# Natural refrigerants

## Carbon dioxide, ammonia and propane

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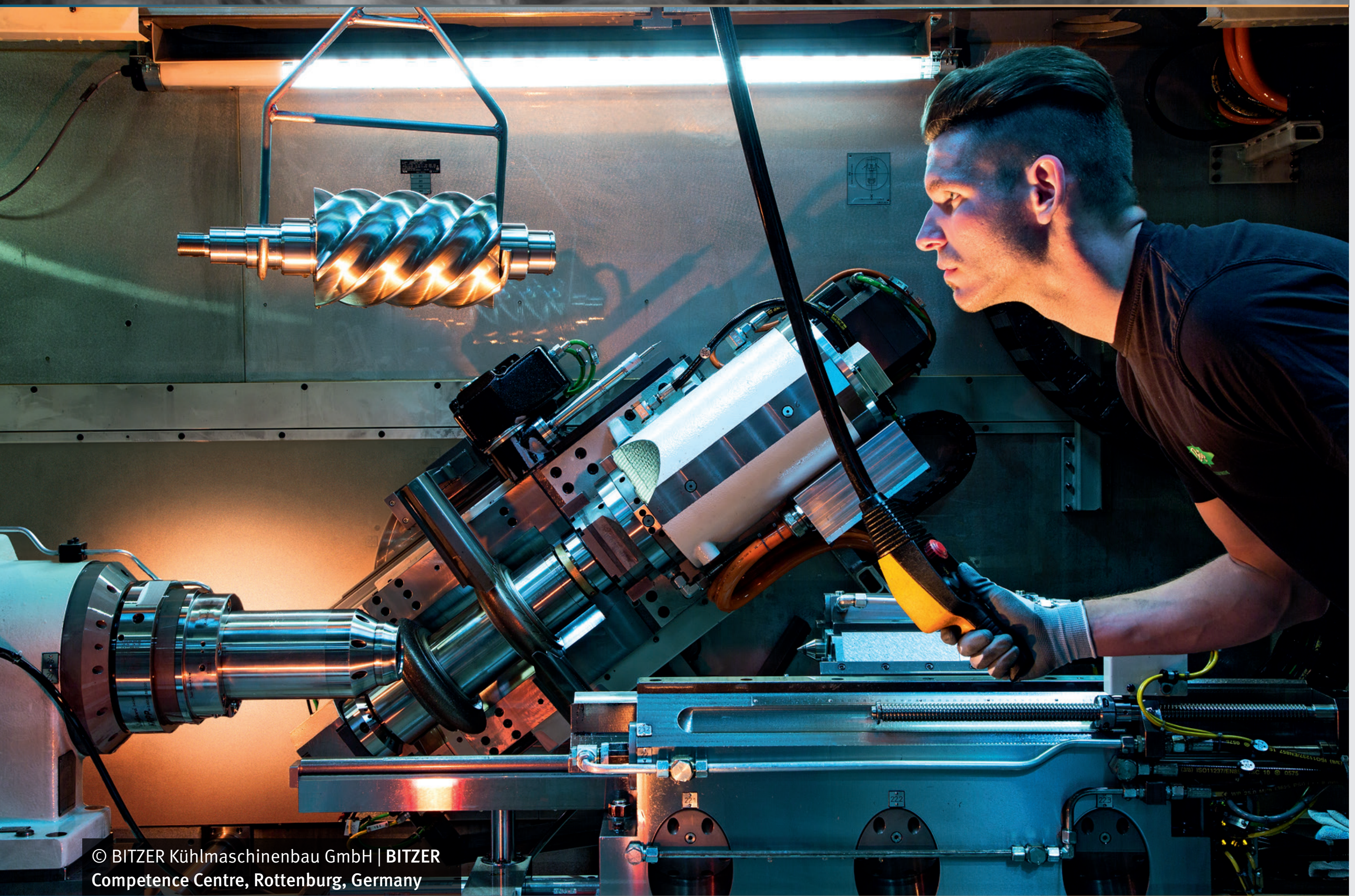

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Fluorinated hydrocarbons, known as F-Gases have dominated the refrigerant gases sector for decades. There has been a progressive transition away from ozone depleting CFCs through to HCFCs that were less damaging to the ozone layer but have a high global warming potential (GWP). HFCs replaced HCFCs and how HFOs are being introduced as the fourth generation of F-Gases. HFO's contain a double bond in the molecule so that UV light from the sun can easily break them down when they are emitted into the atmosphere.

