

ABOUT NATURAL REFRIGERANTS

As a general differentiation, “natural refrigerants” are substances that exist naturally in the environment, while “non-natural refrigerants” or “synthetic refrigerants” are man-made chemicals, not naturally occurring in the environment. The precision of the term “natural refrigerants” is sometimes debated, given that, to be used as refrigerants, ammonia, carbon dioxide, and hydrocarbons also undergo an industrial purification and manufacturing process.

However, today there is a well-established distinction between substances whose chemical properties and safety aspects have been studied in their entirety and those fluorinated gases which, given their chemical complexity and comparatively short period of usage, have confirmed and/or have unknown negative effects on ozone depletion, global warming and ecological safety, and therefore, are subject to continued debate.

The most commonly used natural refrigerants today are ammonia (NH₃, R717), carbon dioxide (CO₂, R744), and hydrocarbons (HCs), such as propane (R290), iso-butane (R600a), and propylene, also known as propene (R1270).

Mixtures of ammonia and dimethyl ether (R723) have been developed, as well as various hydrocarbon blends with optimised performance and safety properties (isobutane/propane, R441 etc.). Water and air are also used to a lesser extent, for example in adsorption chillers and deep-freezing applications.

In addition to their wide availability, their non toxicity, non-flammability and their unbeatable environmental credentials, water and air have shifted into the focus of R&D activities. Natural refrigerants no longer in use are sulphur dioxide (SO₂) and methyl chloride (CH₃Cl).

CARBON DIOXIDE (ODP= 0; GWP= 1)

Carbon dioxide (chemical symbol CO₂, refrigerant designation R744) is colourless, odourless and heavier than air. With a Global Warming Potential (GWP) = 1, CO₂ is the reference value for comparing a refrigerant's direct impact on global warming.

Carbon dioxide carries an A1 safety classification (the same as most fluorocarbon refrigerants), indicating that it has low toxicity

and is non-flammable. CO₂ as a refrigerant is sourced as a by-product from a number of production methods. Although it is nontoxic, if enough carbon dioxide builds up in an enclosed space, it will begin to displace oxygen.

Over a certain period of time, this can cause asphyxiation of those present. With a long atmospheric lifetime, CO₂ does not lead to any byproduct formation or decay products with serious environmental impact.

When used as a refrigerant, carbon dioxide typically operates at a higher pressure than fluorocarbons and other refrigerants. While this presents some design challenges, they can be overcome in systems designed specifically to use carbon dioxide.

Carbon dioxide is compatible with some, but not all, commonly used refrigeration system lubricants. In particular, it is not suited for use with polyol ester (POE) and poly vinyl ether (PVE) lubricants and it only has limited applications with poly alkaline glycol (PAG) lubricants. It is generally regarded as a cheap and easily available refrigerant.

HYDROCARBONS (ODP= 0; GWP < 4)

With zero ozone depleting characteristics and an ultra-low global warming impact, the group of hydrocarbons (HCs) does not form any by-products or decomposition products in the atmosphere.

HC refrigerants can be applied either in systems designed specifically for their use, or as replacements in a system designed for a fluorocarbon refrigerant.

This makes them a cost-competitive solution, and optimal for developing countries. If a hydrocarbon refrigerant is to be used in a system designed for a different refrigerant, it should be noted that modifications are probably required to ensure compatibility. Lubricant compatibility and the issues associated with hydrocarbons' flammability have to be addressed. However, the greatest potential for

hydrocarbon refrigerants lies in new systems. Hydrocarbon refrigerants are flammable and, as a result, carry an A3 safety classification, which means they have a low toxicity but are in the higher range of flammability. HCs are often subject to stricter safety requirements concerning the quantities permitted in occupied spaces.

Hydrocarbon refrigerants are fully compatible with almost all lubricants commonly used in refrigeration and air conditioning systems. One major exception to this rule is lubricants containing silicone and silicate (additives which are commonly used as antifoaming agents).

WATER (ODP= 0; GWP= 0)

Water (chemical symbol H₂O, refrigerant designation R718) is one of the oldest refrigerants used for refrigeration applications. Also known as dihydrogen monoxide, water or water vapour is one of the Earth's most abundant elements. Water has been extensively used as a process fluid (distillation, drying processes), as a heat transfer or energy storage medium (central heating, system cooling, ice storage systems) and as a working fluid in the Rankine power generation cycle.

