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N O R D I C W O R K I N G P A P E R S

Information sheets on natural refrigerants

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INFORMATION SHEETS ON NATURAL REFRIGERANTS

2015

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Foreword

This set of information sheets is an updated version of "Information sheets on natural refrigerants" made on assignment of the Nordic Chemicals Group by the Norwegian association of refrigeration end users "Forum for kuldebrukere (FOKU)" in 2008. It consists of 31 information sheets on natural refrigerants, covering a broad field of technical information.

Non-natural refrigerants like HCFCs and HFCs are strong greenhouse gases. It will be essential in the future to reduce emission of these gases considerably. HCFCs are being phased out and most systems will have to be replaced as the permit to use recycled fluid for servicing purposes ceases on January 1, 2015.

The only way to fully safeguard against HFC emission from refrigeration systems and heat pumps is to change over to other fluids. An extra challenge in the short term is to avoid that the old HCFC systems are replaced by HFC, which often represents the simplest solution. In this situation, natural refrigerants including ammonia, carbon dioxide and hydrocarbons, represent a "green alternative".

Natural refrigerants may already today replace HFCs for a number of applications, and the technology is under continuous improvement. In the future the need for HFCs may disappear.

Properly used, natural refrigerants show additional benefits over the HFCs, such as better energy efficiency in many cases, which also affects global warming.

The use of natural refrigerants differ from using HFCs in many ways, affecting a variety of aspects related to system design and operation, safety requirements etc. To extend the use of natural refrigerants, it is necessary to inform potential users, and the authorities, on the possibilities (and limitations) related to these fluids, and to make technical knowhow and practical experience available for system designers and installers. This is the aim of the information sheets.

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5630 Strandebarne, 22.11.2013
HANS T. HAUKÅS AS

Hans T. Haukås

Some definitions

Absorption system: A refrigeration system where the refrigerant vapour from the evaporator is absorbed by an absorbent (eg ammonia in water). The refrigerant is subsequently driven out at a higher (partial) pressure by heating, and liquefied by cooling.

Cascade heat exchanger: The evaporator/condenser in a cascade system

Cascade system: Two or more refrigeration systems where the condenser heat of one system is rejected directly in the evaporator of another system.

Coefficient of performance (COP): The ratio of the heat absorbed by the system and the supplied work (COP for refrigeration systems), or the ratio of the heat rejected by the system and the supplied work (COP for heat pumps)

Direct system: See Information sheet 3.1.1

Heat transfer fluid: See Information Sheet 3.2.1

Hydrocarbon: See Information sheet 2.3.1

Indirect system: See Information Sheet 3.1.1

Ppm: Parts per million

Transcritical cycle: See Information Sheet 2.2.4

1.1 Overview over natural refrigerants

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Overview over natural refrigerants

“Natural” and “non-natural” refrigerants – what is the difference?

- “Natural refrigerants” are chemicals that exist naturally in the environment
- “Non-natural refrigerants” are man-made chemicals, not naturally found in the environment

Why natural refrigerants?

- No or minor effect on global warming
- In many cases the lowest life cycle cost
 - > Non-natural refrigerants are generally costly (15 - 35 EUR/kg)
 - In Denmark and Norway, they incur a heavy environmental tax
 - > Non-natural refrigerants are often less energy efficient, particularly at high condensing temperatures
- No risk of future use restrictions or environmental taxes

Which refrigerants are natural?

- **Most commonly-used natural refrigerants today:**
 - > Ammonia (NH₃, R-717), Carbon dioxide (CO₂, R-744), Hydrocarbons - eg Propane (R-290), Propylene* (R-1270), Iso-butane (R-600a)
 - Even water and air are used to a minor extent (for special applications)
- **Natural refrigerants no longer in use:**
 - > Sulphur dioxide (SO₂), Methyl chloride (CH₃Cl)

* Also named “propene”

General information on natural refrigerants

Which refrigerants are non-natural?

- **Non-natural refrigerants are found within the following groups of chemicals**
 - > CFCs (chloro-fluoro-carbons , eg CFC-12)
 - > HCFCs (hydro-chloro-fluoro – carbons, eg HCFC-22)
 - > HFCs (hydro-fluoro-carbons, eg HFC-134a)
 - > PFCs (per-fluoro-carbons, eg PFC-218)
 - A constituent of some refrigerant blends)
 - > HFOs (hydro-fluoro-olefines, eg HFO-1234yz)
 - Unsaturated HFCs
 - Low-GWP fluids under development

Importance of refrigerant selection

- **The refrigeration cycle is principally the same, regardless of the type of refrigerant chosen**
- **Type of refrigerant affects:**
 - > Dimensions of components, especially compressor and tubing
 - > System design details and construction materials
 - > Energy efficiency
 - > Investment and running costs
 - > Technical and administrative measures to safeguard against danger to people in the event of refrigerant release
 - > Environmental impact if released to the atmosphere

Harmful effects from refrigerant release

- **CFCs, HCFCs, HFCs and PFCs are hazardous, on a global scale, to the environment, and can also be dangerous on a local scale in the event of high gas concentrations from a release**
 - > Ozone depletion (CFCs, HCFCs)
 - > Contribution to global warming (CFCs, HCFCs, HFCs, PFCs)
 - > Asphyxiation due to oxygen displacement
 - No smell
 - > Toxic break down breakdown products when heated
 - > Low GWP HFCs (HFOs), eg HFO-1234yf, are (mildly) flammable
- **Release of natural refrigerants is virtually harmless to the global environment, but has to be avoided for health and safety reasons:**
 - > Ammonia: Toxicity, flammability, asphyxiation
 - > Carbon dioxide: Toxicity, asphyxiation
 - > Hydrocarbons: Flammability, asphyxiation

General information on natural refrigerants

Measures to reduce the consumption of non-natural refrigerants (in EU/EEA)

- Total ban on the use of CFCs (from 1995)
- Ban on the use of HCFCs in new equipment (from 1997/2004)
- Only reclaimed HCFC permissible for service purposes since January 1, 2010, total ban on HCFC use from January 1, 2015
- Heavy environmental taxes on HFCs in some countries, eg Norway and Denmark
- Restrictions on the use of HFC in some countries, eg Denmark (max 10 kg HFC/charge)
- EU regulations covering the use of HFCs and PFCs (F-gases) are in force:
 - > As part of the EU/EEA countries' efforts to comply with the Kyoto Agreement

Disadvantages of natural refrigerants

- **Ammonia:**
 - > Toxic and corrosive, but easily detectable (through its smell)
 - > Flammable, but only within a narrow band of concentration, and is hard to ignite
 - > Pungent smell can cause panic, but gives an early warning of a leak
- **Carbon dioxide:**
 - > Low critical temperature
 - Challenges with respect to energy efficiency for certain applications, especially in warm climates
- **Hydrocarbons:**
 - > Highly flammable when mixed with air, but the flammability issue is manageable

Where natural refrigerants can be used

- Natural refrigerants can, in principal, be used in most applications – just as they were in the early days of refrigeration
 - > Even though the number of applications has risen substantially since then, and the safety requirements have become much stricter
- An overview of applications is given in Information Sheet 1.3

1.2 Some historical facts

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Some historical facts

The first refrigeration systems

- The first mechanical refrigeration system was built by Jakob Perkins in 1834
 - > Compression/evaporation cycle with ethyl ether as refrigerant
- A refrigerating machine using air was invented by John Gorrie (1844)
 - > Gas cycle with compressor and expander
- Ferdinand Carré used the absorption principle in his refrigerating machine (1859)
 - > Heat driven refrigeration system using ammonia/water
- Up until about 1880, the air and absorption machines dominated
- After 1880, compression/evaporation machines gradually took over
 - > Mainly as a result of the ammonia compression machine
 - > In addition to ammonia, chemicals such as carbon dioxide (CO₂), propane, methyl chloride, sulphur dioxide, etc were used

Typical usage pattern towards the Second World War

- Ammonia was used in industrial systems and (to some extent) on board ships
- CO₂ was primarily used for marine refrigeration
- Methyl chloride, sulphur dioxide and propane were used in domestic refrigerators and other small systems

General information on natural refrigerants

New refrigerants

- **The first refrigerating systems were technically simple and prone to leaking**
 - > For health and safety reasons, refrigerants that were harmless to people were sought
- **New, non-natural refrigerants were introduced around 1930**
 - > CFC-12 and CFC-11 came first: followed by HCFC-22 and CFC-502
 - > The new fluids were neither toxic nor flammable, and they were odourless
 - > Marketed as "safety refrigerants", and reasonably priced
 - > Much easier to handle than the old chemicals
 - > Environmental problems were not known about and recharging without first fixing leaks were not uncommon
- **Natural refrigerants were not competitive**
 - > Practically eliminated by about 1960, with the exception of ammonia, which continued to be used in large industrial systems

Even the new fluids could be dangerous

- **The actual safety of the "safety refrigerants" was in many cases questionable**
 - > Several fatal accidents due to suffocation from air displacement

Depletion of the ozone layer

- **The consumption of CFCs and HCFCs steadily increased**
 - > Exceeded 1 million tonnes per year in the mid-80s
- **By 1974, M.J. Molina and R.F. Rowland had already documented that, in laboratory tests, CFCs could, under certain circumstances, deplete ozone**
- **Measurements demonstrating reduction of the ozone layer over the Antarctic were published in 1985**
- **The findings led to the Vienna-Convention in 1985 and the Montreal Protocol in 1987:**
 - > Binding agreement on phasing out ozone depleting substances
- **HFCs were developed to replace CFC and HCFC**
 - > No ozone-depleting effect

General information on natural refrigerants

Global warming

- **Some gases absorb heat radiation from the earth and thereby affect the earth's heat balance**
 - > Designated "greenhouse gases"
 - > Water vapour and carbon dioxide are the most important greenhouse gases, because they exist in such large volumes
 - > Ozone depleting substances like CFCs and HCFCs are strong greenhouse gases
 - Phasing out CFCs and HCFCs favourable also regarding global warming
 - > Most HFCs are also strong greenhouse gases
 - HFC-134a has 1430 times stronger greenhouse effect than CO₂, HFC-404A is 3922 times stronger
- **Worries about the greenhouse effect of HFCs were already being raised at the time of the Montreal Protocol**
 - > But no other alternatives could replace CFCs and HCFCs fully in the short term

Increasing interest in natural refrigerants

- **Adverse environmental effects of CFCs, HCFCs, and HFCs have greatly increased the interest in natural refrigerants**
 - > Natural refrigerants are offered for an increasing number of applications
 - > No technical limitations to their application
 - > Equipment and systems are constantly improving and the number of applications is expanding
 - > Competitive, in terms of cost and energy efficiency, for an increasing number of uses

1.3 Natural refrigerants – applications

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Natural refrigerants – applications

Domestic appliances

- All domestic appliances made in Europe use iso-butane, a hydrocarbon (R-600a)
- An increasing number of units made in big manufacturing countries like China, India and Brazil also use iso-butane
- Iso-butane fridges available also in the USA
- Heat-driven appliances (portable units, minibars etc) have absorption systems which use ammonia and water
- Units are marked on the back with type of refrigerant and the amount charged
 - > Typically 70 – 100 g

Commercial plug-in units

- **Plug-in units are available with hydrocarbon refrigerant**
 - > Professional appliances: cabinets in shops, supermarkets, restaurants etc., bottle coolers, wine coolers, water coolers, and so on
 - > Refrigerants are iso-butane (R-600a), propane (R-290), propylene (R-1270)
 - > Refrigerant charge up to 150 g
 - > No limitations on where the units can be sited
- **Big multinational companies within in the food and beverage sector, are changing over from HFCs to natural refrigerants**
 - > More than 1 million units in operation with iso-butane, propane and CO₂
 - > Bottle coolers, vending machines, ice cream cabinets etc.

General information on natural refrigerants

Smaller commercial refrigerating systems ("condensing units")

- For use in shops, filling stations, kiosks, restaurants, smaller cooling or freezing stores, etc
- **Use of ammonia is technically possible**
 - > Scroll compressor for ammonia has been developed
 - > But practical hinders
 - costly for small systems
 - components not available for the smallest systems
- **Use of hydrocarbons possible under certain circumstances**
 - > System charge and the location/positioning of equipment are of particular importance
 - > Most suitable for use in indirect systems
- **Condensing units with CO₂ in transcritical cycle have been marketed. A limited number in operation (2013)**

Commercial refrigeration – centralised systems for supermarkets

- **Transcritical CO₂-systems have become the preferred solution by many supermarket chains**
 - > Especially suitable for heat recovery, making the systems very energy efficient
 - > Nearly 3000 systems in operation in Europe
- **CO₂ in the low temperature stage of cascade systems is another common solution:**
 - > Preferably with ammonia or an hydrocarbon in the high temperature stage
 - > Utilising the excellent low temperature properties of CO₂
 - CO₂ for freezing purposes only, conventional heat transfer fluid for cooling
 - CO₂ for both freezing and cooling
- **Ammonia and hydrocarbons (propane, propylene) are suitable for indirect systems**
 - > With conventional brine or heat transfer fluid with phase change (CO₂)
 - > Positioning units outdoors (eg on the roof) is preferable with hydrocarbons
- **Technical solutions based on natural refrigerants are competitive, both in terms of cost and energy efficiency**

General information on natural refrigerants

Industrial refrigeration systems

- **Ammonia is the most commonly used refrigerant in large systems**
 - > Systems erected on site
 - > Packaged systems
 - > Liquid chillers
- **New solutions based on combinations of ammonia and CO₂**
 - > Ammonia as the primary refrigerant and CO₂ as a heat transfer fluid with phase change
 - > Cascade systems using ammonia/CO₂
 - Low temperature requirements covered by CO₂
 - Cooling at intermediate temperature levels (cooling) covered by ammonia or CO₂
- **Hydrocarbons (propane/propylene) can be used for several applications, eg:**
 - > For chillers
 - Placing on the roof often appropriate
 - > For high temperature stage of cascade systems
 - > For ultra low temperature freezers (R-170, ethane) -80C
 - > In equipment sited in a potentially explosive atmosphere, eg within the oil and gas industry
- **Systems using CO₂ as the only refrigerant (transcritical cycle):**
 - > Primarily for small and medium sized systems
 - > Particularly appropriate when combined with heat recovery

