

PRIRODNI RASHLADNI FLUIDI U SVIM APLIKACIJAMA. DA LI JE MOGUĆE?*

NATURAL REFRIGERANTS IN ALL APPLICATIONS. IS IT POSSIBLE?

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Zbog štetnog uticaja sintetičkih rashladnih fluida na životnu sredinu (CFC, HCFC, HFC), u toku su fundamentalne promene u tehnologijama hlađenja i toplotnih pumpi. Ovo doprinosi preuzimanju tržišta za rashladne sisteme i sisteme toplotnih pumpi zasnovane na prirodnim radnim fluidima sa brzinama rasta različitim tempom u različitim segmentima tržišta, iako su se oni uvek primenjivali i bili dostupni do sada. Cilj ovog rada je da predstavi trenutno stanje na tržištu i da se posmatra samo kao pregled napravljen sredinom 2021 godine.

U ovom članku razmatraju se samo budući dokazani radni (rashladni) fluidi, naime supstance koje se prirodno pojavljuju u atmosferi, kao što su CO₂, različite vrste ugljovodonika, NH₃, H₂O i vazduh. Za svako od ovih rashladnih fluida opisane su moguće primene u zavisnosti od temperaturnog opsega, kapaciteta hlađenja, vrste primene itd. Postoje nova inovativna rešenja u cilju poboljšanja primenljivosti, energetske efikasnosti i bezbednosti.

Fluorirani ugljovodonici ponovo su u centru pažnje vezani za njihov uticaj na životnu sredinu u pogledu TFA zagađenja vode za piće i glavni su izvor PFAS-om zagađenja i vode za piće i osnovnih životnih namirnica poput majčinog mleka.

Ključne reči: prirodni rashladni fluidi; ugljen-dioksid; amonijak; ugljovodonici

Due to the harmful environmental impact of the synthetic refrigerants (CFC, HCFC, HFC), there are fundamental changes ongoing in refrigeration and heat pump technologies. This contributes to the market uptake for refrigeration and heat pumps systems based on natural working fluids with growth rates at different pace in different market segments, while they have always been applied and available in others. The aim of this article is to present the current state of the market and is only to be seen as snapshot made in the middle of 2021.

In this article only future proof working fluids/refrigerants are considered, namely substances naturally occurring such as CO₂, different types of hydrocarbons, NH₃, H₂O and air. For each of these refrigerants the possible applications are described depending on temperature range, cooling capacity, type of applications etc. There are new innovative solutions in order to improve the applicability, energy efficiency and safety.

Fluorinated hydrocarbons are again in the spotlight related to their environmental impact with respect to the TFA pollution of drinking water and being the major source of PFAS pollution also of drinking water and essential foodstuff like mother milk.

Key words: natural refrigerants; carbon dioxide; ammonia; hydrocarbons

1. Introduction

The latest report for the Technical Options Committee on *Refrigeration, Air Conditioning and Heat Pumps* of the United Nations Environmental Program was released in 2018. (RTOC-2018). As there are many innovations and transitions ongoing / established within the refrigeration, AC and heat pump sector towards the implementation of system applying natural working fluids, this work is summarizing the current status. The status refers to the above-mentioned refrigerants applied in domestic applications, commercial refrigeration, industrial refrigeration and heat pump systems,

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water and space heating heat pumps, chillers and vehicle air conditioning. Prior the summary part a table summarizes which working fluids are applied within the application sectors mentioned in the RTOC reports.

2. Natural working fluids

To date all the synthetic refrigerants do have harmful environmental impacts, as already stated by Lorentzen 1993 & 1995, Ciconkov 2018, and Kauffeld et. al 2021. Therefore, it is advisable for the refrigeration sector to admit this challenge and acknowledge a paradigm shift: All kinds of heating and cooling services currently supplied are possible, and also more energy efficient, when applying natural working fluids. Such a rapid technology shift will not reduce the need for this kind of services and equipment, as seen in some segments, the business growth rates are enormous and even the health and environmental working conditions of the valuable and qualified technical staff can be improved and secured. Therefore, the following subchapters describe in which areas the natural working fluids currently are applied.

