Background

Natural refrigerants: current developments and trends

by Monika Witt, Chairwoman of eurammon, the European initiative for natural refrigerants

The decision as to which refrigerant should be used in a refrigerating or air-conditioning system is based on the major criteria of safety, costs and environment protection. But against the background of constantly increasing energy prices, the energy consumption of a system also plays an increasingly important role. Ideally, the chosen refrigerant should have excellent thermodynamic properties, high chemical stability and good physical characteristics. Furthermore, it should have no or only a negligible impact on the environment, while also being inexpensive and available worldwide.

However, there is no one refrigerant that fulfils all these requirements. And so in practice, the decision for the most suitable refrigerant depends on a series of different factors. Here the operating area and the operator’s requirements are taken into account, together with the installation site and environmental aspects. But it is above all the actual rating of the overall refrigerating system while taking account of part load conditions that has a crucial influence on energy consumption, as the overall concept of a refrigerating system has a greater influence on efficiency than the choice of refrigerant. However, a number of current projects show that systems operating with natural refrigerants are particularly efficient and environment-friendly.

Ammonia refrigeration convinces with top energy efficiency

Ammonia is the refrigerant with the demonstrably best thermodynamic properties. It is the only natural refrigerant that industry never wanted to dispense with on account of its high efficiency. Ammonia is also unbeatable in ecological terms: it has no ozone depletion potential and no global warming potential (ODP and GWP = 0), with a favourable TEWI balance thanks to the high COP of ammonia systems.

In industrial systems with capacities exceeding 500 kW, ammonia is simply unsurpassed in terms of energy and cost efficiency. And it is also finding increasing use on a smaller scale, for example in systems with a capacity of less than 500 kW where the quantity of ammonia
can be reduced when choosing a suitable secondary refrigerant. At present, intensive research is in progress here in particular in the range of small-capacity systems, with the objective among others of developing small, semi-hermetic and hermetic compressors with output below 100 kW. Reduced quantity heat exchangers are also being developed along the same lines. Furthermore, various research projects are also looking at simplified oil management with soluble oils to facilitate DX systems as well.

Moreover, today ammonia is also being used increasingly in areas that used to be dominated by synthetic refrigerants. For example, all large exhibition buildings in Germany have been equipped with ammonia liquid chillers for air-conditioning. Banks, insurance companies and office buildings also increasingly use ammonia liquid chillers for energy-saving air-conditioning. Even modern airports make increasing use of ammonia systems, in the light of risk analysis results indicating no greater hazard potential for the general public or airport employees than systems using synthetic refrigerants. And so ammonia systems have been installed not only in Düsseldorf's refurbished airport but also in London Heathrow's new Terminal 5 and in Zurich airport. The freight hub in New Zealand's Christchurch airport also saves energy by using ammonia for cooling systems.

**Using carbon dioxide to save energy and money**

The last ten years have brought about a constant increase in the interest shown in CO\textsubscript{2} refrigerating systems. This is due for example to the fact that the global player Nestlé has constantly forged ahead with the development of NH\textsubscript{3}/CO\textsubscript{2} cascade refrigeration plants, demonstrating their energy efficiency with installations in Europe, the USA and Japan. Other companies have followed suit. In addition, this trend has been encouraged by state incentives in some countries. For instance, the Netherlands grant considerable tax relief for CO\textsubscript{2} systems, while taxation on synthetic refrigerants has been increased in Scandinavia. CO\textsubscript{2} is also particularly suitable for heat recovery or heat pump systems. Applications of this kind are already widespread in Asia and other countries can be expected to follow.

How much energy can actually be saved by using CO\textsubscript{2} as refrigerant depends above all on the ambient temperature. The efficiency of a CO\textsubscript{2} system is clearly superior to a plant operating with synthetic refrigerants when used in the subcritical range. But in the supercritical range too, success is also being achieved in optimising system efficiency. This has been confirmed among others by the Coca Cola Company which uses both CO\textsubscript{2} and R134a for its 550-litre refrigerators, with the result that the systems operating with CO\textsubscript{2} consume 20 to 30 percent less energy.
In the trans- or supercritical mode (temperatures > 31.2°C), CO\textsubscript{2} systems are in principle less efficient than those using synthetic refrigerants. Even so, when viewed over the whole year, CO\textsubscript{2} refrigerating systems are frequently more energy-efficient than those with synthetic refrigerants, as most systems operate in the subcritical range most of the time, particularly in latitudes with moderate weather.

