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Low GWP Alternatives to HFCs in Refrigeration

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Low GWP Alternatives to HFCs in Refrigeration

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1. Introduction

1.1 The greenhouse effect and potent greenhouse gases

The potent greenhouse gases (also called the “F-gases”, “fluorinated greenhouse gases” or the three “industrial gases”) are on the list of greenhouse gases, covered by the Kyoto Protocol. In 2010, the emission of F-gases in Denmark was 854 thousand tonnes CO_2 equivalents, which counts for about 1.3 per cent of the total emission of greenhouse gases.

In 2010, the consumption in Denmark was 358 tonnes of HFCs, 3.8 tonnes of SF_6 and 0.9 tonnes of PFSs. The figures indicate that the use of HFCs is the most important issue and is the reason why this report concentrates on HFCs. Only a small amount of SF6 is used for high voltage power switches and a small amount of PFC is used for the production of optic fibres.

The refrigeration industry counts for 331 tonnes (of the total of 358 tonnes) and shows that the use for refrigeration is by far the most important application. Other applications only account for 27 tonnes, including thermostats, medical dose inhalers and propellant in special aerosols. Use in the production of insulation foam has ceased.

More than 92% of the F-gases consumed in Denmark are used for refrigerants. Therefore, this report concentrates on substituting the use of HFCs as refrigerant.

In 1998, the report “Ways of Reducing Consumption and Emission of the Potent Greenhouse Gases (HFCs, PFCs and SF_6)” (Pedersen, 2000) was prepared. It was updated in 2001 and 2006 and printed by the Nordic Council of Ministers (Pedersen, 2007). The report described the application and emission of the potent greenhouse gases in the five Nordic countries and at the same time explained how emissions and the use of alternative substances could be reduced. “Success stories” from the Nordic countries were included, in which alternative technology was introduced instead of technology based on the potent greenhouse gases.

The present report is partly based on the Nordic reports and similar reports made for the Danish Environmental Protection Agency and information recently collected by Danish Technological Institute (DTI).

Purpose
The purpose of the new project is to update the earlier reports and to describe the possibilities of using alternative technology objectively. In addition, all initiatives that have been made in Denmark to reduce the emission of potent greenhouse gases will be described.

Finally, the purpose is to compile the latest results regarding the development of alternative technology. A rapid development is taking place in that area.

Contents
The project is partly based on the results of the previous Danish and Nordic reports as new research is carried out to describe the development level of alternative technology and its rate of implementation.

Summed up, the contents can be described as follows:

- Retrieval of data on the Danish consumption/emission of potent greenhouse gases. The data has been retrieved from the national report from the Danish Environmental Protection Agency.
- New examination of technology for reducing consumption/emission of potent greenhouse gases. The rate of implementation of the new technology has been evaluated and for each consumption area a scenario has been laid down for when the new technology can be implemented by the most advanced part of the industry.
- Description of the national Danish initiatives for reducing emissions.
- Selection of areas where Denmark is in a strong position with regard to alternatives (seen from an international point of view).
- Selection of areas where special efforts should be provided to promote the development of alternative technology.
- Description of the specific problems.

HFCs are used mainly as refrigerant in:

- Commercial refrigeration systems (supermarkets, shops, convenience stores etc.)
- Mobile refrigeration systems (car air-conditioning, reefers etc.)
- Heat pumps
- Air-conditioning systems
- Cryogenic systems

1.2 Participants

The project is being carried out by Per Henrik Pedersen, M.Sc., Danish Technological Institute, Energy and Climate, in cooperation with the Danish Environmental protection Agency.

DTI would like to thank Mikkel Aaman Sørensen, the Danish Environmental Protection Agency for support for working out the report.

Work on the report commenced in May 2011 and ended in April 2012.

2. Danish National Initiatives

The use of F-gases has been significantly reduced!

The Danish regulation has led to a decline in the consumption of F-gases. The most important substances are the HFC substances and the import of bulk HFC substances has been reduced from around 1000 tonnes/year in 2000 to around 350 tonnes in 2010.

In 2001 and 2002, Denmark introduced national regulation on F-gases. The aim was to reduce the consumption and emission of F-gases and the Danish Parliament (Folketinget) agreed on a number of instruments. They comprised a ban on the use of F-gases for certain purposes, F-gas taxation and support for research and development of alternative technology.

In Denmark, taxation was implemented in 2001 and a ban on certain applications was introduced in 2002.

A short description of the tax/refund scheme
The main principle was that a tax of DKK 100 (app. 13 Euro) per tonne of CO_2 equivalent was imposed on the importation of HFC/PFC/SF6. That figure was increased by 50% from January 2011 to DKK 150 (app. 20 Euro) per tonne of CO_2 equivalent. That means that a tax amounting to DKK 195 (app. 26 Euro) per kg is now imposed on the most frequently used F-gas refrigerant (HFC-134a).
The use of HFC for mobile air conditioning is exempt from the tax.

In practice, the system is implemented by taxation on all gas in bulk and on imported products. The tax is administrated by the Danish Customs and Tax Administration, which is an organisation under the Danish Ministry of Taxation.

Information from the market indicates that the tax/refund scheme has led to more awareness from owners as well as operators of the equipment. The tax has also increased the attention on alternative substances (HCs, CO_2, ammonia or other substances or techniques) and has resulted in improved housekeeping of reused gas. Teething troubles were solved through a good cooperation between the industry and ministries and since then the administration of the system has worked satisfactorily.

A short description of the ban
In the Danish Statutory Order, no. 552, on regulation of certain industrial greenhouse gases from 2002 there is a general ban on new products containing or using F-gases from 1 January 2006.

There are some exemptions from this general ban. For instance, the use of HFCs in refrigeration systems is still allowed for cooling equipment with HFC charges between 0.15 kg to 10 kg and the use of HFC for service purposes is exempt from the Statutory Order. In 2002, it was necessary to introduce this “window” of exemptions, because it was estimated it would take longer time to develop alternatives in this area.

The export of HFC containing products is also exempt from the ban.

Support for alternatives

When the regulation was approved it was decided to support R&D projects to ensure a quick development of alternative technology. The Danish Environmental Protection Agency (EPA) conducted the scheme and a number of projects in the refrigeration area were supported financially with app. DKK 20 million. In addition, the "HFC free Centre" was established by the Danish EPA. The Centre offers consultancy services that are free of charge (up to 5 hours of engineering consultancy) for the refrigeration industry and the installers to help them implement alternative technology.

Simultaneously, the education capacity for installers was increased, and hundreds of refrigeration technicians have now been educated to handle refrigeration systems with CO_2, hydrocarbons and ammonia.

Implementation of alternative technology

In this section, some examples are given of the extent of alternative refrigeration technology in Denmark.

Supermarkets:

A number of different centralized refrigeration systems using CO_2 refrigerant were built and tested in supermarkets in Denmark. Soon it appeared that the transcritical systems were well-suited for conditions in Danish supermarkets and today the technology is standard technology and hundreds of systems are installed showing good performance, energy efficiency and economy. There is also considerable export of CO_2 equipment to installers in other countries.

Commercial plug-in cabinets:

Commercial, refrigerated cabinets using hydrocarbon refrigerants have been developed and tested in the past decade. New components (including compressors) were developed and marketed and the technology appeared to be more energy efficient compared to similar HFC refrigeration technology. Today, hydrocarbon technology is standard in bottle coolers, food service cabinets, ice-cream freezers, etc. Several international food and beverage companies use professional refrigerators with hydrocarbon technology.

Industrial refrigeration systems:

In Denmark, ammonia has been used for industrial refrigeration for more than 100 years. Today, only very small industrial refrigeration systems are built with F-gases (< 10 kg HFC).

Chillers for air conditioning and the process industry:
Ammonia chillers have been produced in Denmark for at least 30 years. In addition, two manufacturers have developed and marketed hydrocarbon chillers during the past decade. The ammonia chillers are very efficient and competitive for high-cooling capacity, and the hydrocarbon chillers are very efficient and competitive in the medium to small range. Only very small chillers with F-gases are installed in Denmark (<10 kg HFC).

