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15th Informatory Note on Refrigerants

Carbon Dioxide as a Refrigerant

The Montreal Protocol regulations on gases that deplete the earth's ozone layer have led to phase out of chlorofluorocarbons (CFCs) as refrigerants in industrialized countries. Moreover, hydrochlorofluorocarbons (HCFCs) are only an interim solution in industrialized countries until the year 2020 and certain national regulations prescribe an even earlier phase-out date (for instance, by the end of the year 1999 for R22 in Germany).
Another environmental concern regarding these refrigerants is their behaviour as greenhouse gases in the atmosphere and this also applies for CFC and HCFC substitutes, the newly developed hydrofluorocarbons (HFCs). For this reason, these new refrigerants are placed in a basket with five other gases covered by the Kyoto Protocol on greenhouse gases.
This situation has led to increase use of the "old" refrigerants ammonia and hydrocarbons. Although both are environmentally benign, they can exhibit a certain degree of local danger because of their flammability and/or toxicity. Therefore, carbon dioxide (CO_2), an "old" refrigerant used in industrial and marine refrigeration, was proposed by the late Prof. Gustav Lorentzen in 1990 to be used as an alternative refrigerant, mainly because of its non flammability.[1]

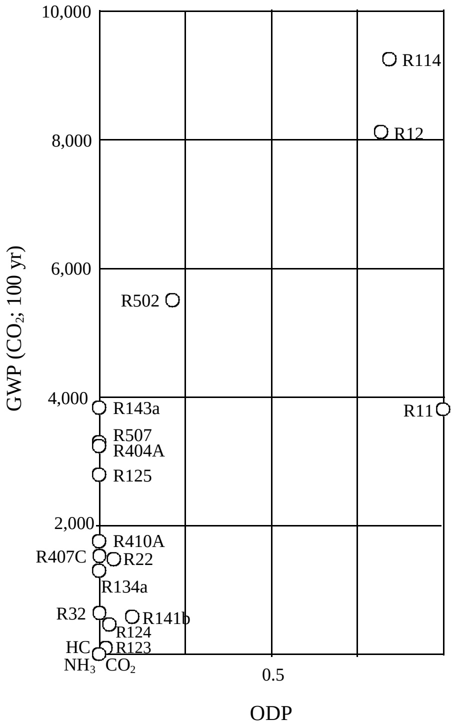

Figure 1. ODP and GWP of several refrigerants

As shown in *Figure 1*, contrary to CFCs and HCFCs, ammonia, hydrocarbons and CO_2 all have an Ozone Depletion Potential (ODP) of zero and a negligible Global Warming Potential (GWP).
As for HFCs, their ODP is zero and their GWP ranges from a few hundred in the case of the flammable HFC32 to several thousand in the case of the flammable HFC143a and the non-flammable R125.
With respect to the local safety of "old" refrigerants**,** only CO_2 can compete with the non-flammable HFCs**.**
If CO_2 exerts a major overall impact on global warming (of the order of 63% of the combined effect of all greenhouse gases)[2], it is because of the large amounts emitted by many industrial applications.
However, contrary to HFCs, its GWP is negligible when applied as a refrigerant.
Therefore, being environmentally benign and locally safe, CO_2 as a refrigerant has major benefits.

Table 1. Comparison of CO_2 properties with those of other refrigerants

Refrigerant	R12	R22	R134a	R290	NH_3	CO_2
Natural fluid	No	No	No	Yes	Yes	Yes
ODP[3]	0.82	0.055	0	0	0	0
GWP (100yr) IPCC values[3]	8100	1500	1300	20	<1	1
GWP (100yr) WMO values[4]	10600	1900	1600	20	<1	1
Critical temp. (°C)[3]	112.0	96.2	101.2	96.7	132.3	31.1
Critical pressure (MPa)[3]	4.14	4.99	4.06	4.25	11.27	7.38
Flammable	No	No	No	Yes	Yes	No
Toxic	No	No	No	No	Yes	No
Relative price	-	1.0	4.0	0.3	0.2	0.1
Volumetric capacity	1.0	1.6	1.0	1.4	1.6	8.4

