Recommendations to safety guidelines and standards for the use of natural refrigerants

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German Environment Agency

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Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety







Abstract

Ozone-depleting substances (ODS) have been used worldwide in a wide range of industrial and consumer applications. Their regulation under the Montreal Protocol has led to an uptake of alternatives, especially in refrigeration and air conditioning, as well as firefighting applications. Hydrofluorocarbons (HFCs) and other fluorinated greenhouse gases – commonly referred to as F-gases – are among the most prominent ODS alternatives. These gases have no measurable effect on the ozone layer and have found widespread application. However, their high global warming potential (GWP) means that they are contributing to climate change and are subject to the Kyoto Protocol under the United Nations Framework Convention on Climate Change (UNFCCC). Due to the requirements of Regulation (EU) No. 517/2014 the uptake of alternative refrigerants with almost no GWP is required. These socalled natural refrigerants, such as hydrocarbons, carbon dioxide and ammonia, are flammable (hydrocarbons, ammonia), toxic (ammonia) or require higher working pressures (carbon dioxide).

This guidance document gives an introduction to the issues regarding the safe handling of natural refrigerants. This includes an overview of existing standards and regulations, as well as relevant properties of alternative refrigerants and necessary safety measures.

The document concludes with three examples of alternative refrigerants applied in practice.

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List of Abbreviations

ATEL	Acute toxicity exposure limit
ATEX	ATmosphères EXplosibles
CEN	European Committee for Standardization
CENLEC	European Committee for Electrotechnical Standardization
CFC	Chlorofluorocarbon
CO ₂	Carbon dioxide: As refrigerant also called R744
CO ₂ eq	Carbon dioxide equivalent
СОР	Coefficient of performance
EPDM	Ethylene propylene diene monomer
ETSI	European Telecommunications Standards Institute
EU	European Union
F-gas	Fluorinated greenhouse gas
GHG	Greenhouse gas
GIZ	Deutsche Gesellschaft für Internationale Zusammenarbeit GmbH (German Association for International Cooperation)
GWP	Global warming potential
НС	Hydrocarbon
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
HFO	Hydrofluoroolefin
IEC	International Electrotechnical Commission
LFL	Lower flammability level
LVD	Low Voltage Directive
MSD	Machinery Safety Directive
NH3	Ammonia (anhydrous): As refrigerant also called R717
ODL	Oxygen deprivation level
ODP	Ozone-depleting potential
ODS	Ozone-depleting substance
OFDN	Oxygen free, dry nitrogen
PFC	Perfluorocarbon
рН	potentia Hydrogenii
PL	Practical concentration limit
PPE	Personal protection equipment
PS	Maximum allowable pressure for components in a refrigerating system

RAC	Refrigeration and air conditioning
TCD	Thermal conductivity detector
UBA	Umweltbundesamt (German Environment Agency)
UNFCCC	United Nations Framework Convention on Climate Change

1 Introduction

The term "natural" in natural refrigerants points towards the origin of the fluids, i.e. nature, where they occur as a result of geological and/or biological processes. These naturally occurring working fluids are typically environmentally friendly as opposed to synthetic refrigerants. Due to their availability, natural substances, ammonia (NH₃), carbon dioxide (CO₂) and hydrocarbons (HC) being among the first, were used as refrigerants at the advent of vapour-compression refrigeration in the second half of the 19th century. Extensive experience has been gained and knowledge has been accumulated since then. However, natural refrigerants require careful handling.

Safety concerns, originating from high working pressures, flammability or toxicity, led to the development of synthetic solutions in the early 1930s (mainly CFCs). These were considered to be safe and easy-to-handle refrigerants and have been rapidly favoured for various applications. The synthetic refrigerants, however, consist of the halogens fluorine and chlorine, which have a high global warming potential (GWP) and deplete the ozone layer.

Rather recently introduced refrigerants with lower GWP, such as R32, hydrofluoroolefins (HFOs) and blends thereof, are often treated as alternatives to presently used hydrofluorocarbons (HFCs). Those gases are flammable and partly decompose to highly toxic substances. There is an ongoing debate whether those gases are sustainable alternatives to HFCs. Safety concerns arising from flammability are also valid for those gases, even though measures are being taken to establish separate guidelines for these alternatives, as they belong to a newly introduced group of "mildly flammable" gases. These gases are not further discussed in this paper.

In the European Union (EU), cooling technologies based on natural refrigerants with negligible or insignificant effect on the environment and climate have experienced a renaissance in recent years, showing a robust development and wide-spread usage in diverse application sectors. In fact, efforts to counteract the progressing greenhouse effect have put natural refrigerants increasingly back into the centre of attention. A variety of highly efficient applications has been developed, and has now reached a technical level that makes their use economically viable. Replacement of current applications based on synthetic working fluids with alternatives based on natural refrigerants will also help resolve the issue of greenhouse gas (GHG) emissions through synthetic refrigerant leakage from the numerous installations and appliances that exist.

The new F-gas Regulation (EU) No.517/2014¹ of the EU and its scheduled HFC phase-down will further promote technologies of this kind. The regulation anticipates a global phase-down of the consumption and production of HFCs. With this new regulation, the EU strengthens its efforts of reducing emissions of fluorinated greenhouse gases (F-gases). The most important instrument of the new EU F-gas regulation is limiting the total amount of F-gases within the EU. Table 1 shows the phasedown schedule. The reduction steps refer to the amount of CO₂ eq (metric tonnes weighted according to GWP) available in 2015.

¹ REGULATION (EU) No 517/2014 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 April 2014 on fluorinated greenhouse gases and repealing Regulation (EC) No 842/2006

Years	Reduction
2015	100 %
2016-2017	93 %
2018-2020	63 %
2021-2023	45 %
2012-2026	31 %
2027-2029	24 %
2030	21 %

 Table 1:
 Phase-down schedule of the new F-gas Regulation (EU) No. 517/2014

Source: Regulation (EU) No. 517/2014, Annex V

As availability of HFC refrigerants will decrease, transition to sustainable low-GWP alternatives, such as natural refrigerants, will increase. Because of safety concerns regarding the use of natural refrigerants, it is essential to provide easily accessible information to show that natural refrigerants can be handled safely and used sustainably. Training provisions on alternatives are also included in the Fgas regulation. The content and availability of such trainings are the subject of a presently ongoing Fgas consultation forum², whose briefing paper stated that training materials are generally available, via the "REAL Skills" platform for example³, but very few technicians are trained⁴.

This guidance document is meant to provide a short overview on the subject, covering major technical and practical aspects in association with the safe use and handling of natural refrigerants and respective equipment. The three main types of natural refrigerants are covered:

- 1. CO₂ (R744)
- 2. HCs, e.g. propane (R290)
- 3. NH₃ (R717).

Other alternatives with lower GWP currently being considered, i.e. R32 as well as HFOs and their blends, are not in the focus of this guidance document.

 $^{^{2}\,}http://ec.europa.eu/clima/events/articles/0106_en.htm$

³ http://www.realskillseurope.eu/

⁴ Ricardo-AEA and Gluckman Consulting (2015b)

2 Relevant safety standards and legislation in the EU

A standard is a document that establishes important requirements for a specific system, product or process. Standards aim to reduce costs, increase performance and improve safety. Standards are developed through a process of sharing knowledge and building consensus among technical experts. They are usually voluntary. However, additional laws and regulations may refer to standards and therefore make compliance with them compulsory.

Directives and regulations are legislative acts of the EU which, in respect to the acquis communautaire, must be legally implemented by the individual member states. Standards which are, by request of the European Commission, formulated in alignment with a given directive are referred to as harmonised standards and are published in the Official Journal of the European Union.

Harmonised standards are voluntary, yet still very useful, as they provide a presumption of conformity to the relevant legislative acts. Manufacturers tend to follow harmonised standards in order to demonstrate the quality of their products and to meet the requirements of the associated directives. On the other hand, non-harmonised standards do not provide a specific interpretation of corresponding directives. In order to achieve conformity, manufacturers have to demonstrate conformity with legislation independent from a standard.

Table 2 illustrates the key EU legislation relevant to safety aspects regarding refrigeration and air conditioning (RAC) equipment and indicates the relationship to standards they are harmonised with. Because all of the quoted EU legislation are directives, they need to be implemented by the member states into their national legislation.

