REFRIGERATORS AND REFRIGERANTS – THE FUTURE

F. Steimle

Department of Applied Thermodynamics andAir-Conditioning Technology, University of Essen, Essen, Germany

After the Montreal Protocol a large discussion started concerning the alternatives for the different CFCs. A number of different points have to be considered carefully. These are e.g. ozone depletion, global warming, flammability and toxicity. Because there will be no fluid with a positive rating for these four points we must be aware of at least one risk per fluid. Development now goes in two directions, on the one hand towards fluorinated hydrocarbons and on the other towards natural fluids like ammonia, propane, butane, CO_2 and water.

Introduction

For some years, in most countries, fully halogenated CFCs containing chlorine have been understood to be the main problem. But, at least in some countries, an early phasing out of HCFCs must be considered. Of the new working fluids only R 134a is now really spread all over the world. The importance of natural fluids like ammonia is increasing especially because other new alternatives are e.g. flammable or have to work at high pressure. To avoid these risks, mixtures are used but they have a higher global warming potential. The main task is therefore to minimise the different risks.

Characteristics of Refrigerants

The negative impact of refrigerants on the environment can be listed as (see IIR 1992):

1. Toxicity to human beings and animals;
2. Influence on biological and genetic areas;
3. Odour;
4. Flammability and explosiveness;
5. Direct impact on the global warming;
6. Energy demand during production and utilisation and the impact on the CO_2-production;
7. Possible influence on the ozone layer.

In addition to the environmental aspects that have been mentioned above, there are demands for appropriate characteristics of several properties:

- near ambient vapour pressure
- high evaporation enthalpy
- high specific heat capacity
- high heat conductivity
- low viscosity
- medium surface tension
- very good solubility in oil
- close to zero corrosiveness
- long stability, even in the upper temperature zone

In the mid-nineteen-thirties, when the first CFCs were introduced, everybody saw in these new fluids chemical products which were not of any direct harm to life. Moreover they were not toxic and not flammable.

Since the CFCs were introduced more than 60 years ago they have been always recognised as very stable fluids. Nowadays, their very low reactivity with other molecules can be a negative influence on the environment via the greenhouse effect. This ecological influence is shown by four different groups of hydrocarbon derived refrigerants:

- CFCs (Chloro-Fluoro-Carbons), fully halogenated without hydrogen in the molecule (e.g. R 11, R 12, R 12 B1)
- HCFCs (Hydro-Chloro-Fluoro-Carbons), partly halogenated with hydrogen contained in the molecule (e.g. R 22)
- FCs (Fluoro-Carbons), with only C-atoms and F-atoms forming the molecule (e.g. R 14, R 116, RC 318)
- HFCs (Hydro-Fluoro-Carbons) partly halogenated without chlorine and with hydrogen in the molecule (e.g. R 32, R 125, R 134 a, R 227, R 245)

Nowadays the influence on the atmosphere, that means the possible depletion of ozone and the impact on the global warming, has become an important issue. Application of these refrigerants however requires a consideration of all influences. The following table shows relative values (R 11 as base) of the Ozone Depletion Potential (ODP) and Global Warming Potential (GWP) for R 11, R 12 and a few of the most often discussed substitutes [UNEP 1992]:

Table 1: Properties of refrigerants

Refrigerant	Property			
	ODP (R 11=1)	GWP (CO_2=1)	Toxicity	Flammability
R 11	1	4000	No	No
R 12	1	8500	No	No
R 22	0.055	1700	No	No
R 32	0	580	(No)	Yes
R 125	0	3200	(No)	No
R 142 b	0.0065	2000	(No)	No
R 143 a	0	4400	No	(Yes)
R 134 a	0	1300	No	No
R 152 a	0	140	No	Yes
R 227	0	2900	No	No
R 717 (Ammonia)	0	0	Yes	(No)
R 290 (Propane)	0	3	No	Yes
R 600 (Butane)	0	3	No	Yes
R 718 (Water)	0	0	No	No
R 744 (CO_2)	0	1	No	No
Helium	0	0	No	No

Chlorine in the molecule causes difficulties with the ozone-layer. Fluorine gives very stable molecules which increase the global warming. Hydrogen gives less stable structures which lead to flammable fluids. Toxicity in this group of chemicals only occurs with molecules including chlorine.