Very recently, a commercially competitive chiller with water as refrigerant has been developed at DTI in cooperation with Japanese companies and it will probably be introduced to the market in about 3 years by Kobelco and Johnson Controls. The chiller is at least as energy efficient as the very best HFC chillers and 10 to 20% better than typical existing installations. Demonstration of the technology will be established shortly.

Domestic refrigerators and freezers:
The introduction of the regulation very soon resulted in an almost 100% penetration of hydrocarbon technology for domestic refrigerators and freezers, for domestically produced as well as imported appliances.

Decline in consumption and emissions
The Danish regulation has led to a decline in the consumption of F-gases. The most important substances are the HFC substances and the import of bulk HFC substances has almost been reduced from around 1000 tonnes/year in 2000 to around 350 tonnes in 2010 (see figure 1).

There is a delay in the impact for emission of F-gases as most of the consumed bulks are filled into refrigeration systems with certain leakage rates. The Danish emission of F-gases declined from 895,000 tonnes CO_2 equivalents in 2008 to 854,000 tonnes CO_2 equivalents in 2010.

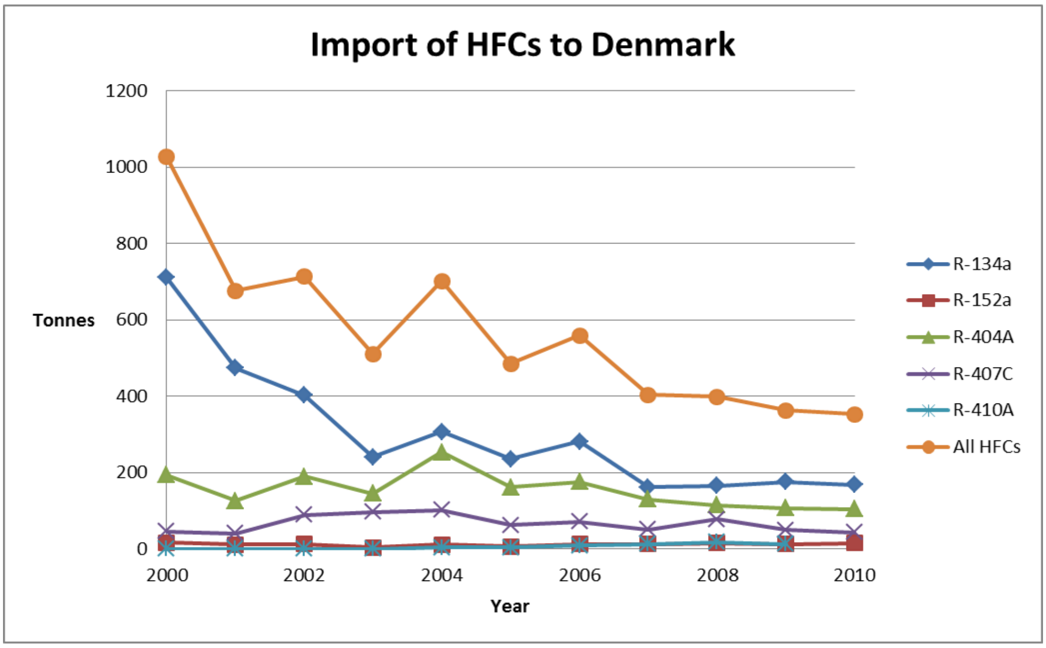

Figure 1: Import of HFC bulk to Denmark 2000 – 2010. Source: Danish Environmental Protection Agency, 2011.

3. The use of HFCs and substitutes in the refrigeration industry

HFC (hydrofluorocarbon) is the name used for a number of substances produced by placing a number of fluoride atoms on hydrocarbons with some hydrogen atoms left in the molecule. The most common HFC substances are as follows:

Table 3.1: The most common HFCs

	Chemical formula	Normal boiling point (C)	GWP (100 yrs)
HFC-23	CHF_3	- 82.1	14,200
HFC-32	CH_2F_2	- 51.7	716
HFC-125	C_2HF_5	- 48.4	3,420
HFC-134a	CH_2FCF_3	- 26.5	1,370
HFC-143a	CF_3CH_3	- 47.5	4,180
HFC-152a	$C_2H_4F_2$	- 24.2	133
HFC-1234yf	$C_3H_2F_4$	- 29.5	4.4

Note: Recently, low-GWP HFCs are being offered by chemical producers. One of them is HFO1234yf, which will be implemented in mobile air conditioning in the near future. This report will not go into further detail about that substance as no (or not much) experience has been gained with that refrigerant in the Danish refrigeration industry.

The commonly used "R" in the designations R-134a, R-125 etc. stands for *Refrigerant*. The designation HFA-134a is also used. It corresponds to HFC-134a.

HFC substances are often used in mixtures of refrigerants, which are assigned the R-400 or the R-500 serial number. A list of refrigerants and refrigerant mixtures is given in Appendix A.

HFCs are not produced in Denmark. All gases are imported and made by international chemical producers.

HFCs are used mainly as refrigerant in refrigerators and refrigeration systems.

Natural refrigerants

Due to the global warming impact from HFC refrigerants there has been great interest in introducing natural refrigerants especially in commercial refrigeration as the refrigerant charges and leakage rates are relatively high.

Natural refrigerants are substances that are already included in nature's own cycle, for instance ammonia, hydrocarbons, CO_2, water and air.

None of the refrigerants in the group of natural refrigerants are perfect and they all have technical limitations. Ammonia is toxic, hydrocarbons are flammable, CO_2 operates at very high pressure and has a low critical point, water has a very low volumetric refrigeration capacity and cannot be used below 0°C and air is only an interesting option at very low temperatures below -60°C.

Therefore, natural refrigerants have to be chosen with care and not only one fluid will cover all applications. This being said it is worth mentioning that there are technical solutions available with natural refrigerants for all applications.

This chapter is divided into 8 sections including all applications in the refrigeration industry.

3.1 Domestic refrigerators and freezers

A large quantity of domestic refrigerators and freezers were made in Denmark by Vestfrost, Gram, Frigor, Derby and Elcold. However, most of this production has moved to low income countries.

In Denmark, two manufacturers (Vestfrost and Elcold) still produce a small amount of chest freezers.

There is also some production of components for refrigerators and freezers, including thermostats, pipe systems and compressor components, but some part of this is also on the move to low income countries.

Ozone-depleting substances were once used when manufacturing refrigerators and freezers. CFC-11 was used for blowing polyurethane foam for insulating refrigerators and R12 (CFC-12) as the refrigerant in the refrigeration system. In a transitional period, different technologies were used instead of CFC, including HCFCs for blowing polyurethane foam. Companies have pursued different paths in their development work. All the manufacturers used R134a (HFC-134a) as a substitute for R12 in their refrigeration systems and are still using it in a large part of their production. R134a was also used by some manufacturers for blowing polyurethane foam.

In 1993, environmental organisations began questioning the environmental impact of HFCs because the substances (like CFCs and HCFCs) are potent greenhouse gases.

In Germany, Foron, together with environmental organisations, introduced refrigerators with hydrocarbons. Other manufacturers soon followed suit. Danfoss was out early with a complete compressor programme for domestic appliances with isobutane (R600a) as refrigerant.

Within just a few months, the entire German market was forced to use hydrocarbons. That also applied to foreign manufacturers who wanted to sell in that market. Many people feared that explosions might occur in some of the refrigerators because there was some risk of an explosive mixture of hydrocarbons and air developing in the cabinet. The mixture could be ignited by a spark from the thermostat, door contact or other spark generator. That problem was solved by placing potential spark generators outside the cabinet and by preventing leakage of refrigerant inside the cabinet.

At present, several hundred million of appliances have been built and the technology has proven to be safe.

Furthermore, refrigerators and freezers with hydrocarbons have proved to be more efficient as HFC models, and refrigerators with hydrocarbons are less noisy than corresponding HFC models because of lower pressure in the refrigeration system.

Today, most of the European production is based on hydrocarbon technology, and the developing work for compressors and new energy efficient appliances is based on hydrocarbons.

Hydrocarbon technology is also gaining momentum in most other countries in Asia, Africa and Latin America.

