



31<sup>st</sup> Informatory Note on Refrigeration Technologies / April 2016

## **Current long-term alternative refrigerants and their possible applications**

*The IIR publishes Informatory Notes designed to meet the needs of decision-makers worldwide, on a regular basis. These notes summarize knowledge in key refrigeration-technology and refrigeration-application domains. Each note puts forward future priority developmental axes and provides IIR recommendations in this context.*

The 26<sup>th</sup> IIR Informatory Note “Overview of regulations restricting HFC use - Focus on the EU “F-Gas” Regulation presented recent regulatory developments at the global level and in some countries in order to limit the use of HFCs due to their impact on global warming. It also specified the requirements and the implications of the EU “F-gas” Regulation, which entered into force on January 1, 2015.

The main consequences for the actors in the refrigeration sector bear on the decisions to be taken regarding the replacement or retrofit of their refrigeration installations and the choice of the most suitable alternative refrigerants to HFCs.

This Informatory Note first provides the characteristics of the main low-GWP refrigerants that can replace HFCs and then lists, application by application, the possible long-term options.

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## Introduction

In the EU, low-GWP alternatives to HFCs have already won a significant market share in some sectors, with over 90% of new domestic refrigerators/freezers <sup>1</sup> and approximately 25% of new industrial air conditioners in 2011 using alternatives [Kau2012]. In other sectors, however, low-GWP technologies are minor players. This may soon change due to the new “F-gas” Regulation and other pending regulations on HFCs, especially in the US, Canada, and Japan. Considering the draft regulations currently discussed in other countries and the current use of low-GWP refrigerants in many countries, the market share of these refrigerants is likely to increase globally.

Low-GWP refrigerants offer a lower impact of direct emissions. Moreover, many low-GWP technologies provide additional indirect emission reductions through increased energy efficiency, as compared to traditional HFC technologies.

Crucially, there is no single alternative that will replace HFCs in all applications, just as there is no single HFC refrigerant that can be used in all applications. The low-GWP technology that is most appropriate will depend on a number of factors including the local economic and regulatory situation, as well as climatic and other factors. Nonetheless the evidence is clear that the use of HFCs can be phased out in the majority of sectors with safe, affordable and energy efficient alternatives in new equipment.

## Overview of low-GWP alternatives

### Ammonia

Ammonia (R717) has the lowest GWP (0) of all refrigerants suitable for refrigeration systems. Ammonia refrigeration systems also usually achieve higher energy efficiency than HFC refrigeration systems. Although ammonia is toxic (Permissible Exposure Limit value (PEL) is 50 ppm or 35 mg/m<sup>3</sup>), it has a pungent odor and thus a strong warning effect. Certain ammonia-air mixtures can be ignited. Ignition limits lie between 15 and 30% vol. in air.

Ammonia is an alkaline gas with a lower density than air. In connection with water the well-known liquid ammonia water (ammonium hydroxide) is created. In connection with carbon dioxide, ammonium carbonate is formed. Steel is the most commonly used material for ammonia refrigeration systems, since ammonia-water mixtures are corrosive to copper and brass. Aluminium can also be used as long as the aluminium alloy is copper- and zinc-free. Aluminium is resistant to ammonia and ammonia containing up to 10% water [Kau1998].

In refrigeration systems, ammonia causes high compression end temperatures, so refrigeration systems for low temperature applications must be designed in two stages with intermediate cooling between both compression stages. On the other hand the high compression end temperatures offer excellent possibilities for waste heat recovery. Ammonia has been the standard refrigerant for industrial refrigeration systems for more than 130 years. Because of its toxicity, it is only used with indirect systems in public access areas, e.g. systems with liquid and, lately, evaporating secondary refrigerant for the medium temperature and/or low temperature range. Recently ammonia has been also used quite often as the higher temperature stage in CO<sub>2</sub> cascade refrigeration systems.

### Carbon dioxide

CO<sub>2</sub> (R744) is a colorless and odorless gas, which is non-flammable and heavier than air. Although it is the largest contributor to manmade global warming, the amount of CO<sub>2</sub> needed in a system would have insignificant impact on climate change if leaked to the atmosphere. CO<sub>2</sub> is non-toxic in low concentrations, but can be harmful in higher concentrations.

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<sup>1</sup> According to the EU “F-gas” Regulation, domestic refrigerators and freezers have to use refrigerants with a GWP lower than 150 starting January 1, 2015.

The maximum allowable concentration (MAC) for a workplace is 5,000 ppm or 0.5 vol.% in air. Immediate danger to health and life (IDLH) exists for CO<sub>2</sub> concentration over 4 vol.% in air (40,000 ppm). Above 10 vol.% in breathing air, CO<sub>2</sub> has a numbing effect and is immediately lethal above 30 vol.% [Rhi2009].

