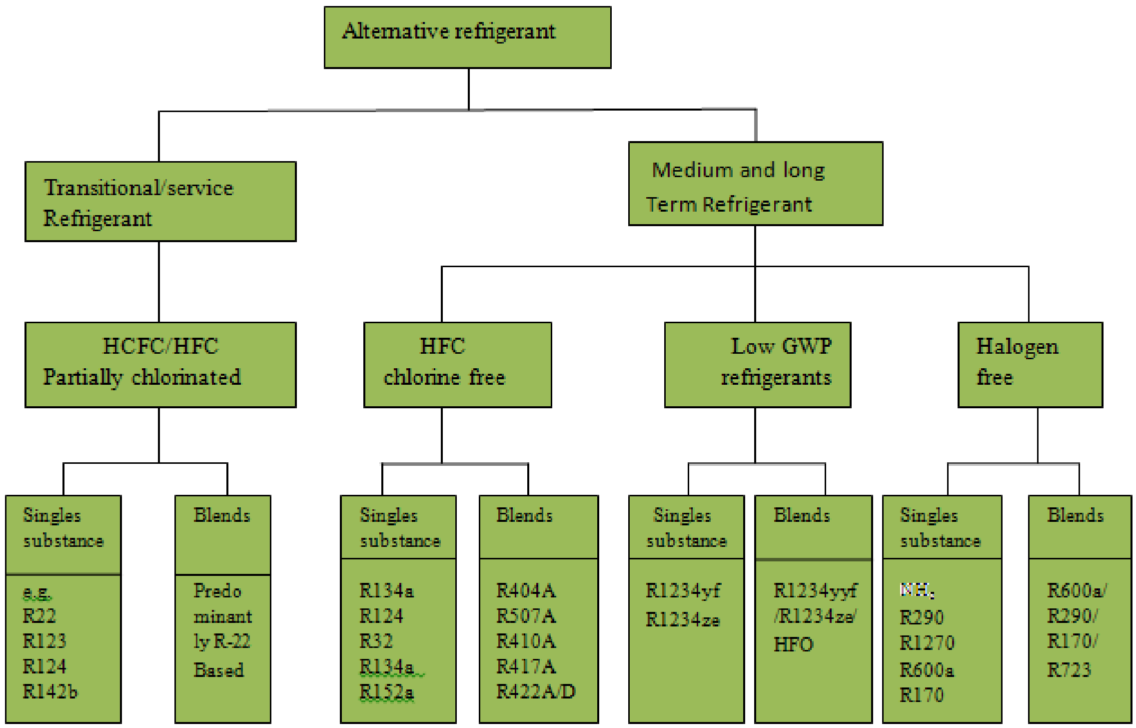

Figure 3: Classification of Alternative Refrigerant

Low Global Warming Refrigerant

Recently, R1234yf (2, 3, 3, 3-Tetrafluoropropene) having chemical formula CH2=CFCF3 has been proposed as a possible alternative refrigerant for HFC134a. R1234yf has zero ODP and excellent life cycle climate performance (LCCP) as compared to HFC134a. HFO-1234yf has the lowest switching cost for automakers among the currently proposed alternatives, although the initial cost of the product is much higher than that of R-134a. Another HFO based refrigerant HFO 1234ze (trans-1,3,3,3-Tetrafluoroprop-1-ene, CF3CH=CHF) is an energy-efficient alternative to traditional refrigerants in air-cooled and water-cooled chillers for supermarkets and commercial buildings, as well as in other medium temperature applications such as heat pumps, refrigerators and CO2 cascade systems in commercial refrigeration. Refrigerant HFO-1234ze is the best medium pressure, zero ODP and low GWP refrigerant on the market when considering the balance of all properties. A unique characteristic of this refrigerant is the absence of flammable mixture with air under 30°C of ambience.

The performance of vapour compression refrigeration system with two next generation environment friendly refrigerants was investigated and compared with the performance of the system with R134a, a third generation refrigerant [Calm and Hourahan, 2001]. Comparison has been made between R1234ze, R1234yf and R134a and it was found that those two environmental friendly refrigerants gave slightly lower performance than that of the R134a. Difference in cooling capacity was calculated between R-134a and both R1234ze and R1234yf. It was found to be 3% - 12% less for R1234yf within the experimented temperature range, whereas this difference was calculated to be less by 4% - 6% for R1234ze. Similarly, COP of the system was also found to be slightly lower for the new refrigerants compared to R134a. Though the performance of the system degraded slightly with these two new refrigerants, they have far less environmental impact compared to R134a. So, those two can replace the existing refrigerant R134a in near future. The variations of cooling capacity and COP with evaporator temperature for the above said three refrigerants have been shown in Fig. 4 and Fig. 5 respectively for different condenser temperatures [Mota-Babiloni et. al., 2014].

R-449A is a non-ODP; lower GWP hydro-fluoro-olefin (HFO) based refrigerant replacement for R-404A/R-507, R-407A/F and R-22. R449A is designed for use in positive displacement direct expansion low and medium temperature commercial and industrial applications. It has a GWP of 1397, which is a 65% reduction and provides energy consumption 8-12% lower than R-404A/R-507. R-449A is presently the best choice to replace 404A for stationary refrigeration systems.