However, in the US, R134a is standard, but hydrocarbon is going to be introduced on the market.

Financial barriers
Hydrocarbon technology exists and has been fully implemented by the large European and Asian manufacturers. As investments already have taken place, there are no additional costs for HFC free technology.

A manufacturer of domestic refrigerators and freezers informs that in general no price difference exists between HFC and hydrocarbon based appliances.

Emission to the surroundings/accumulation in scrapped products
Only a small part of the HFCs used in the manufacture of refrigerators and freezers are emitted directly to the surroundings (estimated to be less than 5%). The remainder is accumulated in the product and gradually released by diffusion from the insulating foam or leakage in the refrigeration system. At the time of scrapping, most of the HFCs still remain in the products.

A small proportion of the HFCs in refrigerators and freezers is presumably collected and incinerated in connection with collection schemes for old refrigerators. Nevertheless, it is assumed that some of the HFCs will be emitted to the atmosphere in the long run – through diffusion and leakage during the lifetime of the appliances and in connection with scrapping.

Situation with respect to alternative technology
HFC free technology has been developed and implemented.

3.2 Commercial refrigerators and freezers (plug-in)

A significant number of commercial refrigerators and freezers are manufactured and installed in Denmark. It is estimated that there are app. 200,000 units, although the specific figure is unknown. The three biggest groups of appliances within commercial refrigerators and freezers (plug-in) are bottle coolers, professional kitchen refrigerators & freezers and ice-cream cabinets. The group also includes vending machines, water coolers, supermarket plug-in display cabinets, minibars, ice machines, wine coolers etc.

Bottle coolers

Glass door bottle coolers can be found in nearly every supermarket, gas station and kiosk. The most common type is the one door 400 litres type, but also bigger (2 or 3 glass doors) and smaller types are on the market. Glass door coolers are often installed by a soft drink company or a beer company and are labelled with the logo of the company.

It is estimated that about 70,000 bottle coolers are installed in Denmark where a significant production also takes place (Vestfrost and Gram Commercial).

Previously, R134a (HFC-134a) was standard as refrigerant in bottle coolers and almost all bottle coolers sold so far use that refrigerant.

But that has changed rapidly during the past couple of years. All ready in 2000, Vestfrost marketed a hydrocarbon version using R600a and has delivered several thousand units to the European marked. Later on, Gram Commercial also started production with R600a.

In 2006 – 2007, a field test was conducted in a co-operation between Carlsberg, Vestfrost and Danish Technological Institute. 9 coolers were operated with CO_2, 5 with R134a and 4 with R600a, and in 2006 they were placed in supermarkets for 3 months and during that time field tests were carried out.

The hydrocarbon coolers as well as the CO_2 coolers showed good performance and the hydrocarbon coolers showed 27.7% reduced energy consumption compared to the R134a coolers, and the CO_2 coolers showed 11.7% reduced energy consumption compared to the R134a coolers. (Pedersen, 2008)

On basis of these results and other investigations, Carlsberg decided to go for hydrocarbon coolers where possible and where educated technicians can service the appliances. Hydrocarbon coolers have proved reliable and Carlsberg is installing bottle coolers in the Nordic countries (Denmark, Finland, Norway and Sweden) and has started installation in Germany and Switzerland. Soon they will also be installed in other countries (Andersen, 2011).

Photo 1: Vestfrost bottle cooler during field test in a Copenhagen supermarket.

Status of HFC free technology:
HFC was standard, but HFC free technology with hydrocarbon refrigerant is very rapidly being introduced to the EU market.

CO_2 based coolers are also a possibility, but these have so far only been produced in limited numbers.

Ice-cream cabinets
Ice-cream cabinets with glass lids can be found in almost every supermarket and kiosk in the Nordic countries. Most of them have been installed by substantial ice cream producers.

Many ice-cream cabinets were earlier produced in Denmark. Most of this production has been moved to low income countries, and Elcold is now the only Danish producer.

HFC refrigerant was standard (R404A and R134a). However, hydrocarbon cabinets have been available for many years and it seems as if hydrocarbon technology now is standard in the EU. Unilever has chosen hydrocarbons for ice-cream cabinets and is implementing hydrocarbon cabinets worldwide.

Unilever started the HC cabinet rollout in Europe (in Denmark) in 2003 (with 800 cabinets). In 2004, we introduced about 15,000 cabinets into 17 countries in the EU, followed by a further

40,000 in 2005. In 2010, the company installed app. 100,000 cabinets with hydrocarbons and Unilever has now installed more than 640,000 units worldwide (van Gerwen, 2011).

Status of HFC free technology:
HFC free technology is available, marketed, implemented and is a standard technology using hydrocarbon refrigerant.

Professional kitchen refrigerators & freezers
It is estimated that about 50,000 professional kitchen refrigerators and freezers are installed in Denmark. Most of them are of the stainless steel upright type, but also counter types are present.

In Denmark, there is one manufacturer of professional kitchen refrigerators and freezers. HFC was standard until 2003.

Since 2002, Gram Commercial in Denmark has marketed appliances with R290, and this type is now standard for the company's products in Denmark and other European countries. Gram has about 50% of the market in Denmark and 85% of the production is exported to mainly UK, Germany, Austria, Holland, Belgium, Sweden and Norway. Other European suppliers have started to offer appliances with R290.

Photo 2: Professional kitchen refrigerator (food service cabinet) from Gram. The refrigerant system uses R290 (propane).

Wine Coolers
To some degree, wine coolers look like bottle coolers. Wine coolers have become popular for professional as well as domestic use. There is a great variety of wine coolers and they use different cooling technologies, including thermoelectric cooling for the smallest units. Other units use compression refrigeration.

Vestfrost is the only manufacturer in Denmark. Vestfrost is producing energy efficient coolers and is using compressor cooling technology, using R600a as standard in production.

Photo 3: Vestfrost wine cooler using R600a (isobuthane).

Minibars
Three different refrigeration technologies are present in minibars for hotel rooms. Absorption minibars are the most common. In Denmark, about 20,000 minibars are in use.

Absorption minibars do not have a compressor. They are quiet but have a high energy consumption and low cooling capacity. The refrigerant is ammonia and the refrigeration system consists of ammonia, water and hydrogen.

Thermoelectric minibars are now expanding. They are quiet but have high energy consumption. Thermoelectric cooling uses a "Peltiér element" which is a semi-conductor.

Compressor minibars are much more energy efficient and have a high sound level, when the compressor is working. At least one type of compression minibar can be controlled, so the compressor runs during daytime and a small ice accumulator cools the contents during night-time. Compressors for R600a of relevant size are available from SECOP (former Danfoss Compressors) and at least one manufacturer is using this compressor and R600a (J. Christensen, 2011).

Vending machines
R134a is standard refrigerant in vending machines. Most soft drink vending machines are purchased by large suppliers of soft drinks. The refrigerant policy of the Coca-Cola Company is going for CO_2 as refrigerant and field tests are on-going.

Water coolers
A great number of water coolers for both bottled water and tap water are installed in the Nordic countries. They are installed with a small compressor refrigeration system and earlier HFC refrigerant was standard. Coolers using hydrocarbon (R600a) are available on the market.

Ice machines
A great number of ice machines are installed in restaurants and bars. So far, HFC refrigerant has been standard. The Japanese company Hoshizaki with production in the UK recently developed the first ice machines with hydrocarbon technology (R290) and the first units are available on the European market.

Supermarket display cabinets
The use of supermarket cabinets of the plug-in type is increasing in Northern Europe. Many small- and medium-sized supermarkets install such units instead of the cabinets for remote cooling machinery.

The plug-in cabinets are cheaper and more flexible. With glass lids they are also economic in use.

The condenser heat is submitted into the supermarket sales area where the cabinets are placed and that might cause high room temperatures during summertime.

AHT from Austria is a major manufacturer of such cabinets. At the "Procool" event in Hannover in April 2006, AHT presented a R290 version of the “Paris” freezer cabinet (724 litres net, 120 grams of R290). Since 2007, hydrocarbon cabinets using R290 have been standard.