CO<sub>2</sub> operates with significantly higher pressures than other refrigerants. In water heating heat pumps, plug-in bottle coolers and transcritical supermarket refrigeration systems CO<sub>2</sub> achieves pressure levels up to 130 bar on the high pressure side. The high operational pressures require stronger materials and/or larger wall thicknesses. On the other hand, the volumetric refrigeration capacity of CO<sub>2</sub> is much higher than that of traditional refrigerants, allowing system designs with reduced volumes and pipes with smaller diameter. Thus, despite the larger wall thicknesses due to increased pressure, the use of material for piping is smaller [Hei2005]. Smaller compressor cylinder displacement still provides adequate system capacity. Pressure drops lead to significantly smaller drops in saturation temperature and thus to smaller losses in energy efficiency. Due to higher heat transfer coefficients, e.g. evaporation temperatures can be increased by about 2 K compared to HFCs [Hei2005].

As the critical temperature of CO<sub>2</sub> is low (31°C), the CO<sub>2</sub> system will operate in a transcritical cycle most of the time in high ambient temperatures<sup>2</sup>. Heat rejection then takes place by cooling the compressed, supercritical fluid at the high-pressure side constantly reducing its temperature. The low-side conditions remain subcritical during normal operation. Usually, the energy efficiency of transcritical refrigeration systems is lower than that of conventional refrigeration systems with condensing refrigerant on the high-pressure side. This characteristic can be partially compensated by application of an internal heat exchanger, which has a greater positive impact on energy efficiency in the transcritical CO<sub>2</sub> process than with other refrigerants. The choice of the high side pressure has an equally critical impact on the energy efficiency. There is an optimal high side pressure for every CO<sub>2</sub> gas cooler exit temperature, i.e., the high side pressure has to be adjusted depending on the temperature of the cooling air or water in order to achieve maximum COP. The control of a CO<sub>2</sub> refrigeration system must account for this characteristic and constantly adjust the high side pressure in order to ensure low energy consumption. Electronic control is able to secure over a wide range of operating conditions that the system is operating with the lowest possible energy consumption [Cec2007].

At ambient temperatures around 26°C, standard air-cooled CO<sub>2</sub> refrigeration systems can achieve comparable energy efficiency to HFC direct evaporation refrigeration systems. At lower ambient temperatures (below 24°C), the CO<sub>2</sub> system achieves even better energy efficiency [Fin2011]. New developments such as small mechanical subcooling refrigeration systems and ejectors as expansion devices with parallel compression move this crossover temperature to higher values, i.e. approximately 30°C for the mechanical subcooling and 40°C for the ejector cycle [Haf2015].

As CO<sub>2</sub> provides very good energy efficiency at low condensing and evaporation temperatures, it is often the refrigerant of choice for the low-temperature stage in commercial and industrial cascade refrigeration systems alongside ammonia or hydrocarbons in the upper stage. The EU “F-gas” Regulation explicitly supports such cascade systems for central supermarket refrigeration systems with its placing on the market prohibitions, where refrigerants up to a GWP 1,500, such as R134a, are allowed in the upper stage of an

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<sup>2</sup> The difference between the refrigerant condensation and critical temperature is important for the efficiency of equipment unless it is explicitly designed for transcritical operation (as it is often the case with CO<sub>2</sub> systems). In the conventional vapour-compression cycle equipment, the condensing temperature is well below the critical temperature, because thermodynamic properties of the refrigerant (such as slope of isentropes in vapour region) and deviation from the Carnot-cycle due to decreasing entropy change at constant temperature result in declining capacity and efficiency as heat-rejection (refrigerant condensing) temperatures increase and approach the critical temperature.

indirect system. Many refrigeration system manufacturers offer such cascade systems as part of their standard product range [Sie2007]. These systems are competitive regarding the investment costs incurred, especially for large supermarkets. In these cascade applications, typical condensing temperatures of the CO<sub>2</sub> system are about 0°C and hence the maximum CO<sub>2</sub> operating pressure is kept below 40 bar <sup>3</sup>. CO<sub>2</sub> cascade systems achieve good energy efficiency especially when combined with ammonia or hydrocarbons in the high-temperature stage.

### Hydrocarbons

Hydrocarbons are substantially less expensive than HFCs. They have global warming potentials below 20 and no ozone depleting potential, are non-toxic, nearly odourless, and satisfy many of the specifications stipulated for refrigerants; however, they are flammable (see Table 1). Nevertheless, they are prevalent in European and Asian household refrigerators and commercial stand-alone cabinets with HC refrigerant charges of up to 150 g, which is defined as the upper limit in IEC 60335-2-89 <sup>4</sup>. For larger charges special requirements are stipulated concerning flammability. Typically a refrigeration system originally designed for HFC will need about 50% to 60% less refrigerant by mass when charged with hydrocarbons [GTZ2010]. A substantial reduction of refrigerant charge is possible, if refrigerant charge minimization is part of the design requirements [IIR2014]. Current plug-in refrigeration units with refrigerant charges below 150 g may achieve refrigeration capacities up to approximately 1,000 watt [Rhi2009 and Pad2015]. Hoehne et al. [Hoe2004] suggest 50 g per kW refrigeration capacity as a limit within reach using plate and/or microchannel heat exchangers; so 150 g hydrocarbon refrigerant charge could achieve 3 kW refrigeration capacity without changes in safety standards. Changes in standard EN378 are on the way and expected to enter into force in 2016 extending the charge limit to 500 g for hermetically sealed equipment if a proper risk assessment is performed [Rinne2015].