Legislation	Year	Title	Scope	Relevant harmonised standards*
Directive 94/9/EC⁵ Directive	2014	ATEX 'Equipment' Directive: equipment and protective systems intended for use in potentially explosive atmos- pheres Recast to react on Regulation	 equipment (both electrical and mechanical) being used in poten- tially explosive atmospheres defines product categories and characteristics products must meet in order to be installed in potentially explosive atmos- pheres dedicated to manufacturers and distributors 	EN 1127-1 EN 13463-1, -5, -6 EN 14797 EN 14986 EN 15198 EN 15233 EN 60079-0, -15, -20-1
2014/34/EU ⁶	2014	(EU) No. 765/2008, entering into force Apr 20, 2016		
Directive 97/23/EC ⁷	1997	Pressure Equipment Directive (PED)	 pressure equipment and assemblies with internal pressure higher than 0.5 bar harmonisation of national law regarding design, manufacture and conformity assessment of pressure equipment more restrictive in regard with flammable refrigerants 	EN 378-2 EN ISO 4126 EN 12178 EN 12263 EN 12284 EN 13136 EN 14276-1, -2

Table 2:EU legislation relevant for safety aspects of natural refrigerants and their applica-
tion

⁵ DIRECTIVE 94/9/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 26 February 2014 on the harmonisation of the laws of the Member States relating to equipment and protective systems intended for use in potentially explosive atmospheres

⁶ DIRECTIVE 2014/34/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 26 February 2014 on the harmonisation of the laws of the Member States relating to equipment and protective systems intended for use in potentially explosive atmospheres (recast)

⁷ DIRECTIVE 97/23/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 29 May 1997 on the approximation of the laws of the Member States concerning pressure equipment

Legislation	Year	Title	Scope	Relevant harmonised standards*
Directive 1999/34/EC ⁸	1999	Product Liability Directive	- liability of defective products	
Directive 1999/92/EC°	1999	ATEX 'Workplace' Directive: occupational health and safety in potentially explo- sive atmospheres	 protection for workers in poten- tially explosive atmospheres classification of working areas where explosive atmospheres ex- ist into zones dedicated to machine owners 	
Directive 2006/95/EC ¹⁰	2006	Low Voltage Directive (LVD)	- applying to any 'electrical equipment' designed for use with a voltage rating of between 50 and 1,000 V for A/C and between 75 and 1,500 V for D/C	EN 60204 EN 60335-1, -2-24, -2-34, -2-40
Directive 2006/42/EC ¹¹	2006	Machinery Safety Directive (MSD)	 machinery and similar equip- ment, safety components risk reduction through integra- tion of safety into design, pro- duction, maintenance, disman- tling etc. of machines 	EN 378-2 EN 1012 EN 1127-2 EN 60204-1 EN 60335-1,-2-40

Source: http://www.newapproach.org/Directives/DirectiveList.asp

A variety of standards address technical aspects of RAC equipment. Some also include environmental requirements (e.g. EN 378). The growing use of technologies associated with natural refrigerants has continuously led to the development of related standards in recent years. Most standards are independent from the refrigerant, yet some define rules regarding specific refrigerants, such as flammable HCs. Annex I provides a list of relevant standards associated to the safety of RAC equipment and the immediate surroundings; industry guidelines and codes of practice may provide helpful additional information.

When it comes to safety, standards may include the following:

- Safety classification of refrigerants (flammability, toxicity);
- Occupancy types, refrigerant charge size limits and room sizes;
- Safe design and
 - Testing of components and pipes (e.g. pressures),
 - Testing of assemblies (systems);
- Electrical safety, ignition sources;
- Installation areas, positioning, pipework, mechanical ventilation, gas detection;
- Instructions, manuals, name plates;
- Servicing, maintenance and refrigeration handling practices.

The most relevant of these aspects are highlighted in detail in the following sections.

⁸ DIRECTIVE 1999/34/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 10 May 1999 amending Council Directive 85/374/EEC on the approximation of the laws, regulations and administrative provisions of the Member States concerning liability for defective products

⁹ DIRECTIVE 1999/92/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 1999 on minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres (15th individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC)

¹⁰ DIRECTIVE 2006/95/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 December 2006 on the harmonisation of the laws of Member States relating to electrical equipment designed for use within certain voltage limits

¹¹ DIRECTIVE 2006/42/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 17 May 2006 on machinery, and amending Directive 95/16/EC (recast)

A briefing paper of the F-gas consolation forum¹² provided an analysis whether legislation and standards are barriers to the uptake of natural refrigerants. It stated that NH₃ and CO₂ do not face significant additional hurdles, whereas there are barriers to using flammable refrigerants. Strict charge size limitations and outright bans in some EU member states obstruct a broader approach to safety measures.

3 Technical guidelines for the safe use and handling of natural refrigerants

3.1 Refrigerant choice and application

The choice of a suitable refrigerant is made up of several factors. The ideal refrigerant should possess the following properties:

- ► No ODP;
- Low or no GWP;
- High volumetric cooling capacity;
- Chemical stability at all temperatures and environments;
- Compatibility with other materials which are used in the system (metals, elastomers);
- Solubility with lubricants;
- Low or no toxicity;
- Low or no flammability;
- Commercial availability;
- Low cost (per kg or per system charge).

Unfortunately, there is no refrigerant today which combines all of the above properties. As different refrigerants possess different properties, the suitability of a refrigerant varies depending on the application.

The natural refrigerants CO₂, HCs and NH₃ are cheap, widely available, and possess many of the qualities listed above. Table 3 indicates a variety of sectors and applications in which they are (or can be) used.

Refrigerant	Sectors of application
CO ₂ (R744)	Commercial and industrial refrigeration, chillers, heat pumps, transport refrigeration, marine refrigeration, vehicle air conditioning, integrals
Propane (R290)	Commercial and industrial refrigeration, chillers, heat pumps, split air conditioners (non-ducted), integrals
lso-butane (R600a)	Domestic refrigerators, small commercial refrigeration systems, heat pumps
Propylene (R1270)	Chillers, heat pumps, integrals
NH₃ (R717)	Industrial and large commercial refrigeration, chillers, industrial heat pumps

Table 3:	Natural refrigerants and sectors of application
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¹² Ricardo-AEA and Gluckman Consulting (2015a)

But natural refrigerants also pose additional risks from flammability, toxicity and high pressures. Table 4 provides an overview, which properties require special attention to ensure safe use.

	Inhalation	Flammability	Operating Pressure
CO ₂ (R744)	non-toxic (asphyxiant, ac- cumulates and re-places air when not vented properly)	non-flammable gas	very high pressure
HCs (R290, R600a, R1270)	non-toxic (asphyxiant, ac- cumulates and re-places air when not vented properly)	extremely flammable gas	lower to similar pres- sure compared to R404A
NH₃(R717)	toxic if inhaled	flammable gas	lower pressure com- pared to R404A

Table 4: Alternatives to F-gases and their properties

CO₂ (R744) has been in use as a refrigerant since the mid-19th century. Its usage was gradually reduced with the introduction of synthetic refrigerants in the 1930s. CO2 is a non-flammable and nontoxic, widely available and inexpensive refrigerant. Compared to HFCs, CO₂ has better heat transfer properties and a negligible GWP. It is compatible with conventional piping materials and lubricants. Because of its high volumetric cooling capacity – 5 to 8 times that of HFCs – a reduction of 50 % may be achieved in respect to the refrigerant charge. Required compressor displacement and pipe sizes are therefore reduced. Due to the high working pressure at which CO₂ is condensed and evaporated, CO₂ has a weaker performance in high ambient temperature conditions. However, the difficulty of addressing the high ambient temperature aspect safely is not as difficult as generally assumed. Due to its low critical temperature of only 31.1 °C, CO₂ refrigeration cycles often operate in the trans-critical state. The physical properties below and above this level differ from each other. Operation below this level refers to CO₂ being in the sub-critical state and being in a trans-critical state above this level. In conventional refrigeration systems, the trans-critical state is less energy-efficient and is reached in the summer months especially in southern Europe. Several technical innovations are worked on to improve the energy efficiency in warmer climates. The so-called "CO₂ equator" where CO₂ systems achieve a comparable energy efficiency to other refrigeration systems is constantly being pushed further south. The refrigerant experiences four cyclic modes of alteration in a refrigeration circuit running in sub-critical state: evaporation, compression, condensation and expansion. Under trans-critical conditions, the CO₂ does not condense as operation is above the critical temperature, instead a gas-cooling without phase change takes place. Systems with CO₂ in trans-critical state require much higher pressure specifications.

Ongoing research aims to improve the energy efficiency of CO₂ refrigeration systems operating in trans-critical state. One of these newly developed measures is the ejector, which is introduced to reduce the pressure after the gas-cooler. The ejector and a following flash tank are inserted between gas-cooler and evaporator. The ejector is using the potential energy of the high pressure stream coming from the gas cooler to pressurize the streaming CO₂ coming from the evaporator.

The ejector could be divided into 3 sections:

- 1. The high pressure CO₂ energy will be converted by a laval nozzle into low pressure but high flow velocity.
- 2. This low pressure allows to suck vapour from the evaporators and accelerate with the high pressure stream.
- 3. The accelerated mixture with high velocity will be converted in a reverse nozzle back into low velocity and higher pressure than suction inlet.