Fishing vessels

- **Ammonia important as replacement for HCFC-22**
 - > Particularly efficient for refrigerated sea water (RSW)
 - > Also suitable for freezing:
 - Used for temperatures down to -54°C
 - In direct, as well as in indirect, systems
 - In case of indirect systems, CO₂ is preferable as heat transfer fluid
- **Cascade systems with ammonia and CO₂ are in use**
 - > Substantial increase in freezing capacity compared to traditional solutions
- **An RSW chiller with CO₂ has been installed in a Norwegian fishing vessel**
 - > Subcritical or transcritical operation depending on sea water temperature
 - > Reliable and energy efficient
 - > Still somewhat more expensive than with HFCs
 - > A promising solutions for the future, especially for smaller vessels

General information on natural refrigerants

Ice sports facilities

- **Ammonia is suitable, and is widely used, in both indoor and outdoor facilities**
 - > In direct systems:
 - Steel piping embedded in a concrete floor
 - Pump circulation
 - > In indirect systems:
 - The preferred solution in new installations
 - With conventional heat transfer medium, for example calcium chloride
 - With CO₂ as heat transfer fluid with phase change
- **Ammonia is also used in heat pumps to boost the temperature of the rejected heat from the condensers**
 - > For space heating and creating hot tap water
 - > For internal use and for sale to neighbouring buildings or district heating systems

Air conditioning

- **In China, production lines for room air conditioners are being converted from HCFC-22 to R-290 (propane)**
- **AC chillers with ammonia and hydrocarbons (propane, propylene) are standard**
 - > Specific requirements apply to the siting of systems and to safety precautions
 - Important that refrigerant selection is made in the early stages of planning
 - > Significantly more energy efficient than with HFC
- **AC systems with CO₂ in transcritical cycle are available**
- **CO₂ is particularly suitable where water leakage may be critical: eg cooling of computer rooms**
- **AC systems should be designed to take advantage of free cooling whenever possible:**
 - > Eg for cooling computer rooms during the winter time
 - > Such systems using natural refrigerants are available

General information on natural refrigerants

Heat Pumps

- **Ammonia is generally the most energy efficient refrigerant to use in heat pumps**
 - > Particularly suitable for large systems:
 - Industrial heat pumps, including heat recovery from refrigeration systems
 - Connected to hydronic heating systems for large buildings, district heating systems, etc
 - > Water temperatures up to 90°C can be achieved with high pressure compressors (60 bar)
 - Even higher temperatures can be reached at 25 bar by using hybrid systems with ammonia and water, combining the compression and absorption cycles
- **Hydrocarbons (propane/iso-buthane) are suitable for many applications:**
 - > Heat recovery from exhaust air
 - > Where standard chillers can be safely used (eg when sited outdoors)
 - > For high temperature heat pumps (up to 80-90C)
- **CO₂ is also suitable for heat pumps**
 - > Particularly where there is a significant rise in temperature in the fluid absorbing the heat, eg for heating tap water
 - > Small CO₂ heat pumps commercially available

Mobile air conditioning systems (MAC)

- MAC is the potentially biggest application area for CO₂ refrigerant
- Some models can be reversed so that they quickly provide heat
- Leading German car manufacturers have announced that MAC systems with CO₂ will be introduced by 2016
 - > May be adopted by other car manufacturers
- Hydrocarbons (propane) technically well suited, but rejected by the car industry for safety reasons

Special applications

- Cascade systems with ethane and propane/ammonia are used for very low temperatures (-80°C and below)

1.4 Energy efficiency

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Natural refrigerants for new applications

TOPIC: Energy efficiency

General measures

- **1: Reduce the refrigeration demand as much as**
 - > Should always be the first step
- **2: Reduce the difference in temperature between the warm and cold sides of the system:**
 - > The energy demand varies in proportion to the temperature difference
 - > A 1°C increased temperature difference increases the energy demand by 2-4 %
- **3: Choose an energy-efficient refrigeration system:**
 - > A direct system is normally more energy efficient than an indirect system
 - > A two-stage system, or a cascade system, should be used where there are big temperature differences (freezing systems, high temperature heat pumps)
 - > The transcritical CO₂-cycle is suitable for heating with large rises in temperature
- **4: Choose an energy-efficient refrigerant**
 - > Ammonia gives (in most cases) the theoretically most energy-efficient cooling or heat pump cycles
 - > Hydrocarbons are often more energy efficient than HFCs
 - > The thermophysical properties of CO₂'s ensure small losses in the practical process
 - CO₂ often proves to be competitive in practice, in terms of energy efficiency, while the theory may suggest otherwise

General information on natural refrigerants

Freezing systems

- **A two-stage system using ammonia is the most energy efficient solution for evaporation temperatures of down to approximately -35°C**
 - > The energy consumption with HFC-404A/507A in a one-stage system is theoretically 15-20 % greater. The actual difference may be significantly higher
- **Cascade systems using CO₂ in the lower stage and ammonia in the upper stage are the most energy-efficient designs for evaporation temperatures below -35°C**
 - > Appropriate solution for all freezing systems where it is considered important to keep all the ammonia in the machinery room
- **Using CO₂ as a heat transfer fluid with phase change creates the most efficient indirect system:**
 - > Lower energy consumption than direct systems using HFC-404A/507A
 - > Significantly lower energy consumption than indirect systems using conventional heat transfer fluids
 - The CO₂ pumps in a freezing system of 500 kW cooling effect will typically consume 2-3 kW electric power compared to 30-40 kW with eg calcium chloride
- **See separate information below about transcritical CO₂-systems**

Refrigeration systems for cooling and air conditioning, heat pumps

- **Using ammonia is the most energy efficient solution for both direct and indirect systems**
 - > Direct systems are normally only found in industrial applications
 - > (Larger) AC-systems and heat pumps are often designed with indirect cooling/heating, with all types of refrigerant
 - Makes the use of ammonia possible, and more cost effective
- **Using ammonia as refrigerant, and CO₂ as a volatile heat transfer fluid, creates the most energy-efficient indirect systems**
 - > Equivalent or lower energy consumption than when using HFCs in a direct system
- **Propane and propylene may be energy-efficient alternatives to HFC:**
 - > In indirect systems
 - Chillers with hydrocarbons are typically 10-15 % more energy efficient than with HFCs
 - > In small, low charge systems
- **See separate information below about transcritical CO₂-systems**

General information on natural refrigerants

Systems using CO₂ in transcritical cycle

- **Particularly energy efficient with large temperatures increases in the heat absorbing fluid, such as:**
 - > Heat pumps for hot tap water production
 - > Refrigeration systems with heat recovery to fresh ventilation air
- **Competitive, as far as energy efficiency is concerned, in many other cases**
- **Experience from supermarket refrigeration:**
 - > Similar or better than HFC in direct systems
 - > Significantly better than HFC in indirect systems
 - > Discharged heat easily utilised due to the high temperature, further improving system energy efficiency
 - > Energy efficiency improved year by year due to improved component and system designs

1.5 Sources of further information about natural refrigerants

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Sources of further information about natural refrigerants

General information on safety and environmental requirements

- **EN-378 Refrigerating systems and heat pumps – Safety and environmental requirements**
 - > European refrigeration standard
 - equivalent international standard: ISO 5149
 - > Covers systems and equipment with any type of refrigerant

Information on natural refrigerants

- **Eurammon**
 - > "a centre of competence for the use of natural working fluids in refrigeration"
 - > Publishes among others information papers on the use of ammonia and other natural refrigerants, including a number of case-studies
 - > Web address: <http://www.eurammon.com>
- **Natural refrigerants industry platforms**
 - > News, products, companies, events, papers
 - CO₂: <http://www.r744.com>
 - Ammonia: <http://www.ammonia21.com>
 - Hydrocarbons: <http://www.hydrocarbons21.com>
 - Water: <http://www.r718.com>

General information on natural refrigerants

Information on alternatives to HCFCs

- **Nordiske indsatser for R-22 i køleanlæg på skibe,**
TemaNor, 2011:503
Nordisk Ministerråd, København 2011
ISBN 978-92-893-2191-4
<http://www.norden.org/no/publikationer/publikasjoner/2011-503>

Companies offering equipment and systems using natural refrigerants

- **Contact details for the trade organisations for refrigeration system suppliers in the Nordic countries:**
- **Sweden:**
Kyl-och Värmepumpföretagen
Box 47122, S - 100 74 Stockholm
Tel.: +46 8 762 75 00
Web address: <http://skvp.se/>
- **Denmark**
Autoriserede Kølefirmaers Brancheforening (AKB)
Vestergade 28, DK - 4000 Roskilde
Tel.: +45 4632 2111
Web address: <http://www.koeleteknik.dk>
- **Norway**
VKE – Foreningen for Ventilasjon, Kulde og Energi
Postboks 5467 Majorstuen, N - 0305Oslo
Tel.: +47 23087701
Web address: <http://www.vke.no>
- **Iceland**
Kælitækni félag Íslands
Icelandic Association of Refrigeration
Smidjuvegi 11E, 200 Kópavogi
Web address: <http://www.kti.is>
- **Finland**
Finnish Refrigeration Enterprises Association (FREA)
Hiihtomäentie 39 A1, FIN - 00800 Helsinki
Tel.: +358 9 759 11 66
Web address: <http://www.skll.fi>

2.1 Ammonia

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Natural refrigerants for new applications

TOPIC: Basic information on ammonia (NH₃) as refrigerant

Characteristics of ammonia refrigerant

- Well-known and well- proven after 150 years of use
 - > Robust systems
- For many applications, the most energy-efficient refrigerant:
 - > Efficient theoretical cycle over a broad temperature range
 - > Small compressor losses
 - > Efficient heat transfer in evaporators and condensers
- Cheap in comparison to HFC refrigerants
- A very pungent odour
 - > Leaks easily detected
- Toxic and flammable
 - > But the smell provides an early warning
- Copper, zinc and alloys containing either of these metals cannot be used as construction material
- Very low miscibility with conventional refrigeration oils

Energy efficient refrigeration/heat pump cycle

- Theoretical energy consumption for refrigeration systems typically 5 – 10 % lower than when using HFCs
- Theoretical energy consumption for heat pumps typically 10 – 20 % lower than when using HFCs
- In practice, the energy efficiency differences are often greater than calculated theoretically

Natural refrigerants – practical use

Health and safety, and environmental issues (HSE)

- **Health and safety**
 - > Dangerous when inhaled in moderate/high concentrations
 - > Ammonia liquid corrosive to skin
 - > Ammonia gas mixed with air may be flammable
 - > The smell may frighten people unfamiliar with ammonia
- **Practical safety**
 - > Ammonia has proved to be safe in practical use
 - The characteristic smell gives an early warning
 - Sound safety procedures established
- **Environmental issues**
 - > In general, ammonia is an environmentally benign substance
 - Is part of nature's own cycle
- More detailed information given in Information Sheet 2.1.2

Design of ammonia systems

- Direct systems are used when feasible (mainly industrial applications)
- Indirect systems are becoming more common:
 - > No ammonia outside the machinery room
 - > Minimised ammonia charge
 - > No risk of polluting goods in store due to ammonia leakage
- Reference is made to Information Sheet 2.1.3 and 3.1.1

New/extended applications for ammonia refrigerant

- Industrial and commercial purposes in combination with CO₂ (cascade systems)
- (Large) commercial cold stores, medium and low temperature
- (Large) air conditioning systems
- (Large) heat pumps
- Refrigeration systems on board ships, especially fishing vessels
- For examples, see Information Sheet 6.1

NMR's Information Sheets

Natural refrigerants for new applications

**TOPIC: Health and safety, and environmental issues (HSE)
with ammonia refrigerant***Aspects that may represent a safety risk*

- **Dangerous to health**
 - > Toxic
 - > Corrosive
- **Flammable at high concentrations**
- **Pungent smell that may create panic**

Safety properties 1 - danger to health

- **Ammonia is dangerous to health in moderate/high concentrations**
- **Toxic**
 - > Acutely dangerous to inhale in concentrations above 1500 – 2000 ppm¹ (0.1 – 0.2 vol.%)
 - > Possible to smell at 5-20 ppm:
 - Less than 1 % of acutely dangerous concentration
 - Efficient warning
 - > TLW = 25 ppm, in most countries (TLW = Threshold Limit Value)
 - Possible to smell for most people
 - > IDLH = 300 ppm (IDLH = Immediately dangerous to Life and Health)
 - Most people will find this level very unpleasant and will quickly leave the room
 - > Ammonia does not accumulate in the body
 - > No long-term health effects (unless exposed to very high gas concentrations)
 - > Serious poisoning very uncommon
- **Corrosive**
 - > In case of direct contact with ammonia liquid
 - May cause severe burns (and frost bite similar to all refrigerants)
 - Eyes particularly vulnerable to severe damage

¹ ppm – parts per million

Natural refrigerants – practical use

- **Irritant**
 - > If exposed to gas (at high concentrations)
 - > Ammonia gas can be absorbed in moist areas of the body, eg eyes and respiratory tract
 - (Severe) irritation of the affected area
 - > Impossible to keep eyes open for long at high gas concentrations
 - Impaired vision may hinder escape

Safety properties 2 - flammability

- **Ammonia gas mixed with air can be ignited:**
 - > But only within a rather narrow concentration range, approx. 15-28 vol. %, corresponding to 105 – 196 gram per m³ room volume
 - > A strong source of ignition is required and a high temperature
 - > Impossible to ignite accidentally by a bystander
 - Ignition only possible at gas concentrations too high for a person to tolerate
 - > Ignition outdoors is practically impossible
- **Ammonia is, in many cases, considered not flammable, eg in hazard classifications**
- **Machinery rooms for ammonia are not classified as areas with potentially explosive atmosphere**
 - > Certain measures to minimize the possibility of fire still need to be taken
 - > Reference is made to Information Sheet 4.2

Safety properties 3 – “bad” smell

- **Ammonia has a very characteristic, pungent smell**
 - > Can be smelled at very low concentrations
 - > Gives an early warning of leakages
 - Encourages good maintenance
 - Important contribution to ammonia safety
 - > The smell becomes very unpleasant for most people at 10 % of acutely dangerous concentration
 - People move away before the concentration represents any immediate health risk
 - Dangerous situations may occur if it is difficult or impossible to escape
 - > Intolerable below half lethal concentration, even for a very short period of time
 - > Panic may ensue if gas leaks into public areas
- **Ammonia has proved to be safe in practical use**
 - > Thanks to its bad smell
 - > Main reasons for serious accidents:
 - Operating/service personnel being insufficiently protected when doing service operations
 - Lack of, or blocked, escape routes
 - Lack of proper training