**Table 1:** Ignition limits and ignition temperatures of some hydrocarbons [AL2007]. Electric sparks are sufficient as ignition source – the required ignition energy is about 0.25 mJ.

	Lower and upper ignition limits in dry air in vol. (%)	Ignition temperature (°C)
Isobutane (R600a)	1.3 – 9.8	543
Propane (R290)	1.7 – 10.9	470
Propene (R1270)	2.0 – 11.1	460
For comparison: gasoline	ca. 1.1 – 7.0	ca. 300

The hydrocarbons used as refrigerant are heavier than air. Ignitable blends with air are therefore predominantly formed in low areas. When larger refrigerant charges are used, appropriate gas sensors and air removal devices need to be installed at the floor level. Hydrocarbons mix very well with mineral oils. The hygroscopic synthetic oils used with HFCs can be avoided.

<sup>3</sup> Without special safety precautions, such as e.g. auxiliary refrigeration system, expansion vessel, cold spot or designated pressure vessel, the CO<sub>2</sub> pressure can rise above 40 bar during longer periods of standstill. CO<sub>2</sub> saturation pressure at 25°C is 64 bar! Appropriate safety valves or components designed for higher pressures should therefore be applied.

<sup>4</sup> IEC 60335-2-89, a standard from the International Electrotechnical Commission specifies safety requirements for electrically operated commercial refrigerating appliances that have an incorporated compressor or that are supplied in two units for assembly as a single appliance in accordance with the manufacturer's instructions (split system).

- **Isobutane (HC-600a)** is the standard refrigerant for European and many Asian domestic refrigerators and freezers. Over 40 million appliances are produced annually with isobutane worldwide. Isobutane is also used for smaller commercial plug-in units, e.g., chest freezers for ice cream. Due to lower pressure levels and pressure ratios, isobutane refrigeration units run quieter than comparable HFC-134a units.
- **Propane (HC-290)** is used by some producers for plug-in bottle coolers, chest freezers and food service cabinets. Those units usually have higher refrigeration capacities than household refrigerators requiring the higher pressure refrigerant propane. When the statutory requirements for safety are met (i.e. IEC 60335-2-89), propane is an excellent refrigerant for such units. It can be used with available components, is well mixable with mineral oils, and causes lower compression end temperatures. Several manufactures reported better energy efficiency for propane units than for comparable HFC units; e.g., [Ger2008] reported 8% better efficiency in field tests of ice cream cabinets (R290 vs. R404A) and Jürgensen [Jür2004] measured 10% efficiency gains in a commercial freezer (R290 vs. R404A). Furthermore, the pressure ratios and pressure differences are lower with R290 than with R404A resulting in lower noise emissions.
- **Propene (HC-1270)** or propylene is a hydrocarbon with one unsaturated carbon bond (double carbon bond). Correspondingly, it is less stable than propane. Systems using propylene may achieve slightly better energy efficiency than the same system running on propane. This was the reason why a German manufacturer of commercial refrigeration systems used propylene in their indirect supermarket refrigeration systems in the 1990s [Rhi2009]. The systems were abandoned in favour of carbon dioxide cascade systems due to the poor energetic performance of liquid secondary refrigerant systems in the low-temperature (freezer) part of the systems. Tests in a prototype transport refrigeration unit showed propylene achieving from 12 to 17% better efficiency than R404A [Bur2011].

5 to 10% energy efficiency improvements compared to HFCs seem to be a reasonable figure creditable to the hydrocarbon fluid properties; publications citing higher energy improvements when changing the working fluid to hydrocarbons usually incorporate component optimization.

### Water

Water (R718) is the most environmentally benign fluid (non-toxic, non-flammable, no ODP, negligible GWP) and the most commonly used liquid as a heat transfer fluid in secondary (indirect) refrigeration<sup>5</sup> and air conditioning (water chillers). The thermophysical properties of water (very low vapour pressure and freezing point at 0°C) limit its use as refrigerant to applications above 0°C. R718 chillers have been announced for market introduction with 45 kW and several hundred kW refrigeration capacity for 2015/2016 by several companies. Development work is also ongoing using those same compressors for (vacuum) ice slurry production. First systems have been installed as sea water heat pumps and snow makers for indoor skiing facilities.