If we want to avoid any ozone depletion, we have to make a choice between the type of risk we face; carbon / fluorine compounds give fluids with high global warming potential, carbon / hydrogen compounds give flammable fluids. At least one of these risks must be faced. The choice can be made only by political decisions because we have, on one hand, an ecological problem and, on the other, a safety problem directly affecting human beings.

The "P" in ODP and GWP refers to potential and not to actual effect; in other words, ODP and GWP are relevant only when and if refrigerants are released into the atmosphere. Consequently, measures against leaks and refrigerant releases, as well as for recycling, should be of first priority [IIR 1993b]. Accurate sealing of systems and reclaiming the refrigerants can significantly reduce not only the global warming impact and the flammability of refrigerants, but also their ozone depletion impact.

The GWP of a refrigerant is not the proper criterion to use in judging the impact of a refrigeration system on global warming, for several reasons. The main reason is that in most countries most of the global warming due to refrigeration systems (including air-conditioning) is due to the CO_2 released during production of the electricity required for their operation. A much better criterion for a refrigerant in a particular system is the TEWI (Total Equivalent Warming Impact):

$$TEWI = GWP \times M + \alpha \times \beta$$

where

GWP = GWP of the fluid, relative to CO_2 (GWP of CO_2 = 1)

M = total mass of the refrigerant released (kg)

α = amount of CO_2 released in generating electricity (kg CO_2/kW h)

β = energy consumption of the system during its whole lifetime (kW h)

The TEWI is directly dependent on how electricity is produced i.e.

- if all energy comes from hydraulic power generation, $\alpha = 0$;
- if electric power derives from fuel, α is around 0.8 kg CO_2/kW h (depending on the type and efficiency of the power station).

Thus, α varies from region to region. (Global warming concerns therefore should influence the strategy of national investments in power generation.)

New substitutes for CFCs out of the group of halogenated hydrocarbons

Even when R134a is widely used world-wide, there is a lot of discussion about substitutes in the middle or long term. In several applications of R 12, R 22 was used in a near term until the year 2000. As R 22 is now banned in those applications (e.g. in Germany from the end of 1999), alternatives for CFCs are:

For R 11	R 123, R 216, R 245 ca	R 245 fa
	R 356	
For R 12	R 152 a, R 227 ca	R 227 ea
	R 245 cb	R 134 a
For R 502	R 125	R 507 (R 125 / R 143 a - 50 / 50)
	R 143 a	
For R 22	R 143 a	R 32
	R 410A (R 32 / R 125 - 50 / 50)	
	R 407C (R 32 / R 125 / R 134 a -	23 / 25 / 52)

Because R 32 is flammable, a lot of blends with non-flammable fluids have been developed (especially in the U.S.) [IIR 1994]. These binary or ternary blends are non-flammable but their global warming potential is higher than that of R 22.

Hydrocarbons as refrigerants

In several countries e.g. in Europe, the GWP is considered more important than the flammability; in different installations hydrocarbons such as propane, butane, isobutane or pentane are used. The big advantage of these refrigerants is that they have a global warming potential and an ozone depletion potential of about zero.

In Germany several thousands of household refrigerators are now built daily with hydrocarbon refrigerants. The first hydrocarbon refrigerant was propane followed by a mixture of propane and isobutane. As well, pure isobutane is used successfully. The quantity of isobutane in a 130-litre refrigerator is only about 20 g, where 12 g of this quantity can be regarded as dissolved in the compressor oil. This must be considered when we are speaking about safety [Hainbach 1993]. These masses are similar to those in cigarette lighters and hand-held hair curlers!

Already in the early 1930s household refrigerators with propane as refrigerant had been built. The differences from the present system design are:

1936	**1998**
Open compressor	Hermetic compressor
Open electric motor	Motor in the hermetic compressor
Expansion valve	Capillary tube
Finned tube heat exchanger	Roll-bond evaporator
250 g propane	20 g isobutane

Hydrocarbons therefore have several advantages but also the disadvantage of flammability and the necessity of high safety standards, especially when handling large quantities of refrigerant.

Ammonia as an old and new refrigerant

Ammonia is the oldest refrigerant successfully used in compression cycles. Even in the days when mainly CFCs were used, ammonia was widespread in special installations all over the world. In 1987 the German DKV published an overview about the application of ammonia (R 717) and R 22 [Table 2 and DKV 1987].