Natural refrigerants – practical use

Other properties concerning safety

- **Ammonia gas is lighter than air**
 - > If released, the gas will rise and dilute as it mixes with air – but
 - > Ammonia-containing air may blow down in unfavourable winds and/or topography
- **Aerosol from a liquid spill is heavier than air and will take time to evaporate and rise**
- **Ammonia gas is effectively absorbed in water**
 - > Water can be used to clean air contaminated by ammonia gas
 - > Water must not be used on a liquid spill (increases the evaporation rate)
 - > Reference is made to Information Sheet 5.2

Safety strategies

- **Avoid equipment and systems with ammonia in areas with public access**
 - > Systems and equipment should be placed in a dedicated machinery room
- **Avoid the possibility of ammonia-contaminated air reaching public spaces, especially where people tend to gather**
- **Reduce the system charge as much as possible, particularly if ammonia is used close to populated areas**
- **Follow the recommendations given in national regulations and relevant (international) standards during system design, construction, operation and maintenance/control**
- **Establish safe routines for all handling of ammonia, including personal protection**
 - > Most incidents and accidents occur during system servicing and during tapping/-charging of systems
 - > Regular training and updating of operators and service/maintenance technicians
- **Provide early warning of leakage by installing gas detectors with automatic alarms**
- **Assess thoroughly where the gas will/may spread in the event of a leak**
- **Set up well-marked escape routes where required**
- **Establish reasonable procedures for raising the alarm, and organising escape and rescue in the event of a major release**
 - > In cooperation with local rescue services
 - > Regular exercises involving all employees
- **Be prepared and equipped to handle minor injuries on site:**
 - > Equipment and routines for first aid to hand
 - > Provide training to all employees

Natural refrigerants – practical use

Environmental issues

- **Ammonia does not contribute to ozone depletion or global warming**
- **Ammonia is very toxic to fish and other organisms living in water**
 - > Absorption of ammonia in water should only be used as a safety precaution
 - > Water that contains ammonia has to be handled with care (special waste)
 - Reference is made to Information Sheet 5.2
- **Ammonia in the air contributes to over-fertilising with nitrogen**
 - > Deliberate release of ammonia into the air should be minimised

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Practical matters when using ammonia refrigerant

High discharge temperature

- **The temperature of ammonia gas rises considerably during compression**
 - > High discharge temperature restricts the pressure increase in one step compression
 - > Two-stage compression with interstage cooling solve the problem:
 - Extensively used for freezing purposes
 - More expensive, but also more energy efficient
 - > Using oil-injected screw compressors is another possibility:
 - The gas is cooled by the oil
 - Appropriate for large systems
 - Less expensive than two stages – but also less energy efficient

Compatibility with construction materials

- **Copper, and alloys containing copper or zinc, cannot be used**
 - > Corroded by (wet) ammonia
- **Steel, stainless steel, and aluminium are all suitable**
- **Ammonia corrodes steel when the surrounding air is moist**
 - > Easily detectable in the vicinity of minor leaks
 - > Corrosion may stick (leaking) safety valves
 - Exposure of safety valves to air has to be prevented, eg by an oil lock
- **Stress corrosion cracking may occur in "completely" water-free ammonia**
- **Ammonia systems do not corrode from the inside, even with water present**
- **Ammonia is compatible with various types of elastomers used in seals and gaskets**
 - > Viton should not be used
- **Ammonia dries out organic seals and gaskets in valves etc. Oil lubrication prevents leakage**

Natural refrigerants – practical use

Ammonia and compressor oils

- **Conventional refrigeration oils (mineral and synthetic) are practically immiscible with ammonia liquid and vice versa**
 - > The oil does not become diluted by the refrigerant and the lubrication properties remain intact
 - > Complicates automatic oil return (to some extent), especially in low temperature systems
 - > Oil management may differ
 - Compact systems, eg chillers, mostly uses automatic oil return
 - (Industrial) systems erected on site mostly use manual oil tapping
- **Oil is heavier than ammonia liquid**
 - > Oil may be tapped manually from the low points where it settles
 - > Normally, tapped oil is not re-used
- **Some synthetic oils, eg polyalphaolefins (PAO), and specially-treated mineral oils, result in less oil from the compressor and maintain viscosity better at high temperatures**
- **O-rings and gaskets shrink when in contact with PAO-oil, after a change from mineral oil**
 - > Leakage may result if the gaskets are not changed at the same time
- **Lubricants which are miscible with ammonia, eg polyalkylene glycols (PAG), are used to a certain extent**
 - > Oil return as with HFCs
 - > Problems due to the PAG's hygroscopicity reported

Water in ammonia systems

- **During operation at sub-atmospheric evaporation pressure, moist air will over time enter the system in the event of a leak**
 - > Water will accumulate in the system, air will be removed by the purger
 - > System capacity and energy efficiency will be reduced
 - > The water must be removed (by distillation)
- **Water in ammonia systems does not result in ice blocking the expansion valve etc**
- **Water content in ammonia prevents stress corrosion**

Natural refrigerants – practical use

Ammonia and other refrigerants

- **Ammonia reacts chemically with HCFC-22 to form a powder (salt)**
 - > May block expansion valves, filters etc.
 - > Care has to be taken to always charge the correct refrigerant
- **Ammonia reacts chemically with CO₂**
 - > Similar results, and consequences, as described for HCFC-22 above
 - > Ammonia/CO₂ cascade heat exchangers have to be secured as far as possible against CO₂ leakage to the ammonia side
 - > The chemical reaction between CO₂ and ammonia can be used to clean a room (eg a cold store) of ammonia gas after a leak
 - Has to be carried out according to specific instructions
- **Ammonia reacts with polyolester lubricants and forms a polymer**
 - > "Ester oils" for HFCs or CO₂ must not be used in ammonia compressors

Ammonia and goods in storage

- **Ammonia leakages in a cold store may/will damage the goods**
 - > Unwrapped goods and goods without diffusion-tight wrapping particularly vulnerable
 - > Valves and other components prone to leakage should be placed outside the room

Electrical installations

- **Electrical installations in rooms with ammonia-containing components do not have to comply with requirements for equipment in possibly explosive atmospheres**
- **Separate rules apply for machinery rooms**
 - > National regulations and refrigeration standards need to be followed
 - > Reference is made to Information sheet 4.2

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Heat pumps using ammonia as refrigerant

Why ammonia for heat pumps?

- Heat pumps normally operate with higher heat rejection temperatures than refrigerating systems
- The process losses increase rapidly as the condensing temperature approaches the critical temperature for the refrigerant:
 - > The coefficient of performance (COP) decreases accordingly
- **Ammonia's critical temperature is much higher than for other refrigerants**
 - > For example: 133°C as opposed to 73°C for HFC-407C
 - > Makes the basis for high theoretical COP for heat pumps
 - Eg at 0/65°C: HFC-407C: COP= 3.4, Ammonia: COP = 4.2 (+ 24 %)
- **Particularly beneficial in heat pumps designed for relatively high temperature heat rejection**
 - > Eg heat pumps in district heating systems
- **Thermally-stable chemical:**
 - > No thermal breakdown even at very high gas temperatures

Natural refrigerants – practical use

Important considerations when using ammonia in heat pumps

- **High discharge temperatures**
 - > May lead to compressor oil coking
 - Choose an oil-type suitable for high temperatures
 - > Apply oil-injected screw compressors
 - > Apply two-stage compression with interstage cooling
 - COP improvement in addition
- **The heat-distribution water becomes corrosive if ammonia leaks into the water**
 - > Use heat exchanger designs that minimise the probability of leaks
 - > Check water quality at regular intervals
 - > Install automatic ammonia detector in the water circuit (bigger systems)
- **Tap water heaters must be designed to prevent any ammonia from leaking into the water**
 - > Use an intermediate water loop
 - > Use double-wall heat exchangers, and externally ventilate the gaps
- **When considering new systems and equipment close to public areas, carry out a thorough risk analysis on the impact, and area, of any gas leak**

Equipment availability

- **The standard design pressure for system components has (until recently) been approximately 25 bar g:**
 - > This limits the leaving water temperature from the condenser to about 50°C
 - Too low a temperature for many applications
- **The availability of components for higher pressures is improving**
 - > Partly as a result of adapting design pressures to meet the needs of high pressure refrigerants, like CO₂ and R-410A
 - > "New" pressure classes are eg: 40 bar, 52 bar, 60 bar, 120 bar
 - > Leaving water temperatures up to approximately 70°C and 90°C can be achieved, for 40 bar and 60 bar systems respectively

Natural refrigerants – practical use

Compression/absorption cycle with ammonia/water

- **The compression/absorption cycle is an alternative to the conventional compression cycle where high temperatures are required:**
 - > Absorption cycle with gas compression ("hybrid heat pump")
 - > Particularly suited for recovery of (industrial) waste heat
 - > An ammonia/water solution is circulated by pump in bypass to the compressor
 - > The condenser is replaced by an absorber
 - > The evaporator is replaced by a desorber
- **Heat delivery at 100°C and above is possible with conventional 25 bar equipment**
- **The principle was first described over 100 years ago**
 - > But not used to any significant extent
- **The first system in Norway was commissioned in 2003:**
 - > Heat recovery in a dairy
 - > A number of systems in operation today, in Norway and abroad

Ammonia in heat pumps for non-industrial space heating

- **Several hundred heat pumps with ammonia installed in Norway since 1990**
 - > The majority for industrial heat recovery
 - > An increasing number for heating of non-industrial buildings
 - > Large systems
 - Heat capacities up to 14 MW
 - > Often in combination with (comfort) air conditioning
- **Systems for any temperature range**
 - > Up to 90°C in the conventional cycle
 - > 100°C and above in absorption/compression cycle
- **Good track record in terms of:**
 - > Technical reliability
 - > Energy saving
 - > Safety
- **Reference is made to Information Sheet 6.1**

2.2 Carbon dioxide (CO₂)

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Basic information on carbon dioxide (CO₂) as a refrigerant

Characteristics of CO₂ as a refrigerant

- **Low critical temperature (approximately 31°C)**
 - > Gas liquefaction above this temperature is impossible
 - The refrigeration cycle becomes transcritical²
 - Sensible heat rejection (no phase change)
 - > Application of the ordinary refrigeration cycle restricted to a condensing temperature of approximately 24 - 26°C
- **Higher system pressures than with other refrigerants**
 - > Eg approximately 68 bar at 28°C condensing temperature
 - > Up to 100 bar (or above) on the high side in transcritical systems
- **High temperatures achievable for heat rejection, eg 80°C**
 - > In transcritical cycle
 - > A large temperature rise is required in the fluid absorbing the heat in order to achieve a high COP
- **Favourable refrigeration properties**
 - > Closer theoretical and practical performance compared to other refrigerants
- **High triple point pressure and temperature**
 - > Converts to solid CO₂ (dry ice) at pressures below approx. 4.2 bar g (-56.6°C)
- **The cheapest refrigerant**
- **Can be applied in direct systems like HFCs**

Ways of using CO₂ in refrigeration/heat pump cycles

- **As heat transfer fluid with phase change in indirect systems**
- **As refrigerant in the low stage cycle of cascade systems**
 - > The CO₂ condenser cooled by another refrigerant in the top cycle
- **As the only refrigerant in an ordinary refrigeration cycle with condensation**
 - > Requires low temperature cooling fluid to be available for the condenser

² Transcritical cycle – Refrigeration (heat pump) cycle operating supercritically on the warm side and subcritically on the cold side

Natural refrigerants – practical use

- **As refrigerant in a transcritical cycle**
 - > No gas condensation, the condenser works as gas cooler
 - Large temperature glide, eg 50–60°C
 - > Can be used, technically, for most purposes
 - > Particularly suitable for simultaneous cooling and heating
 - > Greater throttling loss than for a conventional cycle
 - Can partly be recovered with new technology
 - > Alternating between subcritical and transcritical operation when the heat sink temperature varies over time, eg heat rejection to ambient air

Health and safety, and environmental issues (HSE)

- **Health and safety**
 - > CO₂ is not flammable, nor acutely toxic
 - > Dangerous in higher concentrations
- **Environment**
 - > No ozone depletion
 - > Insignificant contribution to global warming
 - The refrigerant is recovered from other industrial processes
 - > No negative effect on the local environment
- **More HSE details is found in Information Sheet 2.2.2**

Use areas for CO₂

- **As heat transfer fluid in (large) indirect systems, any application**
 - > Eg within supermarket refrigeration and industry
 - > For info, see Information Sheet 3.2.1
- **As low temperature refrigerant in cascade systems**
 - > Industrial applications, in particular large low temperature systems
 - Freezing tunnels, plate freezers etc.
 - > Commercial applications, e.g. supermarkets
- **In transcritical cycle**
 - > Retail refrigeration (supermarkets)
 - With or without heat recovery
 - > Small cooling or freezing units
 - Soft drinks vending machines, bottle coolers, ice cream cabinets etc.
 - > Heat pumps for high temperatures and large temperature glide
 - Eg hot tap water production, up to 90°C
 - > Heat pumps for combined space and tap water heating
 - > Chillers (for air conditioning and other purposes)
 - > Many more applications are being evaluated/tested
 - Eg air conditioning systems for cars (MAC)
- **For examples, see Information Sheet 6.2 and 6.3**

NMR's Information Sheets

Natural refrigerants for new applications

**TOPIC: Health and safety, and environmental issues (HSE)
with CO₂ refrigerant***Important considerations*

- **High pressure**
 - > Parts of the system will (most often) not be capable of holding the refrigerant pressure at ambient temperature
- **Low temperatures**
 - > CO₂ is used in freezing equipment for particularly low temperatures
 - down to approximately -54°C
 - > Dry ice will be formed during liquid discharge to the ambient
 - possible dry ice formation also when discharging vapour, dependent on condition
 - sublimation temperature -78°C
- **Large refrigerant charges are used in industrial systems:**
 - > Possible consequences from major releases have to be considered

Health effects from using CO₂

- **CO₂ is not acutely toxic**
 - > But concentrations above 5 vol. % quickly make you feel unwell
 - Potentially dangerous for persons with weak heart function
- **CO₂ in high concentrations is hazardous due to toxicity, and not only because it replaces oxygen**
 - > Leads to increased CO₂ content in the blood and lowered pH-value
 - natural body reaction
 - > Fatal in high concentrations, at a point before lack of oxygen becomes critical
 - > Breathing in a gas cloud of CO₂ from a major release may be extremely dangerous