### Unsaturated HFCs

Unsaturated HFCs – molecules with double carbon bonds, also called hydrofluoro-olefins (HFOs) – have been developed based on the propylene molecule as alternatives to high-GWP HFCs. Unsaturated HFCs are either used as a single substance, e.g., HFC-1234yf for automotive air-conditioning systems, or in mixtures with HFCs, where they reduce the GWP of the blend. Unsaturated HFCs have high reactivity and therefore shorter lifetimes in the atmosphere resulting in low GWPs.

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<sup>5</sup> For temperatures below the freezing point of water, additives are used such as various salts, alcohols or glycols, but water is usually the largest fraction of such mixtures.

There are concerns about the potential environmental impact of large-scale use and subsequent emissions of HFOs. Trifluoroacetic acid (TFA), for example, is a common by-product when HFCs breakdown; however, HFC-1234yf yields 4-5 times as much TFA as HFC-134a [Lue2010]. The replacement of the current HFCs by unsaturated HFCs is likely to increase TFA concentration. Therefore, the “EU F-gas” Regulation requires “other fluorinated greenhouse gases”<sup>6</sup> to be reported in accordance with article 19, such that the quantity used can be monitored and, if needed, action can be taken.

Unsaturated HFCs have a low global warming impact because they are unstable in the atmosphere due to the double carbon binding. This same instability makes them break up into new chemicals inside living organisms [Sch2010], which could limit certain uses (pharmaceuticals, propellants...). Another concern can be the mild flammability of the HFOs: they are classified as A2L according to ASHRAE Standard 34 and ISO 817 because they have a maximum burning velocity of less than 10 cm/s when tested at 23°C and 101.3 kPa in addition to the class 2 requirements of a lower flammability limit of more than 3.5% by volume in air and a heat of combustion of less than 19,000 kJ/kg. Even if it seems generally negligible, it can be a barrier to certain uses and, in any case, it requires certain precautions. In addition, the decomposition of unsaturated HFC during a fire and subsequent recombination can create decomposition products, e.g., hydrogen fluoride (HF) and carbonyl fluoride (COF<sub>2</sub>, toxicity limit 1 ppm), which are toxic to humans. The IDHL value (immediate danger for life and health) of HF in air is 30 ppm.

In addition to the above, HFOs are rather expensive. The current price for HFOs is somewhat higher than it is expected to be in large scale production, but even in large scale production HFOs are expected to be many times more expensive than the current HFCs.

The long-term future of unsaturated HFCs may therefore be questioned considering these potential risks. HFOs can certainly be an appropriate short-to mid-term alternative in some applications.

### R32 and HFC-HFO blends

R32 (HFC-32) should also be mentioned. It has been chosen by several AC system manufacturers as R407C or R410A replacement, in Asia in particular. R32 is non-toxic but is mildly flammable (ASHRAE/ISO safety classification A2L); however, its mixtures with air have much lower flame propagation velocities than hydrocarbon mixtures. R32 is therefore deemed as not as hazardous as hydrocarbons.

HFC-32 is used as a component of R410A, R407C, and other blends of the R407 series. Its GWP (675) is rather high but presents a significant reduction compared to R410A, HCFC-22, and R407C, which it can replace. Its pressure and volumetric capacity are 1.5 higher than that of HCFC-22 and 10% higher than that of R410A. It is also a component of new HFC-HFO blends with low or intermediate GWPs. These mixtures can especially be justified for retrofitting in cases where the lifespan of the installation is being extended. In the perspective of a phase-down instead of a phase-out of HFCs, it is also likely that both R32 and the aforementioned mixtures, whose range extends rapidly, will be part of possible short-to mid-term solutions.

These are basically all the options that are left as single component refrigerants. As McLinden *et al.* put it after analysing the 100 million compounds in the PubChem database, progressively narrowing down the list of fluids that might be suitable low-GWP refrigerants to 21 candidates as ever more restrictive criteria were applied: “There is not a “magic” fluid that

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<sup>6</sup> Annex II of the “F-gas” Regulation contains a long list of fluorinated substances including many HFOs such as R1234yf and R1234ze(E)

would be a simple drop-in replacement. [...] In other words, we have hit the limits of what chemistry allows.” The authors argue that their 21 candidates identified represent all the viable candidates for single-component, medium-and high-pressure refrigerants [McL2015]<sup>7</sup>.

## Possible options per applications

The second part of this Informatory Note focuses on individual applications and provides some suggestions on feasible technologies, already available in the context of the application of the EU regulations and the HFC phase-down. Various low-GWP refrigerant alternatives are described below.

### Commercial refrigeration

Commercial refrigeration can be divided into three main equipment categories: self-contained or plug-in units (similar to domestic refrigerators) with refrigeration capacities from a few hundred watts to almost 5 kW, condensing units with refrigeration capacities from a few kW to almost 100 kW, and large centralized supermarket refrigeration systems with refrigeration capacities up to 1,500 kW and HFC charges up to 3,000 kg.

#### **Stand-alone (plug-in) units**

Stand-alone units are built with the following low-GWP refrigerants: HC-600a, HC-290 and R744 (CO<sub>2</sub>).