The flash tank separates the gas from the liquid phase and the liquid phase is sent to the evaporator. The gas phase from the flash tank, pre-compressed by the ejector, allows the use of smaller compressors running in a more efficient envelop. The ejector, working like a turbo-charger, does not rely on electrical power. Figure 1 shows refrigeration cycles working in sub- and trans-critical conditions (winter/summer), also in combination with Carrier's ejector technology which compensates for efficiency losses under high ambient temperature conditions. The price for an installation equipped with an ejector is about 15 % higher. If the life-cycle is considered, the investment costs are amortised by the lower operation costs.

Figure 1: Refrigeration cycle with and without ejector technology: (A) Basic principle of hot summer day operation in trans-critical mode, without ejector (B) Basic principle of winter operation in sub-critical mode, without ejector (C) Basic principle on hot summer day operation in trans-critical mode, with ejector¹³



HCs (R290 (propane), R600a (iso-butane), R1270 (propylene), etc.) have been among the first refrigerants to be used. They are non-toxic but highly flammable. Because of their flammability their use was decreased in favour of CFCs and HCFCs. Today, the risk of higher flammability is compensated by refrigerant charge limits. HC refrigerant charges are significantly lower in comparison to CFCs, HCFCs etc. HCs offer high efficiency, even in high ambient temperatures, and are compatible with most compressor lubricants and materials used in conventional refrigerating systems.

NH₃ (**R717**) was commercially used for cooling in the second half of the 19th century and has been in use ever since. Owing to the excellent thermodynamic qualities and high energy efficiencies, it provides a viable alternative to synthetic refrigerants. Its application is concentrated on large installations with high charge sizes. NH₃ has a low flammability but a high level of toxicity. Usually, an NH₃ system is located far from occupied places, because of its high toxicity. Incidents where leakage of NH₃ occurs are rare. NH₃ leakages are easily noticed due to its pungent smell. The adequate and safe handling of the refrigerant requires competent and trained personnel. Particular care has to be taken of NH₃ in combination with water, as it becomes corrosive to copper and other non-ferrous metals. Usually the pipework etc. in an NH₃ system is made of (stainless) steel.

The use of natural refrigerants in general comes with additional safety requirements in comparison to HCFCs and HFCs. Safety concerns and risks, such as flammability, toxicity and pressures, lead to various implications regarding the system design, the choice of components and the placement of the units. Nevertheless, with proper design and responsible maintenance, natural refrigerants are a sustainable alternative for most cooling applications.

3.2 Refrigerant properties and their implication for safe use

In the following, refrigerant properties that have implications on safe handling are discussed in detail. Important physical properties and safety-related characteristics of the essential natural alternatives and a number of synthetic refrigerants most commonly in use are provided in Table 5. Where appropriate relevant standards are cited. However, following a standard is only one way of achieving conformity with applying laws. Alternatively, safety could be documented by a risk analysis. In any case, it is the duty of the manufacturer or importer to demonstrate product safety.

¹³ Carrier Corporation (2015)

	HCFC	HFC				Natural refrigera	nt			
Refrigerant ^a	R22	R134A	R407C	R404A	R410A	R744 (CO ₂)	R290 (pro- pane)	R600a (iso-bu- tane)	R1270 (pro- pylene)	R717 (NH3)
Chemical formula/ composition	CHCIF ₂	CH ₂ FCF ₃	R-32/125/134a (23/25/52)	R-125/143a/134a (44/52/4)	R-32/125 (50/50)	CO2	CH ₃ CH ₂ CH ₃	CH(CH₃)₃	CH ₃ CH=CH ₂	NH₃
Molecular weight (g/mol)	124.0	102.0	86.2	97.6	72.6	44.0	44.1	58.1	42.1	17.0
Heavier than air?	Heavier	Heavier	Heavier	Heavier	Heavier	Heavier	Heavier	Heavier	Heavier	Lighter
Safety classification ^b	A1	A1	A1	A1	A1	A3	A3	A3	A3	B2(L ^c)
Flammability	-	-	-	-	-	-	High	High	High	Low
Temperature class (ATEX) ^d	-	-	-	-	-	-	T1	T1	T1	T1
Explosion group ^e	-	-	-	-	-	-	IIA	IIA	IIA	IIA
PED fluid group ^f	2	2	2	2	2	2	1	1	1	1
PL (kg/m³) ^g	0.30	0.25	0.31	0.48	0.44	0.1	0.008	0.0086	0.008	0.00035
ATEL/ODL (kg/m³) ^h	0.30	0.25	0.31	0.48	0.44	0.036	0.09	0.06	0.0010	0.00035
LFL (kg/m³) ⁱ	-	-	-	-	-	-	0.038	0.043	0.040	0.104
LFL/UFL ^h (Vol%)	-	-	-	-	-	-	1.7/ 10.8	1.5/ 9.4	1.8/ 11.2	15.4/ 33.6
Auto-ignition tempera- ture (°C)	635	743	704	728	-	-	450	460	455	630
Normal boiling point (°C)	-40.8	-26.2	-43.8 to -36.7	-46.5 to -45.7	-51.6 to - 51.5	-78.5°C	-42.1°C	-11.7	-47.7°C	-33.4°C
Critical temperature (°C)	96.1°C	101.1°C	86.0°C	72.0°C	71.4°C	31.0°C	96.8°C	135.0°C	92.4°C	132.4°C
Critical pressure (bar)	49.8	41.7	46.2	35.7	49.5	73.8	42.6	36.5	46.6	112.8

Table 5: General properties relevant to safety characteristics regarding common synthetic and natural refrigerants

Sources: http://gestis.itrust.de/, EN 378-1

^a R-22 is the only refrigerant with an ODP

^b According to ISO 817 and EN 378-1: Refrigerant safety classification

^c proposed in prEN 378-1:2013

 $^{\rm d}$ ATEX temperature class T1 – Ignition temperature of the flammable substance > 450 $^{\rm o}{\rm C}$

^e ATEX explosion group-classification for use of electrical equipment

^f Group 1: flammable to explosive, oxidising to very toxic substances; Group 2: other

^g Practical Concentration Limit- highest concentration limit in an occupied space which will not exhibit any negative effect

^h Acute Toxicity Exposure Limit/Oxygen Deprivation Limit

¹ Lower Flammability Limit – The lower concentration limit of a flammable substance for which air/vapour mixtures can ignite

¹ Upper Flammability limit – Concentration limit of a flammable substance above which there is insufficient oxygen for combustion

3.2.1 Practical limit

The practical limit (PL) is defined as a threshold value for an acceptable concentration of a refrigerant in an occupied space below which no 'escape impairing effects' are to be expected. It is also used for the estimation of a maximum allowable refrigerant charge. For refrigerants with higher flammability, i.e. HCs, the PL is set as 20 % of the lower flammability limit (LFL). ¹⁴ Consequently, the allowed quantity of HC refrigerant tends to be much lower than for most other refrigerants. For other refrigerants, the PL mostly refers to Acute Toxicity Exposure Limit/Oxygen Deprivation Limit (ATEL/ODL) values.

3.2.2 Flammability

Flammable substances are capable of developing an exothermic oxidation reaction, i.e. a fire. For a fire, three components are needed: fuel at the right concentration, sufficient oxygen supply and a source of ignition, e.g. a spark from an electrical component. In order to render these conditions flammable, they must exist in the same position in space and time and the potential source of ignition must be engaged. Depending on the local conditions, the ignition event can extend to various forms of consequences, such as a flash fire or an explosion (which requires sufficient over-pressure) which may lead to damage on property or injuries.

Flammability class	LFL, % of air vol- ume	Heat of combus- tion (kJ/kg)	Flame propagation
1	no flame propagation when tested in air at 60 °C and standard atmospheric pressure (1.013 bar)		
2, lower flammabil- ity	› 3.5	< 19,000	exhibits flame propagation (tested at 60 °C, 1.013 bar)
Proposed: 2L*, lower flammabil- ity	> 3.5	< 19,000	exhibits flame propagation (tested at 60 °C, 1.013 bar) with burning velocity ≤ 10cm/s
3, higher flamma- bility	≤ 3.5	≥ 19,000	exhibits flame propagation (tested at 60 °C, 1.013 bar)

Tablo 6.	Elammability classification	according to EN 278
Table 6:	Flammability classification	according to EN 570

*proposed in prEN 378-1:2013; so far only introduced in ISO 5149

The flammability classification, as defined in EN 378, depends upon whether or not the substances can be ignited. If so, the lower and upper flammability limits (LFL and UFL, respectively) and the heat of combustion (see Table 6) are taken into account. These characteristics, together with the environment they are used in, translate into a variety of risks.