Vaccine coolers
WHO plays an important role in approving vaccine coolers for health stations. A large number of vaccine coolers (several hundred thousands) are installed in health stations around the world. Many of them are placed in rural areas in developing countries.

Vestfrost has a production of vaccine coolers in Denmark.

R134a is the standard refrigerant, but WHO has drafted new standards, which also allow hydrocarbon as refrigerant. The technology for manufacturing hydrocarbon vaccine coolers is available including compressors. Some training of service technicians might be necessary in the countries installing such appliances.

DC coolers
There is some production of DC refrigerators (Direct Current, 12 V or 24 V) for trucks, small boats etc. and for vaccine chillers that are powered by solar cells (photovoltaic). SECOP (former Danfoss Compressors) is a major manufacturer of compressors for this type of appliance, and so far R134a is the refrigerant that is used. SECOP has developed and marketed new DC compressors for isobutane and propane. Up till now, this has been used in a limited number for solar powered vaccine coolers and solar powered ice-cream cabinets.

SolarChill vaccine coolers
Vestfrost in Denmark was first on the global market with a SolarChill vaccine cooler, approved by WHO. This SolarChill vaccine cooler is powered directly by photovoltaic panels, using hydrocarbon refrigerant and has an ice storage which can keep the vaccine cool up to 5 days without any power. Hundreds of SolarChill vaccine coolers are now installed at health centers in areas without grid electricity. The SolarChill technology is developed in a partnership and includes the organizations: WHO, UNICEF, UNEP, PATH, GTZ, Greenpeace International and Danish Technological Institute.

Photo 4: Photo of the SolarChill vaccine refrigerator, produced by Vestfrost. The refrigerant is R600a (isobutane). Ice storage ensures cooling during night-time.

3.3 Commercial refrigeration systems

The area of commercial refrigeration covers a wide range of refrigeration applications. Commercial refrigeration is the part of the cold chain comprising equipment used mainly in retail outlets for preparing, storing and displaying frozen and fresh food and beverages. However, equipment for commercial refrigeration can also be used by small producers of food products and smaller refrigerated warehouses for storage. In some cases, there might be some overlap with the industrial segment for these latter applications.

For commercial systems, two levels of temperatures are typically used (medium temperature for preservation of fresh food and low temperature for frozen products). Commercial refrigeration is the refrigeration subsector with the largest refrigerant emissions calculated as CO_2 equivalents. These represent about 40% of the total annual global refrigerant emissions (IPCC/TEAP, 2005). In 2009, emissions in Denmark for “commercial stationary refrigeration and AC-systems” equalled 590 kt CO_2-eq. out of a total of 858 kt CO_2-eq. for all F-gases (DEPA-2010). Most of this is likely to come from commercial refrigeration systems, and this makes the share of emissions from this sector even bigger in Denmark. This is due to high charges of refrigerant (distributed systems) and high leakage rates. For commercial systems we typically see that the direct emissions of greenhouse gases amount to 40% of the total climate impact from the refrigeration system. In countries with a big share of hydropower and/or nuclear power this figure is even bigger. Taking these considerations into account it is very important to focus on this segment.

R404A was the preferred refrigerant for commercial refrigeration. R404A has a pretty low normal boiling point so it can be used both at low and medium temperature. R134a was also used, but mainly for medium temperatures. However, small HFC systems with refrigerant charges less than 10 kg are built for convenience stores and other small shops.

Commercial refrigeration comprises three main types of equipment:

Stand-alone equipment (plug-in)
Condensing units
Centralised systems.

Stand-alone equipment (plug-in) is described in section 3.2 of this report.

Condensing units are used with small commercial equipment. They comprise one or two compressors, a condenser and a receiver which are normally located in the ambient. The evaporator is placed in display cases in the sales area and/or a small cold room for food storage.

Centralised systems consist of a compressor unit including valves and receivers placed in a machinery room. The unit is connected with distributed piping to evaporators placed in cabinets, cold stores etc. The condenser is typically placed in the ambient. The centralised systems tend to be more effective than the plug-in systems and condensing units.

The centralised system can be sub-divided into 3 groups:

Direct systems, where the primary refrigerant (R404A and now: CO_2) is circulated directly to the evaporators.

Indirect systems where the primary refrigerant and a heat transfer medium (a secondary refrigerant) exchange heat in an extra heat exchanger and the heat transfer medium is pumped to the cabinets and storage rooms. The heat transfer medium can be single-phase brine, but also two-phase fluids such as volatile CO_2 or ice slurry can be used.

The last group is *hybrid systems* where 2 or more different primary refrigerants are combined e.g. in a cascade system, where the high temperature refrigerant is used in the medium temperature level (chilled food) and to cool the low temperature refrigerant in the cascade heat exchanger. The low temperature refrigerant is used at the low temperature level (frozen food). Some cascade systems (increasing in numbers) with CO_2 and a conventional refrigerant use CO_2 even for cooling demand at app. 0 °C.

Centralised systems are normally considered as "best available practice" in supermarkets when focusing on low energy consumption and low initial costs.

A lot of work has been carried out so far regarding the development and implementation of refrigeration systems working on natural refrigerants.

Legislation
The introduction of HFC taxes in Denmark (and Norway) has indirectly established a situation, where direct cooling with HFC refrigerants is economically less favourable.

Since 1st of January 2007 a total ban on the use of HFC refrigerants in Denmark in new systems with charges exceeding 10 kg has been in force. This ban has had a huge impact on the systems implemented especially in supermarkets, where practically all new supermarkets are built with transcritical CO_2 systems.

Leakage rates
The leakage of HFC refrigerant from commercial refrigeration systems is rather high due to distributed piping. The leakage rates have earlier been estimated to be about 15 – 25% of the charge per year. However, a great deal has been done in the past to reduce the leakage. Today, all references indicate that the leakage rate is about 10% per year (including accidents e.g. breaking pipes).

The leakage from more compact systems such as stand-alone and condensing units is smaller. It is estimated to be about 1 - 5% per year (stand-alone) and 5% (condensing units).

Experience with alternative systems
During the past decade a lot of different concepts of supermarket refrigeration systems have been designed, built and tested.

These alternative systems can be divided in three main groups:

Indirect systems with brine. The refrigerant in the primary system can be R134a, R404A, propane or ammonia.
Cascade systems with propane, ammonia, R134a or R404A in the primary system and CO_2 as low temperature refrigerant. Different designs have been tested.
CO_2 used as transcritical fluid. Different designs have been developed and transcritical CO_2 systems are now the standard concept for supermarket refrigeration systems in Denmark.

Transcritical CO_2 systems
The idea of using CO_2 in a transcritical system is not new. For the past 20 years, research and development has been carried out on smaller systems especially for heat pumps and air-conditioning units. However, the know-how required to build an economic transcritical CO_2 system for the supermarket area was limited. A few test installations were made in Sweden, Denmark and Norway until the first half of the first decade in this century. Later on, an increasing amount of

components became available, and increasing experience was achieved, and big installers chose this technology to be standard.