The energy efficiency of hydrocarbon units is frequently claimed to be up to 30-40% better than that of a comparable HFC-unit [Jür2004, Ped2008, Mas2014]; 5 to 10% of this improvement can be accredited to the better thermodynamic and transfer properties of the hydrocarbons – the rest is most likely due to component modifications such as improved compressor or heat exchanger design as well as variable speed drive. An estimated 800,000 commercial HC-units had been manufactured until 2010 [Sch2011].

CO<sub>2</sub> units achieve slightly better energy efficiency than HFC-units under moderate and indoor climate [Sch2011]. Several thousand units with CO<sub>2</sub> have been produced mainly as bottle coolers.

Both options are technically feasible and commercial hydrocarbon plug-in units have been manufactured in several hundreds of thousands with refrigerant charges up to 150 g for most manufacturers. Some European brands commercialize equipment with hydrocarbon charge up to 1 kg and even 2.5 kg depending on national regulation [RTOC2010]. Lately units with water cooled condensers have been introduced on the market. Those units are hooked up to a common water or water/glycol loop for rejecting the heat of all the self-contained plug-in cabinets installed in the market.

#### **Condensing units**

Worldwide approximately 34 million condensing units are in use, mainly in small shops and for individual cold rooms [RTOC2010]. HFC alternatives for condensing units are also hydrocarbons and CO<sub>2</sub>. While hydrocarbons (mainly HC-290) are feasible in direct evaporation (DX) only in smaller systems due to safety concerns (1.5-25 kg HC charge maximum in non-public areas depending on the national regulations), CO<sub>2</sub> can be used universally. From a technical point of view, hydrocarbons could cover the entire range of condensing units and could achieve 5-10% lower energy consumption than HFC condensing units.

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<sup>7</sup> In addition to the fluids described in this Informatory Note, the list of McLinden *et al.* [McL2015] includes dimethylether (the refrigerant used by Jacob Perkins in his apparatus patented 1834) and fluorinated ethers as possible candidates – a series of fluids discussed earlier, e.g., ASHRAE’s 1989 CFC Technology Conference, Gaithersburg, MD.

Due to the flammability of the hydrocarbon refrigerants, special precautions such as leak detectors and ventilation have to be taken, resulting in up to 25% higher initial investment cost [Sch2011].

Due to safety considerations, if hydrocarbons are to be used in areas with public access, e.g., in a grocery store, secondary loop systems (also called indirect refrigeration systems) are needed for larger refrigeration capacities in many countries. Such indirect systems can operate efficiently in the medium temperature range while they tend to use more energy in the low temperature range when operating with liquid secondary refrigerant. Using CO<sub>2</sub> as an evaporating secondary refrigerant allows the use of hydrocarbon condensing units that are also energy efficient for low temperature applications. Special CO<sub>2</sub> pumps required for this are available worldwide.

CO<sub>2</sub> can also be used as the sole refrigerant. Such CO<sub>2</sub> condensing units are expected to operate with greater energy efficiency than HFC condensing units in cold and moderate climates, while they are expected to consume more energy in warm climates. All three options, i.e. direct expansion hydrocarbon, indirect systems as well as CO<sub>2</sub> vapour compression systems, are technically feasible and proven from a few installations for CO<sub>2</sub> to several hundred installations for small direct and indirect systems with hydrocarbons. Any of the alternative systems can achieve similar energy efficiency as the HFC systems.

### **Centralized systems**

Centralized systems are the preferred option in supermarkets, because they usually achieve better energy efficiency than plug-in cabinets and condensing units. They operate with racks of compressors installed in a machinery room, typically using HFC in direct expansion refrigeration systems. Because all cabinets/evaporators are connected to all compressors in one compound system, HFC charges are quite high – up to 3,000 kg for hypermarkets – with resulting high emissions in the case of component failure like pipe rupture due to excessive vibration. In addition, the thousands of joints of large systems are prone to constant leakage, hence such systems often have HFC leakage rates in the order of 10-15% [Sch2011].

For centralized supermarket refrigeration systems, at least seven or eight HFC-free alternatives exist [Rhi2009]. Alternative refrigerants used are ammonia, CO<sub>2</sub> and hydrocarbons – mainly propane (HC-290) and propylene (HC-1270). While CO<sub>2</sub> can be used inside the sales area, all other alternatives are confined to the machinery room or an outdoor installation due to toxicity (ammonia) or flammability (HC-290 and HC-1270) of the refrigerant.