R718 is an environmentally benign, cheap, totally safe refrigerant with zero ozone depletion potential and zero global warming potential. It is odourless, colourless, nontoxic, non-flammable, non-explosive, easily available, and it is the cheapest refrigerant.

In refrigeration applications, water requires state-of-the-art technology. Its use as a refrigerant has been mostly limited to compression chillers with steam injection compressors, absorption systems built around a binary fluid comprised of lithium bromide as the absorbent and adsorption systems using water as the refrigerant and the mineral zeolite as the adsorbed.

From an environmental and thermodynamic point of view, water is an ideal refrigerant for applications above 0°C. R718 has a higher latent heat of evaporation (2,270kJ/kg) than other natural refrigerants. R718 absorbs significantly larger amounts of energy in the form of heat, during a change of phase from liquid to gas, without a change in temperature. An obvious limitation is the high freezing rate at atmospheric pressure. Water leads to corrosion and oxidation of many metals. Water is more reactive than other refrigerants and choosing the right materials or the R718 system during the design phase requires special attention.

AIR (ODP= 0; GWP= 0)

Air (refrigerant designation R729) is a refrigerant that is environmentally benign, cheap, totally safe and nontoxic. Environmental concerns about ozone depletion, global warming, and increasingly stringent legislation have renewed the interest in alternative refrigeration technology globally. However, the use of air cycle refrigeration systems is not new. It was

used on refrigerated cargo ships around the turn of the last century.

Air cycle refrigeration works on the reverse Brayton or Joule cycle. Air as a refrigerant does not undergo phase change (condensation/evaporation) at the temperature levels encountered in conventional refrigeration applications. The COP value of air is low because of its light weight, but air cycle cooling systems can provide relatively high temperature heat recovery without the efficiency set back experienced by vapour compression systems. Air cycle units, compared to vapour-compression units, can also produce a much higher temperature difference between the hot and cold sides. As a result, very cold air can be produced for near cryogenic processes. The performance of an air cycle unit does not deteriorate as much as that of a vapour-compression unit when operating away from its design point.

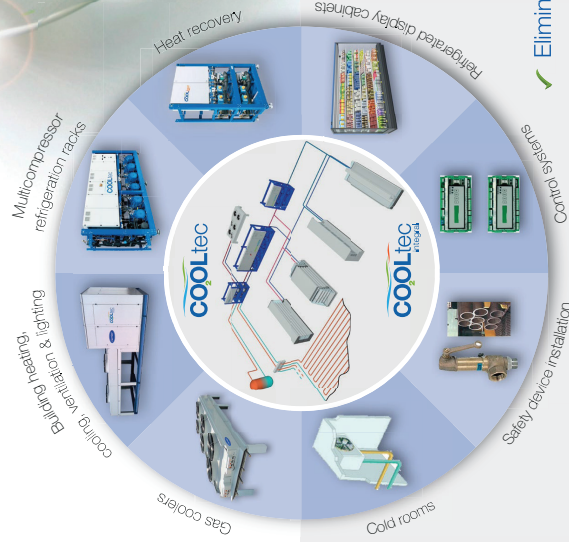
When operating in a refrigeration cycle, an air cycle unit can also produce heat at a useful temperature. Air has been used commercially for aircraft cooling for a long time. In spite of the low COP, air is used because of the specific operating conditions of aircraft (e.g., availability of compressed air and ram effect) and stringent specifications (e.g., low weight, small size, absolute safety, zero toxicity etc.). Air has also been used as a refrigerant for residential and automobile air conditioning and cooling. In some refrigeration plants, air is used in the quick freezing of food products.

REFRIGERANTS	REFRIGERANTS NUMBER	CHEMICAL FORMULA	GWP (100 YEARS)	ODP	NORMAL BOILING POINTS (°C)	CRITICAL TEMPERATURE (°C)	CRITICAL PRESSURE (BAR)	SAFETY GROUP	MOLECULAR WEIGHT (G/MOL)
Ammonia	R717	NH ₃	0	0	-33.3	132.4	114.2	B2	17.03
Carbon dioxide	R744	CO ₂	1	0	-78	31.4	73.8	A1	44.0
Propane	R290	C ₃ H ₈	3.3	0	-42.1	96.7	42.5	A3	44.1
Isobutane	R600a	C ₄ H ₁₀	4	0	-11.8	134.7	36.48	A3	58.12
Propylene	R1270	C ₃ H ₆	1.8	0	-48	91	46.1	A3	42.08
Water	R718	H ₂ O	0	0	100	373.9	217.7	A1	18
Air	R729	-	0	0	-192.97	-	-	-	28.97

NATURAL LEADERS IN SUSTAINABILITY

At Carrier, we incorporate sustainability into all that we do. To us, it's only natural.