2.1. Carbon dioxide, CO₂, R744

CO₂ has a low critical point (31 °C). It means that there is not condensation above the critical point, i.e. therefore, systems operate in a transcritical process at elevated heat rejection temperatures. In such a refrigeration cycle, when the temperature before expansion is relatively high, the COP is lower compared with other refrigerants performing in a conventional system configuration. 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. However, during last two decades, the R&D on CO₂ systems contributed to significant improvement of their energy efficiency. The transcritical operation can be improved with the following modifications (Hafner, 2015; Ciconkov, 2017): by installing parallel compressor(s); by implementing an internal heat exchanger; by utilizing an external subcooler; by utilizing expansion losses with ejectors or other expansion devices, etc.

CO₂ has gained a lot of attention and has become the new norm for domestic hot water heat pumps in Japan[†] and in supermarkets, mainly in Europe but getting acceptance in most parts of the world. The technology has developed over the years and currently the 4th generation of supermarket CO₂ units are entering the stage. For the layman, the refrigeration systems build in racks look very identical independently of the various suppliers.



Figure 1: A unit from Advansor, one of the first in the market in 2006

One of the first suppliers of CO₂ racks for mainly centralized refrigeration systems in the market was Linde, now part of Carrier Global. Another early adopter of the technology was ENEX and Advansor, now part of Dover Corporation as well as Epta, Costan, Arneg, etc. Many other suppliers are now suppliers to the market some only suppliers in the region e.g. compact Kältetechnik in Dresden, Germany and others are still growing into new markets e.g. Teko in Germany, SCM Frigo, now part of Beijer Ref, Sweden and Carnot Refrigeration, Canada. The only true global suppliers are probably Carrier and Beijer Ref., however, also Enex, Teko, Epta and Arneg are supplying CO₂ systems out of Europe to both South America and Asia and

Australia. The first demonstration projects started about 2004 and in 2021 the number of installed CO₂ units on a global base exceeded 35,000 systems, as shown in Figure 2 from 2020. There is no

[†] More than 5 million eco-cute heat pumps with R744 are applied in Japan to produce hot water for apartments.

region on this planet where it is technically impossible to implement a CO₂ refrigeration system. For a single rack, the capacity range for the CO₂ supermarket refrigeration systems is between 10 kW and up to 1000 kW of cooling capacity including both freezing and chilling of foodstuff.

Carbon dioxide is also used in cascade systems with other natural working fluids, however, mainly in combination with ammonia, NH₃ or R717. Cascade systems are widely used on board ships, warehouses and for industrial refrigeration and heat pump systems located in warm climate regions. The exact number of installed systems globally is not known; however, the total installed cooling capacity is constantly growing. One of the larger systems is phase one for a factory currently built in Russia with a capacity of 89 MW for freezing meat products, in phase two and three even more capacity will be added.

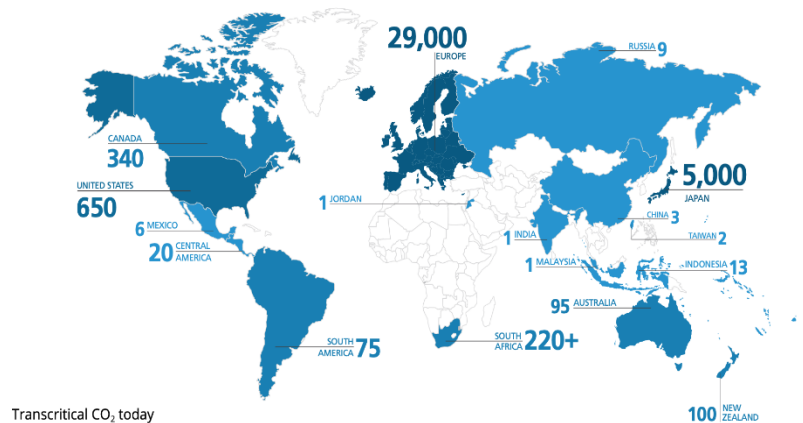


Figure 2: An overview created by Shecco (status middle of 2020)



Figure 3: A packaged cascade system in a plug-and-play type of system

Cascade systems, as shown in Figure 3, have been installed in all parts of the industrialised world and on the inhabited continents. At high ambient temperatures, cascade systems are less sensitive to the ambient temperature compared to the transcritical CO₂ systems and yield a higher energy efficiency. In the cascade system, the ammonia charge is reduced to about 10% of what was normally used in ammonia systems with similar refrigeration capacities. This part of the charge has

been substituted with CO₂, which can be distributed safely within the process plants or building and storage places. In short, it can be said that the two natural refrigerants are applied at the temperature levels where they yield the best energy efficiency, i.e. CO₂ at the low temperature part/heat uptake, NH₃ at the heat rejection circuit.