With CO<sub>2</sub> as the only refrigerant in a remote DX-system, annual energy consumption in moderate climates is usually lower than that of an HFC-system [Fin2011, Saw2008]. The energy efficiency of standard CO<sub>2</sub> systems is better than that of comparable HFC systems at temperatures below 22°C, about equal at temperatures between 22°C and 26°C, and lower at higher ambient temperatures [Fin2011]. The technical feasibility is well proven with an estimated more than 4,000 such systems spread throughout Europe, another 1,000 in Asia + Australia, and more than 100 in Northern America [Masson2014]. Shifting from HFCs to CO<sub>2</sub> can reduce the carbon footprint of supermarkets by 25% [EPA2010]. With new developments like economized systems (two-stage expansion with recompression of the flash gas), mechanical subcooling unit, ejector systems and expansion machines, the efficiency of CO<sub>2</sub> systems may be improved in the future to the extent that such systems will be more energy efficient even in warmer climates [Huf2012 and Haf2015].

Ammonia and hydrocarbons require secondary loop (indirect) systems in areas with public access. Traditionally liquid (water-based) fluids have been used for both medium (MT) and low-temperature (LT) applications. Due to the high viscosity of water-based fluids in the LT-application, energy consumption is higher for indirect LT-systems than for comparable DX-systems. Therefore liquid secondary fluids are mainly applied in MT-applications where

they achieve similar energy efficiencies as HFC direct expansion systems at 10 to 30% higher cost [Sch2011]. The LT-loop of an indirect ammonia or hydrocarbon system is now usually built as a cascaded CO<sub>2</sub>-system achieving better energy efficiency than HFC-systems. All indirect systems as well as the CO<sub>2</sub> cascade solution are technically feasible, and well over several thousand such supermarket systems can be found all over the world, with concentrations in Canada, Germany, Luxemburg, Scandinavia and Switzerland [for cascade systems: Masson2014]. Indirect systems are also gaining significant market share in the USA [EPA2010].

Distributed systems, whereby the compressors are installed close to the display cases either inside or very close to the sales area (rather than in a separate machine room), are also popular in the USA and were promoted at the 2014 Euroshop fair in Düsseldorf, Germany by several manufacturers. If installed inside the sales area, compressors are housed in sound-proof boxes, and condensers are cooled by a water loop. These systems can significantly reduce refrigerant charge and, provided the necessary safety precautions are taken, can also use hydrocarbon refrigerants. Distributed systems (with HFC refrigerant) account for 40% of new installations in the USA [EPA2010]. As well as reducing refrigerant charge, the close proximity of the compressors to the cases and coolers allows these systems to use considerably less piping than traditional direct-expansion systems resulting in reduced suction line pressure loss.

### Industrial refrigeration

Industrial refrigeration systems are characterized by heat extraction rates in the range 10 kW to 10 MW, typically at evaporating temperatures from -50°C to +20°C. About 75% of all industrial refrigeration capacity is installed in the food industry, the rest in industrial processes and leisure applications [Sch2011]. Over 90% of the large industrial refrigeration installations use ammonia (R717) whereas the market share of ammonia is only 5% (India and China) to 25% (Europe and Russia) for smaller industrial refrigeration systems [RTOC2010]. Industrial ammonia systems are in general 15% more energy efficient than their HFC-counterparts, and 40% of the European industrial refrigeration systems use ammonia [Sch2011].

Hydrocarbons are not widely used, other than in situations where safety measures are already required, e.g. in a petrochemical plant. "They offer excellent efficiency, and compatibility with most materials and lubricants. However the precautions required to prevent ignition are significantly more expensive than those required for ammonia systems." [RTOC2010]

CO<sub>2</sub> is used with excellent efficiency in systems as the low-temperature stage to a cascaded upper ammonia system especially in the food industry where the refrigerant has to evaporate in freezing equipment in the factory. In colder climates CO<sub>2</sub> is as energy efficient as the sole refrigerant.

Air can be used with good energy efficiency in low-temperature applications, namely below 50°C. At least one manufacturer is offering such systems and claims energy efficiency improvements over R22 by 20% at -50°C and 33% at -60°C [Mac2011].

### Transport refrigeration

Natural refrigerants have been commercialized to a small extent aboard marine vessels worldwide (ammonia, CO<sub>2</sub>) [RTOC2010]. For European fishing vessels highly efficient ammonia-CO<sub>2</sub> cascade systems are the systems of choice, using approximately 6% less energy [Sch2011].

Initial field tests with small fleets of containers using CO<sub>2</sub> have started. In the future hydrocarbons may also be a technically feasible option for reefer containers.

CO<sub>2</sub> is offered with two-stage compression for intermodal reefer containers by one manufacturer [RTOC2014]. The units achieve comparable energy efficiency as HFC-systems in cold and moderate climates [RTOC2014]. Current and previous tests with containers and trucks using CO<sub>2</sub> suggest that larger scale introduction of CO<sub>2</sub> will take place when more efficient compressors with more than one compression stage (under development) become commercially available [RTOC2014].