Natural refrigerants – practical use

- **Typical effects from increasing CO₂ concentration in air**
 - > 2 vol. %: Breath rate increases 50 %
 - > 3 vol. %: Breathing laboured: headache: increased blood pressure and pulse rate
Breath rate increases to the double of normal
- But a busy person is not likely to realise this increase
 - > 5-10 vol. %: Breathing very laboured: physical exhaustion: "visual disturbance":
possible loss of consciousness. Risk to acute reaction similar to a stroke
 - > 10 + vol. %: Respiratory distress: loss of consciousness within minutes: lethal if not
brought into fresh air or given oxygen
- **A person who has been exposed recovers quickly in fresh air**
- **Cannot be smelled in low/moderate concentrations**
 - > Irritant to nose and throat (pungent smell) at higher concentrations (5-10 vol. %)
- **CO₂ vapour is heavier than air. Highest concentrations at low levels**
 - > Mixes effectively by diffusion and minimal air movements
- **Published/accepted concentration limits:**
 - > "Sick building syndrome" (headache) : 2000 ppm (0.2 vol. %)
 - > Practical limit (long term, according to EN 378): 70 g/m³ room volume (approx. 4000 ppm)
 - > Short term exposure limit (15 min., STEL): 15000 - 30000 ppm (varying figures)
 - > Immediately dangerous to life and health (IDLH): 40000 ppm

Flammability

- **CO₂ is not flammable:**
 - > Used in fire extinguishers
 - > Chemically very stable

Environmental issues

- **CO₂ does not deplete the ozone layer**
- **CO₂ is a weak greenhouse gas (GWP is per definition equal to 1.0)**
 - > But CO₂ is regarded as the most serious greenhouse gas because vast amounts are released when burning fossil fuel
- **CO₂ refrigerant is made from recovered and cleaned CO₂ from various industrial processes**
 - Net direct climatic effect of using it as refrigerant becomes zero
- **Indirect effect from power production to run the systems has to be considered**

Natural refrigerants – practical use

Gas detection

- The CO₂ content in the air has to be measured by a special CO₂-detector
 - > An oxygen detector should not be used
 - If, for example, the setting for the oxygen detector is 18 % O₂ (usual setting), the air could be very dangerous to breathe in if the oxygen was replaced by CO₂
- A gas detector must be installed in the machine room and in rooms defined as "human occupied spaces"³ if the CO₂ concentration in the air could exceed a practical limit of 70 gram/m³ room volume
- If a dangerous CO₂-concentration can be reached (above IDLH), a gas detector should be installed whether or not the room is an occupied space (similar to any refrigerant that cannot be smelled at very low concentrations)

Safety issues with high pressures and low temperatures

- Only the high pressure side of transcritical systems can normally withstand CO₂ pressure at ambient temperature
 - > All system parts that may contain liquid CO₂ have to be secured against rupture when at standstill
 - Unless the liquid has been transferred to a high pressure receiver
- Combinations of high pressure and low/high temperatures may occur under certain circumstances
 - > Presents challenges when choosing appropriate materials
- Dry ice may form during (instantaneous) venting of system parts containing CO₂ liquid when the pressure drops below 5.2 bar(a)
 - > May lead servicing personnel to believe that the system, or part of system, has been emptied when this is not the case
 - > Uncontrolled pressure rise can result if the system, or system part, is shut off and heated
- Dry ice may form during discharge from safety valves to ambient air
 - > Will occur during discharge of liquid (particularly) and high pressure (saturated) vapour (above approximately 24 bar)
 - increasing dry ice formation with increasing vapour pressure
 - > May block the downstream line
 - Connections for safety valves should always be placed above the liquid level
 - Safety valves should be installed at the downstream end of the discharge pipe
 - Internal pressure relief should be preferred for liquid filled piping or components
- Severe frost-bite may result from contact with CO₂ dry ice from a liquid leak
 - > The sublimation temperature is -78°C

³ Human occupied space = A space which is occupied for a significant period by humans

Natural refrigerants – practical use

Other safety issues

- **CO₂ and ammonia react chemically to form ammonium carbonate and ammonium carbamate (salts)**
 - > Forms a powder at temperatures below 60°C, evaporates at higher temperatures
 - found on the low temperature side
- **May occur during a major CO₂ leak into the ammonia side of a cascade heat exchanger**
 - > Leakage can be prevented by choosing appropriate technical solutions and resistant materials
 - > Practical experience has shown that the problem is less than anticipated at the early days of CO₂/ammonia cascade technology

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Practical matters when using CO₂ refrigerant*Effects on the refrigeration process of low critical temperature*

- Application of the ordinary refrigeration cycle restricted to a condensing temperature of approximately 24 – 26°C
- At temperatures above 31°C, the cycle becomes transcritical
 - > Reference is made to Information sheet 2.2.4

Consequences for the refrigeration process related to high pressures

- High pressures is, in many ways, advantageous to the practical process
- Dense vapour results in high volumetric capacity
 - > Small compressor volumes and small diameter gas piping
 - > Required swept compressor volume is 80-90 % less than with other refrigerants
 - > Suction line and return line diameters are more than halved
- Smaller temperature losses due to pressure drop in piping and heat exchangers than with other refrigerants
- High compressor efficiencies and efficient heat transfer
 - > Energy consumption can be lower than that of other refrigerants even if CO₂ is less efficient theoretically
- The pressure at ambient temperature is higher than the design pressure for the entire system or parts of it
 - > Potential overloading of components and piping needs to be considered
 - > Measures have to be taken to limit system pressure at standstill
 - Eg a small, independent refrigeration system ("cold finger" or stand still cooling)
 - > As long as the evaporators are cold, the low side pressure will be determined the evaporator pressure

Natural refrigerants – practical use

- **The higher the pressure is, the more easily vapour bubbles form in evaporators**
 - > Contributes to very high heat transfer coefficients in pool boiling of CO₂
 - CO₂ evaporators are very efficient
 - > Bubbles/foaming can easily occur during fast pressure reduction in liquid separators

Other effects of high pressure

- **The systems may be more prone to leaks**
 - > But practical leak rates similar to HFCs are reported
- **Higher design pressures for piping and components will often be required**
 - > Relevant components for high pressures are now available
- **Materials will be loaded closer to maximum allowable pressure during normal operation**
- **Pressure testing has to be done carefully and in full accordance with written procedures**
 - > As for all types of pressurised systems

Effects of high triple point pressure

- **Evaporation temperature restricted to (slightly above) the triple point temperature (-56.6°C)**
- **CO₂ in solid form (dry ice) may be used for freezing/cooling**
 - > Must be handled with care due to very low temperature (-78°C)
 - > Dangerous CO₂ concentrations may occur if used in confined spaces
- **System parts containing liquid should be emptied in vapour phase: or the liquid should be transferred to a container/bottle with pressure above 4.2 bar (g)**
 - > Pressure control required during emptying of liquid-containing systems or components
 - > Valves/piping can become blocked if liquid is discharged to the ambient

Construction materials

- **Suitable materials for piping and components are, in general, similar to those for HFCs**
 - > Material properties should be considered carefully, particularly for low temperature systems
 - Combinations of high pressure and low temperature may occur
 - Temperatures as low as -78°C during pressure equalisation with the ambient (fast discharge, tube rupture)
 - Construction materials, in particular carbon steel, may become brittle at low temperatures, may cause accidents
 - Copper and austenitic stainless steels suitable for low temperatures
- **CO₂ is not corrosive in pure form**
 - > Carbonic acid (H₂CO₃) forms in contact with water
 - May corrode various metals, but not a big problem in practice
 - > Refrigeration grade CO₂ has to be used
 - Water-content should be guaranteed no more than 10-15 ppm
 - > With appropriate routines for system drying and evacuation, corrosion will not pose a significant problem

Natural refrigerants – practical use

- **Leaks in gaskets etc not uncommon in the past**
 - > Valves and other components have to be designed for, and tested with, CO₂
 - > Some types of gaskets need to be lubricated to stay leak tight. Also some valves need lubrication. (This was more an issue in the early days of CO₂)
 - > O-rings and gaskets may rupture from internal pressure if pressure is relieved too quickly

Compressor lubricants

- **Conventional (synthetic) compressor oil (PAO) may be used**
 - > Only slightly miscible with CO₂: keeps its lubrication properties
 - > Lighter than liquid refrigerant: complicates oil management
- **Polyolesters (ester oils) can be used**
 - > Miscible with CO₂ in the most important temperature range
 - > Oil return similar to HFC refrigerants
- **Various other lubricants are suitable, including polyglycols (PAG):**
 - > Eg for mobile air conditioning systems and hot tap water heat pumps
 - > Improved PAG-formulations are in development
- **CO₂ is a very efficient solvent**
 - > Dissolved pollutants are caught by the oil
 - > Thorough system cleaning prior to charging is essential

CO₂ and other refrigerants

- **CO₂ reacts chemically with ammonia:**
 - > Forms ammonium carbamate (minor part) and ammonium carbonate (major part)
 - > In the event of a cascade heat exchanger leak
 - In particular, CO₂ will enter into the ammonia side
 - But some ammonia will also enter the CO₂ side
 - Problems caused by the reaction products will occur in the ammonia system, mostly on the suction side and in the compressor
- **No chemical reactions between CO₂ and HFCs**
- **Charging the wrong type of refrigerant will always have a detrimental effect and must be avoided**

Goods in storage

- **Leakage of CO₂ into a cold store will not have an adverse effect on goods in storage**
 - > Dry ice is often used for keep frozen food cold in direct contact

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: The transcritical CO₂ cycle*Transcritical cycles*

- All fluids have a so-called "critical point" for pressure and temperature
 - > At the critical point, liquid and vapour merge into one common phase
 - > At pressures above the critical pressure, the fluid will exist in one phase, independent of the temperature
- Refrigeration and heat-pump cycles are said to be "transcritical" if the state of the high pressure fluid belongs to the supercritical region, while subcritical conditions apply to the low pressure side
- The CO₂-cycle easily becomes transcritical due to the low critical temperature (31.1°C)
- Transcritical cycles are not normally sought
 - > But they may be used positively in some applications
- Other refrigerants have significantly higher critical temperatures than CO₂
 - > For most, this is between 70°C and 130°C
 - > The transcritical cycle is not relevant for these fluids

Characteristics of the transcritical cycle

- Gas cooling replaces condensing on the high pressure side
 - > Condenser becomes a gas cooler
 - > Pressure and temperature are independent of each other
 - > Gas temperature is (much) reduced through the gas cooler
- The cooling effect (and heating effect for a heat pump) increases with increasing compressor discharge pressure
- The cooling effect falls considerably when the fluid temperature leaving the gas cooler exceeds the critical temperature
 - > May be (partly) compensated for by increasing the pressure

Natural refrigerants – practical use

- **Greatest energy efficiency occurs at a certain (optimum) discharge pressure**
 - > The lowest possible discharge pressure is normally not the most energy efficient
 - > The optimum pressure varies depending on the fluid temperature at the gas cooler outlet
 - The warmer the fluid, the higher the optimum pressure

Energy efficiency

- **The transcritical CO₂-cycle is less efficient than the conventional cycle for most applications**
 - > Transcritical systems are normally designed to operate subcritically, if possible, when this is the most energy efficient
- **Solely transcritical operation may be the best choice under certain conditions:**
 - > When there is a large temperature rise in the fluid absorbing the rejected heat
 - Favourable temperature match between the two sides results in low energy losses
 - Eg heat pump for heating tap-water
 - > When there is simultaneous demand for heating and cooling
- **Optimum pressure control on the warm side is a prerequisite for achieving good results**
- **Fluid conditions close to the critical point before throttling must be avoided**
 - > Results in low capacity and low system efficiency
 - > Difficult to determine the fluid state for controlling the system
- **Significant technical developments in components and systems have taken place**
 - > Heat exchangers, as well as compressors, have been improved
 - > Various methods for reducing the throttling loss have been introduced
 - > The energy efficiency of transcritical CO₂-cycles is competitive for an increasing number of applications, especially for supermarkets
- **High energy efficiency is dependent on low fluid temperature from the gas cooler**
 - > A technical challenge when the temperature of the cooling fluid, eg ambient air, is high
 - > The average annual temperature is key
 - > Moderate annual ambient temperatures, such as those of Northern Europe, are best
 - > Hotter climates (tropical) are a bigger challenge
 - But system optimization have brought the "CO₂-equator" steadily further south
- **Mobile air conditioning systems (MACs) with CO₂ have proved to be the most energy efficient systems even in climates that are periodically extremely hot**
 - > A good example of what is possible with component development and process optimisation

Practical issues

- **The pressure in the gas cooler is controlled by throttling after the cooler**
 - > Constant pressure is simple to achieve, but not the most energy efficient
 - > Dynamic pressure control required for maximum coefficient of performance

Natural refrigerants – practical use

- **The gas temperature at the gas cooler exit may approach that of the heat sink**
 - > Thanks to the temperature glide
 - > 1–3 K temperature difference achievable
 - > A key to energy-efficient operation
- **The gas cooler design is important**
 - > The temperature curve through the cooler bends
 - > Faulty design may give pinch point within the cooler
 - high temperature of the leaving CO₂
 - reduced system efficiency
- **Sub-optimal conditions during operation may affect energy efficiency more adversely than with a conventional system**
 - > Gas cooler conditions close to the critical point particularly detrimental
 - > The gas cooler has to cope with the extreme temperatures, not only nominal values
- **Alternating between transcritical and subcritical operation often advantageous**
- **The transition between transcritical and subcritical operation may be achieved in one pressure step, or by continuous pressure regulation**
 - > Continuous regulation implies that the condensing pressure, under certain operating conditions, is kept above the minimum possible pressure
 - Liquid subcooling contributes to favourable energy efficiency

Technical solutions

- **Various technical solutions possible as for the conventional cycle**
- **One-stage system with the liquid receiver after the evaporator (low pressure receiver system)**
 - > Common throttling valve for controlling gas cooler pressure and for feeding liquid into the evaporator
 - > Suitable for small systems with only one cooler
 - > Used in heat pumps, small commercial units, mobile air conditioning systems etc.
- **One-stage system with the liquid receiver at intermediate pressure (transcritical operation) or condensing pressure (subcritical operation)**
 - > Typical for larger systems
 - Simple to connect more than one cooler
 - Two-stage throttling in transcritical mode. "Economiser" arrangement improves energy efficiency
 - > Separate throttling valves, coupled in series, for controlling gas cooler pressure and evaporator feeding
 - > In regular subcritical operation, the gas pressure control valve is fully open
- **Two-stage systems**
 - > For freezing purposes only
 - > Or for both freezing and cooling
- **More information is given in Information Sheet 3.3.3**

2.3 Hydrocarbons

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Basic information on hydrocarbons as refrigerants

What is a hydrocarbon?