LFL and UFL describe the lower and upper concentration limit of a flammable substance in which air/vapour mixtures can ignite or burn. Below the flammability limit, the concentration is too low for combustion, however, above it, there is insufficient oxygen for it to occur. These parameters are critical for ventilation air-flow rates and set-values of refrigerant leak detectors. Moreover, they are important for relating the space an application may be placed in to the size of refrigerant charge (see maximum refrigerant charge below).

¹⁴ Colbourne et al. (2010)

Minimum ignition energy and auto-ignition temperature are primarily associated with a source of ignition. Potential ignition sources need to be eliminated in both the RAC equipment and, in certain cases, the surrounding area. This includes, amongst others, the avoidance of surfaces with temperatures in the range of the auto ignition temperature and use of devices which could produce sparks with a charge above the minimum ignition energy. Service and maintenance technicians are required to handle their tools with care as these may be potential additional ignition sources, aside from electrical devices that are part of the equipment itself (see Table 7). The risk of a fire is 10 to 1,000 times higher during servicing than during normal operation, e.g. by unintentional damage to components, leaking refrigerant cylinders, servicing equipment as ignition sources. During normal operation, safety can be part of the system's design. During servicing, safety is far less easily regulated therefore proper training of service personnel is indispensable.

Electrical devices	Tools/equipment
Switches (manual, time, defrost, oil differ- ential, etc.)	Brazing equipment
Condensate pumps	Some electronic leakage testers
Thermostats	Unsealed switches on equipment (e.g. vacuum pumps)
Fan speed controllers	Generators
Contactors and most on/off switches	
Thermal overload	
Relays	

Table 7:	Example	s for potenti	al ignition o	of electrical	devices a	and tools/	equipment/
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Source: Coulbourne (2010)

In the EU, the two ATEX directives (see Table 2) prescribe the use of designated equipment and/or appropriate behaviour in atmospheres which are likely to ignite or explode. No matter what the degree of flammability for a product or substance is, the directives must be followed in any case.

EN 378 is not harmonised with the ATEX directives, nor does it contain any specification that ATEX applies. However, EN 378 refers to the standard EN 60079 (explosive atmospheres), which ATEX is harmonised with. Other relevant product standards are: 60335-2-24, -2-40, -2-89 (household and similar electrical appliances – safety), which are more important to those product groups than the more general EN 378.

3.2.3 Toxicity/Asphyxiation

Inhalation of any refrigerant vapour can have various effects on health. The toxicity classification for refrigerants according to EN 378 is based on whether toxicity has or has not been identified at certain concentrations for specific time periods. Class A is defined as exposure to refrigerant concentrations which do not have an adverse effect on health for 8 hrs/day and 40 hrs/week with values from 400 ppm. Class B addresses the same time frame of exposure, although no adverse effects should be monitored below 400 ppm.

Among natural refrigerants, NH₃ has a high toxicity and is thus assigned toxicity class B according to EN 378. Although being exposed to NH₃ may be poisonous, it is difficult not to detect NH₃: Due to its pungent smell, concentrations of 5 ppm can already be noticed, far before seriously dangerous concentrations of 400 ppm and higher are reached. At low concentrations it already has a distinctive smell, therefore leaks can be detected easily and refrigerant loss minimised. It is lighter than air and

leaked refrigerant will rise upwards, displacing oxygen in that direction. The most serious damage NH₃ can inflict is to the eyes. Direct contact can result in blindness. NH₃ irritates the skin, deteriorating the tissue through chemical burns, as well as potential freeze burns when in contact with liquids.

Accidents with NH₃ have occurred, however nobody outside a close proximity to the system has been injured in the past. Persons harmed were at the point of the leakage and were working on the system. Injuries can be prevented by wearing appropriate protection (no bare arms or legs etc.). Particular care must be taken during servicing of the systems to avoid a release of the refrigerant into areas where people are working.

According to EN 378, in refrigeration plants charged with more than 500 kg of NH₃, the occurrence of the refrigerant in all connected water or fluid circuits (referring to indirect systems) must be tracked by detectors and an alarm must be triggered in the machinery room in case of emergency. Since NH₃ is lighter than air the ventilation system should be placed in a higher position. NH₃ must be kept from entering the sewage system. Measuring the pH is the most common method for detection as the pH value increases with the presence of NH₃. Measuring the chemical composition of the water is even more accurate.

CO₂ exhibits no toxicity and naturally occurs in the atmosphere at concentrations around 350 ppm. People usually do not notice any differences in concentrations between 300 and 600 ppm. CO₂ however is not noticeable when leaking from a system. It is non-toxic and odourless, although higher concentrations can cause physical impairments, such as suffocation as it is an asphyxiant and displaces oxygen This implies that enclosed facilities (e.g. machinery rooms, cold rooms, etc.) where CO₂ may leak must be equipped with sensors that trigger an alarm when the concentration level exceeds its PL (0.1 kg/m³; > 5,000 ppm). Due to the fact that CO₂ is 1.5 times heavier than air it tends to pool and the distribution of CO₂ concentration in the ambient air is usually not homogenous. Because of this the exposure to CO₂ when standing up right might be lower than at ground level. Gas detection and ventilators should therefore be placed near the floor, approx. 30 cm above it. The sensor must be installed at a level close to the floor, which means that it will measure higher concentration than at a level where it might be breathed in by e.g. a service technician. This will provide earlier warning in case of a leakage and more time to escape. The enclosed area around a CO₂ system should always be well-ventilated. Ear protectors should be worn when venting the facility as higher noise levels will occur during the process.

All refrigerants can replace breathable air if trapped and thus act as an asphyxiant.

3.2.4 Working pressures

CO₂ needs distinctively higher operating pressures and, therefore, requires specific safety requirements in connection with these pressure levels. CO₂'s critical temperature is at 31 °C while its critical pressure or the critical point is ~74 bar (i.e. 31.0 °C/73.8 bar). The critical point is the condition above which distinctive liquid or gas phases do not exist. Beyond the critical point CO₂ is in trans-critical state. In comparison to other refrigerants CO₂'s critical point is low; in addition, the triple point at which solid, liquid and gas phase co-exist is high (5.2 bar/-56.6 °C).

These higher operating pressures require specific technical equipment, from pipe thickness to appropriate tools etc. Operating and standstill pressures are significantly higher than for all other refrigerants. A common issue for CO₂ systems in supermarkets is the high pressure at standstill. If the plant is stopped for maintenance the refrigerant inside the system begins to heat up. The pressure inside the system consequently increases. Components of CO₂ employed in a (subcritical) cascade system may not stand the high pressure as they are usually designed for operating pressures of approx. 35 bar. ¹⁵

¹⁵ Huehren (2015)

The most common and also easiest counter-measure is to purge some of the CO_2 in the system, so pressure and temperature in the plant are reduced.

At certain conditions, for instance during venting or charging, solid CO₂ (dry ice) can be formed when pressure/temperature drops below the triple point. This is also relevant for the selection and positioning of pressure-relief valves, through which liquid CO₂ must not pass, as the forming of dry ice might block the valve (with subliming dry ice, pressure rises rapidly). CO₂ has a very high coefficient of expansion. Trapped liquid CO₂ expands rapidly which can result in a very high pressure increase. As a rule of thumb for every 1 °C rise in the temperature of the trapped liquid CO₂, the pressure rises by 10 bar. It must be avoided that liquid CO₂ is trapped between closed valves before venting the system. This can be done by moving the liquid CO₂ to another part of the system by means of high pressure gas.

3.2.5 Occupancy and limitation of refrigerant charge

The charge size limit of any refrigerant is closely connected to that refrigerant's safety requirements. For any refrigerant, according to EN 378, it is derived from the occupancy category (Table 8) and on the placement of the refrigerant-containing parts, such as:

- An entire system within space occupied by humans which is not a machinery room;
- A compressor and liquid receiver in an unoccupied machinery room or in the open;
- All refrigerant containing parts in an unoccupied machinery room or in the open;

including an additional factor based on the system design, being either a direct or indirect expansion system.

Class	Type of occupancy	Examples
A	General occupancy not restricted at all, dwellings and public places	Hospitals, hotels, prisons, restau- rants, supermarkets, theatres, transport termini, etc.
В	Supervised occupancy restricted to a certain number of people, some of whom are aware of general safety pre- cautions	Laboratories, Offices, places of work, etc.
С	Occupancy with authorised access only, authorised persons are aware of general safety precautions	Cold stores, manufacturing facili- ties, non-public areas in supermar- kets, refineries, etc.