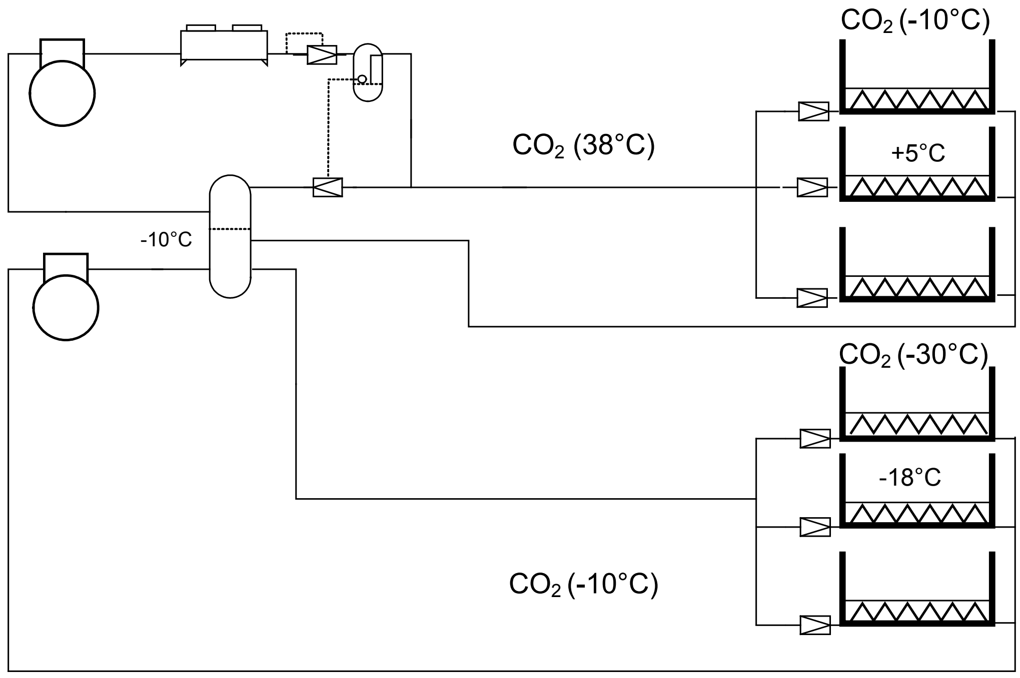

Figure 2: Refrigeration system for supermarket using transcritical CO_2 as refrigerant. This piping diagram shows the first transcritical CO_2 installations in Denmark.

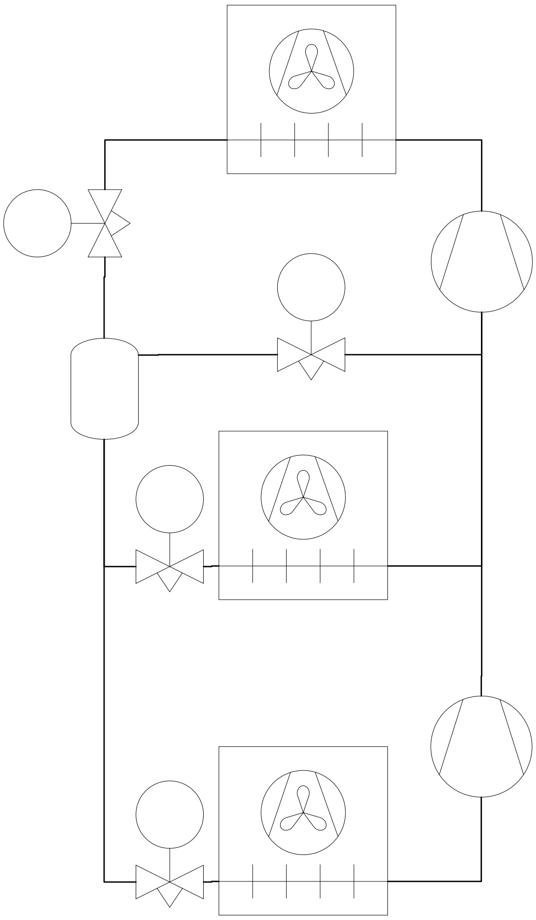

Figure 3: Principal piping diagram for supermarket transcritical CO_2 booster system. Today, this is the most frequently used system.

The system operates under transcritical conditions during higher ambient temperature (e.g. 25°C). A transcritical CO_2 system is an attractive option for supermarkets because they are much simpler than the cascade systems. The system comprises a high-pressure compressor that compresses the CO_2 to 120 bar. The compressed gas then enters a gas cooler and is cooled to a temperature close to ambient. The cooled, high-pressure gas then passes through a high-pressure valve, which allows the gas to expand and reduces pressure to a level below the critical point where saturated liquid can exist (under the critical point). The liquid is circulated towards the low- and high-temperature refrigeration cabinets. The liquid is then allowed to expand to 25 bar in the high-temperature cabinets and to 15 bar in the low-temperature cabinets by the expansion valves. The liquid evaporates in the cabinets and the resulting gas from the low-temperature cabinets is removed by the low-pressure compressor and, after compression, mixed with the gas from the high-temperature cabinets. The mixture is then led to the high-pressure compressor and the closed cycle starts again.

Status of supermarket refrigeration systems, 2011
Transcritical CO_2 systems need high pressure components and the availability was very limited until about 2005, where the first mass-produced commercially available compressors and regulation valves were launched on the market.

When this happened it became clear to a number of people and companies that there is a great potential in this technology. The technology became competitive and superior because of the following issues:

Only one refrigerant is necessary in the supermarket (CO_2)
No need for additional heat exchangers (and the related loss caused by temperature differences in the exchangers)
Environmental properties are very fine
Properties for working environment are fine
Good thermo physical properties for the refrigerant
Good energy efficiency at normal ambient temperatures.

In Denmark, the conditions for quick implementation of this technology became present because of the high tax on HFC refrigerants and the introduction of the ban on building new systems with more than 10 kg HFC.

In the years 2005 to 2009, a total of about 150 systems were installed in Denmark and a similar number in Europe, outside Denmark. In 2010, about 200 systems were installed in Denmark and the total figure for Europe is more than 400 units.

In 2011, more than 800 systems will be installed in Europe. The total amount of transcritical CO_2 systems in supermarkets will ultimo 2011 be about 2000 systems in Europe, whereof app. 500 systems will be installed in Denmark (K. G. Christensen, 2011).

Photo 5: Photo from the production of "remote refrigeration packs" for CO_2 at the Advansor Company in Aarhus.

Supplier of transcritical CO_2 components and systems
The fast development of this technology has resulted in new business areas.

Danfoss has developed a full programme for valves and controls for transcritical (and subcritical) CO_2 systems. Danfoss offers these components worldwide and the business is increasing.

There are a number of suppliers of compressors, including Bitzer, Bock, Copeland, Dorin and Frascold as well as several manufacturers of heat exchangers, covering evaporators and gas coolers as well as plate heat exchangers for heat recovery and special applications.

New qualities of pipes (Wieland K65) have been available and can manage the high pressure in the systems as well as inline components from different manufacturers.

In Denmark, at least three companies are building transcritical CO_2 systems:

Knudsen Køling A/S is building as well as installing the refrigeration systems in the supermarkets in Denmark.
Carrier (formerly Birton) is also building and installing the system in supermarkets in Denmark.
Advansor A/S.

The company Advansor was founded in 2006 by former employees at Danish Technological Institute and has achieved great success with developing a "remote refrigeration pack" for transcritical CO_2 refrigeration systems for supermarkets.
The packs are mass-produced at the factory in Aarhus and are sold to big installers in Europe. The packs are sized in modules, and Advansor has a full programme for all supermarket sites. In 2011, about 300 supermarket refrigeration systems will be build, and about 80% will be exported (K. G. Christensen, 2011).

During 2009, a second generation of systems was developed and went into production with new and better components and higher energy efficiency.

Advansor is now the world's biggest producer of transcritical CO_2 systems for supermarkets, and the production capacity is about 500 units per year.

The biggest installer in Denmark is Superkøl, which covers 35 – 40% of the market. Superkøl has installed more than 100 transcritical CO_2 packs from Advansor and is monitoring about 2,000 supermarket refrigeration systems. The second generation transcritical CO_2 systems use app. 10% less energy compared to similar HFC systems and the technology has proved to be reliable (Gøttsch, 2011).

Economy and energy efficiency

The second generation systems use about 10% less energy in Northern Europe.

In Central Europe the figure is around 5% less energy.

In Southern Europe, the systems have to be tailor-made due to higher ambient temperatures, and in some cases cascade systems with subcritical CO_2 systems have to be used.

In 2011, the price was 4 to 5% higher (for the total refrigeration system) compared to similar HFC systems, and the payback time is 1 to 2 years in Denmark and Norway (because of the HFC tax) and 3 to 5 years in other countries (K. G. Christensen, 2011).

3.4 Air conditioning

In many office buildings and hospitals, chillers are installed for distribution of cold water in the buildings. The air in the individual rooms is cooled in heat exchangers by means of the cold water.

Various refrigeration systems are available for this purpose, and previously CFCs, HCFCs and HFCs were used. Some small systems based on HFC refrigerants (with charge below 10 kg) are still being sold. In the past few years, however, a large number of ammonia-based and hydrocarbon based refrigeration systems have been installed for this purpose.