Whilst the transition to HFOs has reduced the environmental risk of using refrigerant gases, there are







alternatives that are even less risky to the environment. They are the so-called 'natural refrigerants'. The most common three are carbon dioxide (R774), ammonia (R714) and propane (R290). Also included in this category are water (R718) and the hydrocarbons isobutane (R600a), n-butane (R600), n-pentane (R601), isopentane (R601a) and cyclo-pentane.

Whilst ammonia, propane and $CO_2$ are commonly used industrial gases, when they are used as refrigerant grade gases they must comply to the appropriate specification. Using a cylinder of patio gas propane in a refrigeration system is not an option. R744, refrigerant grade $CO_2$ is generally supplied with less than 10 ppm (parts-per-million) of water and less than five ppm of incondensable inert gases such as nitrogen. Moisture would result in corrosion of the refrigeration equipment and incondensables reduce the energy efficiency of the system. Grades of $CO_2$ used for welding do not generally need to confirm to this specification.

### Using carbon dioxide to reduce greenhouse gas emissions

Carbon dioxide ($CO_2$) is a greenhouse gas. It is rated with a GWP of one and all other greenhouse gases are referenced back to $CO_2$ according to their relative climate impact. R134a, one of the most used F-Gases has a GWP (on a 20-year basis) of 3,830 meaning that 1kg of R134a in the atmosphere has the same global warming effect as 3,830kg of $CO_2$ emissions.

Liquid $CO_2$ is used as a cryogenic refrigerant in applications such as food freezing. In this application it is released to the atmosphere as it vaporises to release its cold energy. $CO_2$ can also be used in closed circuit refrigeration loops as an alternative to F-Gases such as R134a. In this case, the charge of $CO_2$ remains in the refrigeration system throughout the life of the equipment – it is not intentionally released to the atmosphere.

**"Refrigeration contractors often transport common refrigerant gases in their van so that they can react quickly to serving jobs. However, they are not willing to take the risk of having an ammonia cylinder on board"**

On the other hand, if there is a problem on the refrigeration system and a gas leak develops the climate impact of releasing the charge of $CO_2$ is significantly less than a release of R134a or another F-Gas with a high GWP. Similarly, if the refrigerant gas contained within the closed system is accidentally released to the atmosphere during maintenance decommissioning, the climate impact of a $CO_2$ release will be less than the damage done by accidentally venting an equivalent amount of an F-Gas.

### Ammonia – a zero, zero refrigerant gas

Amongst all refrigerant gases, the premium environmental credentials of 'zero ozone depletion potential and zero global warming potential' can only be assigned to water and ammonia. The main disadvantage of using ammonia is its toxicity. The Permissible Exposure Limit for ammonia set by the US Occupational Safety and Health Administration (OSHA) is 50 ppm averaged over an eight-hour day. In contrast, the limit for the F-Gas R134a is 1,000 ppm.

Refrigeration contractors often transport common refrigerant gases in their van so that they can react quickly to serving jobs. However, they are not willing to take the risk of having an ammonia cylinder on-board. This has limited the field of application for ammonia to larger industrial systems, for example on oil refineries or pharmaceutical plant refrigeration systems where expert engineers and strict safety protocols are in place to protect lives in the event of an inadvertent ammonia gas leak.

### Climate impact through the full lifecycle

Refrigeration units consume electrical power to operate the gas compressor and evaporator heat exchanger air →

Ammonia refrigeration piston compressor

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BITZER $CO_2$ refrigeration compressor

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BITZER $CO_2$ or Propane refrigeration compressor

fan. Use of an efficient refrigerant gas reduces the electrical power consumption. Over a period of 20 years of operation, a small percentage increase in system efficiency can mean a significant decrease in the power consumed.