- A hydrocarbon is a chemical compound consisting entirely of hydrogen and carbon
 - > Common petroleum gases such as propane and butane are examples of hydrocarbons

Which hydrocarbons are suitable as refrigerants?

- Hydrocarbons suitable for use as refrigerants include among others (refrigerant designation and normal boiling point in parenthesis):
 - > For very low temperatures: Ethane (R-170, -88.3°C), Ethylene (R1150, -103.7°C)
 - > For ordinary freezing/cooling/heat pump applications: Propane (R-290, -42.1°C) and propylene (R-1270, -47.7°C)
 - Propylene is mainly for use with evaporation temperature below -10°C
 - > For freezing/cooling (small units): Iso-butane (R600a, -11.7°C)

Health and safety, and environmental issues (HSE)

- Favourable environmental properties (no ODP, low GWP)
- Low toxicity and no toxic break down products
- Very high flammability
 - > Specific safety precautions required
- Reference is made to Information Sheet 2.3.2

Natural refrigerants – practical use

Advantages of hydrocarbons

- **Cover the entire temperature range** – from low temperature freezing to heat pumps
- **Favourable refrigeration properties:**
 - > Moderate system pressures (–42/+68°C within a pressure range 1-25 bar g for propane)
 - > Energy-efficient theoretical cycle
 - > Low discharge temperature
 - > Low viscosity
 - > Other properties similar to HCFC-22
- **Well-known technology**
 - > Knowledge and experience gained from using traditional systems with eg HCFC-22 is useful

Disadvantages of hydrocarbons

- **Safety measures needed due to the flammability**
 - > Specific requirements given in regulations, and standards have to be followed carefully (as for all refrigerants)
 - > Potential loss of efficiency, and increased costs, due to "over-safeguarding" the systems
 - a threat to the technology

Uses – general

- **Small systems (less than 150 g charge)**
 - > Can be used without restriction and is already in use in large scale
- **Commercial refrigeration systems**
 - > Shops, supermarkets, hotels, restaurants, small cold stores etc.
 - Indirect systems
 - > Chillers available from several manufacturers
- **Heat pumps**
 - > Bigger systems for heating of buildings
 - Based on standard chillers
 - > Smaller systems for one family houses etc.
 - Often situated/installed outdoors
- **Air conditioning**
 - > Standard chillers
 - Often sited on roofs of buildings
 - > Propane and propylene are technically well suited for conversion of existing systems using HCFC-22
 - Many examples of such conversions in Asia – to save energy
 - Mainly systems placed on the roof
 - Not recommended (in general) for indoor systems, for safety reasons
- **Process cooling within industries handling flammable material**
 - > Eg the oil and gas industry and the petrochemical industry

Natural refrigerants – practical use

Uses - small units

- Refrigerators, freezers etc for domestic and commercial use
 - > Appliances manufactured in Europe use hydrocarbons (mainly iso-butane)
- Cabinets in retail areas, eg in shops, kiosks, petrol stations etc
- Spot coolers (air conditioners) for offices, shops etc and for private use
- Low-temperature freezers (– 80°C) for medical applications etc

NMR's Information Sheets

Natural refrigerants for new applications

**TOPIC: Health and safety, and environmental issues (HSE)
with hydrocarbon refrigerants***Health risks*

- **Primary health risks are burn injuries and asphyxiation (as the hydrocarbon displaces air)**
 - > The gas itself may also have an anaesthetising effect
 - which also the case with HCFC and HFC

Flammability

- **Hydrocarbons are flammable/explosive**
 - > Explosion limits for e.g. propane in air are 2.1 – 9.5 vol. %, corresponding to 38 – 171 g/m³ room volume
 - > However, the gases are not easy to ignite
- **Dilution of refrigerant into the compressor oil requires careful handling**
 - > Compressor oil, tapped from the compressor, contains a considerable amount of hydrocarbon
 - especially if no measures are taken to boil off the hydrocarbon, eg installation of a compressor oil heater
 - > Hydrocarbon evaporating from the oil represents an explosion hazard

Environmental issues

- **Negligible adverse effect on the global environment**
 - > Atmospheric lifetime only days (for hydrocarbons applied as refrigerants)
 - > No ozone depletion
 - > Low global warming potential
- **Hydrocarbons are volatile organic compounds (VOC)**
 - > Contributes to smog formation in big cities under certain atmospheric conditions
 - > A minor problem under Nordic conditions
 - Additionally, only very small amounts of hydrocarbons are released from refrigeration systems and heat pumps

Natural refrigerants – practical use

Safety issues

- **Variable warning properties**
 - > Propane and (iso)butane are practically odourless
 - > Propylene has a distinct smell
 - One of few refrigerants that can be smelled in low concentrations
 - A useful safety feature, make people leave the room
 - > Chemicals (certain mercaptans) added to commercial propane and butane to make them smell will be absorbed by the compressor oil and the filter drier
 - Adding mercaptans will not work satisfactory with hydrocarbons
- **Small leaks can be revealed by oil sweating at the leaking spot (as with other refrigerants)**

Refrigerant vapour is heavier than air (but not as heavy as HFCs)

 - > Collects at floor level/in low areas in case of leakage
 - > Zones containing explosive gas/air mixture may occur locally even with moderate leaks
 - But they are easily vented away
 - > Quickly diluted to non-flammable concentrations by ventilation
- **Refrigeration standards (eg EN-378) require specific precautions to be taken avoid to fire/explosion**
 - > If the hydrocarbon concentration could exceed 20 % of the lower flammability limit (LFL) assuming the total charge was to leak into the room
 - For propane and propylene this corresponds to 8 g per m³ room volume
- **Long term exposure limit for propane is 500 ppm, for propylene 250 ppm (in Norway)**

Reported incidents and accidents

- **The incidences of fires in domestic refrigerators and freezers is no more frequent with hydrocarbon refrigerants (iso-butane) than with HFCs**
- **Some incidents and accidents have been reported in bigger systems:**
 - > Almost all have been traced back to operational (servicing) issues
 - > As a result of insufficient training/poor practice

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Practical matters when using hydrocarbon refrigerants

Overview

- **Components and equipment are readily available on the market**
- **Cheaper than systems using ammonia or CO₂**
 - > Extensive safety measures may in some cases even out the price differences
- **Somewhat more expensive than units using HFCs**
 - > Lower cost may result along with increasing production volume
- **Small refrigerant charge**
 - > Approximately half the charge by weight compared to HCFC-22
- **Miscibility with conventional compressor oil secures easy oil return**
- **Materials and technology normally used to construct refrigeration systems can be used**
 - > Materials for o-rings and gaskets require special consideration
- **Oil dilution by the refrigerant will affect lubrication properties**
 - > Can be compensated for by using more viscous oils
 - > Generally not a big problem for piston compressors
 - Provided dry suction is secured and compressor pump-down is used
 - > A bigger challenge in relation to screw compressors
 - Lubricants that dissolve less refrigerant should be used, eg based on polyalkylene glycols (PAGs)

Natural refrigerants – practical use

Technical measures to prevent fire/explosion

- **Use indirect systems**
 - > Low charge
 - > Place all refrigerant containing parts in the machinery room (or outdoors)
 - Avoid refrigerant spreading into critical areas
- **Employ a means of detecting refrigerant leakage into secondary cooling/heating circuits**
 - > Microbubble separator in the supply line will ensure refrigerant free liquid to enter the space to be cooled or heated
- **System location**
 - > Avoid basement and other low-level locations without natural air change
 - > Ideally site outdoors (in a protected space) or in a machinery room set apart from other buildings
 - Roof installation is often ideal (but proximity of fresh air intakes needs to be considered)
 - > Use gas-tight, ventilated enclosures, if systems must be located indoors
 - Practicable solution also for units located outdoors
- **Safeguarding against leaks:**
 - > Use hermetic and semi-hermetic compressors
 - > Avoid detachable joints (only braze/weld)
 - > Check that piping and components do not vibrate during operation (as for any refrigeration system)
- Prevents pipe rupture from material fatigue
- **Safeguarding against explosion in the event of a leak**
 - > Prevent flammable concentrations from occurring
 - Put systems in large volume spaces or outdoors
 - Split the system into two, or more, independent refrigeration circuits when practical and efficient
 - Provide good ventilation, including emergency ventilation activated by gas detectors
 - > Use EX-classified equipment in areas with a potentially explosive atmosphere
 - But also minimise the EX-zone (through technical measures)
 - > Install a gas-tight wall between classified and non-classified areas
 - > Place equipment which may create sparks outside the machine room or container/-machine cabinet
 - > Keep electrical cabinets under overpressure
- **Ensure that machinery room/system location is only accessible to authorised personnel**
- **Post relevant warning signs, especially about the fire/explosion risks**
 - > On the machinery room door/entrance to the location area, and on the system itself
- **Keep the room/system environment tidy, clean and easily accessible**

Natural refrigerants – practical use

Measures to minimise danger and damage caused by fire/explosion

- Place fire extinguishing equipment in, or by, the machinery room/location area
- Label equipment and enclosures, and mark all safety exits/escape routes, very clearly
 - > For the safety of employees/contractors as well as to assist fire fighters

Training and information

- Provide adequate training for all personnel
 - > Including those working on system installation, operation and maintenance/servicing
- Draw up operational manuals and special safety instructions
- Establish system-specific routines with qualified personnel for maintenance
- Adhere carefully to rules and regulations:
 - > Local/national authorities' regulations and approved refrigeration standards

3.1 Systems

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: System types

Direct and indirect cooling/heating

- Refrigeration systems and heat pumps are divided into two main groups according to the method of heat transfer between the refrigerant and the substance that is going to be cooled or heated
- **Direct system**
 - > Direct heat transfer between the fluids. The refrigerant is circulated on one side of the heat exchanger (evaporator or condenser) and the substance to be cooled or heated on the other side (Figure 1)
- **Indirect system**
 - > A heat transfer fluid circulates between the evaporator and an external cooler which absorbs heat from the air, or substance to be cooled: or between the condenser and an external heater which rejects heat to the air, or substance to be heated (Figures 2 – 4)
- **Types of indirect systems:**
 - > Partly indirect system
 - Indirect on the cold side (Figure 2)
 - Indirect on the warm side
 - > Fully indirect system
 - Indirect on both sides (Figure 3)
 - Double indirect system (on the warm side, Figure 4)

Technical solutions with natural refrigerants

Figure 1 Direct system

Figure 2 Indirect system on the cold side, direct system on the warm side

Figure 3 Indirect system on both sides

Technical solutions with natural refrigerants

Figure 4 Indirect system on the cold side, double indirect system on the warm side

Characteristics of each system type

- **Direct systems**
 - > Less costly solution
 - > The most energy efficient solution, theoretically
 - > Often needs large refrigerant charge
 - > Potential for leaks of refrigerant into humanly occupied space/area
- **Indirect systems**
 - > All refrigerant may be kept in the machinery room (or outdoors)
 - > The risk is much smaller of refrigerant release into humanly occupied space
 - > Makes it possible/easier to apply toxic and flammable refrigerants
 - > Low refrigerant charge – typically 85 – 90 % less than in direct systems
 - > Often easier to obtain theoretically calculated performance in terms of capacity and energy efficiency

More information

- Using natural refrigerants in direct and indirect systems is discussed in Information Sheet 3.1.2
- Information about heat transfer fluids is found in Information Sheet 3.2.1 and 3.2.2

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Natural refrigerants in direct and indirect systems

When can direct systems be used?

- **Ammonia can be used in direct systems in certain circumstances:**
 - > Eg for systems not in "humanly occupied spaces"⁴ – eg cold stores, tunnel freezers etc
 - > Can be used, with charge limitations, in systems serving production areas etc, where people are familiar with escape routes and escape procedures
 - > But can normally not be used in systems serving rooms, or areas, open to the public
- **CO₂ can be used in both system types much the same way as HFCs**
 - > Requires special safety measures when used with large charges (as with HFCs)
- **Hydrocarbons can be used in direct systems in certain circumstances:**
 - > When the charge is so small that it will not make the air explosive, even if all of it leaks out
 - > When the system is designed and positioned to minimise the risk of explosion if a leak should occur
 - But national regulations need to be observed – may vary from country to country

When are indirect systems better?

- **Indirect systems are used, when:**
 - > They are the preferred technical solution
 - > Direct systems are not to be used for safety reasons
 - > Indirect systems are the most appropriate for other reasons
 - Facilitates free cooling easily
 - Less requirements on personnel for system operation and for modification of the (secondary) cooling system
- **An indirect system should be used when in doubt about safety**

⁴ Space which is occupied for significant periods by humans

Technical solutions with natural refrigerants

Possible consequences of refrigerant leaking into the heat transfer circuit

- **Ammonia:**
 - > Becomes absorbed in water-based heat transfer fluids – no, or low, pressure increase
 - > The heat transfer fluid becomes very corrosive, especially at high temperatures and with air present
 - > Corrosive to skin
 - > The heat transfer fluid becomes a special waste
- **CO₂ and hydrocarbons (and HFCs):**
 - > Not absorbed by the heat transfer fluid
 - > Leakage will generate pressure increase
 - a safety valve relieving to the free is mandatory
 - > A micro-bubble separator must be used
- **Greatest risks when producing warm/cold tap water**
 - > In reality, a kind of direct system
 - > Refrigerant in the circuit will be released during tapping
 - > Direct heat exchange between ammonia and tap water can be done but a dual circuit is more safe

Safety measures for indirect systems

- **Prevent refrigerant from leaking into the heat transfer circuit:**
 - > Choose heat exchanger designs with lowest possible leakage risks
 - > Prevent evaporators from freezing by choosing an adequate freezing point for the heat transfer fluid and by installing a low temperature switch
- **Put measures in place to avoid damage, or danger, from refrigerant leaks into the heat transfer fluid**
 - > Check the heat transfer fluid regularly
 - > Employ (automatic) detection of refrigerant in the heat transfer fluid
 - With gas separation, and discharge, when the refrigerant is not absorbed by the fluid
 - > Use a pressure sensor to detect increases in pressure
 - > Safeguard the heat transfer circuit against overpressure
 - > Use double indirect systems in particularly critical situations

Technical solutions with natural refrigerants

Changing over from direct to indirect systems

- **In most countries, direct systems have been the traditional way of building refrigeration systems**

Indirect systems have been used for specific purposes, eg:

- > (Large) air conditioning systems and heat pumps
- > Systems employing heat recovery
- > Reversible systems (alternating cooling/heating)
- > Industrial ammonia systems when direct refrigeration cannot be used for legal or other reasons

- **A significant shift towards indirect systems has occurred over the last two decades**

- > Reducing the refrigerant charge
- > Making natural refrigerants like ammonia and hydrocarbons suitable for new uses

- **Indirect systems are currently also used for:**

- > Refrigeration systems in supermarkets
- > Cooling in food production and distribution (production areas, cold stores, distribution centres etc.)
- > Industrial ammonia systems – to minimise ammonia charge

Heat transfer fluids in indirect systems

- See Information Sheet 3.2.1 and 3.2.2 about heat transfer fluids

3.2 Heat transfer fluids for indirect systems

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Information about heat transfer fluids

What is a heat transfer fluid?