Table 2: Installations with Ammonia (R717) and R22

Application	Value distribution (%)	Proportion of installations in which particular refrigerants are used (%)		
		R 717	R 22	other
1. Cold stores	20	70	30	-
2. Slaughterhouses and meat processing industry	15	60	30	10
3. Soft-drink and beer industry	15	80	15	5
4. Special food-processing, chocolate, ice-cream etc.	30	50	40	10
5. Chemical industries	20	40	40	20
Total	100			

Therefore there is a lot of knowledge and experience available in ammonia technology. This refrigerant also can be used in other applications where e.g. R 22 is widely used. Compared with R 22 and R 502, ammonia has some advantages:

- lower cost,
- better cycle efficiency in most temperature ranges,
- higher heat transfer coefficients,
- higher critical temperature,
- immediate detectability of leaks,
- lower pumping cost for liquid recirculating systems,
- great tolerance to water contamination,
- no effect on the ozone layer and global warming,
- smaller pipe dimensions required for the same refrigeration capacity.

Ammonia is also used in chiller units for air-conditioning in a capacity range from 200 kW to 3 MW. Several installations are running with very good economic results. Sometimes it is difficult to convince the users, because they are afraid of the toxicity. Ammonia is however a strongly self-warning refrigerant. It can be smelt at very low concentrations.

–	Limit of smelling	1 - 5 ppm
–	TWA[1] value in different countries	25 - 50 ppm
–	Serious irritation level approx.	250 ppm
–	Limit to tolerable breathing	500 - 1,000 ppm
–	Danger from short exposure	2,500 ppm
–	Severe risk of fatalities	> 5,000 ppm

[1] Time weighted average – the airborne concentration of a material that workers may not exceed for an eight-hour day of a 40-hour week.

It is important to remember that ammonia is very soluble in water. About 0.3 litre of ammonia can be stored in 1 litre of water.

Other problems that may arise with ammonia are:

- behaviour with oil, solubility aspects,
- incompatibility with various materials,
- high discharge temperatures.

But all these problems can be solved by the correct system design and the correct choice of the oil and a lot of experience (IIR 1993a).

Water as a refrigerant

In absorption systems water has been used as a refrigerant for a long time. Newly developed systems are also using water in compression cycles. The whole system works at much lower than normal pressure. The pressure difference between condensing temperature and evaporation temperature is very small but the pressure ratio is fairly high. This means that the large volume flow needs centrifugal compressors and the pressure ratio demands several stages. These systems are now being developed and the first installations are going into operation, e.g. at the University of Essen. The cooling capacity of this water chiller is about 800 kW.

Carbon dioxide as a refrigerant

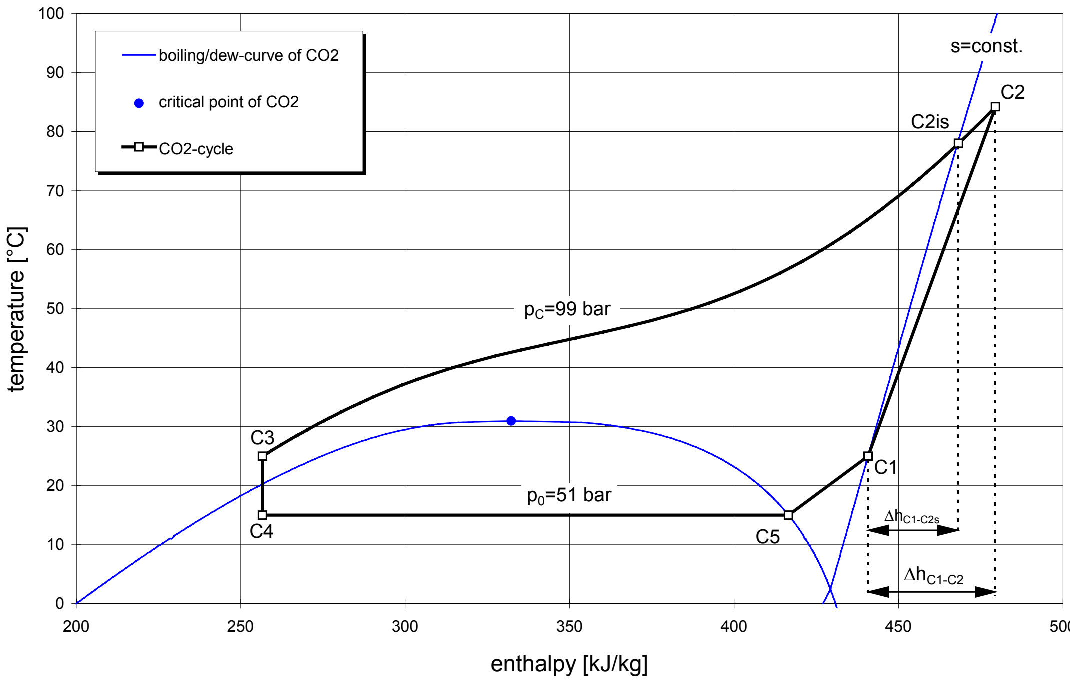
The application of carbon dioxide as a working fluid in refrigeration and heat pump systems is regaining increasingly importance in view of the need to substitute CFCs. Both ecologically and economically it is an attractive alternative to the HFC working fluids in practical use.[Lorentzen, 1994]