**Climate-neutral cooling with hydrocarbons**

Hydrocarbons such as butane, propane and propene are ideal refrigerants. Butane for example is very successful in the more than 300 million domestic refrigerators currently being used. Furthermore, butane can also increasingly be found in smaller commercial refrigerating systems. The beverages company Pepsi for example compared the efficiency of small drinks chillers with up to 150 g coolant and found that units operating with butane consumed up to 27 percent less energy than those using R134a. Since then, the beverages manufacturer has given preference to butane in these chillers – and is not the only one. Ben & Jerry used butane for their ice-cream freezers for the first time in the USA, with most satisfactory results.

Propane has very similar thermodynamic properties to R22. Some Asian countries have therefore replaced R22 with propane in central air-conditioning systems and report cut-backs in energy consumption between 10 and 30 percent with only minimum modifications necessary to the systems. Unilever has also recognised the advantages of propane as a refrigerant: already during the 2000 Olympic Games in Brisbane and Sydney the company performed a field study with 360-litre ice-cream freezers, comparing operation with propane to operation with R404A. On average, the propane freezers permitted energy savings of about 9 percent.

Hydrocarbons have excellent thermodynamic properties, which is why refrigerating and air-conditioning systems operating with these substances are particularly energy-efficient. They are well miscible with conventional refrigerating oils and have a relatively high critical temperature. While the flammability of hydrocarbons requires hermetically sealed systems with explosion protection for electrical components, all components are easily available and current technology copes well with the demands of safe operation. Given the high energy saving potential of systems with hydrocarbons, a number of companies have announced their intentions of operating new refrigerating systems with hydrocarbons.

Up to now, Europe has imposed a 150 gram filling restriction of hydrocarbons. However, this value was determined arbitrarily, so that it would be preferable to make the filling restriction
dependent on the prevailing conditions in each case. Recommendations for such site-dependent limit values could be compiled and developed for example in the framework of a scientific research project. Larger filling quantities could probably be permitted if the propane filling is located up high on the roof of a building, or in large, well ventilated rooms.

In the USA there seems to be a willingness to rethink the situation: while the use of hydrocarbons was restricted hitherto to industrial applications, this restriction may possibly be lifted in future. For the first time, the US Environmental Protection Agency (EPA) with its highly critical stance on substances that pose a safety risk on account of the product liability laws, has approved of a field study that will test up to 2000 chest freezers operating with flammable refrigerants. This could lead to a real breakthrough.

**Water refrigeration with up to 25% potential savings**

The evaporation of water has always been used as a means of cooling. But this method that functions quite naturally in the human body through perspiration presents a challenge on an industrial scale. A huge flow of water vapour is needed to achieve an adequate cooling effect, which in turn requires the use of turbo-compressors. Suitable machines here consist either of axial compressors with a relatively small base area and many stages, or radial compressors connected in series. However, these are sensitive to load fluctuations and need operation to be as constant as possible. The situation is further complicated by the fact that operation takes place in a deep vacuum which requires a system that is absolutely tight. Even so, these stringent technical requirements are offset by huge energy saving potential of about 25 percent compared to currently available R134a liquid chilling units. This is why research is currently in progress in France and Dresden/Germany on prototypes for both radial and axial compressors.

**Air: fast refrigeration at low energy costs**

Air is interesting as a refrigerant for temperatures below -50°C. Systems with a closed air circuit are convincing above all on account of their particularly rapid cooling at low energy costs. But air has not become widely accepted as a refrigerant because of the comparatively high costs for the overall system. To achieve the necessary mass flow density, expensive turbo-compressor/expander systems are necessary together with special shaft seals to minimise leakage. However, at the same time air-cooled systems are also very compact. This is why today they are primarily used for gas liquefaction on tankers, where the high costs are justified in view of the confined space available.
Double advantage for the environment and corporate balance sheets

Natural refrigerants are inexpensive, available in abundance and can cover nearly every refrigeration application already today. Furthermore, they have a very low global warming potential (GWP) compared to synthetic refrigerants. This alone is reason enough to recommend their use. However, it is just as important that they are highly energy-efficient: after all, more than 80 percent of the global warming potential posed by refrigerating and air-conditioning systems results from system energy consumption and not from refrigerant leaks. At present, around 15 percent of global electricity consumption is used to generate refrigeration – resulting in huge savings potential. Measures to save energy throughout the entire service life of refrigerating systems are therefore acquiring increasing significance and can help considerably to relieve the burden on the environment. Here the use of natural refrigerants offers a double incentive for companies: by reducing their energy consumption, they not only cut back on costs but also help to protect the environment. And so in future, everything points towards the use of natural refrigerants in both ecological and economical terms, in order to safeguard both capital expenditure and the environment in the long term!
Annex