CO₂ is also successfully used in heat pumps as working fluid. One of the new start-up companies working with CO₂ heat pumps is Fenagy, now part of Beijer Ref.



Figure 4: A Fenagy CO₂ heat pump type H-600. The projected temperature range will be up to 90 °C or higher

These heat pumps, as shown in Figure 4, has been installed in district heating networks in Denmark. They are especially interesting for markets where the district heating is relatively well developed and also where the district heating temperatures (both supply and return) are now becoming lower. The 5th generation of heating networks are predicted to have supply temperatures around 40°C, and

where there are auxiliary solutions in the apartments/houses for heating the domestic hot water to the final temperature.

Figure 5 shows the simplified system layout of a CO₂ heat pump chiller, developed within the EU funded project MultiPACK and available in the market since 2020. The unit can produce hot water and simultaneously provide chilled water. If heating is not required excess heat can be rejected to the ambient, via an external gascooler.

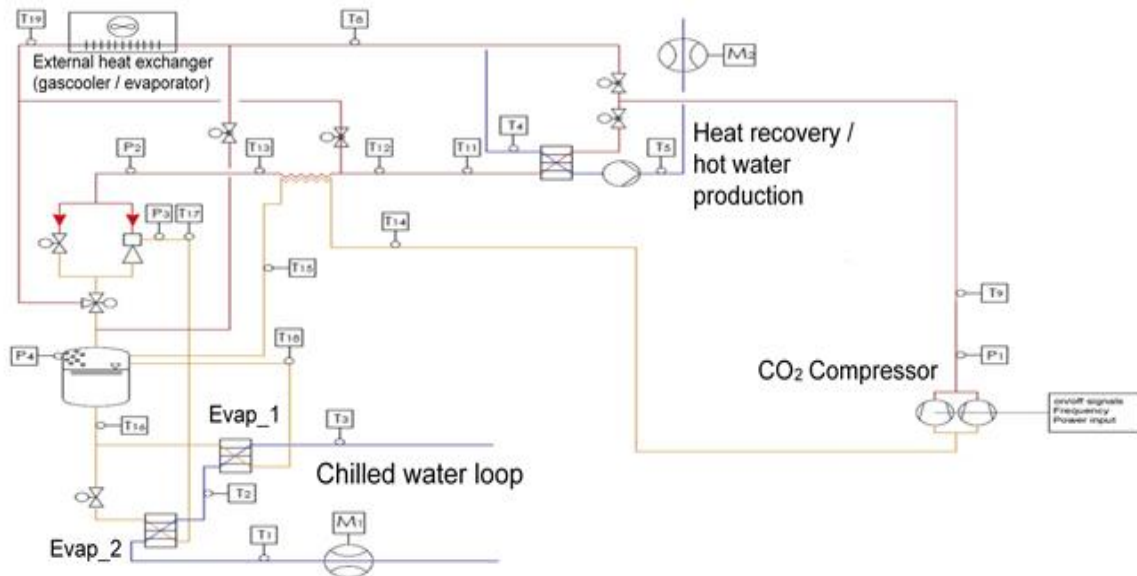


Figure 5: MultiPACK (enex) heat pump chiller unit with ejector supported evaporators.

In case the chilled water loop cannot supply the heat required to produce hot water, ambient air can be the heat source, as the external heat exchanger can also be operated as an evaporator. The innovative concept includes an ejector supported chilled water loop which consists of two evaporators in series to absorb heat from a secondary fluid. The secondary fluid is pre-cooled in Evap₁ which is gravity fed, i.e. liquid refrigerant is supplied from the receiver. The pressure level in the receiver represents the suction pressure of the compressor as well as the corresponding evaporation temperature (Evap₁). The second evaporator (Evap₂) is further reducing the temperature of the secondary loop with a lower evaporation temperature as in Evap₁, as the ejector utilises expansion work to pre-compress all the evaporated CO₂ of Evap₂. The pressure level in the receiver is adapted by the control unit and compressors accordingly to achieve the required supply temperature level for the secondary loop. The ejector capacity is self-adjusting, i.e. at low load conditions and low heat rejection temperatures, mainly Evap₁ is in operation. Compared to traditional chiller units, the suction pressure can be significantly higher and thereby improving the energy efficiency accordingly. This kind of heat pump chiller systems are very applicable for high performance buildings like hotels etc., which do have both heating and cooling demands. In case of time-staggered production and demand, appropriate energy storage devices must be implemented on both sides of the heat pump unit.