Table 8:Classification of occupancy

Where the PL refers to the maximum allowable mass of refrigerant for a given occupied space, the maximum charge size is represented by the upper boundary limit of the PL (in certain cases this may be more strict). This is typically based on the assumption that in a worst-case scenario, the entire refrigerant charge from a circuit will be released almost instantaneously into a room without, however, resulting in a local flammable concentration for anything more than a brief moment. Especially for flammable refrigerants, this leads to rather small permitted charge sizes. The strict limitation of charge sizes is one measure to ensure safety. Other measures, currently not mentioned in standards, include in-depth analysis of refrigerant flow in the room in case of a leakage, taking into account the position of a leakage, air mixing rates (also due to ventilation) and measures like compressor shut-off to avoid more refrigerant reaching the leakage.

Minimum Ventilation Requirements in Machinery Rooms (Category C occupancy)

Mechanical ventilation is a necessity for all refrigerant systems. Mechanical ventilation is mandatory within a machinery room where larger quantities of refrigerant occur. EN 378 specifies certain ventilation rates for machinery rooms. According to EN 378, every machinery room with installations of more than 25 kg of refrigerant charge must be equipped with a refrigerant detection system. For refrigerants with a recognisable smell below the ATEL/ODL value (e.g. R717), no detectors are necessary, as a leakage is easily noticed. If the concentration of refrigerant within a machinery room (or any other Category C occupancy) exceeds the PL, an alarm has to be triggered and the mechanical emergency ventilation must set in.

The ventilation should be started at a concentration of no more than 20 % of the LFL¹⁶ / 50 % of the ATEL/ODL. In the case of flammable refrigerants, it is necessary to ensure sufficient ventilation so that the refrigerant is dispersed rapidly in the event of a leakage. The pre-set value or limit for any oxygen deprivation detector must be 18 % of oxygen concentration. For CO2 the ATEL/ODL is 0.036 kg/m³, so the alarm should be set at 0.018 m³ (approximately 20,000 ppm). Ideally there should also be a pre-alarm at 5,000 ppm because, due to the high pressure in CO₂ systems, the concentration will rise rapidly in the event of a leakage.

3.2.6 Requirements to components

Natural refrigerants can require different equipment according to the safety requirements. A summary of necessary component adjustments according to given refrigerant properties, are listed in Table 9. More detailed information is available in various legal requirements, standards, codes of good practice, etc. ¹⁷

The very high working pressures of CO₂ poses some technical challenges. Components must withstand pressures by a factor of 5 to 10 times higher than synthetic refrigerants. As a result, materials, component thickness, jointing methods and mechanical operation of components such as the compressor must be adapted.

Hydrocarbons require a safety environment that prevents the risks of fire from potential ignition sources. This concerns in particular the selection and placement of electrical devices and materials. It must also be ensured that the fan and casing of the evaporator do not interact as that might produce sparks. Standards EN 378, IEC 60335-2-24, IEC 60335-2-40, IEC 60335-2-89 indicate all electrical devices that could be ignition sources.

Due to NH₃'s chemical properties, pipework and other components consisting of copper and other non-ferrous metals (e.g. zinc) and rubber/plastics are not suitable. In connection with trace water or moisture, NH₃ is highly corrosive towards these materials. It is recommended to use (stainless) steel instead.

¹⁶ Colbourne et al. (2010), EN 378

¹⁷ Guidance through the process of component adjustments can be found in Colbourne et al. (2010): "Guidelines for the safe use of hydrocarbon refrigerants. A handbook for engineers, technicians, trainers and policy-makers". <u>https://www.giz.de/expertise/downloads/giz2010-en-guidelines-safe-use-of-hydrocarbon.pdf</u>.

Table 9:	Safety concerns and adaption of equipment in regards to CO2, HCs and $\rm NH_3$ refrig-
	erants.

Refrigerant	Safety concern	Component	Requirements
CO ₂	Leakage	Refrigerant detector	CO ₂ and health implications: facilities where CO ₂ may leak must be equipped with sensors that trigger alarm when the concentration level exceeds 5,000 ppm
	Pressure	Pressure relief valves	Reducing over-pressure through venting
	Pressure	Compressor	Smaller displacement, protection against over-pressure
	Pressure	Piping	Thicker walls, smaller diameter
	Pressure	Joints	Brazed or welded; mechanical joints should be avoided
HCs	Leakage	Piping	Pipework must be enclosed or protected to prevent mechanical damage
	Material compa-tibil- ity	Material	EPDM, natural and silicone rubbers are incompatible with HC; chloroprene (neo-prene) particularly with unsaturated HCs
	Ignition	Electrical components	Any leaked refrigerant should not flow or stagnate where electrical components could be a source of ignition
	Ignition	Fan/casing	Fan blades and casing should be of ma- terials that do not cause sparks when in- teracting (e.g. no stainless steel, no steel alloy and brass pairing)
NH3	Corrosion (external)	Pipework and other components	Using steel or carbon instead of copper (internal corrosion not a significant is- sue)
	Leakage	Joints	Welded joints should be preferred over flanged joints to reduce risk of leakage, socket weld connections over butt- welded joints
	Leakage	Shut-off devices	Shut-off valves should be installed to reduce risk of NH_3 loss

4 Selected practical recommendations for the safe use of natural refrigerants and equipment

4.1 General

A refrigerant and the equipment it is used in, is handled during four major stages: (1) installation and commissioning, (2) maintenance, (3) servicing and repair, and (4) decommissioning, dismantling and disposal. These stages comprise of activities, such as:

- Refrigerant charging;
- Leakage checks and gas detection;
- Recovery of refrigerant, venting or evacuation;
- General handling of cylinders.

When handling natural refrigerants, it is important to accurately follow the safety rules. In addition, technicians must be well trained and have knowledge of RAC system technologies in general. They should also be competent in handling synthetic refrigerants.

No matter which type of refrigerant, some common hazards apply to all of them, for instance:

- ► Pressurised gases and liquids can cause injuries, e.g. freeze burns, when released under atmospheric conditions. Therefore, appropriate personal protection equipment must be worn.
- Refrigerant, when released, displaces air and poses a risk of asphyxiation, etc. Therefore ventilation is required and technicians must be aware of necessary actions to take in case of leakage.

Since it is difficult to anticipate all eventualities, further precautions may be appropriate, depending on the conditions and the equipment.

In the following, best practices for the safe use of natural refrigerants shall be outlined by the example of HCs. Most of the procedures are similar with other natural refrigerants.

4.2 Warnings, markings and instructions

Warning signs, marking and detailed instructions are a requirement of safety standards and regulations. Comprehensive signs and instructions warn about hazardous substances and make workers aware of relevant risks and how to appropriately behave. Figure 2 provides examples of common signs related to safety requirements. Signs and labels for hazardous refrigerants are attached to refrigerant containers and storage areas. Warning signs may be attached to both working areas and equipment and are mandatory in manuals (e.g. installation or servicing manuals). Manuals and other instructions should also include additional information on improving the safe handling of the equipment. For example, in the case of flammable refrigerants, it is important to know whether a part of the equipment can safely be used in a certain area.



Figure 2: Signs relating to refrigerant safety

Source: Federal Office for Occupational Safety and Health (Bundesamt für Arbeitsschutz und Arbeitsmedizin). http://www.baua.de/de/Themen-von-A-Z/Arbeitsstaetten/ASR/pdf/ASR-A1-3.pdf (last accessed: 01 Oct 2015)

4.3 Working with flammable refrigerants

When working with flammable refrigerants, design features and operational practices must be established to minimise risks. Knowledge of the properties of the various refrigerants is required. Raising the awareness of practices for safe handling and storage of flammable refrigerants and appropriate system designs are measures that can prevent possible accidents. Precautions need to be taken to prevent the occurrence of leakages and to prevent a dangerous degree of released refrigerant. In the case of flammable refrigerants, potential ignition sources must be eliminated.

4.3.1 Work routine

Technicians carrying out various activities, such as installation of equipment, commissioning of installations, routine maintenance, service and repair or dismantling should follow a strict work routine. Figure 3 illustrates situations technicians encounter while working on a system. During these activities technicians may come into contact with released refrigerant which bears certain risks in the case of flammable refrigerants.





4.3.2 Risk assessment

Risk assessment is a general tool for gaining understanding of potential hazards and consequently eliminating them. It provides a useful medium for achieving a rational understanding of the risk associated with the use of flammable refrigerants. In general, if there is little knowledge and understanding of risks and the components of the risks associated with the use of a particular technology, the safe design, use and operation of equipment will have many uncertainties associated with it. This leads to a more risky situation. However, if those involved attain a greater knowledge and understanding of the issue, then a much higher level of certainty in the safe design, use and operation will be achieved. This ultimately leads to a reduced level of risk¹⁸. For the case of flammable refrigerants, such an assessment must include:

- Hazardous properties of the substance;
- Risk of exposure to individuals;
- Probability of an explosive atmosphere to occur and to persist;
- Probability of ignition sources to exist and to trigger;
- Necessary action in the event of a fire or explosion and the degree of expected effects.