- A heat transfer fluid is a fluid which is used to carry heat from the air, or substance, to be cooled to the evaporator of the refrigeration system or heat pump, or to carry heat from the system's condenser to the air, or substance, to be heated
- The heat transfer fluid is normally a liquid:
 - > Heat is absorbed and rejected under temperature glide, without phase change
- A fluid with phase change can also be used:
 - > Heat is absorbed and rejected at (approximately) the same, constant temperature
 - > CO₂ is the most frequently used heat transfer fluid with phase change

Characteristics a good heat transfer fluid

- Large volumetric heat capacity:
 - > Low flow rate, small pipe dimensions, small pump energy demand
 - > Evaporation of 1 kg CO₂ (at -30°C) binds the same amount of heat as heating 15 litres of water 5°C
 - Greatly reduced pipe costs and pumping work
- Low viscosity, even at the lowest temperatures
 - > Efficient heat exchangers, little pump work
- Neither corrosive towards metals, nor aggressive towards elastomers for o-rings, gaskets etc
- Favourable health, environmental and safety properties:
 - > Neither toxic nor allergic
 - > Inflammable
 - At least has a high flame point
 - > Easily bio-degradable
- Low price
 - > Indirect systems may require very large quantities of heat transfer fluids

Technical solutions with natural refrigerants

The most common heat transfer fluids

- **The most commonly used heat transfer fluids consist of water-added:**
 - > Alcohols
 - > Glycols
 - > Salts (organic and inorganic)
 - > Ammonia/water solutions
 - > More specific information about the various kinds of heat transfer fluids is given in Information sheet 3.2.2
- **Non-water based fluids are used for very low temperatures**
- **In practice, CO₂ is the only fluid used as heat-transfer fluid with phase change**

General issues

- **Many heat transfer fluids are chemically-active substances:**
 - > Unwanted chemical reactions may occur if inappropriate materials are chosen
 - > Pumps and other components have to be designed to work specifically with the heat transfer fluid being used
- **The ratio between active substance and water has to be adapted to the relevant operating conditions**
 - > Freezing must be avoided
 - > (Unnecessarily) high concentrations should also be avoided
 - High viscosity increases pump work and lowers heat-exchanger efficiency
- **Inhibitors are added to prevent corrosion**
 - > Manufacturers use different kind of inhibitors, some are toxic
 - > Inhibitors are consumed
 - Binds oxygen if air present
 - Regular inhibitor control required
- **Various types of heat transfer fluids should not be mixed**
 - > Even within the same group of chemicals

Technical solutions with natural refrigerants

Safeguarding against freezing

- **The freezing point of cold heat transfer fluids should be a little lower than the minimum anticipated evaporation temperature**
 - > Suitable freezing point for cooling systems and heat pumps – approximately -15°C
 - > Suitable freezing point for freezing systems – approximately -42°C
 - At room temperatures down to -37°C
- **The freezing point for a heat transfer fluid which changes heat with ambient air should be approximately 5°C lower than the dimensioning outdoor temperature for the area**
- **An unnecessarily low freezing point should not be chosen, as:**
 - > The heat transfer fluid becomes more viscous
 - > The heat exchangers becomes (far) less efficient
 - > The pumping work increases (much)
- **Heat transfer fluids based on water freeze over a temperature interval**
 - > The freezing point is defined as the temperature at the start of freezing
 - > The fluids do not form compact ice at the point of freezing
 - Reduces the risk of damage to the heat exchanger from "light" freezing
- **CO₂ can be used down to below -50°C**
 - > Solidifies at -56.6°C
 - Does not expand during formation of dry ice: no mechanical frost damage
 - But can damage any CO₂-pumps

Corrosion in heat transfer fluids

- **Water-based heat transfer fluids are corrosive**
 - > Corrosion is the major practical challenge with many heat transfer fluids
 - > The liquid level area is the most prone to corrosion
 - > Salt solutions are the most corrosive, alcohols the least
- **Corrosivity increases greatly when there is air (oxygen) in the system:**
 - > Closed circuits are necessary
 - > Piping and hoses have to be diffusion-tight
 - > The circuit should be evacuated before charging
 - > The system has to be kept fully charged all the time
 - > All system parts have to be kept at overpressure
- **Corrosivity increases greatly when the temperature rises**
 - > The corrosion rate doubles for every 10-20°C rise in temperature (rule of thumb)
 - > Salt solutions can be particularly difficult
 - > Great care should be given to the choice of warm heat transfer fluid

Technical solutions with natural refrigerants

- **Avoid spillages:**
 - > Rust results when heat transfer fluids leaks and are in contact with metals
- **Corrosion products, and decomposed inhibitors, may create secondary problems:**
 - > Damage to pump shaft seals
 - > Tend to settle, creating favourable conditions for further corrosion
- **Possible leakage of ammonia into the heat transfer fluid will increase corrosivity**
 - > Especially in compounds containing copper and/or zinc, eg brass

Measures to prevent corrosion and damage from corrosion

- **Select the right materials**
 - > Materials have to be suitable for the selected heat transfer fluid
 - > Metallic materials should be of similar nobility to avoid galvanic corrosion
 - Materials with different nobility should not be in electrical contact
- **Keep the systems clean**
 - > Particles, and other pollutants, which settle increase the risk of corrosion
 - Also risk of damage to pump shaft seals
- **Use water of appropriate quality**
 - > The water quality has to be adapted to the heat transfer fluid in question
 - > The chlorine content has to be checked if glycols are to be used
 - > Many heat transfer fluids are marketed pre-mixed with water. Recommended
- **Guard against "creep currents"**
 - > May generate galvanic corrosion
- **Keep the heat transfer fluid properties under control**
 - > Measure pH and freezing point at least once a year
 - > Have samples chemically analysed at regular intervals
 - To check the contents of inhibitors, and the pH value

Charging and disposal

- **Water- based heat transfer fluids must be completely mixed before charging**
- **Used heat transfer fluid should be considered as industrial waste and be disposed of properly:**
 - > Must not be emptied into municipal sewers
 - In some cases acceptable, but only with permission from the authorities

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: The most commonly used heat transfer fluids

Alcohols

- **Denatured ethanol is the most important alcohol:**
 - > Commonly used as cold heat transfer fluid in heat pumps
 - > Generally appropriate for cooling/freezing purposes, down to approximately -40°C
 - > Less suitable as warm heat transfer fluid due to flammability (low flame point)
 - > Flammable - flame point between 12 – 30°C, or higher, depending on concentration
 - > Moderately corrosive
 - > Should be mixed with ordinary drinking water, not deionised or distilled
 - Less risk of corrosion
 - > Not injurious to health (when used correctly)
 - > Easily bio-degradable

Glycols

- **Correctly handled, glycols are generally unproblematic in use**
 - > The substances are corrosive, but the corrosivity is moderated by the use of inhibitors
 - > Can attack eg gaskets in pumps if used with the wrong materials
 - > Diluted glycol mixtures (< 20 %) should be avoided, even where there is no risk of freezing
 - Algae may grow in the system
- **Ethylene glycol**
 - > The same substance as the antifreeze fluid used in car cooling systems
 - But antifreeze fluid for cars will damage pump shaft seals and must not be used
 - > Suitable as cold heat transfer fluid down to approximately -40°C
 - > Suitable as warm heat transfer fluid
 - > Toxic

Technical solutions with natural refrigerants

- **Propylene glycol**
 - > More viscous than ethylene glycol and less suitable for low temperatures
 - Unsuitable below approximately -25°C
 - > Approximately similar viscosity as ethylene glycol at temperatures above 20°C
 - Suitable as warm heat transfer fluid
 - > Non-toxic
 - Useful for food cooling
 - No risk of poisoning even if a liquid spill on unpacked food went undetected

Brines – general information

- **Brines are the most efficient water-based heat transfer fluids for low temperatures**
 - > Less viscous than glycols and alcohols
 - Resulting in a more efficient system
 - > Can be used to -50°C
- **Brines are generally less suitable as warm heat transfer fluids**
 - > Due to the risk of corrosion
- **Brines are generally very corrosive in the presence of oxygen (air)**
 - > More corrosive than glycols
 - > Attack galvanised steel, zinc, soft soldering (even with inhibitor added)
 - > Deionised water should be used to reduce corrosion risks
 - > Particularly important to keep the fluid condition under good control
 - > Corrosion is particularly a problem (aesthetics) when leaks occur
- **Serious damage from corrosion may occur:**
 - > If the wrong materials are used
 - > Air gets into the system
 - > The system gets dirty etc
- **High fluid velocity can lead to turbulence corrosion (erosion)**
 - > At tube inlets in the shell and tube heat exchangers
 - > In the return bends of tubes in fin batteries
 - The velocity in copper tubes with return bends should be restricted to 1 m/s

The most commonly used brines

- **Calcium chloride:**
 - > Traditional heat transfer fluid for heavy industrial uses and large ice sport facilities
 - > The content of chlorine puts particular demands on material quality
 - > Applied inhibitors may be toxic (e.g. chromium compounds)
- **"New" organic salts:**
 - > Include potassium formate: potassium acetate: and a mixture of the two
 - > Thermal properties fairly similar for all types
 - > Non-toxic
 - > More environmentally-friendly than calcium chloride
 - Quickly bio-degradable
 - > Used in eg the food industry

3.3 Technical solutions with CO₂

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: CO₂ – technical solutions

Overview

- CO₂ as low temperature heat transfer fluids with phase change
- CO₂ as refrigerant in the bottom cycle of cascade systems
- CO₂ as the only refrigerant
 - > In ordinary refrigeration cycle
 - > In transcritical cycle

CO₂ as heat transfer fluid with phase change

Technical solutions with natural refrigerants

- **Differences with conventional heat transfer fluids (liquids):**
 - > Heat absorption at constant temperature
 - > Higher evaporation temperature (normally)
 - > Smaller flow rates
 - > Smaller pipe dimensions
 - > Smaller pump work
 - > Higher pressure
 - Pressure rating up to 40 bar for equipment for cooling
 - The standstill pressure, at room temperature (approximately 80 bar), higher than the system design pressure
 - Measures to limit the pressure at standstill required, eg by use of a small separate cooling unit, see the figure above
- **Typical uses**
 - > Commercial and industrial low temperature cold stores where ammonia is used in the primary refrigeration cycle

CO₂ in the bottom cycle of cascade systems

- **Advantages over solutions using one type of refrigerant:**
 - > Large reduction in compressor volume and gas pipe dimensions
 - > Easy to achieve particularly low evaporation temperatures, eg -50°C
 - > More energy efficient
 - At temperatures below -35/-40°C compared to two-stage ammonia systems
 - For all freezing purposes compared with other alternatives
 - Small temperature losses from pressure drops – an important reason for efficient practical solutions
 - > Equipment containing ammonia (or hydrocarbons) is kept within the machinery room
 - > Much reduced ammonia (or hydrocarbon) charge

Technical solutions with natural refrigerants

- **Typical applications:**
 - > Freezing purposes in supermarkets
 - > Industrial freezing
 - Freezing tunnels, quick freezing equipment (with ammonia in the top cycle)
 - Faster freezing – increasing capacity
 - > Commercial and industrial low temperature cold stores (with ammonia in the top cycle)
 - > Examples of installations are given in Information Sheet 6.2.

CO₂ as the only refrigerant

Ordinary refrigeration cycle: The pressure control valve (3) fully open

Transcritical cycle: The pressure in the gas cooler kept at the desired level with the help of the pressure control valve (3)

Alternates between transcritical and conventional operation according to the available temperature for cooling the condenser/gas cooler, eg by air cooling. Various designs of transcritical systems applied, dependent on purpose. (See Information sheet 3.3.3)

- **Comparison with conventional solutions:**
 - > Needs a much smaller compressor volume and smaller gas pipe dimensions
 - > Very high design pressures, eg:
 - High pressure side: 120 bar
 - Intermediate pressure side: 60–80 bar
 - Low pressure side: 30–60 bar
 - > Competitive with respect to energy efficiency for an increasing number of applications
 - > Particularly suitable for heat pumps with large increases in temperature in the heat absorbing fluid
 - CO₂ heat pumps for hot tap water heating a common product in Japan
 - Appropriate for heating fresh air
- **Investments**
 - > Somewhat higher than for conventional direct systems
 - > Lower than for indirect systems
- **Applications and practical examples**
 - > See Information Sheets 1.3 and 6.3

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Technical solutions for cascade systems using CO₂

Alternative 1. CO₂ dry expansion for freezing, conventional indirect system for cooling

Characteristics

- The least expensive solution for smaller systems
- Simple technology
- Used in, for example, smaller supermarkets/shops

Technical solutions with natural refrigerants

Alternative 2. CO₂ dry expansion for freezing, pump circulation of CO₂ for cooling

- 1 – compressor, top stage
- 2 – condenser
- 3 – throttling valve
- 4 – cascade heat exchanger
- 5 – CO₂ receiver
- 6 – compressor, bottom stage (CO₂)
- 7 – throttling valve
- 8 – air cooler (freezing)
- 9 – CO₂ pump
- 10 – air cooler (cooling)

Characteristics

- The least expensive solution for bigger systems
- Energy efficient
- Used in, for example, larger supermarkets

Alternative 3. Pump circulation of CO₂ both for freezing and cooling

- 1 – compressor, top stage
- 2 – condenser
- 3 – throttling valve
- 4 – cascade heat exchanger
- 5 – CO₂ receiver
- 6 – compressor, bottom stage (CO₂)
- 7 – throttling valve
- 8 – CO₂ liquid separator
- 9 – CO₂ pump (freezing)
- 10 – air cooler (freezing)
- 11 – CO₂ pump (cooling)
- 12 – air cooler (cooling)