The use of HC-290 in truck refrigeration units has been tested with a small number of vehicles both in the UK and Germany. Safety concerns have until now prevented a wider application, even though many trucks are equipped with an auxiliary heating system running on hydrocarbons, making the fear of hydrocarbon refrigerants somewhat difficult to understand. A new refrigerated truck with propylene (HC-1270) was developed by a German company and is now in field tests for a supermarket chain in Germany. The refrigeration unit uses an innovative inverter technology and is very energy efficient [Bur2011]. It was awarded the German Refrigeration Award in 2011. For a broader market introduction, manufacturers and customers still see a need for specific legal rules and standards for hydrocarbons in mobile applications. From an energetic point of view hydrocarbons are the preferred choice as they can result in lower energy consumption than R404A units [Bur2011]. Calculations show energy efficiency potentials for hydrocarbons [Bur2011, Vieth2012].

Cryogenic or open loop systems which evaporate the liquid CO<sub>2</sub> or nitrogen (N<sub>2</sub>) charged to an insulated container aboard the truck are a low maintenance alternative to the standard vapor compression cycle. Besides the possibility of high local CO<sub>2</sub> or N<sub>2</sub> concentrations with the associated risk of asphyxiation, the technology as a whole needs more energy as the liquefaction of the cryogenic liquid takes place at much lower temperatures than the normal evaporation temperature of a vapor compression system. Furthermore, the systems need frequent refilling, consequently the user needs to provide storage and refilling infrastructure for the liquefied gases. Thus, open loop systems are usually only used for local distribution.

### Air Conditioning

Air-conditioning systems can be divided into stationary and mobile air-conditioning systems for vehicles. Stationary systems can again be divided into unitary systems designed for air conditioning of single rooms (single split and moveable systems), multi-split systems servicing several rooms or entire buildings (often equipped with VRF technology – variable refrigerant flow) and central air-conditioning systems with distribution of cold by air (central air handling units or ducted systems) or water (chillers). The refrigeration capacity varies depending on the number of rooms to be air conditioned and ranges from less than 1 kW for unitary systems to several MW for large central systems (chillers).

#### **Stationary Air Conditioning**

Air conditioners for cooling and heating ranging in size from 2.0 kW to 420 kW (the majority less than 35 kW) comprise a significant segment of the air-conditioning market [RTOC2010]. Most air-conditioning systems in the EU use HFC refrigerants with charges from a few hundred grams (factory sealed moveable units), to a few kg for split units, to several tonnes for large central chillers. Leakage rates range from 1% for new chillers over 2.5% for small factory sealed units to approximately 8% for multi-split units. Due to an ever increasing demand for air-conditioned spaces – triggered by the large proportion of air-conditioned cars – the European HFC demand in the stationary air-conditioning market is expected to grow significantly. It has to be noted though that the fastest growing refrigeration and air-conditioning market is in emerging countries like China, India, Malaysia and the like.

“Hydrocarbons are a perfect alternative in many air conditioning and heat pumps systems. It seems that the number of producers using hydrocarbons as refrigerants has decreased during the last few years. One important reason for this seems to be the limited supply of compressors, which is at least partly a result of the new Pressure Equipment Directive. Another significant factor is the increasingly strict requirements that are specified within European and International safety standards that make it difficult to design systems with a competitive market price.” [Pal2008]

### ***Factory Sealed Units including Moveable Units***

Factory-sealed units are self-contained systems and single-split systems with flexible refrigerant hoses with cooling capacities of one to 10 kW. Most of them operate with HFC as refrigerant at charges of 0.3-3 kg [Sch2011]. HC-290 is used in several small moveable units with 5-10% higher energy efficiencies as comparable HFC-units. The cooling capacity of those units ranges from 500 to 3,200 W and the refrigerant charge is 100-500 g [Pal2008].

### ***Split Air Conditioners***

Hydrocarbons are being used with existing safety standards, especially for wall and ceiling mounted single-split units with up to approximately 7 kW cooling capacity especially in China and India [Sch2011]. Actual production costs are 0.5 to 1.5% lower than for comparable HFC products. If initial investment cost for production line regarding safety and training of production and service staff is considered, i.e. approximately 0.5% higher cost per produced unit, the total price of HC units is approximately the same cost per unit at the end. A replacement of about 50% to 65% of all HFC refrigerant mass is considered technically feasible in Europe given current safety regulations [Sch2011]. The flammability risk associated with larger refrigerant charges prohibits the use of hydrocarbons in larger systems in occupied spaces under current safety regulations. Although technically feasible and not more expensive [Sch2011], these restrictions currently hinder the wider use of hydrocarbon refrigerants in air-conditioning systems.

For larger multi-split units, current safety regulations hinder the application of hydrocarbon refrigerants in occupied spaces due to the larger refrigerant content in multi-split systems. CO<sub>2</sub> might be an alternative for larger split systems and should result in similar energy efficiencies at least for moderate climates, taken the experience with commercial refrigeration systems into account.

### ***Ducted Systems***

Ducted air-conditioning systems cover several categories including rooftop-ducted systems, central ducted systems and close-control systems. In the EU, those systems typically use HFC refrigerants with charges of 5 to 150 kg. The same technical options described for multi-split systems apply to ducted systems, although due to the larger refrigerant charges, hydrocarbons will mostly be limited to indirect applications.