The thermophysical properties and characteristics of carbon dioxide are quite different from those of refrigerants used in conventional vapour compression cycles (Fig. 1). Its application in conventional vapour compression refrigerating systems is limited by its critical parameters (t_c = 31.1°C and p_c = 73.8 bar (7.38 MPa).

A better use of the thermophysical properties of carbon dioxide can be achieved by the development of applications in a transcritical cycle. This transcritical cycle seems to be a promising possibility from the ecological and also from the safety engineering viewpoint. Transcritical carbon dioxide processes offer new possibilities of application in the operating range of air-conditioning, heating, heat recovery and drying technology.

One application, built at our institute using carbon dioxide in a transcritical cycle, is a commercial laundry dryer [EC 1999]. The experiments and parameter studies have shown that the use of heat pumps in laundry dryers exhibits a considerable energy saving potential. The use of CO_2 as working fluid gives the advantages of safe operation and enhanced performance.

Figure 1: The transcritical CO_2 heat pump cycle in a t/h chart. (Note: 100 bar = 10 MPa)



Absorption systems

Beside the compression systems, absorption systems have always had some importance in the refrigeration. The main thermodynamic principles of the absorption heat pump are shown in Fig. 2. The apparatus of the real installations are shown in Fig. 3. There are five energy flows in this type of heat pump. The drive of the solution pump, L, must be of high quality energy (exergy). The other four energy flows occur at several temperature levels. The ratio of the pump energy to the total heating capacity is of special interest, because this ratio varies from 1% to 10% according to the working fluid couples. The energy ratio of an absorption heat pump can be derived from the heat flow of the condenser and the absorber, divided by the heat input to the generator.

Up to the present, absorption heat pumps are used only on a very large scale (above 1 MW). In the range lower than 20 kW, there are some pilot plants operating with NHK_3/H_2O and H_2O/LiBr. Both pairs present some difficulties. NH_3/H_2O produces a high pressure in the condenser under heat pump conditions and needs rectification after the generator to ensure no water enters the evaporator. H_2O/LiBr has a narrow working range. It is limited in the lower range by the freezing point and has an upper limit at the crystallisation line.

Some criteria for the choice of working fluid pairs are:

- a high difference in the boiling point between solvent and refrigerant
- a low viscosity of the solvent and the mixtures
- good pressure range
- no toxicity in any component of the mixture
- no crystallisation in the working range, and
- a good stability