**Ammonia (NH₃)**
Ammonia has been successfully used as a refrigerant in industrial refrigeration plants for over 100 years. It is a colourless gas, liquefies under pressure, and has a pungent odour. In coolant technology, ammonia is known as R 717 (R = Refrigerant) and is synthetically produced for use in refrigeration. Ammonia has no ozone depletion potential (ODP = 0) and no direct global warming potential (GWP = 0). Thanks to its high energy efficiency, its contribution to the indirect global warming potential is also low. Ammonia is flammable. However, its ignition energy is 50 times higher than that of natural gas and ammonia will not burn without a supporting flame. Due to the high affinity of ammonia for atmospheric humidity it is rated as “hardly flammable”. Ammonia is toxic, but has a characteristic, sharp smell which gives a warning below concentrations of 3 mg/m³ ammonia in air possible. This means that ammonia is evident at levels far below those which endanger health (>1,750 mg/m³). Furthermore ammonia is lighter than air and therefore rises quickly.

**Carbon dioxide (CO₂)**
Carbon dioxide is known in refrigeration technology as R 744 and has a long history extending back to the mid 19th century. It is a colourless gas that liquefies under pressure, with a slightly acidic odour and taste. Carbon dioxide has no ozone depletion potential (ODP = 0) and negligible direct global warming potential (GWP = 1) when used as a refrigerant in closed cycles. It is non-flammable, chemically inert and heavier than air. Carbon dioxide has a narcotic and asphyxiating effect only in high concentrations. Carbon dioxide occurs naturally in abundance.

**Hydrocarbons**
Refrigeration plants using hydrocarbons such as propane (R 290, C₃H₈), propene (R 1270, C₃H₆) or isobutane (R 600a, C₄H₁₀) have been in operation all over the world for many years. Hydrocarbons are colourless and nearly odourless gases that liquefy under pressure, and have neither ozone depletion potential (ODP = 0) nor significant direct global warming potential (GWP = 3). Thanks to their outstanding thermodynamic characteristics, hydrocarbons make particularly energy efficient refrigerants. Hydrocarbons are flammable, however, with currently available safety devices, refrigerant losses are near zero. Hydrocarbons are available at low cost all over the world; thanks to their ideal refrigerant characteristics they are commonly used in small plants with low refrigerant charges.

**Ozone Depletion and Global Warming Potential of Refrigerants**

<table>
<thead>
<tr>
<th>Refrigerant Type</th>
<th>Ozone Depletion Potential (ODP)</th>
<th>Global Warming Potential (GWP)</th>
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</thead>
<tbody>
<tr>
<td>Ammonia (NH₃)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Carbon dioxide (CO₂)</td>
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<td>1</td>
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<tr>
<td>Hydrocarbons (propane C₃H₈, propene C₃H₆, isobutane C₄H₁₀)</td>
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<td>Water (H₂O)</td>
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<tr>
<td>Chlorofluoro-hydrocarbons (CFCs)</td>
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<tr>
<td>Partially halogenated chlorofluoro-hydrocarbons (HCFCs)</td>
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<td>76–12100</td>
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<tr>
<td>Per-fluorocarbons (PFCs)</td>
<td>0</td>
<td>5820–12010</td>
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<tr>
<td>Partially halogenated fluorinated hydrocarbons (HFCs)</td>
<td>0</td>
<td>122–14310</td>
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</tbody>
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**Ozone Depletion Potential (ODP)**
The ozone layer is damaged by the catalytic action of chlorine, fluorine and bromine in compounds, which reduce ozone to oxygen and thus destroy the ozone layer. The Ozone Depletion Potential (ODP) of a compound is shown as chlorine equivalent (ODP of a chlorine molecule = 1).

**Global Warming Potential (GWP)**
The greenhouse effect arises from the capacity of materials in the atmosphere to reflect the heat emitted by the Earth back onto the Earth. The direct Global Warming Potential (GWP) of a compound is shown as a CO$_2$ equivalent (GWP of a CO$_2$ molecule = 1).

**About eurammon**
eurammon is a joint European initiative of companies, institutions and individuals who advocate an increased use of natural refrigerants. As a knowledge pool for the use of natural refrigerants in refrigeration engineering, the initiative sees as its mandate the creation of a platform for information sharing and the promotion of public awareness and acceptance of natural refrigerants. The objective is to promote the use of natural refrigerants in the interest of a healthy environment, and thereby encourage a sustainable approach in refrigeration engineering. eurammon provides comprehensive information about all aspects of natural refrigerants to experts, politicians and the public at large. It serves as a qualified contact for anyone interested in the subject. Users and designers of refrigeration projects can turn to eurammon for specific project experience and extensive information, as well as for advice on all matters of planning, licensing and operating refrigeration plants. The initiative was set up in 1996 and is open to European companies and institutions with a vested interest in natural refrigerants, as well as to individuals e.g. scientists and researchers.

Internet URL: [www.eurammon.com](http://www.eurammon.com)

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