The carbon dioxide refrigerating cycle

The following question remains: is CO_2 also well suited for application in refrigeration, air-conditioning and heat pump systems?
Here, because of its thermodynamic properties, CO_2 differs from the other refrigerants mentioned. Its vapour pressure is much higher and its critical temperature is around 31°C, so that heat discharge into the ambient atmosphere above this temperature is impossible through condensation as happens in the normal vapour compression cycle: CO_2 can only be used in the classic very efficient refrigeration cycle when heat discharge temperatures are lower than the critical temperature e.g. when used in the lower stage of a cascade system, with another refrigerant being used in the higher stage.
For heat rejection at supercritical pressure, only gas cooling, not condensation, is possible, leading to the cycle known as the transcritical cycle proposed by Gustav Lorentzen and his co-workers for automotive air conditioning and heat-pump systems.[1,5]
This transcritical cycle is not new: it has been well-known since last century as the Linde-Hampson process for air liquefaction based on the Joule-Thomson effect. In this context, it shows a certain lack of efficiency. In classic refrigeration, air-conditioning and heat-pump applications, this principal energetic drawback of the transcritical cycle with CO_2 has to be taken into account. Therefore, it should only be applied where the environmental advantage is obvious and/or local safety is necessary, either of these measures compensating for the energetic drawback.

Applications of carbon dioxide

Refrigerant (direct effect) and CO_2 emissions from energy supply to refrigerating systems (indirect effect) both contribute to greenhouse gas emissions expressed by using Total Equivalent Warming Impact (TEWI). Therefore, refrigeration systems with a high degree of emission are preferred application areas for CO_2 as alternative refrigerant, as long as the energy efficiency, defined as Coefficient of Performance (COP), can be kept at the same level.[6]
In the 1991 Technical Options Report of UNEP,[7] the field of automotive air conditioning was identified as the application with the largest refrigerant consumption worldwide (see *Figure 2*) and the highest direct effect on TEWI, expressed as a percentage (see *Figure 3*).
Therefore, Lorentzen and his co-workers first drew attention to this application for CO_2 as a refrigerant, necessarily employing the transcritical cycle because of higher outside air and heat discharge temperatures when running mobile air-conditioning systems. But the entire transport sector can be a main application for CO_2 as a refrigerant.

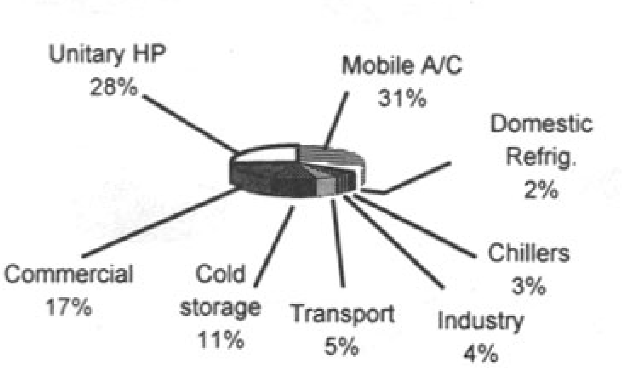

Figure 2. Consumption of refrigerants in 1991 (worldwide 484 200 tonnes/year) [8]

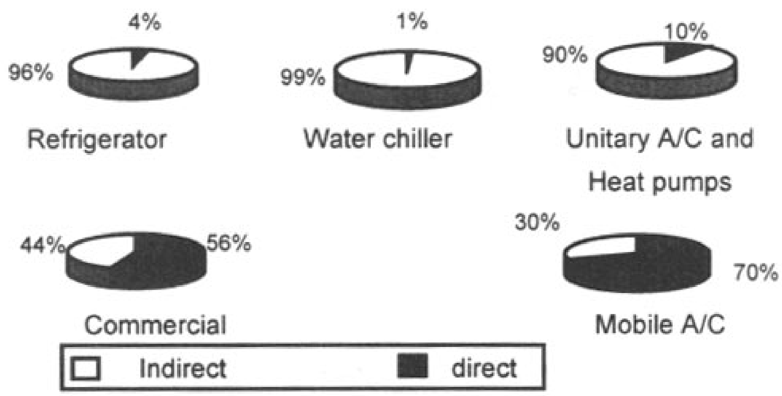

Figure 3. Direct (fluid)/indirect (energy) part of TEWI (100 years)[8]