Figure 2: Schematic absorption process

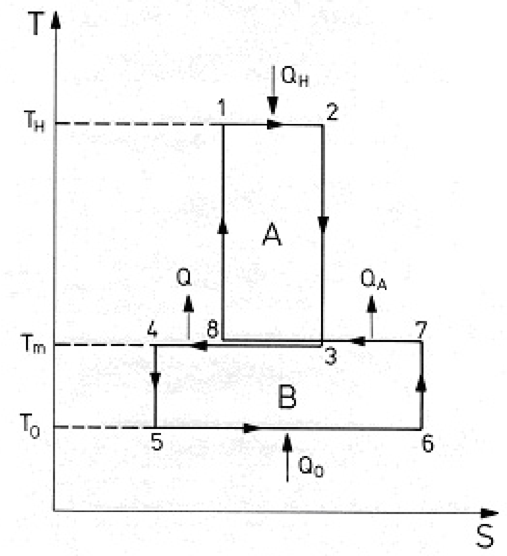
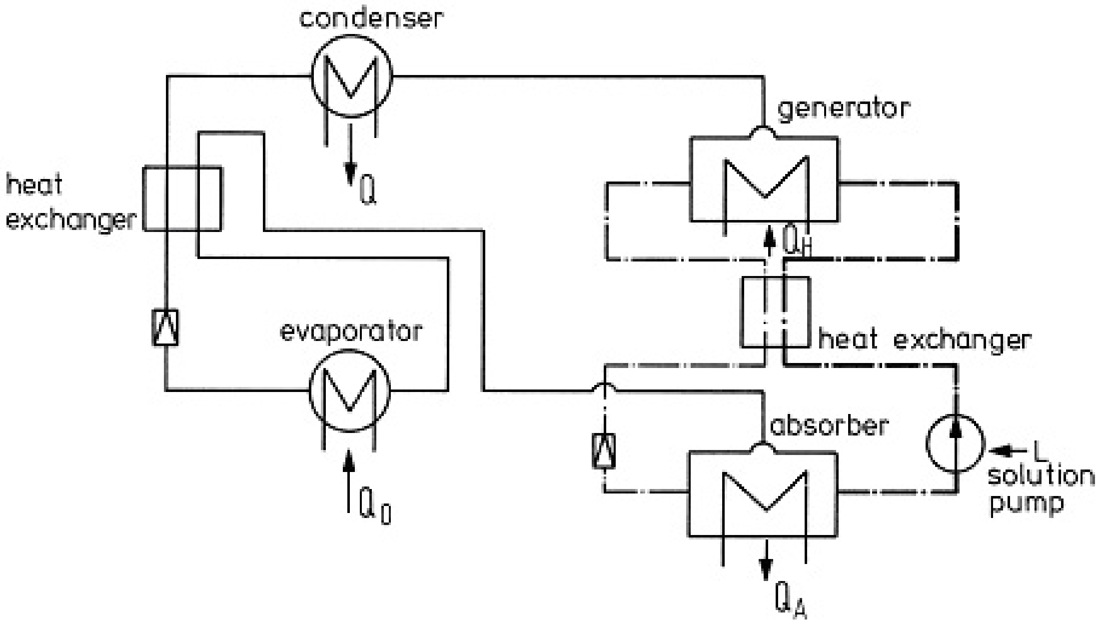


Figure 3: Absorption refrigeration cycle



There are several other working pairs possible. The primary energy demand of the absorption heat pump in comparison to compression systems is shown in Fig. 4.

The absorption refrigeration systems have a new future especially in combination with total energy systems. The waste heat of these systems can be used in winter for heating and in summer this waste heat and heat from district heating systems can be used to drive absorption systems especially for air-conditioning with H_2O/LiBr as the working fluid. The cooling capacity depends strongly, however, on the hot water temperature (Fig. 5). The decrease of the temperature from 120°C down to 80°C causes a drop of the refrigeration capacity to about half of its maximum.