After decades of R&D by major car manufactures and their suppliers since 2016, mobile CO₂ AC systems are standard equipment in Mercedes cars. As Volkswagen now develops and introduces new car platforms for their electric cars, even this global car manufacture utilizes CO₂ systems applicable both in summer for cooling the passenger compartment as well during the cold period to enhance the performance when the CO₂ heat pump system is in operation. CO₂ is the most energy efficient, non-flammable refrigerant, which enables to apply the heat pump function to ambient temperatures below -20°C, and therefore auxiliary electrical heater can be avoided.

During the embargo against Cuba, it was not allowed to export CFC and HCFC to the island. Therefore, in Cuba people were still using CO₂ and hydrocarbon systems installed before WWII. CO₂ as refrigerant was not unknown to Prof. Gustav Lorentzen when the rival took place in the late

1980s; he had worked with CO₂ as refrigerant in his young days. The last reported fishing vessel applying a traditional CO₂ unit registered in a UK harbour was in the 1980's. So even CO₂ has always been used, however, was suppressed to a large extent by the fluorinated hydrocarbons.

2.2. Ammonia – NH₃– R717

Ammonia has been the preferred refrigerant in industrial refrigeration for more than 130 years. Due to some accidents not related to refrigeration in 2013, the suppliers of these applications are forced by different stakeholders to reduce the refrigerant charges in the systems. This has led to new designs and innovations in the packaged Ammonia systems offered to the market.

The low ammonia charge levels can be achieved mostly by using new types of heat exchangers and circuit arrangements avoiding receivers and pumped systems. The following solutions can be used:

- Dry expansion (DX) evaporators where the refrigerant evaporates in tubes (this requires miscible oil).

- Plate heat exchangers (PHEs) as evaporators and condensers. New types are developed with stainless steel welded modules and nickel brazed PHEs.

- Shell-and-plate heat exchangers are new types of heat exchangers applicable in R717 systems. These are combining the shell-and-tube and PHE arrangement, resulting in a very compact structure able to operate with a small refrigerant charge (see Fig. 6).

- The microchannel type of heat exchanger design is an excellent option for ammonia and CO₂ units. New designs in microchannel heat exchangers enable much lower refrigerant charges compared to conventional heat exchangers. Aluminium is very suitable for manufacturing of these types of heat exchangers, compatible with ammonia and allow for a simple recycling after usage.

Low charged R717 chillers, as shown in Figure 6, are offered and installed in many different types of applications e.g., airports, hospitals office buildings but also for chilled– and cold-water

production in industrial applications. The shown type is from Sabroe in Denmark, part of Johnson Controls Intl.

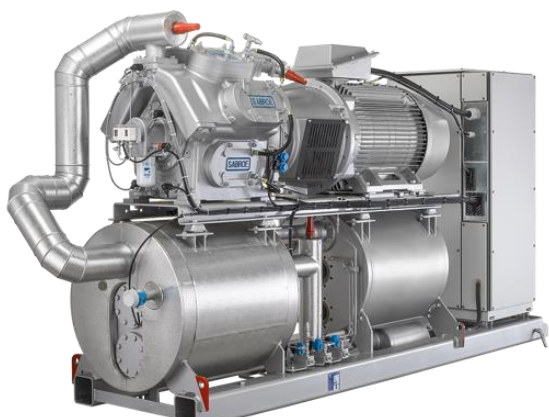


Figure 6: A packaged low charged water cooled NH₃ chiller

Ammonia systems are used onboard ships, in fish processing factories, meat processing plants, slaughterhouses in general, in chemical and pharmaceutical installations, in breweries and dairies and many other industrial facilities. In the USA alone, it is estimated that more than 9000 sites are applying Ammonia as refrigerant.

Ammonia is also widely used as working fluid in heat pumps up to a supply temperature of about 90 °C. These units are installed in numerous district heating systems in Europe. Ammonia is also used in industrial heating and cooling applications where it performs very well, yields a very

high energy efficiency and satisfied end-users.