From innovative solutions to green factories to services developed to increase efficiency, Carrier is a leader in sustainability. We pioneered the use of natural refrigerants in the food retail world, and continuously invest in research and development to improve our products and processes while protecting the natural environment.



Carrier's CO₂OLtec® Integral system uses natural refrigerant CO₂ for refrigeration, heating and space cooling.

- ✓ Eliminates the need for traditional heating systems
- ✓ Reduces greenhouse gas emissions by up to 58%
- ✓ Delivers up to 35% energy savings

vs. R404A systems with gas boiler

GUIDE CHILLVENTA 2014 - MARKET TRENDS

The European market for natural working fluids is buoyant, with over 400 European companies providing components, systems and services linked to the use of CO₂, ammonia, hydrocarbons and water as refrigerants in the refrigeration, heating and air conditioning sectors.

A preference for CO₂, confirmed by major European retailers: will R744's success continue into the heating and mobile air conditioning sectors?

Worldwide, the number of retailers using CO₂ refrigeration technology is constantly growing, with Europe leading this trend. Latest figures indicate a minimum of 2,885 stores use transcritical CO₂ refrigeration systems in Europe and that 1,639 stores use CO₂ / HFC cascade systems. Research by shecco, the leading publisher of natural refrigerant news worldwide, suggests that in just two years the number of CO₂ transcritical commercial refrigeration systems has increased by 117%. What is more, almost two-thirds of large supermarkets in Germany, France, Denmark, Norway and the UK confirm that they now use natural refrigerants in their stores¹.

The recently adopted EU F-Gas Regulation, introducing EU-wide bans on HFCs in certain sectors is expected to further increase demand for natural refrigerant-based systems in Europe and beyond. Some of the major system manufacturers expect that Europe will see over 6,000 CO₂-only stores annually by 2018, with more and more installed in Southern Europe, as solutions for warmer climates become increasingly available².

For many large food retailers, who have an average technology investment cycle of 14 years, CO₂ systems are considered to have achieved parity with HFCs in terms of return on investment and life-cycle costs. For example, data from one CO₂ transcritical store in Norway indicates that the system reduces energy consumption by 30%, compared to similar supermarkets in the same chain that use HFC refrigeration systems. The gap between CO₂ and HFC systems' initial capital cost and investment is also narrowing and will be bridged as development gains pace.

In the light commercial refrigeration sector, The Coca-Cola Company has decided to phase out HFCs by adopting CO₂ technology and has already installed over 1 million units globally, a large number of these in Europe.

The growing trend towards CO₂ doesn't stop with commercial refrigeration. Following the success of CO₂ heat pump technology in Japan, where 600,000 units are sold on average each year, manufacturers in Europe are hoping to reach annual sales of tens-of-thousands by 2015.

For CO₂, mobile air conditioning (MAC) is a final application area seeing significant development activity. Leading OEM (Original Equipment Manufacturers) Daimler has, since 2013, stood firmly behind its decision to develop CO₂ MAC systems³.

Hydrocarbon freezers and fridges: the future-proof solution for FMCG and supermarket chains

Alongside CO₂, hydrocarbon refrigeration systems represent another growth market for natural refrigerants. Outside the domestic refrigeration market, where hydrocarbons have become the standard refrigerant, more and more companies are investing in low temperature freezers using R290. Perhaps the biggest player in this market, Unilever has already purchased over 1 million hydrocarbon units and plans to purchase 1.3 million by 2015. Supermarket chains are also investing in this technology, with German retailers such as Lidl and Aldi Sud having purchased over 40,000 freezer cabinets using hydrocarbons in 2013⁴.

Whilst The Coca-Cola Company has chosen CO₂ as its preferred option for its cooler fleet, companies like Heineken and Red Bull have purchased over half a million hydrocarbon fridges and coolers between them.