Ammonia

In the first Nordic report (Pedersen, 2000), hundreds of ammonia-based chillers in the Nordic countries were listed. The list referred to includes systems installed in the period from 1990 to 1998.

Because of data confidentiality it has not been possible to update the reference lists in later reports, but according to the biggest installer in the Nordic countries (Johnson Control International, former Sabroe) many new ammonia chillers have been installed since then to cool office buildings, hospitals, airports and other big buildings.

Johnson Control International, which is a major manufacturer of chillers offers a wide range of ammonia chillers (air and liquid cooled plants) in the range from 300 to 6.500 kW cooling capacity (Pachai, 2011). The production takes place at the factory in Aarhus.

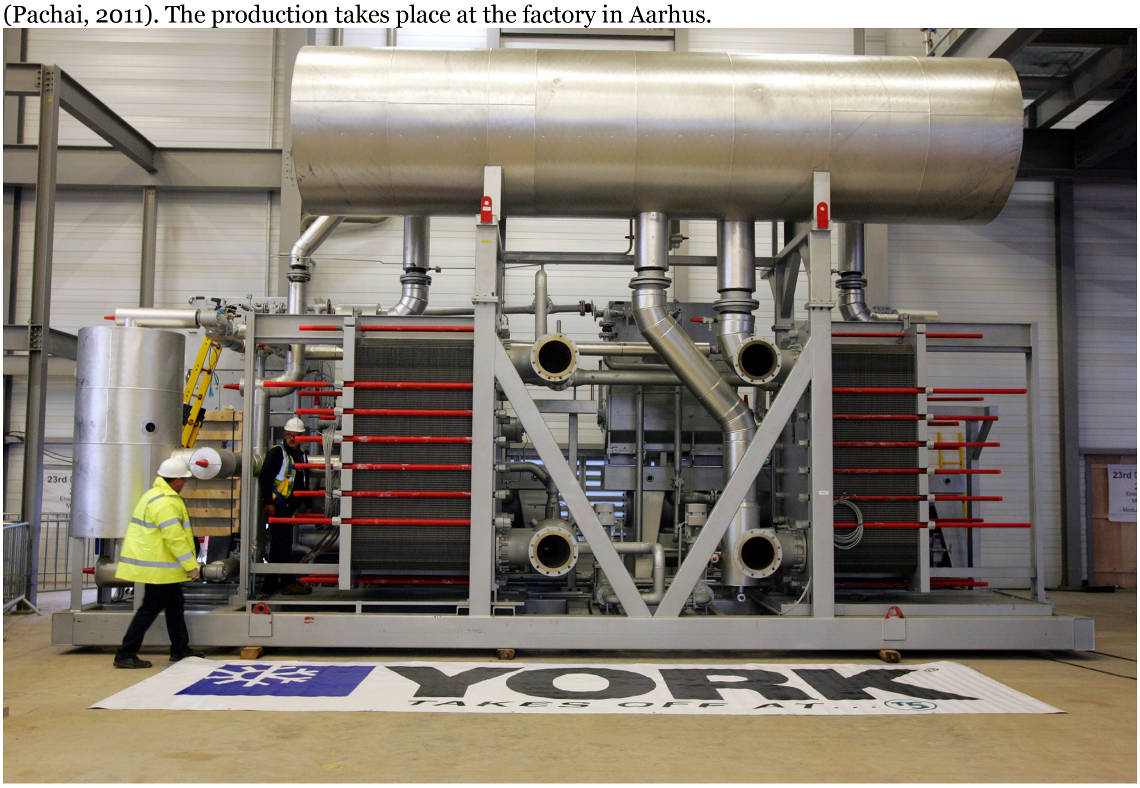

Photo 6: Assembly of ammonia chiller at Johnson Control International (formerly Sabroe and York Refrigeration).

Photo 7: The shopping mall “Fields” in Copenhagen is cooled by ammonia chillers.

The price of ammonia chillers is higher than HFC chillers. The difference depends on the size. Ammonia chillers are often competitive because of the higher energy efficiency.

Hydrocarbon
Two Danish companies (Bundgaard Køleteknik and Johnson Control International) have started a production of hydrocarbon chillers in the medium to larger range (50 – 400 kW). Annually, the two competing companies produce about 150 units and most of what is produced is installed in Denmark, but some is exported to e.g. Norway, UK and Germany.

The energy efficiency is better than in HFC systems (about 10%) and the price is about 20% higher compared to HFC systems. In Denmark (and Norway), the price is equal to HFC systems due to the tax on HFC refrigerant in the chillers. The payback time for countries without tax will typically be 1 to 2 years (Pachai, 2011).

Hydrocarbon chillers cool the new University Hospital in Aarhus (Skejby).

Photo 7: Hydrocarbon chiller produced by Bundgaard Køleteknik. The refrigerant is R290 (Propane).

Absorption
There are also systems that use absorption refrigeration (often lithium-bromide water absorption refrigeration systems). One example is the use of cooling water from an incineration plant in Trondheim, Norway. This “cooling water” is warm and runs a huge absorption refrigeration plant at the University Hospital in Trondheim.

Recently, an absorption refrigeration system was installed in central Copenhagen. It will in combination with huge ammonia chillers distribute cold water for district cooling of buildings in central Copenhagen.

Energy efficiency
The energy efficiency is a very important issue for chillers. As the leakage rate is relatively small, the energy use is the most important factor for the environmental impact. Danish Technological Institute carried out a small analysis in the Nordic report from 2007 (Pedersen, 2007). The Analysis compared the energy efficiency of chillers with different refrigerants (HFCs, HCs and ammonia).

A calculation tool "CoolPack", developed at Danish Technical University has been used to analyse the energy efficiency. CoolPack is used by thousands of refrigeration engineers around the world and contains thermodynamic properties for different refrigerants and algorithms for calculation of refrigeration systems. The calculations have been carried out for two different situations:

a) Evaporation temperature - 10 °C and condensation temperature + 35 °C
b) Evaporation temperature + 5 °C and condensation temperature + 45 °C
The evaporation temperature refers to the temperature the liquid is cooled to, and the condensing temperature refers to the ambient temperature. A small temperature difference will always occur between the heat exchangers.

For the compression cycle, the isentropic efficiency is set to 0.60 and heat loss from the compressor is set to zero.

Table 3.2: Comparison of the COP (Coefficient of Performance) for refrigeration systems with different refrigerants. COP expresses the energy efficiency of refrigeration systems. The higher the value, the more energy efficient the cooling system.

Refrigerant	COP, **Situation a)** T_0=-10^{0}C, T_C=+35^{0}C	COP, **Situation b)** T_0=+5^{0}C, T_C=+45^{0}C
R134a	2.78	3.30
R404A	2.53	2.94
R407C	2.71	3.15
R410A	2.65	3.05
R717 (ammonia)	2.82	3.41
R290 (propane)	2.74	3.25
R600a (isobutane)	2.80	3.36
R1270 (propylene)	2.73	3.21

Note: The refrigerants with mixtures (R404A, R407C and R410A) have temperature glides by evaporation. R407C has a significant glide, making an explicit comparison with refrigerants without glide difficult. No pressure drop in condenser and evaporator and no internal heat exchange.

Table 3.2 shows a variety in the energy efficiency of about 11% in situation a) and 15% in situation b). In both situations, ammonia (R717) shows the best efficiency with isobutane in the second place.

The comparison shows that R410A is inferior in terms of theoretical efficiency. Nevertheless, a great share of the marked is turning towards R410A in smaller AC applications. The main advantage of R410A is the volumetric efficiency that results in smaller components and better price competitiveness.

Emissions to surrounding environment/accumulation in scrapped products
The systems in question are compact, factory-made systems with a relatively small charge and limited emissions. The leakage rate is estimated to be 4 – 5% per annum.

With a lifetime of 15 to 20 years, there is some leakage of refrigerant. A large part of the refrigerant will remain in the system when it is scrapped. It is assumed that this refrigerant will be collected and reused in other systems. However, a small part of it will be emitted when the refrigeration system is opened during the scrapping process.