Characteristics

- Typically used in large-scale industrial systems
 - > Especially when it's important to avoid ammonia outside the machinery room
 - > Energy efficient

Technical solutions with natural refrigerants

Alternative 4. Pump circulation of CO₂ for freezing: pump circulation of ammonia for cooling Characteristics

- Typically used in large-scale industrial systems
 - > When the use of ammonia outside the machinery room is acceptable
 - > Similar to alternative 2 with respect to energy efficiency

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Technical solutions using CO₂ in transcritical cycle*Alternative 1. One stage system with low pressure receiver* *Characteristics*

- Designed to operate in transcritical and subcritical mode
- Full gas cooler pressure upstream of the throttling valve
- Suction line heat exchanger to evaporate oil containing refrigerant bled from the low pressure receiver
 - > Also to improve system efficiency
- Originally developed for mobile air conditioning (MAC)
- Also used in other (mass produced) small units
 - > Heat pumps for heating tap water, and combined systems for space and water heating
 - > Bottle coolers, vending machines, ice cream cabinets etc

Technical solutions with natural refrigerants

- **Several methods for improving efficiency:**
 - > Compressor with two stage compression and inter-stage cooling
 - > Pre-compression of the gas through the use of an ejector driven by high pressure fluid
 - > Expansion machine driven by high pressure fluid coupled to the compressor shaft
 - Under development

Alternative 2. One-stage system with high pressure receiver Characteristics

- **Designed to operate in transcritical and subcritical mode**
- **Natural or controlled receiver pressure**
 - > Possible to keep the receiver pressure below 40 bar through pressure control (see figure)
 - Better availability of standard refrigeration components and equipment
 - Lower liquid pressure in public areas
 - > A separate flash gas compressor will improve system efficiency (see alternative 3)
- **Commonly used in commercial systems (supermarkets etc):**
 - > Separate systems for cooling and freezing purposes
 - > One-stage compression for cooling; two-stage for freezing

Technical solutions with natural refrigerants

Alternative 3. Transcritical booster system (with heat recovery) Characteristics

- Fairly simple design
- Covering both cooling and freezing demands
- Simple and efficient heat recovery
- The pressure control valve (8) can be replaced by a flash gas compressor to improve energy efficiency (see Alternative 4)
- Established at the generally preferred CO₂ system design for supermarkets in the Nordic coun

Technical solutions with natural refrigerants

Alternative 4. Two-stage system (with flash gas compressor)

- 1 – high stage compressor
- 2 – gas cooler (condenser)
- 3 – pressure control valve
- 4 – receiver
- 5 – flash gas compressor
- 6 – high pressure float valve
- 7 – throttling valve, cooling
- 8 – air cooler (cooling)
- 9 – low stage compressor
- 10 – intermediate pressure receiver
- 11 – throttling valve (freezing)
- 12 – air cooler (freezing)

Characteristics

- Refrigeration at two temperature levels
- The upper stage transcritical: the lower stage subcritical
> Subcritical operation of the upper stage, if possible and energy efficient
- Flash gas compressor improves energy efficiency
- Used in commercial systems (supermarkets, etc)

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Where to site refrigeration systems and heat pumps using natural refrigerants

The paragraphs below outline some important issues, but are not exhaustive. Readers should refer to national regulations and refrigeration standards for more detailed information.

Overview

- Refrigeration systems and heat pumps can be located in populated rooms/areas, in machinery rooms, in ventilated enclosures, or in the open air.
- Location has to be considered carefully, regardless of the type of refrigerant used:
 - > For safety reasons
 - > To guard against entry by non-authorised personnel (with larger systems)
 - > To comply with requirements of the authorities
- **Primary factors to consider:**
 - > Type of refrigerant and refrigerant charge
 - > Whether or not the room, or area, has public access
 - > The likely spread of gas if refrigerant is released
- **National regulations apply**
 - > May differ from country to country
- **Guidelines can be found in Refrigeration Standards**
 - > EN 378 "Refrigerating systems and heat pumps – Safety and environmental requirements"

Location of systems and equipment

Systems and units using ammonia

- **Industrial ammonia systems are often erected on site**
 - > Compressors and high pressure vessels, etc are generally situated in a separate machinery room (see Information Sheet 4.2)
 - > Components and piping containing ammonia can be located in occupied spaces so long as they comply with specific regulations
 - Depending on: pressure level: refrigerant charge: room category and occupation density
 - > A growing trend for indirect systems
 - All ammonia-containing equipment placed in the machinery room
- **Factory-made unit systems, eg chillers and heat pumps, and other systems with a limited charge can be located in occupied spaces**
 - > Charge limitations dependent on room category and occupation density
 - > Location in machinery rooms often the most practicable also for unit systems

Systems and units using CO₂

- **Follow similar rules as for the location of systems using HFCs**
 - > No restrictions on the location if the release of the entire charge is considered to be harmless to people
 - I.e if the charge does not exceed an upper limit of 70 grams per m³ room volume
 - > Greater charge acceptable if access is restricted to the room/area in question
 - Detectors activating alarm are required if the concentration could exceed said limit
- **Heavy machinery, as used in large systems, is generally placed in separate machinery rooms for practical reasons**

Systems and units using hydrocarbons

- **Small, sealed units with less than 150 grams charge carry no restrictions on location**
- **Location of systems, or components, with bigger charges depends on charge size – absolute and relative to the room volume**
 - > No restrictions, provided that an average gas concentration of 25 % of the lower flammability limit will not be exceeded – even if the entire charge leaks out
 - For propane and propylene this corresponds to 8 gram per m³ room volume
 - Bigger charges allowed with additional requirements, see EN-378 for details
 - > Charge limits of 1 – 2.5 kg in addition, dependent on room category
 - > Up to 25 kg charge permitted by EN-378 under certain conditions in locations restricted to persons with authorised access
 - Comment: Hydrocarbon charges of this size are not recommended in direct systems
- **If the requirements cannot be complied with, the system has to be located in a machinery room or in a ventilated enclosure (indoors or outdoors)**
 - > See Information Sheet 4.2 for machinery room requirements
- **Outdoor locations are preferable wherever possible**
 - > For additional safety, detectors should be installed that activate an alarm alerting appropriate personnel

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Machinery rooms for systems using natural refrigerants

The paragraphs below outline some important issues, but are not exhaustive. Readers should refer to national regulations and refrigeration standards for more detailed information.

Overview

- Refrigeration machinery rooms are spaces intended for, and equipped for, housing refrigeration systems and heat pumps, or components of such systems
- **Required when the system, or the operation of the system, could be hazardous due to:**
 - > Refrigerant release
 - > Rotating machinery
 - > Components under high pressure
 - > Low temperatures
 - > Electrical hazards, and so on
- **Many of the risks are the same regardless of the type of refrigerant used**
- **Separate, detached, and ventilated containers/enclosures can be used as machinery rooms**
 - > Facilitates the location of hydrocarbon and (small) ammonia units
 - Fewer constraints on location
 - The requirements apply to the container/enclosure itself

Purpose of machinery rooms

- To prevent gas spreading to other parts of the building in the event of a (major) leak
- To prevent fire/explosion as a result of a release of flammable refrigerants
- Hinder access to unauthorised people
- Various practical purposes (not related to safety)

Location of systems and equipment

General requirements of machinery rooms

- Their relationship with other rooms or buildings needs to be considered in terms of access, likely gas spread, noise etc
- Good escape routes are required
 - > Preferably two (emergency) exits, one at each end of the room
 - With ammonia, it is especially important that escape routes avoid the need to pass the leakage point
 - > Doors shall open outwards and be equipped with anti-panic systems
 - One door should open directly to the outside of the building
- Rooms should be efficiently organised to facilitate system operation, servicing and maintenance
 - > Easy access to equipment for system operation
 - > Enough space for servicing the system
 - > Satisfactory lighting
- Specific requirements regarding the fire resistance of walls, floor, roof, and doors
- Ventilation requirements:
 - > Mechanically driven
 - Background ventilation
 - Emergency ventilation
- Goods not related to system operation or servicing should not be stored in machinery rooms
 - > Flammable material, in particular, should not be stored there
- Machinery room doors need to carry information about type and charge of the refrigerant(s) being used, and be clearly marked with relevant warnings

Special requirements for ventilated enclosures

- Ventilated enclosures are primarily intended for units with flammable refrigerants, in particular hydrocarbons
- A high ventilation rate minimises the risk of explosion by diluting gases
 - > Minimum fan capacity according to type and charge of the refrigerant
 - > Fan function and gas concentration needs to be constantly monitored
 - > System needs to be switched off in case of failure/high alarm
- Main electrical equipment must be located on the outside of the enclosure
 - > Ventilating fan must not create sparks
 - > Electrical equipment inside the enclosure has to be sealed
- Charge limitation for hydrocarbons
- Suitable for outdoor (roof) location
- Installing the enclosure within a machinery room may be practicable
 - > Simplifies compliance with the safety requirements

Location of systems and equipment

Measures to prevent the spread of gas

- **Design the room/enclosure so that it is gas tight, and keep it constantly below atmospheric pressure**
 - > Background ventilation from an extraction fan
- **Suitable location of air outlets**
 - > Ammonia is lighter than air
 - Ventilation outlets should be placed high up
 - > CO₂ and hydrocarbons are heavier than air
 - Ventilation outlets should be placed low down
- **Check that heavy gases cannot flow into rooms/areas below**
 - > Eg stairs, windows, drains etc
- **Activate powerful (emergency)ventilation in the event of a leak**
 - > Independent of other ventilation systems in the building
 - > Preferably automatically, initiated by a gas detector alarm
 - Obligatory with ammonia or hydrocarbon refrigerants
- **Avoid situations whereby the ventilation outlet from a machinery room could feed into the fresh air intake for ventilation**
 - > Neighbouring buildings should also be taken into consideration
- **Absorb the gas in a suitable absorbent if external ventilation is not desirable**
 - > Relevant for ammonia
 - > Easily absorbed in water (see Information Sheet 5.2)

Measures to prevent fire/explosion

- **Relevant for hydrocarbons and ammonia**
- **No special requirements for equipment intended for normal use in ammonia machinery rooms**
 - > Equipment that is in operation during a (heavy) leak must not generate sparks
- **If the lower flammability level could be exceeded, a machinery room for hydrocarbon refrigerants must be classified as a zone with a potentially explosive atmosphere**
 - > Only equipment designed for used in such atmosphere to be used
 - > Explosion relief measures need to be provided (wall or roof)
 - > Does not apply to ventilated enclosures
- **Automatic activation of emergency ventilation (at full capacity) at 25 % of lower flammability level**
 - > A ventilated enclosure may operate with full-fan capacity all the time
 - > Helps keep the gas concentration below flammable levels
- **Power to the system must automatically cut out, if 25 % of lower flammability level is exceeded**
 - > This includes other electric equipment in the machinery room
 - If not intended to operate in a potential explosive atmosphere

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Handling of ammonia leakage into the machinery room

The paragraphs below outline some important issues, but are not exhaustive. Readers should refer to national regulations, refrigeration standards, and other specialist literature for more detailed information.

Overview

- **Ammonia which leaks into a machinery room has to be taken care of in a safe manner**
 - > Gas must be prevented from penetrating neighbouring rooms or areas
 - > Spilled liquid must be prevented from entering lower floors or the sewage network
- **Disposal of ammonia in case of leakage is discussed in information folders from eurammon**
 - > <http://www.eurammon.com>
 - > eurammon-Information No.5, March 2009

Handling ammonia gas

- **The normal procedure is to ventilate out the gas**
 - > Fan activated automatically when ammonia is detected in the air
 - > High velocity flow, directed upwards, gives the best gas dilution
 - Ammonia is lighter than air, moves upwards
- **The potential for ammonia-containing exhaust air to spread has to be considered**
 - > Air outlets need to be located well away from fresh air inlets
 - > Particular care is needed if systems are located close to institutions such as schools, kindergartens, old people's homes etc
- **Absorption of the ammonia gas in water is a possible alternative when it is not desirable to ventilate out the polluted air**
 - > Water absorbs ammonia gas very efficiently
 - > For more information, see Information Sheet 5.2

Handling ammonia leakage

Handling liquid ammonia

- **A portion of the liquid will evaporate immediately due to the reduction in pressure**
 - > $\approx 25\%$ if leakage from the high pressure side (30°C)
 - > $\approx 10\%$ if leakage from the low pressure side of cooling systems (-10°C)
 - > Small amounts if the leak is from the low pressure side of freezing systems (-30°C)
- **To prevent a liquid spill from flowing out of the machinery room, the floor should be liquid-tight, or a basin/trough should be placed underneath the equipment**
- **Liquid caught in the room will evaporate over time**
 - > The boiling rate proportional to the surface of the liquid pool
 - > The boiling intensity decreases quickly
 - > Covering the liquid surface with foam (with low water content!), or a cover of tarpaulin or plastic, may reduce the boiling rate
 - > Smaller spills should be left to completely gasify
 - > Bigger spills may require the ammonia to be recovered by specialists
- **Water must not be used on liquid spills**
 - > Will result in heavy boiling
 - > Ammonia machinery rooms must not have automatic sprinkler system

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Absorption of ammonia gas in water

The paragraphs below outline some important issues, but are not exhaustive. Readers should refer to national regulations, refrigeration standards, and other specialist literature for more detailed information.