For heat pump applications, R290 remains a niche application, but is considered a good technology for the residential renovation market, as a substitute for gas or oil boilers.

Ammonia, the stalwart of the industrial refrigeration sector

In Europe, about 95% of large industrial applications use ammonia, a situation expected to continue over the next decade, although reduced charge NH₃/CO₂ solutions will become increasingly competitive. Other key technological trends, besides minimising refrigerant charge through cascade systems or innovative heat exchangers, include increased efficiency by means of frequency control, advanced valve control systems or multi-stage systems, as well as heat recuperation and improved safety features.

Applications that rely on ammonia refrigeration include food processing plants such as dairies, bakeries, slaughterhouses, ice cream and chocolate manufacturers, breweries and fishing vessels. Whilst such NH₃ refrigeration systems are commonplace, ammonia is also thought to have a significant market potential in industrial heat pump applications using waste heat to provide space heating or process heat in large scale applications such as waste treatment, the automotive sector, chemical industry or metal processing. District heating using ammonia is also gaining popularity. For example, several hundred ammonia heat pumps have been installed in Norway since the early 1990s.

As with CO₂ and hydrocarbons, changes in legislation represent a significant opportunity for ammonia growth in the refrigeration market. In this respect, the ban on R22 that will enter into force in 2015 in Europe, will require cold stores, warehouses, ice rinks and food and beverage processing facilities to switch to ozone and climate friendly alternatives, such as ammonia.

1. Masson N., et al. (2014) GUIDE, 2014: Natural Refrigerants - Continued Growth & Innovation in Europe. Brussels, shecco publications. <http://publication.shecco.com/publications/view/2014-guide-natural-refrigerants-europe>
2. Topley Lisa J., Chasseroit M., Girard-Reydet C. (2014) ATMosphere America 2014 - Summary Report of International Conference. Brussels, shecco publications. <http://publication.shecco.com/publications/view/atmosphere-america-2014-report>
3. R744.com (07 March 2013). "Daimler, Audi, BMW, Porsche and VW to develop CO₂ MAC systems - Third time lucky?" R744.com. http://www.r744.com/articles/daimler_audi_bmw_porsche_and_vw_to_develop_co2_sub_mac_systems-third_time_lucky

Enhancing **energy efficiency** and enabling the industry to achieve **refrigerant goals**



Affordability, safety and environmental concerns are the cornerstones of **sustainability**

Danfoss encourages the further development and use of low-GWP refrigerants to help slow – and ultimately reverse – the process of global warming. Our goal is to ensure continued global well-being and economic development along with the future viability of our industry.

Meet Danfoss experts at Chillventa 2014. They are ready to offer advice and guidance on the refrigerants and technologies of both today and tomorrow.

Visit us at Chillventa 2014 booth 102, hall 4.

For more information, please visit www.refrigerants.danfoss.com

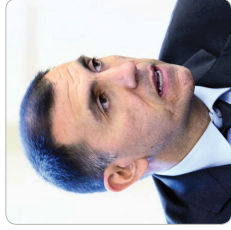
ENGINEERING
TOMORROW



EXCLUSIVE INTERVIEWS

INDUSTRY LEADER INSIGHTS INTO THE LATEST NATURAL REFRIGERANT TECHNOLOGIES

Ahead of Chillventa 2014, shecco publications interviewed Alessandro Greggio of Carel, Group Head of Marketing – Retail & Refrigeration; Giovanni Dorini, Marketing Manager at Dorini; Pedro Ollala of Huayi Compressor Barcelona, Vice General Manager Sales & Purchasing; Eric Delforge of Mayekawa Europe, Corporate Business & Policy Officer and Nicola Pignatelli, Sales Director, SCM FRIGO. In the following section of this GUIDE, these industry-leading companies reveal their product showing at Chillventa 2014 and how they think the natural refrigerant market has evolved in the last 6 years, since the first Chillventa in 2008. Increasing product energy efficiency demands, together with retailers asking for natural refrigeration solutions for small convenience stores and warm climates, have created a dynamic market for natural refrigerant technologies, spurring rapid product innovation.



Nicola Pignatelli
Sales Director
SCM Frigo S.p.A.

What natural refrigerant products have you chosen to showcase at Chillventa and why?