There are several methods for risk assessments available, as well as standards that may be directly or broadly applicable to the situation or equipment under consideration.¹⁹

4.3.3 Temporary flammable zone and safe working area

Certain locations should be marked as 'temporary flammable zone' when working on systems with flammable refrigerants. This temporary zone should range from about half a metre radius from the system to a distance appropriate in relation to the maximum amount of refrigerant which could be released during the working procedure. The 'safe working area' begins three metres away from the system. No ignition sources should exist in a two metre radius; a gas detector should be used to be aware of HC concentration in the air before and after work is carried out.

Tools used in temporary flammable zones must be suitable to work with in potentially explosive atmospheres.

4.3.4 Service and repair

For the duration of servicing on a system, the use of a portable gas detector without 'zero background' function is recommended (attached to clothing or placed on the floor). The pre-set value for the alarm should be 15 % of LFL. Technicians will be warned early on and can react immediately according to emergency procedures.

¹⁸ Colbourne et al. (2010)

¹⁹ For example EN 15198: Methodology for the risk assessment of non-electrical equipment and components for the intended use in potentially explosive atmospheres. Explosion prevention and protection; EN 15233: Methodology for the functional safety assessment of protective systems for potentially explosive atmospheres

4.3.5 Refrigerant recovery

Recovering refrigerant is mandatory for synthetic refrigerants such as ODS and F-gases, but under all circumstances recommended for all types of refrigerants. Recovering HCs from the refrigerant circuit is no different from procedures applied with synthetic refrigerants. However, it should be ensured that the recovery machine is compatible with HCs and does not have any ignition sources, the same being true for the recovery cylinder.

It is important to stress that HC refrigerants in liquid form occupy more than twice the volume of fluorinated refrigerants due to only half of the density. If this is not considered during recovery the recovery cylinder might burst. Therefore, the cylinder must only be filled to 75 % of its capacity. It is also important to consider that the cylinder might be exposed to higher ambient temperatures and the liquid HC might expand. The maximum filling should therefore not exceed 40 % of the amount of fluorinated refrigerants in kg.

4.3.6 Refrigerant venting

Venting from a system (to a safe place) is only done with small quantities of HC (less than 150 g). According to legislation, the venting of a system may not take place in a public area. The hose for venting must be compatible with HCs and extend at least 3 m outside of the building. It needs to be ensured that there are no ignition sources near the hose discharge.

4.3.7 Refrigerant charging

Charging procedures used with HCs are similar to any other refrigerant, although certain aspects are important to consider. The connection of hoses needs to be checked and secured, including checks for any potential ignition sources within the temporary flammable zone. Use of a four-way manifold is recommended to avoid interchanging of hoses whereas the hoses should be as short as possible. The refrigerating system must be earthed before charging takes place and a leakage check must be carried out. The system needs to be labelled properly.

4.3.8 Leakage detection with HCs

Leakage detection is particularly important when working on systems which run on HCs. However, leakage detection is not to be confused with gas detection which is itself only a means to detect leakages. A variety of methods for finding leakages connected to HCs are listed in Table 10.

Method	Used as	Not recommended	Necessary	Recommended
Soapy water bubble test with refrigerant pressure (only)	Leakage check	Х		
Using an appropriate electronic gas detec- tor, e.g. thermal con- ductivity detector (TCD)	Leakage test		х	
OFDN* pressurised system and soapy wa- ter (Bubble test)	Tightness test Test pressure at 10 bar sufficient		Х	
N ₂ /H ₂ Forming gas pressurised system and trace gas detector	Tightness test Test pressure at 5 bar sufficient			х
Pressurising the Sys- tem with OFDN	Pressure (Strength) test PS x 1.1, e.g. refrigerant cir- cuit components are repaired or re- placed		Х	
Fixed refrigerant de- tection systems	Fixed refrigerant leakage monitor- ing system. Man- datory for charges ≥ 500 t CO ₂ eq ac- cording to EU F- gas Regulation		Х	

 Table 10:
 Suitable methods for finding leakages with regards to HCs

Source: Huehren (2015)

*oxygen free, dry nitrogen (to impede formation of oxides)

4.3.9 Storage of refrigerant cylinders

Refillable and non-refillable cylinders are available for HCs. The handling of cylinders filled with flammable substances is usually subject to national legislation. In general, the following precautions should be followed.

- ► Storage: in specific locations, at ground level, never in residential premises, preferably outside in dry, cool, and well-ventilated areas, in an upright position.
- Access: marked location with restricted access to authorised persons only.
- Restriction: The storage limit to certain amounts of flammable substance needs to be kept.
- Prohibition: no smoking or open flames near the storage location.
- ► Flammability: avoid ignition sources.

5 Practice examples for the use of natural refrigerants

Natural refrigerants are already used in various applications from industrial applications to room air conditioners. A lack of information about the technology is often accompanied by misconceptions about the additional safety risks associated with natural refrigerants. However, many countries are rapidly picking up on implementing systems based on natural refrigerants. Handling large charges of them is a safety concern and specific practises and handling procedures are required. Reducing refrigerant charge sizes via the use of indirect refrigerating systems is a solution to addressing safety concerns. The continued development of these systems is necessary to guarantee safe use on a larger scale.

Reasons for choosing natural refrigerants are mostly gains in energy efficiency and independence from requirements of F-gas regulations (mandatory leakage checks, uncertain cost and supply of F-gas refrigerants in the future, bans). Presently, investment costs are usually higher than for systems using F-gases. Often, this is because equipment is not (yet) produced on a large scale and therefore more expensive. In most cases, the higher investment cost is balanced by lower energy costs.

Example 1: Air conditioning-Chiller using R290 - Ohara GmbH, Hofheim

Flammable refrigerants such as propane not only find employment as alternative to conventional refrigerants in smaller applications but increasingly in cooling applications of larger proportions. One example is a HC chiller unit cooling a building with a total of 630 m² room area distributed on two floors. The cooling load accounts for 26.5 kW (40–50 W/m²). There are two compressor circuits charged with 3.1 kg of propane each. The components of the system containing propane are located in a machinery box in a safe distance outside of the building. Hence, flammability of the refrigerant poses no risk to people and the interior of the building. If it were placed on the roof an additional fire security installation would be required.

A cooled water-glycol mixture circulates from the outside machinery box into the building and back, serving ceiling cassettes for air conditioning. At low outside temperatures (below 0 °C) heating is supported by a condensing boiler, powered with natural gas. Surplus cooling or heating can be stored in buffers in the basement and supply the demand of the building in times of higher energy prices.

The system is also linked to the manufacturer who is able to monitor the performance of the installation without local inspections.

Example 2: Propane-/CO₂-based ice slurry refrigerating system – Technical University of Applied Sciences, Karlsruhe

Another quite exotic example, is the R290/CO₂-based ice-slurry machine of the student union (Studierendenwerk) at the Technical University of Applied Sciences in Karlsruhe servicing the University's canteen. The use of propane for the generation of ice slurry is unique to date. Ice slurry is generated within 6 cylindrical generators (14 kW cooling capacity, 3 refrigerant circuits with 10 kg of charge each) by means of R290 as primary refrigerant. Each ice generator is equipped with an individual pump to support a storage tank. The ice is stored in a tank where it is continuously stirred. The ice slurry consists of bean-shaped ice pellets in the size of up to half a millimetre which are suspended in a solution of water, ca. 8 % ethanol, as well as glycol. Simple pumps usually used for heating systems distribute the secondary refrigerant to cabinets and cold rooms. The ice slurry is pumped through a duct system made of polyethylene. The ice-slurry provides the refrigerated counters in the canteen, as well as the cold storage rooms. For freezer storage rooms, a compact CO₂ refrigeration system is set as a cascade into the refrigeration circuit to provide further freezing capabilities below -20 °C.

The main advantages compared to a conventional direct expansion system is a) the reduced leakage due to avoiding extensive piping through the building and b) the substantial cut in peak load energy consumption by de-coupling cooling "production" and cooling "use" by means of the ice-slurry storage.

The machinery room is situated outside of the building (no risk due to flammability) and has two compartments, separated by an air tight wall. One compartment contains the propane compressors, the other the electric control system. Due to the separation, off-the-shelf components can be used for the control system, without special ignition prevention measures. Additional safety is also provided through air suction. The cold storage rooms are equipped with CO2-alarms.

