There's a future for natural refrigerants

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The question as to how to prevent food from going off is probably as old as humanity itself. Way back in the Stone Age, people knew that food could be kept for longer in the cold, and stored meat and fruit in cool caves protected from heat and the sun. More than 5,000 years ago, the Egyptians used what must be the world's oldest natural refrigerant to cool their food and drinks: ice.

Development of industrial refrigeration

The use of natural ice was common practice through to the second half of the 19th century. Industrial developments made it possible to use machines for refrigeration. The first refrigerating system to operate with the natural refrigerant CO_2 was installed in 1869 by the American Thaddeus S. C. Lowe in Jackson, Missouri. In 1876, Carl von Linde, Professor for Mechanical Engineering at the Polytechnic School in Munich, developed the first compression refrigeration machine with the natural refrigerant ammonia, which became widely accepted on account of its good thermodynamic properties. The first large refrigerated warehouses were built from 1881.

Synthetic refrigerants on the advance

Natural refrigerants need to be handled carefully. Ammonia for example is toxic, even if its characteristic pungent smell has a high warning effect already in low concentrations. For this reason, the chemical industry started to develop synthetic refrigerants in the early 1930s, using the halogens fluorine and chlorine to completely replace the hydrogen atoms. The chlorofluorocarbons (CFCs) were stable, non-flammable and also neutral in smell and taste, and were therefore propagated as safe, easily handled alternatives. Even if some companies continued to use the natural refrigerant ammonia in particular, due to its good thermodynamic properties and efficiency, from this time onwards, industrial refrigeration systems were filled increasingly with CFCs. However, just 50 years later, chemists issued warnings that the chlorine contained in the anthropogenic CFCs could destroy the ozone layer, as confirmed in 1985 by the discovery of the ozone hole.

Protecting the ozone layer: a global task

This development led to the Montreal Protocol which came into effect in 1989. In the multilateral treaty which is binding under international law, 196 countries undertook to adopt measures to protect the ozone layer. In order to reduce the harmful effect of the refrigerants, partly halogenated chlorofluorocarbons (HCFCs) with lesser ozone depletion potential (OPD) were produced. Since 1996, the use of CFCs has been banned in industrial countries. From 2015, HCFCs may also only be used in existing systems and also only in those cases where there is no interference in the refrigerant circuit or no replenishment.

Global warming and the greenhouse effect are becoming social issues

While newly developed substitute refrigerants called fluorocarbons (FCs) no longer contain chlorine compounds that are harmful to ozone, they still contribute to global warming. The global warming effect could be mitigated by producing partly halogenated refrigerants, so-called HFCs. However, the contribution to global warming (GWP value) is still between 120 and 14,000 times higher than that of the natural refrigerant carbon dioxide. This is why the FCs and HFCs referred to as fluorinated gases are featured together with other greenhouse gases in the international Kyoto Protocol to the United Nations Framework Convention on Climate Change, with mandatory target values stipulated for industrial countries for the first time.

On the European level, the EC Regulation on fluorinated greenhouse gases stipulates specific measures to be taken to reduce refrigerant emissions, including for example regular maintenance and leak checks of the refrigeration and air-conditioning systems. However, a review of the defined objectives in 2011 revealed that the measures currently adopted by the Member States cannot reduce fluorinated greenhouse gas emissions but just keep them constant on the current level - and only if the regulations are implemented consistently by all 27 Member States. But it is precisely the lack of consistent implementation that is criticised by the Review Panel. In turn, this revives the debate about tightening up the Regulation or even banning the refrigerants.

Renaissance of natural refrigerants

Efforts to counteract the progressing greenhouse effect is putting natural refrigerants increasingly back on the agenda again. They have no ozone depletion potential and either no global warming potential (ammonia) or their global warming potential is negligibly low (carbon dioxide: 1, hydrocarbons: 3). Furthermore, systems with natural refrigerants today operate with just the same energy efficiency as systems with synthetic refrigerants.

Natural refrigerants remain the more viable solution

The chemical industry reacted to the increasing legislation and standards aiming to counteract the use of refrigerants with high GWP by developing unsaturated HFCs, called hydrofluoro-olefins (HFOs). They have a shorter lifecycle in the atmosphere which gives them just a low global warming potential. On the other hand, opponents of the new refrigerants argue that their long-term impact on the environment is not clear and that their decomposition in the atmosphere releases harmful by-products such as trifluoroacetic acid. Furthermore, there are additional safety risks in terms of combustibility and flammability. And yet there are adequate supplies of alternatives available, such as natural refrigerants.

We at eurammon are convinced that in future too, natural refrigerants will continue to be the most environmentally friendly option for refrigeration applications. One thing is certain: today, for every refrigeration application, there is also a solution with natural refrigerants which is convincing in both ecological and economical terms. And so, natural refrigerants are a safe investment in the future.

Annex

Ammonia (NH_3)

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/m^3 ammonia in air possible. This means that ammonia is evident at levels far below those which endanger health (>1,750 mg/m^3). Furthermore ammonia is lighter than air and therefore rises quickly.

Carbon dioxide (CO_2)

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, C_3H_8), propene (R 1270, C_3H_6) or isobutane (R 600a, C_4H_{10}) 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

	Ozone Depletion Potential (ODP)	Global Warming Potential (GWP)
Ammonia (NH_3)	0	0
Carbon dioxide (CO_2)	0	1
Hydrocarbons (propane C_3H_8, propene C_3H_6, isobutane C_4H_{10})	0	<3
Water (H_2O)	0	0
Chlorofluoro-hydrocarbons (CFCs)	1	4680–10720
Partially halogenated chlorofluoro-hydrocarbons (HCFCs)	0.02–0.06	76–12100
Per-fluorocarbons (PFCs)	0	5820–12010
Partially halogenated fluorinated hydrocarbons (HFCs)	0	122–14310

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.
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