Figure 4: Exergy fluxes of compression and absorption heat pumps

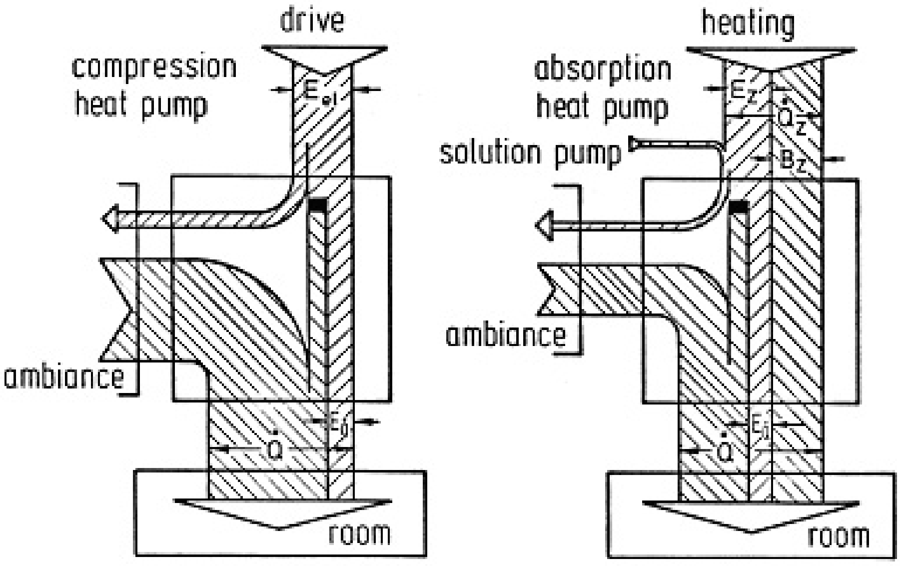
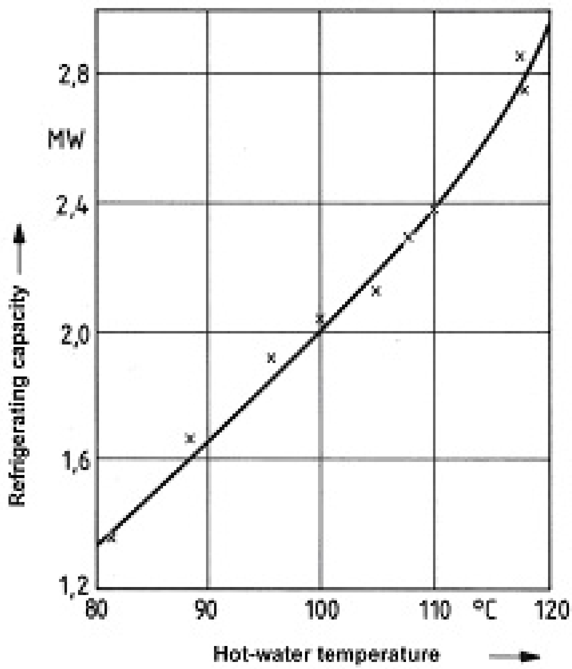


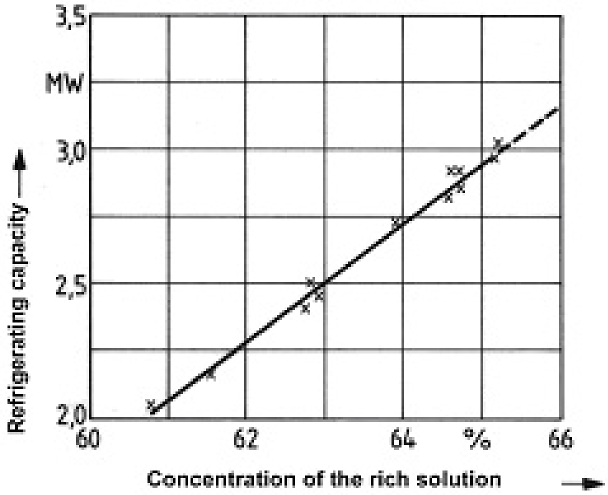
Figure 5: Influence of generator temperature on refrigerating capacity



The control of absorption refrigeration systems can easily be handled by changing the concentration of the solution. Figure 6 shows that a concentration change from 65% to 61% results in a capacity change from 100% to 65%.

In the near future absorption systems for air-conditioning will also be developed in the power range between 20 kW and 100 kW. This will give many more possibilities for absorption systems on the market but always in combination with total energy systems.

Figure 6: Load Control



Stirling refrigerators as an alternative to cold vapour compression systems

Stirling refrigerators may be a possible alternative to Perkins-Evans cycle machines for refrigeration at temperatures below –30°C.

The essential feature of Stirling refrigerators is the fact that a closed gas cycle is realised. Thus the working medium does not change its phase during the cycle. Typically two pistons periodically compress and expand a closed gas volume - usually helium - while the refrigeration capacity is transferred to a cooling agent in a tube bundle heat exchanger. Figure 7 shows a schematic Stirling refrigerator and Figure 8 an experimental machine.