Example 3: Centralized systems for supermarkets using CO₂ – EDEKA Nolte, Koenigstein

EDEKA forms the largest group in the German retail industry and consists of various franchisers (hence EDEKA Nolte). The refrigeration system of the supermarket EDEKA Nolte in Koenigstein is a CO₂-based system from Carrier which has been in operation since the second half of 2013. It was EDEKA's first CO₂-based solution in their markets. The second market with a CO₂-based refrigeration system was opened in the beginning of 2015. The refrigeration system is able to air condition the supermarket's interior (cooling and heating), as well as to supply cooling to the refrigeration cabinets in the market. Additional air-conditioning in the market is necessary because of the glass front of the building. The supermarket was newly build and also utilizes an energy-efficient LED lighting system.

The energy savings including those from the LED lighting accounts for roughly 50 % in comparison to a conventional state-of-the-art supermarket refrigeration system. Approximately 35 % comes from the refrigeration system alone. The amortisation period of the initial investment costs is difficult to assess, since subsidies are included into the overall calculation. Roughly, amortisation is possibly reached within a time frame of about 3–5 years. The amortisation of LED technology is less than 2 years. The difference in investment costs to a conventional F-gas system is also difficult to estimate but may be 30–40 % higher.

Routine maintenance of the refrigeration system is required twice a year. Mandatory leakage checks are not required. In order to maintain the high efficiency of the system, the whole building is being monitored online, so that small deviations of standard performance are noticed and early action can be taken.

6 Where to start?

The knowledge on handling natural refrigerants is already part of the formal (theoretical) education of refrigeration technicians. Limited practice due to the presently limited application may have led to a reluctance against the wider application of natural refrigerants. Practical training on natural refrigerants may motivate refrigeration technicians to use natural refrigerants more often.

According to a study carried out in 2014²⁰ to assess the situation in Germany, the following applications show potential for the use of HC refrigerants: room air conditioners, household heat pumps, refrigerated trucks and trailers and chillers of up to 1 MW. In order to accelerate the dissemination, the following measures were found promising:

- Green public procurement of chillers;
- Adaptation of relevant technical standards to promote a wider use of HC refrigerants, in particular regarding the application air conditioning;
- Reviewing the interpretation of the product liability law in Germany with respect to HC refrigerants, which positively affects all applications;
- Establishing a professional contact point which serves as an independent and objective consulting centre for HC refrigerants (This will have an effect on three of the main applications);
- Developing and publishing guidelines for the use of HCs in heat pumps and for the use of components which are not certified for HCs yet.

Several of these measures aim to improve the confidence in existing standards by developing guidelines for specific product groups or investigating the legal consequences potentially arising from the product liability law. Similar measures are possible to increase the number of installations of CO₂ and NH₃ based equipment.

Without detailed investigation regarding the transferability to Bulgarian circumstances some general guidance can be deduced from these findings:

- ► Identify the applications, where introduction of a natural refrigerant is promising in terms of readiness of the technology and expected emission reduction;
- Analyse current legislation and standards regarding the specific application;
- Develop and disseminate guidance documents for those specific application;
- ► Financial support programmes to balance the price premium attributed to low units numbers could accelerate the uptake of new technologies.

7 References

Publications

Arias, Jaime (2005). Energy Usage in Supermarkets – Modelling and Field Measurements. Doctoral thesis, Royal Institute of Technology, Stockholm, Sweden.

https://www.kth.se/polopoly_fs/1.301522!/Menu/general/column-content/attachmont/PhD% 20Thesis_laime% 20Arias_ndf

ment/PhD%20Thesis-Jaime%20Arias.pdf

Hasse, Volkmar; Ederberg, Linda; Colbourne, Daniel (2008; reprint: 2012). Natural refrigerants – sustainable ozone- and climate-friendly alternatives to HCFCs. Deutsche Gesellschaft für Internationale Zusammenarbeit GmbH, Eschborn, Germany.

<u>https://www.giz.de/expertise/downloads/giz2008-en-natural-refrigerants.pdf</u> (last accessed: 01 Oct 2015)

Colbourne, Daniel (lead author); Huehren, Rolf; Schrempf, Bernhard; Ederberg, Linda; Meenen, Sabine (2010; reprint: 2012). Guidelines for the safe use of hydrocarbon refrigerants. A handbook for engineers, technicians, trainers and policy-makers – For a climate-friendly cooling. Deutsche Gesellschaft für Internationale Zusammenarbeit GmbH, Eschborn, Germany.

https://www.giz.de/expertise/downloads/giz2010-en-guidelines-safe-use-of-hydrocarbon.pdf (last accessed: 01 Oct 2015)

Colbourne, Daniel; Huehren, Rolf (lead author); Ederberg, Linda (2011). Operation of split air conditioning systems with hydrocarbon refrigerant. A conversion guide for technicians, trainers and engineers. Deutsche Gesellschaft für Internationale Zusammenarbeit GmbH, Eschborn, Germany. <u>https://www.giz.de/expertise/downloads/giz2011-en-split-air-conditioning.pdf</u> (last accessed: 01 Oct 2015)

Hasse, Volkmar; Ederberg, Linda; Kirch, Rebekka (2010; reprint: 2012). Good practices in refrigeration. Deutsche Gesellschaft für Internationale Zusammenarbeit GmbH, Eschborn, Germany. <u>https://www.giz.de/expertise/downloads/giz2010-en-good-practices-in-refrigeration.pdf</u> (last accessed: 01 Oct 2015)

Heubes, Jonathan; Papst, Irene; König, Holger; Usinger, Jürgen; Gschrey, Barbara; Kimmel, Thomas; Schwarz, Winfried (2014). Kohlenwasserstoffe sicher als Kältemittel einsetzen – Entwicklung einer Strategie zum vermehrten Einsatz von Kohlenwasserstoff-Kältemitteln als Beitrag zum deutschen Klimaschutzziel unter Berücksichtigung des Energieziels 2050. German Environment Agency, Dessau-Roßlau, Germany.

<u>https://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/cli-</u> <u>mate change 30 2014 kohlenwasserstoffe sicher als kaeltemittel einsetzen.pdf</u> (last accessed: 01 Oct 2015)

REAL Alternatives Europe (2015a). REAL Alternatives Europe programme module 1 – Introduction to Alternative Refrigerants – safety, efficiency, reliability and good practice.

http://www.realalternatives.eu/learning-platform

(last accessed: 01 Oct 2015)

REAL Alternatives Europe (2015b). REAL Alternatives Europe programme module 2 – System design using alternative refrigerants.

http://www.realalternatives.eu/learning-platform

(last accessed: 01 Oct 2015)

REAL Alternatives Europe (2015c). REAL Alternatives Europe programme module 6 – Checklist of legal obligations when working with alternative refrigerants.

http://www.realalternatives.eu/learning-platform

(last accessed: 01 Oct 2015)

Ricardo-AEA and Gluckman Consulting (2015a). Topic A Briefing Paper: Barriers related to standards and legislation. 1st meeting of Consultation Forum according to Art. 23 of Regulation (EU) No. 517/2014 on fluorinated greenhouse gases. Brussels, Belgium. September 2015. <u>http://ec.europa.eu/clima/events/docs/0106/m01/ta_paper_en.pdf</u>

(last assessed, 04 Oct 2015)

(last accessed: 06 Oct 2015)

Ricardo-AEA and Gluckman Consulting (2015b). Topic B Briefing Paper: Barriers related to training. 1st meeting of Consultation Forum according to Art. 23 of Regulation (EU) No. 517/2014 on fluorinated greenhouse gases. Brussels, Belgium. September 2015.

http://ec.europa.eu/clima/events/docs/0106/m01/tb_paper_en.pdf (last accessed: 06 Oct 2015)

UNEP Division of Technology, Industry and Economics (2010). Alternatives to HCFCs in the refrigeration and air conditioning sector. Practical Guidelines and Case Studies for Equipment Retrofit and Replacement.

http://www.unep.org/pdf/hcfc-alternatives .pdf (last accessed: 01 Oct 2015)

Presentations

Colbourne, Daniel (2014). Possibilities of the RAC sector transformation – a technical perspective. The Delegation of the European Union in India and GIZ Proklima. New Delhi, India, 2014. <u>http://ec.europa.eu/clima/events/docs/0102/possibilities_en.pdf</u>

(last accessed: 01 Oct 2015)

Colbourne, Daniel (2015a). Challenges to the use of natural refrigerants. Workshop on 'Climatefriendly technology alternatives to HCFC/HFCs', Tel Aviv, Israel, May 2015.

http://www.sviva.gov.il/English/env_topics/climatechange/Mitigation/Documents/Chal-

lenges%20to%20the%20use%20of%20natural%20refrigerants%20-%20D%20Colbourne%20-%20May%202015.pdf

(last accessed: 01 Oct 2015)

Colbourne, Daniel (2015b). Safety standards and risk assessment. Workshop on 'Climate-friendly technology alternatives to HCFC/HFCs', Tel Aviv, Israel, May 2015.

http://www.sviva.gov.il/English/env_topics/climatechange/Mitigation/Documents/climatefriendly%20alternatives%20to%20HCFC-HFCs%20-%20Safety%20stand-

ards%20and%20risk%20assessment%20-%20D%20Colbourne%20-%20May%202015.pdf (last accessed: 01 Oct 2015)

Colbourne, Daniel; Peixeito, Roberto (2015c). Air-to-air air conditioners and heat pumps. UNEP Workshop on hydrofluorocarbons (HFC) Management. Bangkok, Thailand, April 2015.

http://conf.montreal-protocol.org/meeting/workshops/hfc_management-02/presentations_speakers/English/Session%202%20-%202%20-%20Colbourne%20and%20Peixoto.pptx (last accessed: 01 Oct 2015)

Huehren, Rolf (2015). Safe handling of natural refrigerants- safety concerns in installation and maintenance. Workshop on 'Climate-friendly technology alternatives to HCFC/HFCs', Tel Aviv, Israel, May 2015.