Ammonia heat pumps for high temperature lifts are normally made in a two-stage design. These systems can be either site– or factory built. The factory-built solutions, as shown in Figure 7, are often delivered with a factory test, so capacity has been tested/verified and the control settings have been checked prior to shipment.

Over the last 20 years, there has been a trend to reduce the charge size in ammonia systems. There has been a lot of talk about low charge systems, and the industry has been lowering the charges significantly in many new installations. This move has come after two major accidents in China and one in West Texas, all three happened in 2013. One of the accidents in China caused about 70 deaths to a large extent because emergency doors had been locked in violation with local law. The second accident in China was a matter about poor welding violating local design rules and

performed by a non-qualified welder. The accident in Texas was not even related to refrigeration, it was fertilizer, ammonium nitrate, that exploded causing several deaths and lots of damage. After this accident, the then president of the United States Barack Obama and his administration put a limit of 10,000 pounds (4536 kg) of ammonia in refrigeration systems. Now years later every plant with less than 10,000 pounds has become low charge. There is no real definition of low charge.

The chiller shown in Figure 6 is the lowest charged ammonia chiller in the market, however, the development of new technologies such as direct expansion systems and new microchannels heat exchangers are driving the charges further down. The latest innovations for ammonia systems are the emergence of semi-hermetic compressors for ammonia from several market players. The suppliers are both from Europe but also from China,

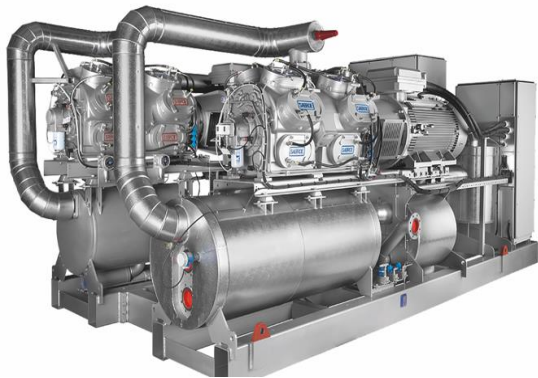


Figure 7: A two stage unit with front compressor for the low temperature part and rear compressor for the high temperature part of the heat pump system

which can make the competition more intense and drive down the cost for the user of the systems. The main advantage of the semi-hermetic compressors is to avoid the shaft seal, which theoretically can be a risk. However, semi-hermetic design also comes with some disadvantages, mainly related to the motor efficiency or lack of it if the process changes out of the normal operation range envisioned by the designer of the system. The strength of the open type of compressor is the flexibility of choice of motor. As an example, it is very advantages to be able to isolate the motor and keep the compressor very warm (insulated) if applied in heat pumps to avoid condensation of refrigerant inside the compressor housing.

With such a demand for the high temperature side of a heat pump, the motor of a semi-hermetic type of compressor will be a problem and will suffer on the efficiency.

One of the reasons for ammonia being accepted globally as refrigerant is that it is available in all parts of the world and it an inexpensive refrigerant and yields the highest energy efficiency values compared to most other working fluids in most operating conditions. However, during the last years not much effort has been done to further increase the energy efficiency of the vapour compression cycle with ammonia, compared to the effort made with carbon dioxide-based units. This issue is being addressed and some innovation can be expected to emerge in the market targeting a further improvement of the energy efficiency and further reduction of refrigerant charge.

The increased focus on safety around the ammonia plant is also pushing the industry to better education and training of staff to ensure that the systems are designed, installed and maintained in such a way that accidents are prevented in the best possible way. The Seveso directive has in some countries been used as reference for regulating the use of NH₃ in refrigeration, but this is overregulating the issue because the European standard EN-378 (ISO 5149) already cover the safety related to refrigeration systems. When following regulations and standards ammonia applied as a refrigerant is safe. Most accidents happen when ammonia is handled as fertiliser.

2.3. Hydrocarbons

Very often, when hydrocarbons are mentioned as alternative refrigerants, most people think about propane (R290) and in some cases iso-butane (R600a). Propane is often used in heat pumps and in commercial refrigeration and freezer applications. Due to the phase-down of HFCs (Kigali Amendment), R290 is the only viable and future-proof choice for single-split ACs and, furthermore, it is more energy efficient. When following design and operational standards (e.g. EN378), a safe operation can be performed even at higher system charges and capacities for R290 and other flammable working fluids. Several global suppliers manufacture a high number of R290 AC systems annually. Midea made the first Eco-friendly air conditioner certified by Blue Angel in 2018, now also available in Europe, as shown during the Green Cooling Summit 2021.