Due to the company vision to be "a leader in the production of refrigeration systems with natural refrigerants", SCM FRIGO will present at Chillventa 2014 its latest generation of CO₂ boosters for supermarket applications, our Emerald line. We think that CO₂ boosters are the most efficient systems today in this sector, capable to perform well in various climate scenarios, according to the latest technology.

What are the key product features and how do they help end users save energy and money and/or change the market?

With experience of more than 1000 CO₂ units installed, SCM FRIGO has arrived to develop the latest generation of CO₂ boosters, focusing especially on the end user's needs: easy management, easy maintenance, easy to install. Also, there is the possibility to install it outside with our sound-proof container box. Energy saving is guaranteed by inverters by leading compressors and heat recovery availability.

How do you think the natural refrigerant product offering at Chillventa has evolved over the last few last years?

At the beginning of this journey, almost 10 years ago, there were very few components available and only prototypes for parts such as valves and exchangers. Moreover, not all the players really believed in CO₂'s growth potential. It was a "development phase". At Chillventa 2012, 90% of the producers were CO₂ or natural fluids-oriented and most of the news was related to either CO₂, NH₃ or propane etc. So the components market became ready and system producers started the "optimisation phase".

What other components for CO₂ / hydrocarbons / ammonia / water / air does SCM FRIGO manufacture?

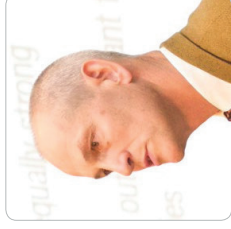
SCM FRIGO also produces Water Chillers with CO₂ as the refrigerant in our Amethyst line. They are compact chillers for outdoor installation (with an integrated condenser).

For which region in Europe do you see the biggest growth/interest for NatRef products?

The future will be green all around Europe. We are improving our export of natural refrigerant products to all European countries, a forecast of +40% next year, from Spain to the Baltics, and Norway to Italy. Today, it is possible to find the right/efficient/reliable CO₂ system for any geographical area in Europe.

What influence has the new F-Gas Regulation on your business?

The F-Gas regulation influence can be positive for our business because it is increasing the interest of installers and end users for natural refrigerants, even in countries where natural refrigerant products have not been considered as an alternative so far.



Eric Delforge
Corporate Business and Policy Officer
MAYEKAWA EUROPE

What natural refrigerant products have you chosen to showcase at Chillventa and why?

Aside from solutions for our core business of industrial refrigeration applications we also display our capability in industrial heating solutions. Mayekawa will even occupy a prominent space at the European Heat Pump Association booth to showcase industrial heating applications. The reason for this choice is obvious: as a leading industrial solutions provider for combined cooling and heat pump applications using natural refrigerants we want to underline our capabilities and the fact that we are ready to fulfill the fast growing need for industrial heating solutions.

What are the key product features and how do they help end users save energy and money and/or change the market?

There are many, but I can highlight one that both saves money and will change the market. It is the introduction of semi-hermetic compressor/motor blocks. This combination enables efficient part load operation and best in class permanent magnet motors. Furthermore, this physical integration eliminates what was formerly a potential problem: shaft seal refrigerant leakage. This is a game changer, especially for ammonia applications.

How do you think the natural refrigerant product offering at Chillventa has evolved over the last few last years?

It has been Mayekawa's mission to promote natural refrigerants in industrial applications for decades. Because of their proven energy efficiency, this hasn't been too hard. The challenge though is to multiply this logic to smaller applications such as commercial and eventually domestic markets. This is exactly what is happening now. More and more manufacturers are discovering the multitude of natural refrigerant offerings, with astounding energy efficiencies and combined with unmatched environmental advantages.

What influence has the new F-Gas Regulation on your business?

Since its introduction it triggered a lot of demand for information from new customers and novel applications. Mayekawa is benefiting from having been at the forefront of defending natural refrigerants. For instance the majority of old R22 installations that will be replaced by natural refrigerant based technology (NRBT) from now on will be a real challenge to keep up with, but we are prepared.

Many entrepreneurs being faced with the question of which refrigeration technology to choose will realise that taking into account that the new F-Gas Regulation, they are facing a real HFC phase down scenario. As a result they need to choose long term, sustainable and energy efficient solutions, and this will ultimately mean choosing natural refrigerants.