### ***Chillers***

Chillers cool water, which is pumped throughout a building in order to provide cooling in multiple rooms. Chillers can be divided according to the compressor used, i.e., positive displacement compressors (reciprocating piston or screw) and centrifugal compressors. In the EU most of them use HFCs with charges from 5 to 10,000 kg, although there are chillers in the EU using ammonia, hydrocarbons and water. In many other countries CFCs and HCFCs are still used in chillers.

Any alternative low-GWP refrigerants are technically feasible as the distribution in the building is via water loops. Ammonia and hydrocarbon chillers are already on the market, with increased energy efficiency of about 10% in small hydrocarbon chillers to 20% for small ammonia chillers. CO<sub>2</sub> is expected to have the same energy efficiency in moderate

and 10% lower energy efficiency in warm climates. For large centrifugal chillers, water as refrigerant is an environmentally benign solution, with 5-10% better energy efficiency [Mad2011]. Recently, global companies are offering HFO chillers using R1234ze or R1233zd as refrigerant with slightly better COPs than R134a.

### Heat Pumps (heating only)

Heating only heat pumps are used for heating spaces and/or drinking water. Ground water, soil and outdoor air are the most common heat sources of these heating devices. Typical coefficients of performance of such systems are around four, meaning that they produce four times more heating than the electricity used to drive the compressor. Depending on the energy mix of a country, i.e., the CO<sub>2</sub> emissions associated with the electricity production, heating with a heat pump system can substantially reduce CO<sub>2</sub> emissions compared to heating with fossil fuels. Approximately 98% of European heat pumps today use HFCs as a refrigerant in charges of 1.5-15 kg for achieving 5 to 50 kW heating [Sch2011].

Most heating-only heat pumps heat tap water or water which then heats the space via a hydronic heating system. For these systems hydrocarbons are a technically feasible option with excellent energy efficiency. Heat pumps with HC-290 or HC-1270 were used in the 1990s and 2000s when CFCs were banned. However, the majority of production was stopped due to the introduction of the Pressure Equipment Directive (PED), which imposed additional certification of the compressors used with HCs, imposing an additional cost on manufacturers. As a result, the use of HFC blends- R407C, R404A and R410A- took over [Sch2011]. Today heat pumps with hydrocarbons (HC-290, HC-600a) are available for capacities <20 kW from at least 18 European manufacturers [Pal2008]. Unit prices are expected to be 5% higher due to safety requirements [Sch2011].

CO<sub>2</sub> heat pumps are marketed especially in Japan. The thermodynamic characteristics of CO<sub>2</sub>, with its uniform heat capacity<sup>8</sup> during gas cooling in the transcritical process (see section "Carbon dioxide") resulting in a good temperature glide match to the water to be heated, make it the ideal refrigerant and cycle for water-heating heat pumps for high water temperature demands. In these cases, CO<sub>2</sub> emissions are cut by about 50% compared with conventional combustion type water heaters [FEPC2011]. Over 2 million "eco cute" heat pumps had been sold by the end of October 2009 [Mor2009] – also supported by noticeable subsidies by the power companies and the Japanese government who wanted to replace electric resistant heaters in order to lower the load on the power grid.

## Conclusions

It is technically and economically feasible to build and operate refrigeration systems with a reduced impact on the climate. This can be done in several ways as described above. Which way is selected depends on personal preferences, local regulations and safety standards, the availability of components and skills as well as on the willingness to maybe pay a slightly higher system price to begin with. In many cases, the higher investment can be recovered by lower operating and/or maintenance costs of improved systems.

Energy efficiency of such alternative refrigeration systems can be at least as good as the state-of-the art HFC technology. In countries with a history of progressive environmental laws, e.g. Denmark and Sweden, many HFC-free or HFC-reduced systems have already been built and operated with good energy efficiency.

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<sup>8</sup> Except for a sharp peak near the critical point as is the case for most substances.

## Disclaimer

Since the performance of various types of systems is dependent on a large number of design and operation parameters, it is not possible to generalize the relative performance of different refrigerants in an exact way. All figures in this Informatory Note are thus indicative, but the authors believe they give a balanced view on the situation.

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## Recommendations

- Introducing low-GWP refrigerants, especially natural refrigerants, in the various refrigeration and air-conditioning systems should be done to the greatest possible extent. The effort to further advance low-GWP technologies should increase.
  - Natural refrigerants are already used in many applications and offer good energy efficiency and reliable safety. They should be promoted in order to limit the climate change impact of refrigerant emissions.
  - Barriers still hinder implementation of low-GWP solutions in some applications where technologies must be improved in order to offer adequate equipment at reasonable prices, especially in warm climates.
  - Standards and safety regulations should be adapted to low-GWP technologies. The adoption of new international standards and national regulations is needed especially regarding the safe use of flammable refrigerants.
  - Participation in the definition of standards by developing countries in hot regions should be improved.
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