The standard refrigerant in most domestic refrigerators is iso-butane, in-fact it is estimated that about 95% of all fridges in Europe are now based on this natural working fluid. However, some American style fridges are still supplied to the market based in a fluorinated hydrocarbon.

In plug-in and self-contained units used in smaller shops and supermarkets propane has become mainstream with charges as low as or below 150 g. However, these low levels are not required anymore when the equipment is located inside the sales area, as the volume inside the sales area is sufficiently large. These units have undergone many changes, upgrades and with a water-cooled condenser, the refrigerant charge becomes again comparably low, even for higher cooling capacity units, as required in larger display cabinets. The systems are used in both normal temperature (chilled food) and for low temperature cabinets (frozen food).

For lower temperatures, propene (previously called propylene) or R1270 is used down to -45°C. R1270 is the preferred working fluid in the operation range from -45°C up to -10°C, however, it can be applied even at higher temperature levels. It must be noted that propane yields in a higher energy efficiency above -10°C evaporation temperature and is therefore in many cases preferred for higher operation temperatures. On the commercial side: propane as working fluid requires a larger swept volume at similar cooling capacities compared to propene. Therefore, some manufacturers prefer the propene enabling them to select a smaller and less expensive compressor.

For temperatures down to about -80°C, ethane or R170 is a good and energy efficient working fluid. It is often used in cascade systems with propane on the higher temperature stage and the systems yield a better efficiency than the systems using R23 in cascades with another HFC, which can be seen in Table 1

Table 1 By investigating suppliers of ultralow temperature freezer (-80°C) documentation this will be the result

Manufacture	Refrigerant Type	Volume (liter)	Power cons. (kWh/day)	(Wh/d)/Liter	Relative
Brand 1 cascade	HC	729	7.87	10.8	1.1
Brand 2 cascade	HC	729	7.06	9.7	1.0
Brand 3 cascade	HFC	815	17	20.9	2.2
Brand 4 cascade	HFC	793	17.8	22.4	2.3
Brand 5 Stirling	H ₂ /C ₂ H ₆	780	6.67	8.6	0.9
Brand 6 auto cascade	HC blend	556	16.3	29,3	3.0
Brand 7 auto cascade	HC blend	300	5.2	17.3	1.8
Brand 8 auto cascade	HC blend	74	5	67.6	7.0

Auto cascade systems are systems containing only one compressor compressing a blend of refrigerants. The refrigerants condense in turns by evaporating another fluid. This concept is applied in both laboratory freezers as reported in Table 1, but also in large industrial systems onboard ships and in petrochemical sites. In the table the information collected for this comparison show that from an energy efficiency point of view auto cascade is not the most efficient solution, however, it has an investment cost advantage.

In special cases where the required temperature needs to be even lower, R1150, ethylene, can be applied. For near absolute zero systems Helium is applied on the lowest stage with nitrogen and methane on the next stage and on the higher stages the above-mentioned gases, all in a multi-cascade construction are applied.

Other hydrocarbon refrigerants are suitable for high temperature heat pumps reaching up to about 250°C. An analysis, Pachai 2021, shows that the way up in temperature is possible by applying butane, pentane and for the very high temperatures heptane is the best choice. That is for the general market, however, optimised blends for different processes and applications with dedicated temperature glide requirements are possible to generate and utilize. These blends of different hydrocarbons are common working fluids in chemical process plants as well.

The stability of the fluorinated hydrocarbons has been questioned when it comes to high temperature heat pumps. Of other uncertain points can also be the possible lubricants. The currently

used lubricants produce soot at about 180°C and coke about 200°C, however, new lubricants are under development and soon ready for the market and these high temperature heat pumps applying hydrocarbons. Also, valves and other components needs to be clarified for operation conditions at such elevated temperatures.