According to *Figure 3*, commercial refrigeration, including systems used in supermarkets, also has a rather large impact on TEWI due to the long refrigerant lines and the big charge. Cascade systems with CO_2 as the low-temperature refrigerant in a classic vapour compression cycle, or CO_2 as secondary refrigerant are possibilities enabling reduction of greenhouse gas emissions of refrigerants without the disadvantage of higher energy consumption.
The third largest quantity of refrigerant emission per system is shown by the unit air-conditioning and heat-pump systems (see *Figures 2* and *3*).
In the heat-pump application, unit systems and chillers offer good perspectives for CO_2 as a refrigerant, thanks to use of the transcritical cycle; the heat rejected on the high-temperature side is used for space heating or hot-water production.
Since the transcritical cycle also shows a temperature glide in the gas cooler, the temperature profiles of the refrigerant and the secondary fluid can be advantageously adapted in order to minimize heat-transfer loss and hence improve energy efficiency. Good results can be achieved only with similar and rather large temperature intervals on both sides, so the preferred application should be hot air or water production.

Advantages of carbon dioxide

In the transcritical cycle, gas cooler pressure and temperature are not linked as in the subcritical two-phase region.
Since the high-side pressure greatly affects, via the pressure ratio, compressor work and efficiency, high temperatures can be achieved with reasonable compressor power. Therefore, the application of CO_2 in heat pumps, e.g. for hot water at 90°C, can be an excellent goal.
The high vapour pressure leads not only to a low pressure ratio with the advantage of high compressor efficiency, but also to high heat-transfer coefficients and low relative pressure losses. Thus, despite the lack of efficiency of the theoretical transcritical cycle, the CO_2 supercritical refrigeration cycle may still compete with the vapour compression cycle using other refrigerants.
A further advantage related to the use of CO_2 is its higher volumetric capacity due to its high working pressures enabling small equipment components and small-diameter lines to be used. Also, the fact that one is not forced to recover, reclaim or recycle the CO_2 refrigerant (as is necessary with HFC refrigerants) means that CO_2 appears to be very attractive in certain applications where the infrastructure is poor or too expensive, as in developing countries.

Drawbacks of carbon dioxide

The main drawback of carbon dioxide as a refrigerant is its inherent high working pressure: this pressure is much higher than that of the other natural and synthetic refrigerants mentioned. On one hand, this means that for CO_2 cycles, newly developed components must be redesigned. Since CO_2 offers a much higher volumetric capacity, the problem of the higher working pressure can be overcome by optimal design involving smaller, stronger components.
Nevertheless, newly designed components have to be produced and can only be manufactured at reasonable prices if mass produced in sufficient numbers. This can be a big hurdle to surmount before CO_2 technology is introduced in refrigeration, air-conditioning and heat-pump systems. If for instance the automotive and transport industries decided to move to this technology, other fields would benefit from mass-produced low-price components.

Conclusion

CO_2 technology is very attractive as it is environmentally benign and locally safe, but needs a breakthrough enabling mass production of the necessary components in order to be cost-competitive compared with conventional refrigeration, air-conditioning and heat-pump technology with either inherent global environmental or local safety problems.
Extensive research and developmental work on CO_2 technology has been performed internationally over the past 8 years since the revival of carbon dioxide, especially within two large European Community projects: the EC RACE Project for the development of CO_2 automotive air-conditioning systems and the EC COHEPS Project for CO_2 heat pumps.
These projects have shown that CO_2 technology can compete with common technology in automotive and transport air conditioning as well as in heat pumps providing high temperatures for hydronic systems and for the production of hot water at temperatures of up to 90°C as well as for industrial drying processes.[9] However, it should also be mentioned that there are some applications in which the nature of the less efficient transcritical cycle can not be compensated for by taking advantage of the particular operating conditions of the system.
In conclusion, CO_2 technology can meet the environmental and safety requirements of today's challenges for refrigeration, air-conditioning and heat-pump systems, but only in suitable applications where the advantages outweigh the drawbacks of this technology.

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