<u>http://www.sviva.gov.il/English/env_topics/climatechange/Mitigation/Documents/Safe%20han-dling%20of%20natural%20refrigerants%20-%20R%20Huehren%20-%20May%202015.pdf</u> (last accessed: 01 Oct 2015)

Ricardo-AEA and Gluckman Consulting (2015a). Topic A: Barriers to the uptake of low GWP alternatives to HFCs related to standards, codes and legislation. Preliminary findings of external study carried out for DG CLIMA. 1st meeting of Consultation Forum according to Art. 23 of Regulation (EU) No. 517/2014 on fluorinated greenhouse gases. Brussels, Belgium. September 2015. <u>http://ec.europa.eu/clima/events/docs/0106/m01/ta_slides_en.pdf</u>

(last accessed: 06 Oct 2015)

Ricardo-AEA and Gluckman Consulting (2015b). Topic A: Barriers to the uptake of low GWP alternatives to HFCs related to lack of training. Preliminary findings of external study carried out for DG CLIMA. 1st meeting of Consultation Forum according to Art. 23 of Regulation (EU) No. 517/2014 on fluorinated greenhouse gases. Brussels, Belgium. September 2015.

http://ec.europa.eu/clima/events/docs/0106/m01/tb_slides_en.pdf

(last accessed: 06 Oct 2015)

Standards and codes of practice

EN 378-1: Refrigerating systems and heat pumps - Safety and environmental requirements -Part 1: Basic requirements, definitions, classification and selection criteria

EN 378-2: Refrigerating systems and heat pumps - Safety and environmental requirements -Part 2: Design, construction, testing, marking and documentation

EN 378-3: Refrigerating systems and heat pumps - Safety and environmental requirements -Part 3: Installation site and personal protection

EN 378-4: Refrigerating systems and heat pumps - Safety and environmental requirements -Part 4: Operation, maintenance, repair and recovery

See Annex below for a detailed list of relevant standards

The Institute of Refrigeration (2009; revised 2015). A1 Refrigerant (HFC) Code of Practice.

The Institute of Refrigeration (2009; revised 2013). Carbon Dioxide (R744/CO2) as Refrigerant Code of Practice.

The Institute of Refrigeration (2009). A2 & A3 Refrigerants (flammable including hydrocarbons and HFOs) Code of Practice.

The Institute of Refrigeration (2009). Ammonia Refrigeration Systems Code of Practice.

Web Sources

GESTIS Database on chemical media (Stoffdatenbank)

http://gestis.itrust.de/nxt/gateway.dll/gestis_de/000000.xml?f=templates\$fn=default.htm\$vid=gestisdeu:sdbdeu\$3.0

REAL Alternatives Europe

http://www.realalternatives.eu/

REAL Skills Europe

http://www.realskillseurope.eu/

8 Annex

Relevant standards associated to the safety of RAC equipment (derived from Heubes et al. 2014)

Standard	Title
EN 378	Refrigerating systems and heat pumps – Safety and environmental requirements
	Part 1: Basic requirements, definitions, classification and selection criteria Part 2: Design, construction, testing, marking and documentation Part 3: Installation site and personal protection Part 4: Operation, maintenance, repair and recovery
EN 1012-1, -2	Compressors and vacuum pumps – Safety requirements Part 1 : Air compressors Part 2 : Vacuum pumps
EN 1127-1	Explosive atmospheres – Explosion prevention and protection Part 1: Basic concepts and methodology (2011)
EN 1736	Refrigerating systems and heat pumps – Flexible pipe elements, vibration isolators, expansion joints and non-metallic tubes – Requirements, design and installation
EN ISO 4126	Safety devices for protection against excessive pressurePart 1: Safety valvesPart 2: Bursting disc safety devicesPart 3: Safety valves and bursting disc safety devices in combinationPart 4: Pilot operated safety valvesPart 5: Controlled safety pressure relief systems (CSPRS)Part 6: Application, selection and installation of bursting disc safety devicesPart 7: Common data
EN ISO 9001	Quality management systems – Requirements
EN ISO 12100	Safety of machinery – General principles for design – Risk assessment and risk reduction
EN 12178	Refrigerating systems and heat pumps – Liquid level indicating devices – Requirements, testing and marking
EN 12263	Refrigerating systems and heat pumps – Safety switching devices for limiting the pressure – Requirements and tests
EN 12284	Refrigerating systems and heat pumps – Valves – Requirements, testing and marking
EN 12693	Refrigerating systems and heat pumps – Safety and environmental requirements – Positive displacement refrigerant compressors
EN 13136	Refrigerating systems and heat pumps – Pressure relief devices and their associated piping – Methods for calculation
EN 13313	Refrigerating systems and heat pumps – Competence of personnel
EN 13463-1, -5, -6	Non-electrical equipment for use in potentially explosive atmospheres Part 1: Basic method and requirements Part 5: Protection by constructional safety 'c' Part 6: Protection by control of ignition source 'b'
EN 13980	Potentially explosive atmospheres – Application of quality systems
EN 14276-1, -2	Pressure equipment for refrigerating systems and heat pumps Part 1: Vessels – General requirements Part 2: Piping – General requirements
EN TR 14739	Scheme for carrying out a risk assessment for flammable refrigerants in case of household refrigerators and freezers
EN 14797	Explosion venting devices
EN 14986	Design of fans working in potentially explosive atmospheres
EN 15198	Methodology for the risk assessment of non-electrical equipment and components for intended use in poten- tially explosive atmospheres
EN 15233	Methodology for functional safety assessment of protective systems for potentially explosive atmospheres
EN 15834	Refrigerating systems and heat pumps — Qualification of tightness of components and joints
EN 16084	Refrigerating systems and heat pumps – Qualification of tightness of components and joints

EN ISO/IEC 17020	Conformity assessment Requirements for the operation of various types of bodies performing inspection
EN ISO /IEC 17024	Conformity assessment General requirements for bodies operating certification of persons
EN ISO / IEC 17025	General requirements for the competence of testing and calibration laboratories
EN 50110	Operation of electrical installations Part 1: General requirements Part 2: National annexes
EN 50402	Electrical apparatus for the detection and measurement of combustible or toxic gases or vapours or of oxygen – Requirements on the functional safety of fixed gas detection system
DIN EN 60079-0, -10- 1, -14, -15, -17, -19, -20-1	Explosive atmospheres Part 0: Equipment – General requirements Part 10-1: Classification of areas – Explosive gas atmospheres Part 14: Electrical installations design, selection and erection Part 15: Equipment protection by type of protection 'n' Part 17: Electrical installations inspection and maintenance Part 19: Equipment repair, overhaul and reclamation Part 20-1: Material characteristics for gas and vapour classification – Test methods and data
DIN EN 60204-1	Safety of machinery – Electrical equipment of machines Part 1: General requirement
DIN EN 60335-1, 2- 24, -2-34, -2-40, -2- 89	Household and similar electrical appliances – Safety Part 1: General requirements Part 2-24: Particular requirements for refrigerating appliances, ice-cream appliances and ice makers Part 2-34: Particular requirements for motor-compressors Part 2-40: Particular requirements for electrical heat pumps, air conditioners and dehumidifiers Part 2-89: Particular requirements for commercial refrigerating appliances with an incorporated or remote refrigerant condensing unit or compressor
EN 60812	Failure Mode and Effects analysis
EN 61160	Design review
EN 62502	Analysis techniques for dependability – Event tree analysis
IEC 61882	Hazard and operability studies
ISO 817	Refrigerants – designation and system classification
ISO 5149	Mechanical refrigerating systems used for cooling and heating – Safety requirements