2.4. Water – R718 – H₂O

Water applied as refrigerant is emerging the market for some air-conditioning applications as shown in Figure 8. In addition, high temperature heat pumps are another application area, e.g., when producing steam for process plants by utilizing surplus heat in combination with a cascade heat pump. Water, in comparison to other refrigerants, has a relatively high boiling point at atmospheric pressure, 100°C. At Air Conditioning temperatures, the pressures in the water cycle will be sub-atmospheric and the swept volume in the compressor needs to be relatively large compared to similar systems e.g. based on ammonia. This drawback is reversed when the operation temperatures increase to levels above 100°C or even 200°C. In this temperature regions water becomes a viable and energy efficient solution for high temperature heat pumps. New technology and innovations have demonstrated water is a solution especially for cooling in server environments at higher temperatures levels than normal AC units can be applied for.



Figure 8: The eChiller from Efficient Energy is based on water as the working fluid.

A lot of R&D is ongoing for system applying water as the working fluid in vapour compression systems. It is a cheap and present in most markets in a usable quality. In the current available heat pump cycles the temperatures levels can reach 160°C, which ensures any bacterial activity will stop. In a project in Denmark, the low stage in a heat pump cascade is a water vapor system supplying heat towards the high stage heat pump for the production of district heat for a new part of the city.

With water as the working fluid heat pumps, designed in a conventional vapour compression cycle, will potentially be able to reach temperatures close to 350°C, critical temperature 374.14°C at 220.9 bar(a), and if used as a transcritical fluid there is no limit, however, the challenge will be to build a compressor for the purpose.

2.5. Air – R729

Atmospheric air can also be used in a special loop to create temperatures from -40°C and down to about -130°C but it is possible to reach as low as -160°C. Such air cycle systems are being

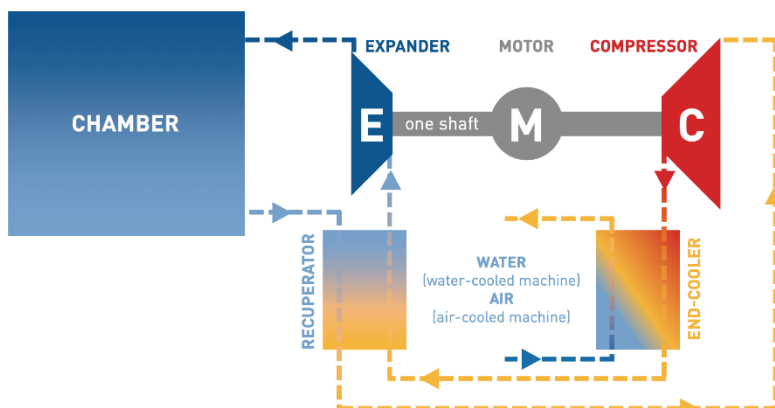


Figure 9: The open air cycle as shown by Mirai Intex

used to store frozen tuna at about -60°C in Japan, where the traditional sushi tuna requires very high-quality sushi tuna flesh. Air cycles are energy efficient compared to traditional vapour compression units at very low temperatures. The need for low temperature storage of some vaccines at -70°C +/-10°C has triggered a new application area for this kind of system, too.

As shown in Figure 9, the compressor and expander are connected to the same motor. Through the connecting shaft, the expander contributes to the driving force to operate the compressor. The air from the refrigerated area enters the compressor. After compression the air temperature is reduces in a cooler and even further reduced in a recuperator before it enters the expander part at high pressure.

The air temperature drops significantly as the pressure drops downstream of the expander before entering the refrigerated space/chamber.

The air cycle shown in Figure 9 is often used for storage and process cooling. This cycle is the open type. A closed loop is very common and most used onboard airplanes of any kind and some train AC systems. It is basically the same cycle but here also heating is often needed as most airplanes are flying in high altitudes where the ambient temperature often still is about -50°C . The heat is recovered from both the combustion in the engine and from the passenger cabin.

3. Standards and regulations

The natural refrigerants have been used for more than 100 years, most known is ammonia but also the hydrocarbons have been used in the petrochemical sector, and there is a lot of knowledge on how to work with and apply these fluids. The challenges with the barriers in the market today is the influence and market position of the manufacturers of fluorinated hydrocarbons, which virtually have made it impossible to install natural refrigerants in many cases. Based on the real environmental impact of these synthetic fluids, most of them classified as PFAS, this must end, and the unnecessary barriers must be removed.