Refrigerants R-513A, DR-55, R-452A are non-ODP, low GWP HFO based refrigerants. R-513A is developed to replace R-134a in positive displacement, direct expansion, medium-temperature commercial and industrial, including centrifugal chillers. DR-55 will be the leading low GWP replacement for R-410A as it is easily convertible from R-410A designs while offering the optimal balance of energy performance.

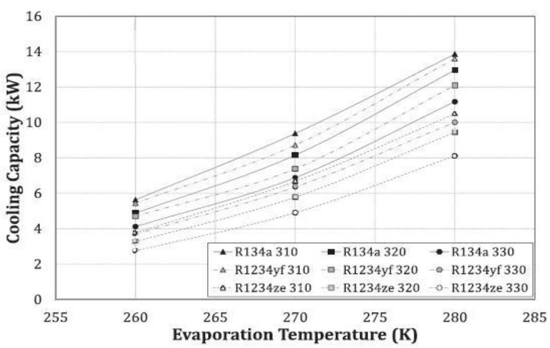

Figure 4: Cooling capacity versus evaporation temperature

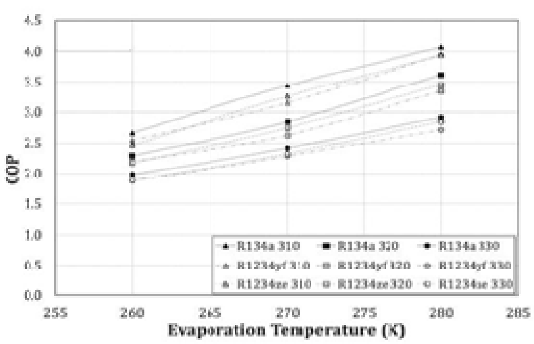

Figure 5: COP versus evaporation temperature

HFC/HCFC Blends

R-407F is a non-ODP replacement for R-22 and lower GWP (1825) replacement for R404A in various air-conditioning applications particularly in low-temperature applications. Since it is a close match to

R-22, it also serves as a retrofit fluid in applications where R-22 is used. R-407F contains HFC-32, HFC-125, and HFC-134a. R-409A (a HCFC blend) containing HCFC-22 (60%), HCFC-124 (25%) and HCFC-142b (15%) is an interim replacement for R-12 in stationary positive displacement air-conditioning and refrigeration systems such as walk-in coolers, beverage dispensers and supermarket systems. Its ODP is 0.046 and GWP is 1909. R-401B may act as an interim replacement for R-12 in low temperature commercial refrigeration systems, for transport refrigeration, low temperature retrofits, retrofits including air conditioners and dehumidifiers. It is made up of HCFC-22 (61%), HFC-152a (11%) and HCFC-124 (28%). The ODP and GWP values for this mixed refrigerant are 0.036 and 1288 respectively. R-422D is a non-ozone depleting replacement for R-22 in low- and medium-temperature commercial refrigeration systems suitable for direct expansion evaporators. It contains HFC-125 (65.1%), HFC-134a (31.5%), and HC-600a (3.4%).

Benefits of Alternative Refrigerants

Modern refrigerants are more beneficial financially and environmentally over commonly used old refrigerants. Hydro chlorofluorocarbons (HCFCs) and chlorofluorocarbons (CFCs), the commonly used refrigerants in the 20th century, are phasing out in more recent years because of their harmful effects on the ozone layer. Similarly, these fluorocarbons such as CFCs add harmful greenhouse gases to the atmosphere. Such gases are thousands of times more harmful than carbon dioxide and continue to increase global warming. With modern-day energy standards increasing, new methods of refrigeration are being implemented and are continuing to be developed to provide residential refrigeration with less emission.

Alternative refrigerants such as R-32 and R-410A are phasing out the older refrigerants (more harmful and less efficient). R-22 is harmful to the ozone layer and was discontinued for use in new AC units in 2010 which is then replaced by R-410A. R-410A is an HFC (hydro fluorocarbon) that does not contribute to ozone depletion and will be the new standard for U.S. residential AC systems as of 2015 because R-410A can absorb and release more heat than R-22. R-410A also functions at a higher pressure than R-22, so new compressors are built to withstand greater stresses, reducing the chance for cracking. R-32 is an even newer refrigerant that will likely gain popularity over the next few years. R-32 efficiently conveys heat; it can reduce electricity consumption up to approximately 10% compared to that of AC units using R-22. Compared to R-22 and R-410A, R-32 has a global warming potential (GWP) that is one-third lower and is remarkable for its low environmental impact.

The next generation refrigerants should be developed based on zero ODP and low GWP. In the future further research, regulation changes, the design of new systems suitable for the use of newly developed and natural refrigerants and the optimization of the system can be expected. There cannot be any ideal refrigerant but it is very important that the refrigerants should do less harm to the environment. The return to natural refrigerants at a new, high technology level should not be forgotten.

CONCLUSION

The following conclusions can be drawn from this review on next generation refrigerants:

1. The next generation refrigerants should be developed based on zero ODP and low GWP
2. R1234ze and R1234yf are suitable replacements for R134a
3. HFC/HCFC Blends R-407F and R-422D are Non-ODP replacement for R-22 and R-409A replacement for R12
4. The return to natural refrigerants at a new, high technology level should not be forgotten.

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