Figure 7: Schematic Stirling refrigerator

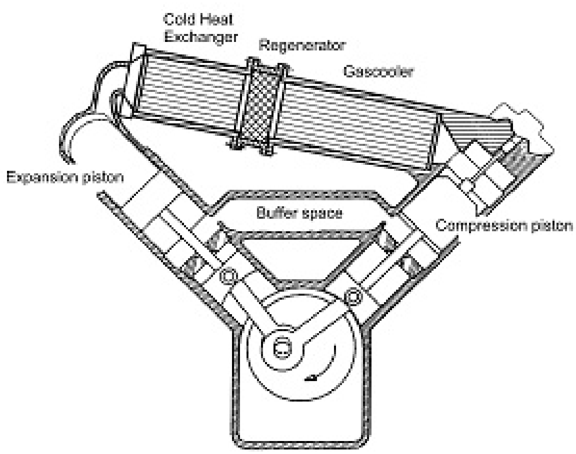
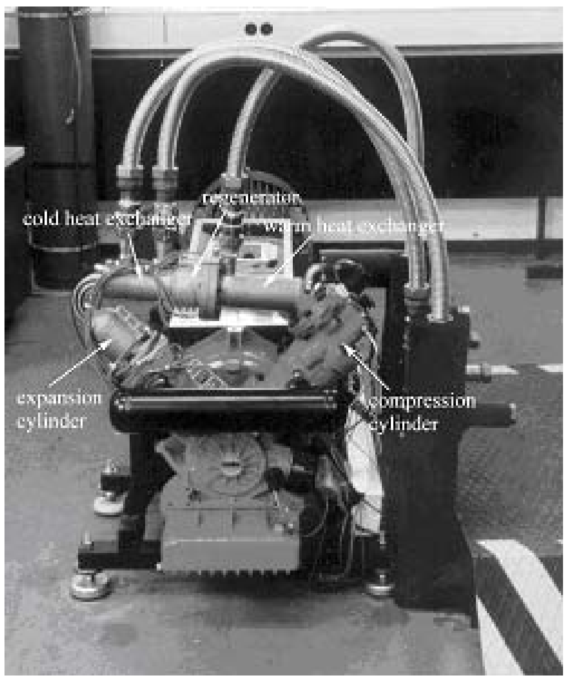


Figure 8: 161-Stirling refrigerator



From today's viewpoint Stirling refrigerators can be used sensibly at temperatures of refrigeration below -30°C. At higher temperatures the thermodynamic losses rise, thus Stirling refrigerators cannot compete with refrigeration systems used so far. At temperatures below -60°C Stirling refrigerators reach the highest COP (co-efficient of performance i.e. heat extraction per second divided by electrical power input) of all refrigeration systems. A proof for this statement is the fact that Stirling refrigerators have been used for a long time for air liquefaction and for the cooling of infrared sensors (temperature of refrigeration about 80 K).

Conclusion

At present different points of view, in various countries, of the importance of the possible risks lead to different approaches. It is not necessary to decide completely one way or the other. We will have to go several ways simultaneously towards the goal of minimising the ecological changes under serious consideration of the risks for mankind.

References

EC (1999) EC-Project: Contract JOE3-CT-950006. *Energy efficient and environmental friendly heat pumping systems using CO2 as working fluid*. COHEPS Final Report of WP12: Prototype System Design.

DKV (1987) *Deutscher Kältetechnischer Verein – Statusbericht No. 2*. Das FCKW-Ozon-Problem und Möglichkeiten der Emissionsreduzierung von Fluorkohlenwasserstoffen für die Kälte-, Klima- und Wärmepumpentechnik, ISBN 3-929-429-91-2

Hainbach, C. (1993) Doctoral thesis, University of Essen, *Experimentelle und theoretische Untersuchung der Alternativ-Kältemittel R290 und R134a unter Einbeziehung des Verdichterverhaltens.* ISBN 3-927882-07-0

IIR (1992) *International Institute of Refrigeration - Informatory Note on CFCs No. 8*. The Environmental Impact of the Molecules used as Refrigerants, see www.iifiir.org

IIR (1993a) *International Institute of Refrigeration – Brochure.* Thermodynamic and physical properties of refrigerants - R717 (ammonia). see www.iifiir.org

IIR (1993b) *International Institute of Refrigeration - Informatory Note on CFCs No. 9*. Replace R22? When and How? see www.iifiir.org

IIR (1994) *International Institute of Refrigeration - Informatory Note on CFCs No. 10*. Refrigerant Mixtures. see www.iifiir.org

Lorentzen, G. (1994) Revival of carbon dioxide as a refrigerant. *International Journal of Refrigeration*. 17 (5) 292-301.

UNEP (1992) UNEP-Document prepared for the Copenhagen Conference 1992. *Compression Cycles for Environmentally Acceptable Refrigeration, Air-Conditioning and Heat-Pump Systems.* see www.iifiir.org