The standards are now being revised to allow for larger charges of flammable fluids for indoor applications. For chillers located outside, there is no charge limit unless the local fire inspector requires special attention on the installation. The main challenge is the education and training levels regarding the natural refrigerants, which has in many countries been neglected far too long. This is now changing thanks to a strong base of committed trainers in most countries, and due to the fact that also the newly introduced non-natural low GWP working fluids are flammable.

4. Application sectors and natural working fluids in a nutshell

Table 2. Applications and the applied working fluid

	CO ₂ (R744)	NH ₃ (R717)	HC	H ₂ O (R718)	Air (R729)
Domestic applications	Domestic hot water heat pumps	-	Refrigerators, AC units (split units) including heat pumps (liquid to liquid, air to liquid, and air to air)	-	-
Commercial refrigeration	Centralized systems, integrated units providing also AC and heating to the building, condensing units and standalone units (for convenience stores) No regional restrictions	As the upper stage of CO ₂ -NH ₃ cascade systems, applied in some stores and warehouses	Self-contained cabinets, water cooled cabinets, refrigeration systems for indirect systems, AC part of the building Safe in operation when following EN378 and other standards	-	-
Industrial refrigeration and heat pump systems,	Freezing applications within food processing from -53° to $+5^{\circ}\text{C}$, Industrial heat pumps providing high temperature lifts, warehouses and distribution centre cooling and freezing	All kind of freezing, chilling and heat pump applications	ultra-low temperature applications, in process plants, high temperature heat pumps, steam producing heat pumps	Data centre cooling, heat pump applications including high temperature heat pumps	
Water and space heating heat pumps	Domestic hot water heat pumps for hotels and other high performance buildings	Space heating, roof mounted units for distribution centres and warehouses.	Indirect systems providing hot water and space heating		
Chillers	Ejector supported chillers (10kW to 1 MW)	From small capacities to several MW units	From small capacities to several MW units	Large industrial chillers	
Vehicle air conditioning	AC only or reversible system having heat pump function	-	Applied as drop in fluid in Australia. Indirect compact systems	-	Applied in aircrafts and trains

5. Conclusions

All temperature levels and most applications can be cooled by applying natural refrigerants. There is no technical barrier to replace currently used synthetic fluorine containing refrigerants with natural working fluids in new systems. It is more about seeing the possibilities than the ghosts when selecting the optimal refrigerant for the project or a product. No single refrigerant can cover all applications; however, the group of natural refrigerants can cover all the applications which can be covered by fluorinated hydrocarbons and even more. None of the fluorinated hydrocarbons can go as low in temperature or as high as the natural refrigerants, they only cover the most profitable markets in the middle temperature range.

The short life HFC blends containing HFO are claimed to be simple and compatible with HFC systems designs, therefore some manufactures are preferring to utilize them. However, as these fluids become flammable when lower GWP values are required, objective information and promotion of natural refrigerants towards end-users are necessary, as they might accept a natural solution when informed about all the risks related to the environmental impact of the fluorinated substances.

With respect to PFAS pollution on earth, the refrigeration sector does have all possibilities to spearhead a complete phase out of HFCs contributing to the PFAS accumulation in our biosphere, without compromising safety, food supply and human comfort.

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References

- [1] **Ciconkov R.**, 2018. Refrigerants: There is still no vision for sustainable solutions, International Journal of Refrigeration 86 (2018), pp. 441–448
- [2] **Hafner, A.**, 2017. Integrated CO₂ system for refrigeration, air conditioning and sanitary hot water, Ammonia and CO₂ Refrigeration Conference, IIR, Ohrid, R. Macedonia.
- [3] **Kauffeld M., Dudita M.**, 2021. Environmental impact of HFO refrigerants & alternatives for the future <https://www.openaccessgovernment.org/hfo-refrigerants/112698/>
- [4] **Lorentzen G.**, 1993, Revival of carbon dioxide as a refrigerant. Int. J. of Ref., 17 (5) (1993), pp. 292-301
- [5] **Lorentzen G.**, 1995, The use of natural refrigerants: a complete solution to the CFC/HCFC predicament Int. Journal of Refrigeration, 18 (3) (1995), pp. 190-197
- [6] **Pachai, A., Norman J., Arpagaus C., Hafner A.**, 2021. Screening of future-proof working fluids for industrial high-temperature heat pumps up to 250 °C. Proceedings of the 9th IIR Conference: Ammonia and CO₂ Refrigeration Technologies, Ohrid, 2021