Considering that grid power in almost every nation has a substantial $CO_2$ footprint refrigeration system efficiency is very important to minimise upstream (Scope 2) greenhouse gas emissions from refrigeration plant.

Scroll compressor internal element

On the other hand, the most efficient refrigerant gas may have a high GWP when it is released to the atmosphere. The ideal regime would be to use an efficient refrigerant gas, with a low GWP and avoid leaks of the refrigerant gas during operation, maintenance, and decommissioning.

In large commercial refrigeration units such as centralised supermarket freezing and chilling systems, the motivation for energy efficiency justifies the used of more complex and capital-intensive hybrid cascade systems. This means that two different refrigerant gases are used in high and low temperature circuits. It is common to use ammonia in the warmer part of the system and $CO_2$ at the low temperature end. Alternatively, an F-Gas or hydrocarbon can be used in place of the ammonia if toxicity concerns exist.

Many commercial refrigeration systems have been switched from F-Gases to natural refrigerants in recent years. The change in refrigerant gas has also meant new equipment is required. Compressors and evaporators must be replaced to work with the new chemicals and their operating pressure profiles. Companies such as Bitzer have been at the forefront of this wave of innovation, providing both equipment and the required training to ensure supermarket operators can modernise and use natural refrigerants in an energy-efficient manner.

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### Electrification: more heat pumps

Domestic heating using gas boilers has been popular in countries such as the UK and NL, where North Sea gas has been abundantly available in recent decades. The recent energy crunch, driven by the Ukraine war, has seen a surge in natural gas prices. Also, heating with gas releases $CO_2$ greenhouse gas emissions to the atmosphere from the domestic boiler.

For these reasons, the increased uptake of heat pumps which can be powered by renewable electricity from wind farms or solar parks has been strongly advocated and is now a firm trend. The natural refrigerant propane (R290) is the most likely candidate to replace R410A and R134a in small heat pumps for domestic applications. It is well suited to moderate climates, such as Europe where ambient air is used as the heat sink.

In larger district heating systems where sea or lake water can economically be used as the heat sink, the natural refrigerant $CO_2$ (R744) can be used. For such applications, very large $CO_2$ compressors are required, such as the specialist machines produced by MAN Energy Solutions. These multi-stage $CO_2$ compressors are also used for supercritical $CO_2$ pipeline transmission in enhanced oil recovery (EOR) and carbon capture and storage (CCS) applications.

### Climate change is increasing the demand for air conditioning

As summer temperatures are on the rise in many locations, the attraction of air conditioning is becoming more widespread. Recent regulatory changes in Europe (EN 378) have made it possible to use flammable refrigerants in domestic and commercial air conditioning applications. The natural refrigerant propane (R290) is lined up to play an increasing role in air conditioning systems.

EN 378 is the European standard that specifies safety and environmental requirements for refrigerating systems and heat pumps. Flammable refrigerant gases were previously banned under EN 378 due to safety concerns related to the use of flammable gases in domestic homes and commercial offices. The drive towards natural refrigerants and the increasing mechanical integrity of refrigeration equipment has led to a relaxation of the policy.

### The future of F-Gases

Regulations in the European Union have led the world in the transition from F-Gases to natural refrigerants and other regions are following. In the EU, domestic refrigerators predominantly switched to using propane (R290) more than a decade ago. Propane is ideal for spanning the temperature range between the general European ambient temperature and the temperature at which chilled and frozen food is stored.

Scroll compressor

Despite the trend to use more natural refrigerants, F-Gases remain dominant and represent about 70% of the refrigerant gas tonnages sold each year. Whilst R1234yf, which is becoming the default mobile air conditioning gas for cars only has a GWP of 4, many other F-Gases such as R32, which is very common in air conditioning systems, has a GWP of 675. The climate benefits of the three most common natural refrigerants (ammonia with a GWP of zero, $CO_2$ with a GWP of one and propane with a GWP of only three) will be difficult to match with the current generation of F-Gases. As a result, natural refrigerants will continue to penetrate market share, and F-Gases will continue to transition towards lower GWP molecules.



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