Overview

- **Water absorbs ammonia gas very efficiently**
 - > But adding water to liquid ammonia will greatly increase the boiling rate and must be avoided
- **The ammonia does not react chemically with the water**
 - > The ammonia vapour pressure over the mixture increases as the ammonia concentration increases
 - > Restricts the practicable absorption capacity of a given amount of water
- **Absorption of gas may be utilised in various situations**
 - > To reduce the ammonia concentration in air in emergency situations
 - > When it is not desirable to ventilate out ammonia-containing air
 - > To reduce the ammonia content in the exhaust air
- **The ammonia- water must be disposed of properly**
 - > Must be treated as special waste
 - > Must not be drained to surface water systems
 - > Drainage into municipal sewer only possible with the agreement of the local authorities
 - Neutralising the ammonia-water, or binding the ammonia chemically, may be required
- **The ammonia will be bound chemically by adding diluted sulphuric acid to the water**
 - > Forming ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, (a salt, fertiliser)
- **Absorption of ammonia in water is discussed in detail in an information folder from eurammon**
 - > <http://www.eurammon.com>
 - > eurammon-Information No.5, March 2009

Handling ammonia leakage

- **Ammonia vapour can be removed by chemical reaction with CO₂**
 - > Forming ammonium carbamate (a salt - corrosive)
 - > Can be utilised in difficult situations
 - eg removing ammonia from a cold store after leakage
 - > Special procedures have to be followed

Methods overview

- Using a water screen
- Bubbling ammonia-containing air through a water bath
- Leading the air through a simple scrubber with water
- Leading the air through an absorption column

Water screen

- **Water hose with spray nozzle**
 - > Additional protection equipment required (full-face mask, gloves etc.)
- **Can be used as an emergency measure in critical situations, in order to reduce the ammonia concentration in air, in order to:**
 - > Rescue an injured person
 - > Gain access and shut off valves to stop the release
- **Also applicable in less critical situations**
 - > Eg to "knock down" gas outdoors when spread could result in a very unpleasant atmosphere
- **Possible negative consequences (polluted water) need to be weighed against the benefits of the water screen**
- **Local authorities would need to be informed as soon as possible**

Bubbling through water bath

- **An alternative to ventilating out contaminated air**
- **Suitable for small/moderate amounts of gas**
- **Maximum practicable ammonia concentration in water 10–12 %**
 - > 100 l water may absorb up to approximately 12 kg ammonia gas

Scrubber

- **Used to reduce the ammonia concentration in exhaust air**
- **Neutralising the ammonia water may be required before it can be released into the sewage system**
 - > Release into sewers requires agreement from local authorities

Handling ammonia leakage

Absorption column

- Used to remove practically all ammonia from the exhaust air
- More than 99.5 % of the ammonia may be removed
- Neutralising the ammonia water–may be required before it can be released into the sewage system
 - > Only with the agreement of local authorities

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Natural refrigerants for new applications

TOPIC: Examples of systems using ammonia

Example 1. Heat pump for district heating system

- The world's largest ammonia heat pump, 14 MW heat output
- Situated in Drammen, Norway
- Two stage system with single screw compressors based on sea water as heat source
- Three heat pump units in series
- Designed for up to 90°C leaving water temperature, 65 bar high side pressure
- Measured COP > 3.0 at design conditions
- In operation since 2012
- Reference: Andy Pearson: "District Heatpumps and Rivers of Gold", www.tinyurl.com/NH3-totalenergy

Example 2. Heat pump for heating of buildings

- High pressure heat pump, 50 bar
- Screw compressors
- Two-stage system
- Hot water production up to 82°C
- Heat source: Ice water production for comfort and computer cooling
- Treated sewage water in addition during winter
- Design heating capacity 2950 kW
- Annual heat production (2011): 13 GWh
- COP (annual average): 2.9
- In operation since 2010
- Reference: Therma Industri AS, www.therma.no

Practical examples

Example 3. Heat pump for hot process water in a factory

- Ammonia heat pump with solution circuit
 - > Combined compression/absorption system
 - > Standard design pressure (25 bar), standard piston compressor
- Heating water up to 85°C in one of the biggest abattoirs in Norway
- Heat source: Waste heat (water) of 40–50°C
- Design heating capacity: 650 kW
- COP (annual average): 4.5
 - > Energy saving: 3.400.000 kWh per year
 - > Reduction in oil consumption: 350.000 l/year
 - > Reduction in CO₂-release: 850 tonnes/year
- In operation since 2007
- Referencee: Hybrid Energy AS, www.hybridenergy.no

Example 4. Heat pump/air conditioning system

- For heating and cooling Gardermoen Airport (outside Oslo)
- 7.5 MW heating capacity, 6 MW cooling
- Uses ground water as a heat source during the winter and as a heat sink during the summer
- The machinery room is situated 1 km from the other buildings
- Refrigerant charge: 2500 kg
- Coefficient of performance (COP) for heating and cooling combined: 5.5
- In operation since 1998
- Reference: Eggen, G. and G. Vangsnes: "Heat pump for district cooling and heating at Oslo Airport Gardermoen", Proc. From the 8th IEA Heat Pump Conference, May 2005, Las Vegas, USA

Practical examples

Example 5. Air conditioning of large office buildings in London

- Many examples exist of replacing standard CFC and HCFC AC units with ammonia units
- **Example 1: Heathrow Airport, Terminal 5**
 - > Four big chillers with screw compressors working in parallel
 - > In total, over 26 MW cooling effect
 - > Ammonia found to be the most sustainable alternative
 - > Installed after in-depth risk analysis and safety considerations
 - > Concluded to be as safe as conventional, big AC units
- **Example 2: Major bank**
 - > Conventional chillers, used for air conditioning, replaced with ammonia units in 2000
 - > Existing equipment had caused operational problems in hot weather
 - > Mounted on the roof
 - > No problems during extreme temperature of 38°C in the summer 2003
- **Example 3: IMO's Headquarters (IMO = International Maritime Organization)**
 - > Two old CFC-11 units replaced by ammonia units in 2001
 - > Cooling capacity 1400 kW
 - > Refrigerant charge 280 kg
 - > Mounted on the roof
 - > Evaporative condenser
 - > Noticeable reduction in power consumption after the replacement
- **Reference: Pearson, A: "Ammonia's Future", ASHRAE Journal, Febr. 2008, pp. 30–36**
[www.eurammon.com, "Case studies"](http://www.eurammon.com/Case%20studies)

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Examples of cascade systems using CO₂ usage in the bottom stage
Example 1. Low temperature system for freeze-drying of coffee

- Built in Hayes (UK) in 2001
- Possibly the first example of an operational cascade system with CO₂ in the bottom stage
- Refrigerant in the top stage: Ammonia
- Total refrigeration demand (at -48°C and -54°C): 2400 kW
- Investment 13 % lower than for an ordinary two stage ammonia system
- Energy efficiency calculated to be 5 % better than with ammonia in two stages
- Oil-free compressors were used
 - > Due to lack of experience with oil handling in CO₂ systems, and the use of oil-injected screw compressors with CO₂. (Oil-lubricated compressors commonly used today)
- Reference: Star Refrigeration, star@star-ref.co.uk

Example 2. Refrigeration system for a small supermarket

- Situated in Beder, Denmark
- Installed in: 2002
- Refrigerant in the top stage: Propane
- Refrigeration demand (cooling/freezing): 10 kW/35 kW
- Conventional indirect system for cooling (propylene glycol)
- Investment compared to direct system with HFC-404A: +12-20 %
- Energy consumption compared to direct system with HFC-404A: ± 0
- Reference: K.G. Christensen, P. Schneider: „ Developments in the field of refrigeration in Denmark“, Dansk Teknologisk Institutt, Århus, 2003

Practical examples

Example 3. Freezing system on board fishing vessel

- MS Kvannøy (Norwegian trawler)
- Installed in 2002
- The first cascade system with CO₂ on board a vessel
- Refrigerant in the top stage: Ammonia
- Freezing capacity: 200 tonnes per 24 hours in 11 plate freezers, -49°C
 - > Also includes a freezing store and an ice machine
 - > 25 % increase in freezing capacity compared to conventional systems with -40°C evaporation temperature
 - > Actual freezing capacity greater than predicted
- Hot-gas defrosting
- Six CO₂ piston compressors (40 bar), and a separate defrosting compressor (50 bar)
 - > Lubricant: Polyolesther (POE)
- Two screw compressors for ammonia
- A small separate cooling unit with HFC-404A ("cold finger") to limit the pressure during system standstill
- Coefficient of performance (calculated) better than with one-stage screw compressor using ammonia, operating at -40°C
- Reference: Per Skærbek Nielsen: "Nyt ammoniak/CO₂ højeffektivt kølekoncept for fryseanlegg for fiskebåter", Norsk Kjøleteknisk Møte 2003 (In Danish)

Example 4: Refrigeration system for supermarket

- Situated in Auckland, New Zealand
- Refrigerant in the top stage: Propylene
 - > Machinery room on the roof
 - > Two separate refrigeration circuits with propylene, each with 20 kg charge
 - > Continuous ventilation to remove any gas in the event of a propylene leak
 - > Intrinsically safe electrical circuits for instrumentation
- Refrigeration demand (cooling/freezing): 90 kW/190 kW
- CO₂ both for freezing (-35°C) and cooling (-7°C)
 - > Cooling by CO₂ liquid pumped from the CO₂ system receiver
- Heat recovery from hot gas in the top stage
- Energy demand compared to HFC-404A in direct system: - 7 % (calculated)
- Reference: Alexander Cohr Pachai: "The first CO₂ Supermarket Plant in New Zealand", gtz Proklima, Natural Refrigerants, Sustainable Ozone- and Climate-Friendly HCFC alternatives, Provisional Version – April 2008

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Natural refrigerants for new applications

TOPIC: Examples of systems using CO₂ in transcritical cycles*Example 1. Hot tap water heat pumps*

- In production in Japan since 2001
- Leaving water temperature 85°C
- Heat source: Air
 - > Operates down to -20°C air temperature
- Advanced compressor technology
- More than 1 million units sold
 - > Primarily for the domestic market
- Steadily improvements in efficiency
 - > COP at nominal conditions increased from 3.5 in 2001 to more than 5 in 2008
- Reference: www.R744.com

Example 2. Small unit systems

- Coca Cola has chosen CO₂ as the HFC-free refrigerant of choice for its bottle coolers and vending machines
- Several tens of thousands of units in operation world wide
- Complete HFC phase out in new equipment by the end of 2015
- 8 % less energy consumed than with HFC-134a
- Reference: www.R744.com

Practical examples

Example 3. Supermarkets, general

- Transcritical CO₂ solutions are becoming market standard for European supermarkets
- Nearly 3000 systems in operation
- Improved component and system design have made transcritical solutions competitive in warmer climates
 - > Parallel compression
 - > Ejector systems
 - > Mechanical subcooling after gas cooler
 - > Low pressure receiver/flooded evaporators
- Reference: www.r744.com

Example 4. Large-scale supermarket (Hypermarket)

- Situated in Wettingen, Switzerland
- Installed in 2004
- Refrigeration capacity (cooling/freezing): 116 kW/322 kW
- Investment compared with reference system (DX-system, HFC-404A): +10-20 %
- Energy consumption compared with reference system: -(5-10) %
- Energy consumption compared with indirect system using HFC-404A for cooling, direct system for freezing: -(15-20) %
- Reference: B. Heinbokel, A. Gernemann: Eine neuentwickelte CO₂-Kälteanlage für den Tief- und Normalkühlbereich in einem Schweizer Hypermarkt, DKV 2005, Würzburg (sited in: M. Kauffeld: Trends and Perspectives in Refrigeration Technology, – Co₂ol Food, Berlin, 2007)

Example 5. Supermarket

- Situated in Charlottenlund, Danmark
- Installed in 2007
- Refrigeration capacity (cooling/freezing): 30 kW/110 kW
- Condenser/gas cooler with adiabatic pre cooling of inlet air
 - > 4-6 K temperature reduction
- Receiver designed for 90 bar
 - > The refrigerant is collected in the receiver during service - no refrigerant release
- Energy efficient operation
 - > Condensing temperatures 10-15°C during winter (subcritical operation)
- Reference: "Vidensenter for HFC-fri køling", Denmark, www.hfc-fri.dk

Practical examples

Example 6. Supermarket in Migros Bulle, Switzerland

- 5000 m² sales area
- Refrigeration capacity 120 kW (medium temperature), 55 kW (low temperature)
- Transcritical CO₂ booster system with parallel compression, ejector and flooded evaporators
- Evaporation temperature increased from -8°C to -1.5°C
- Energy consumption reduced by 12 % compared to conventional booster system, referred to central Europe conditions. 16 % reduction referred to southern Europe conditions
- Reference: Jonas Schönberger: "Advanced CO₂-booster system for warm climates". Atmosphere, natural refrigerants, 15–16 October, 2013, Brussels

NMR's Information Sheets

Natural refrigerants for new applications

TOPIC: Examples of systems using hydrocarbons

Example 1. Refrigerators and (chest) freezers

- In Europe and Japan iso-butane is the preferred refrigerant in domestic refrigerators and freezers
 - > Several hundred millions of appliances are in operation
- Hydrocarbons increasingly also used in commercial units of the plug-in-type
 - > Iso-butane and propane
- Considerable reduction in energy consumption compared to HFCs
- Reference: www.hydrocarbons21.com

Example 2. Ice-cream cabinets

- Unilever has chosen hydrocarbons (R-290, propane) for its ice cream cabinets
- Field tests started in 2000/2001
- 9 % efficiency improvement compared to HFC-404A
- Today 800 000 units in operation world wide
- Reference: www.hydrocarbons21.com

Example 3. Other professional refrigeration units

- A number of cooling products for the professional market are available with hydrocarbons:
 - > Bottle coolers
 - > Commercial kitchen refrigerators and freezers
 - > Display cabinets of plug-in-type in supermarkets
 - > Wine coolers, water coolers, ice machines for restaurants and bars etc.
- Reference: "Low GWP Alternatives to HFCs in Refrigeration", Environmental Projekt no. 1425, Miljøstyrelsen, København, 2012

Practical examples

Example. Air conditioning of office building, Herlev, Denmark

- Chiller for cold water production, 12/7°C
- Type of refrigerant: Propylene
- Cooling capacity: 100 kW
- Details of the cooling unit:
 - > Located outdoors, at ground level
 - > Placed in a ventilated enclosure (machine cabinet)
 - > Piston compressors
 - > Equipped with two independent circuits, each with 9 kg charge
 - > Type of lubrication: Polyolester (POE)
 - > Ex-classified gas detector and fan
 - > Ventilation activated at 10 % of lower flammability limit (LFL)
 - > Power supply cut at 25 % of lower flammability limit (LFL)
- In operation since 2007
- Operational performance good
 - > Also true for other propylene systems from this manufacturer
- Somewhat higher investment than for a standard unit using HFC
- Reference: "Propylen chiller hos VWR – Bie & Berntsen A/S", (In Danish), Videncenter for HFC-fri køling, Danmark, www.hfc-fri.dk

Example 4. Air conditioning

- Church House, Westminster Abbey, London
- Type of refrigerant: Propane
- Installed in 2007
- Cooling capacity: 600 kW
- Screw compressors
- Type of lubricant: Polyalkylene glycol (PAG)
- Floating condenser pressure and liquid subcooling for improved energy efficiency
- Energy saving compared to conventional unit with HFC-134a: 32 % (calculated)
- Investment compared to conventional unit +16 %
- Reference: www.earthcareproducts.co.uk