Some very inexpensive, small HFC chillers are expected to have a shorter lifetime.

Situation with respect to alternative technology
Alternative technology with natural refrigerants already exists and is now standard for all applications. Only small HFC chillers with refrigerant charges < 10 kg are installed. Such chillers are used in areas, where the cooling need does not exceed app. 35 kW.

Small air-conditioning systems
No production of small air-conditioning systems takes place in Denmark. Although the climate in the Denmark does not necessitate air-conditioning, there is a growing tendency to set up small split systems – in almost each case, the systems are made in Asia. The refrigerant is R410A.

The systems are often reversible systems, which means combined A/C and heat pump systems (air to air), where it is possible to switch mode. Many of the small air to air heat pumps sold in the Nordic countries can also be switched to A/C-mode.

Hydrocarbon-based systems are being developed in Asia with refrigerant charges of 250 – 300 g. So far, there is no experience with these systems in Denmark, maybe because nobody has tried to install the system.

De Longi in Italy also offers a small local air conditioner with propane. So far, Danish Technological Institute has not heard about the installation of such an air conditioner in Denmark.

Dehumidifiers
A great number of small dehumidifiers for domestic use have been installed in the Nordic countries. Earlier, Vestfrost (Vesttherm) produced such appliances, but that has stopped and the products are imported from Asia. The refrigerant used is R134a.

A production of professional dehumidifiers takes place at Danterm A/S. The refrigerant used is HFC.

3.5 Industrial refrigeration systems

Normally, industrial refrigeration systems are very large systems. They are used for process refrigeration and cold storage within the food industry and in the chemical/ biochemical industry. Industrial refrigeration systems are built on site, using components suited for ammonia refrigeration systems.

Ammonia
In Denmark and other Scandinavian countries, traditional ammonia refrigeration systems are used for these purposes. Probably all dairies, slaughterhouses, breweries and fishery companies have ammonia refrigeration systems. There is a 100-year-old tradition for this.

There is a growing trend towards the use of indirect refrigeration in order to reduce the refrigerant charge and avoid ammonia in working areas etc.

CO_2
The installation of industrial refrigeration plants with CO_2 for low temperature purposes in cascade system is growing rapidly. Ammonia is used in the high temperature stage and CO_2 in the low temperature stage. Johnson Control International has built many such systems (Pachai, 2011).

Financial barriers
There are normally no financial barriers to using ammonia as refrigerant in large industrial refrigeration systems. In the case of small systems, the situation corresponds to the situation for commercial refrigeration systems or air-conditioning systems.

Situation with respect to alternative technology
Alternative technology using natural refrigerants is available; it has been widely implemented and is today standard for industrial systems.

3.6 Mobile refrigeration systems

Mobile refrigeration systems should be understood as the refrigeration systems installed in cars, trains, aircrafts, ships and containers.

Air-conditioning systems in cars
Since the mid-1990s, R134a has been used for mobile air conditioners (MAC).

Great efforts have been made by the car manufacturers and sub-suppliers to develop MAC for CO_2. This technology is mature and ready for production.

In the meantime, new low GWP HFCs have been introduced into the market, and the car manufacturers now work for implementing the new low GWP substances which include “HFO-1234yf”. It would be easy to change to this substance as the existing refrigeration system can be used with no (or very simple) changes. However, the fluid will be more expensive.

There is no car production in Denmark.

It should be mentioned that in some countries hydrocarbons are used (by DIY – do it yourself enthusiasts) in car air-conditioning systems. This is for instance the case in Australia and USA. The refrigerant is a mixture of propane and butane that can be used as drop-in substitute for R12 in existing systems.

The risk of fire and/or explosion in connection with the use of hydrocarbons in car air-conditioning systems has been debated. Hydrocarbons could be a natural choice as several kilos of hydrocarbons in the form of petrol, diesel oil or gas are already present in the car. However, it is important that the system is designed correctly so an explosive mixture cannot occur inside the car.

The EU directive 2006/40/EF, adopted in May 2006, put a ban on the use of refrigerants in MACs with a GWP higher than 150, and from 2011 there will be a ban on refrigerants with a GWP higher than 150 in car air-conditioning systems in new types of cars and from 2017 in all new cars.

HFC consumption: There is no specific data on consumption for this application, but the typical refrigerant charge is 0.8 kg for an existing car (0.6 kg for new cars), 1.5 kg for a truck and 5 to 12 kg for a bus.

Emission to the surroundings/accumulation in scrapped products: There is a relatively large leakage of refrigerant from mobile air-conditioning systems – in the order of 20 - 30% of the charge per year. The leakage used to be even bigger. The leakage is due to seals and leaky hoses, but it has been reduced in recent years by means of tighter hoses. The leakage rate for new systems is now 10 - 20% per year.

The relatively large leakage amount means that almost all the refrigerant used will be emitted to the atmosphere during the lifetime of the vehicle. The remainder should be collected when the vehicle is scrapped.

Situation with respect to alternative technology: Alternative technology is being developed.

Integral reefer containers
The company Mærsk/Sealand Line is the world's leading carrier of refrigerated goods and has a big fleet of reefer containers in traffic at global level.

Since 1993, all new refrigeration systems have been installed with R134a as refrigerant. Mærsk Container Industry had a considerable production of integral reefer containers in Denmark, but this production has moved to low-income countries. CO_2 has been suggested as a refrigerant in reefer containers and development projects have been conducted. But it is unsure what will happen.

Emissions to the surroundings/accumulation in scrapped products: There is a relatively large leakage from integral reefer containers because of the violent actions they are subject to in ports and at sea. The leakage rate is of the same order of magnitude as from air-conditioning systems in cars - probably 20 – 30% of the charge per year. Therefore, most of the refrigerant used for this purpose will be emitted to the atmosphere. When a container is scrapped, the remaining refrigerant will be collected, cleaned and reused in another container.

Ships
HFC refrigerant is standard on ships today. There is a large leakage of refrigerant from these ships because of rough physical actions at sea. Experts estimate a substantial annual leakage rate for reefer ships.

Large, new or retrofitted ships use ammonia as refrigerant, but ammonia cannot be used in old ships.

In Iceland and Norway, about 20 - 30 fishing vessels have been built/rebuilt with an ammonia-based refrigeration system.

In Norway, at least two large fishing vessels have CO_2/ammonia cascade systems (Pedersen, 2007).

Air-conditioning in aircrafts
For many years, cold-air refrigeration systems were used to cool passenger cabins in ordinary airplanes. A simple joule process is used, in which air is compressed and cooled through heat exchange with the surroundings. Afterwards, the air is expanded in a turbine, whereby it becomes cold. The process is not particularly energy efficient but is used in aircrafts because of the lightness of the components.

Air-conditioning in trains
R134a is normally used as the refrigerant in air-conditioning systems in trains. In Germany, however, a cold-air refrigeration system has been developed for trains in which, as in aircrafts, air is used as refrigerant. The project has been successful and many units have been made for ICE trains. CO_2 systems might also be interesting for this purpose.

3.7 Heat pumps

The function of heat pumps is similar to that of refrigeration systems, as heat is collected from a source (e.g. fresh air, soil, stable air, process water, etc.). At a higher temperature the heat is rejected to a heat carrier - for example, a hydronic heating system.

The following main types of heat pumps are used in Denmark: domestic heat pumps, industrial heat pumps and large heat pumps for district heating systems. Domestic heat pumps are used for space heating and for heating of water for domestic use in single family homes or in apartment buildings.

Domestic heat pumps
In Denmark, about 100,000 heat pumps are installed. Most of them are air/air heat pumps. The yearly sale is about 20,000, where off ground source heat pumps are estimated to be ca. 5,000 per year and slightly increasing in numbers (DEA, 2011).

The domestic heat pumps can be divided into 5 categories:

- Air to air (Heat source: Outside air / Heat sink: inside air)
- Air to water (Heat source: Outside air/ Heat sink: hydronic system with water)
- Liquid to water (Heat source: heat from ground/ Heat sink: hydronic system with water)
- Exhaust air heat pumps: (Heat source: exhaust air from the house/ Heat sink: hydronic system with water and/or inlet air to the house)
- Sanitary hot water heat pump: (Heat source: mostly exhaust air from house/ Heat sink: Tap water for local use in the building).

The most important types are liquid to water and exhaust air heat pumps. Liquid to water heat pumps are mostly produced with R407C as refrigerant. A small number of units are produced with propane (R290).

Exhaust air heat pumps are often produced with R134a, though some have chosen propane (R290) as refrigerant. The charge is about 400 grams of R290.

Most air to air heat pumps are imported from Asia. They use HFCs as refrigerant (preferably R410A). This type of heat pump can normally also be switched to A/C-mode.

In Denmark, Vestterm (Nilan) and Genvex produce tap water heat pumps. So far, R134a has been used.

The Danish ban on HFC does not cover domestic heat pumps, and this is probably the reason why most heat pumps still use HFC.

Large heat pumps
Johnson Control International and other companies e.g. use ammonia or propane as refrigerant. CO_2 is also interesting for large heat pumps and the company Advansor is offering large CO_2 heat pumps.

Financial barriers
It is possible to make domestic heat pumps for propane without major additional costs. Precautions have to be taken to eliminate the risk of fire. When the necessary infrastructure and service is in place, the additional cost of propane heat pumps is expected to be modest.

As mentioned, CO_2 is very interesting for heat pumps, and some manufacturers are committed to offering heat pumps with this refrigerant. The current price for CO_2 heat pumps in the small and medium sized range is significantly higher than for HFC systems. This is due to a lack of mass produced components (compressors) at the moment. In the long term, it should be possible to deliver CO_2 heat pumps with modest additional costs.

HFC consumption
There is a consumption of HFC for this application. A typical liquid/water heat pump is charged with 2.5 kg HFC, a tap water heat pump with 0.8 kg HFC. A typical split type air to air heat pump is charged with about 1 kg R410A.

Emissions to surrounding environment/accumulation in scrapped products
The leakage from heat pumps has become quite small, a few per cent annually, due to compact refrigeration systems and good quality. When a heat pump is scrapped, the remaining refrigerant should be collected and reused or incinerated.
Some cheap split type air to air heat pumps have been sold from supermarkets. Educated refrigeration technicians are required for the installation of such systems, but it is assumed that many systems have been installed by DIY people resulting in a considerable part of the refrigerant being emitted to the atmosphere. In those cases the heat pump might not work or it will work with poor efficiency because of lack of refrigerant. Finally, air might have come inside the refrigeration cycle and that will also reduce the efficiency of the appliance.

Situation with respect to alternative technology
Heat pumps that use natural refrigerants have been developed, but a lack of compressors and other components approved by the manufacturer for hydrocarbons have practically limited the use of hydrocarbons to exhaust air heat pumps.

It is still legal to install HFC heat pumps in Denmark, and this is probably the reason why HFC is still standard.

3.8 Cryogenic systems and low temperature freezers

Cryogenic systems have a relatively small area of application. They are used to cool laboratory specimens and other small specimens to low temperatures.

The equipment normally consists of a cascade system; the high temperature stage can be a R507 system. During the high temperature stage of the process, temperatures down to approximately -50 ^{0}C are reached. During the low temperature stage, hydrocarbons are used as refrigerants - either ethane (R170) down to app.
-80 to -90 ^{0}C or ethene (R1150) down to app. -100 to -120 ^{0}C.

Some foreign manufacturers use R23 or R508 in the low temperature stage. These refrigerants have very high GWP values.

York Refrigeration has supplied cascade systems with R1270 on the high temperature stage and R170 on the low temperature stage for cooling blood plasma at
-70 ^{o}C (Pachai, 2006).

There is a production of small plug-in units with one-stage cooling systems, cooling down to -80 ^{o}C. The refrigerant is a mixture of at least three different substances, of which one or more are potent greenhouse gases. The refrigerant mixture is delivered by the customer of the products. Danish Technological Institute has information about prototypes with refrigerant mixtures of hydrocarbons used for the same purpose.

Elcold has developed and is manufacturing low temperature chest freezers
(-85° C) using hydrocarbon refrigerants (Elcold, 2011).

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Appendix A: Refrigerants and refrigerant mixtures

The following table shows the most common refrigerants consisting of single substances. ODS and GWP figures for HFCs and PFCs are from UNEP, RTOC 2010 report.

Substance	R-number	Chemical formula	ODP value	GWP value (100 yrs)
Halon-1301	R-13B1	$CBrF_3$	15.9	7,140
CFC-11	R-11	$CFCl_3$	1.0	4,750
CFC-12	R-12	CF_2Cl_2	0.82	8,500
CFC-115	R-115	$CClF_2CF_3$	0.57	7,230
HCFC-22	R-22	CHF_2Cl	0.04	1,790
HFC-123	R-123	$C_2HF_3Cl_2$	0.01	77
HCFC-124	R-124	CF_3CHClF	0.02	619
HCFC-142b	R-142b	$C_2H_3F_2Cl$	0.06	2,220
HFC-23	R-23	CHF_3	0	14,200
HFC-32	R-32	CH_2F_2	0	716
HFC-125	R-125	C_2HF_5	0	3,420
HFC-134a	R-134a	CH_2FCF_3	0	1,370
HFC-143a	R-143a	CF_3CH_3	0	4,180
HFC-152a	R-152a	$C_2H_4F_2$	0	133
HFC-227ea	R-227ea	C_3HF_7	0	3,580
HFC-236fa	R-236fa	$C_3H_2F_6$	0	9,820
HFC-245fa	R-245fa	$C_3H_3F_5$	0	1,050
PFC-14	R-14	CF_4	0	7,390
PFC-116	R-116	C_2F_6	0	12,200
PFC-218	R-218	C_3F_8	0	8,830
Isobutane (HC-600a)	R-600a	$CH(CH_3)_3$	0	(20)
Propane (HC-290)	R-290	C_3H_8	0	(20)
Ethane (HC-170)	R-170	C2H6	0	(20)
Ethene (Ethylene)	R-1150	CH_2CH_2	0	(20)
Propylene (HC-1270)	R-1270	C_3H_6	0	(20)
Ammonia	R-717	NH_3	0	0
Carbon dioxide	R-744	CO_2	0	1
Air	R-729	-	0	0
Water	R-718	H_2O	0	< 1

The following table shows refrigerant mixtures in the 400 series (zeotropic mixtures). The ODP and GWP values can be calculated on the basis of the values in the table for single substances, weighing on the basis of the mix ratio between the individual substances.

R-number	Substances	GWP (100 yr.)	Concentration in weight-%
R-401A	HCFC-22/HFC-152a/HCFC-124	1200	53/13/34
R-402A	HCFC-22/HFC-125/HC-290	2700	38/60/2
R-403A	HCFC-22/PFC-218/HC-290	3100	75/20/5
R-403B	HCFC-22/PFC-218/HC-290	4400	56/39/5
R-404A	HFC-143a/HFC-125/HFC-134a	3700	52/44/4
R-406A	HCFC-22/HC-600a/HCFC-142b	1900	55/4/41
R-407C	HFC-32/HFC-125/HFC-134a	1700	23/25/52
R-408A	HCFC-22/HFC-143a/HFC-125	3000	47/46/7
R-409A	HCFC-22/HCFC-142b/HCFC-124	1600	60/15/25
R-410A	HFC-32/HFC-125	2100	50/50
R-412A	HCFC-22/HCFC-142b/PFC-218	2200	70/25/5
R-413A	HFC-134a/PFC-218/HC-600a	2000	88/9/3
R-414A	HCFC-22/HCFC-124/HCFC-142b/HC-600a	1500	51/28.5/16.5/4
R-415A	HCFC-22/HFC-152a	1500	82/18

The following table shows refrigeration mixtures in the 500 series (azeotropic mixtures).

R-number	Substances	GWP (100 yr.)	Concentration in weight-%
R-502	CFC-115/HCFC-22	4600	51/49
R-507	HFC-143a/HFC-125	3800	50/50
R-508A	HFC-23/PFC-116	13000	39/61
R-508B	HFC-23/PFC-116	13000	46/54
R-509A	HCFC-22/PFC-218	5700	44/56

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