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EUROPEAN SEMINAR – CO_2 AS A REFRIGERANT

PROPERTIES OF CO_2 AS A REFRIGERANT

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Summary: *In the beginnings of mechanical refrigeration, at the end of the nineteenth century, Carbon Dioxide was one of the first refrigerants to be used in compression type refrigerating machines, later gaining widespread application mainly onboard of refrigerated ships, but common in other sectors of refrigeration as well.*

It was only immediately after World War II that CO_2 rapidly eclipsed as a refrigerant, due to the advent of the synthesised halogenated working fluids, addressed as safe and ideal refrigerants at that time.

Because of the stratospheric Ozone depletion environmental issue, CFC and HCFC working fluids are now phased out of use in Europe under EU Regulation 2037/2000. The Global Warming environmental issue casts concern over the use of the new HFC fluids as substitute refrigerants, because of their high GWP values, which make them subject to regulations under the Kyoto Protocol.

In this mixed situation, CO_2 is being revisited as a fully environmentally friendly and safe refrigerant. An intense research activity on its prospective applications is underway in many research establishments in Europe, Japan and North America, and important results have already been reached in exploiting the peculiar characteristics of this high-pressure fluid operated with a transcritical cycle. In some applications CO_2 systems have been already commercialised; this yields for heat pump water heaters, as a brine in indirect systems and in the low temperature stage of cascade systems.

The paper critically analyses the prospects for the future return of CO_2 as a working fluid, or sometimes as a brine with change of phase, in important application areas. These include air conditioning and heat pump systems in the residential and commercial sectors, commercial and transport refrigeration and mobile air conditioning.

Keywords: Carbon Dioxide, CO_2, Refrigerants, Refrigeration, Heat Pumps.

1. HISTORICAL HINTS

The dawn of mechanical refrigeration preceded the possibility of recurring to chemical synthesis to obtain compounds foreign to nature, and therefore surely the first refrigerants have been natural fluids. Some of them have completely disappeared, others are still widely applied today, and some others, although abandoned in the past, are now reconsidered. This happens under the emergency of the environmental issues put forth by the use of synthesised refrigerants, that is the depletion of the stratospheric ozone and the display of the antropogenic greenhouse effect.

A compound certainly disappeared in the use as a refrigerant is the stinky distillate of caoutchou, called caoutchoucine, very first working fluid in a vapour compression refrigerating machine built (although with limited success) by John Hague. This happened shortly after 1834, when Hague's mentor Jacob Perkins applied in London for the first patent relative to this kind of machine; actually Jacob Perkins had thought of ethyl ether (then called sulphuric ether) as the refrigerant for his new machine.

The dangerous sulphuric dioxide too is a natural fluid used in the past as a refrigerant, and then abandoned without any chance of reconsideration. It permitted the birth of domestic refrigeration, but it was used also in the commercial sector and even in big air-conditioning plants, as in the Rio de Janeiro Opera House in 1904.

Ammonia and some paraffinic hydrocarbons are instead among the working fluids that, already used since the beginning of mechanical refrigeration, never lost their importance in this application. Hydrocarbons are still extensively used in industrial refrigeration (where local safety issues, due to their high flammability, can be adequately addressed), and find new applications (at least in Europe) in domestic refrigeration and low-charge unitary air conditioners. As to ammonia, it is still widely used in the sector of treatment and preservation of foodstuffs, while new applications have already entered the market, as for example in the sector of water chillers for air-conditioning (mainly for installation in the open air). The refrigerant substitution issue opens new interesting perspectives for all these natural fluids.

Carbon dioxide too has been a natural agent extensively used in the past as a working fluid in compression-type refrigerating machines, above all in the initial forty years of the past century. Phased out after World War II, this fluid is now revisited and vastly investigated as a possible working fluid for a wide variety of applications. This action is driven by the search for natural fluids fully compatible with the environment and intrinsically safe even in the immediate surroundings, as a substitute for the old generation synthetic fluids.

Old Physics books report that carbon dioxide was solidified for the first time in 1835 by the French physicist Thilorier, and in turn used as a cooling agent (dry ice) to solidify mercury. In 1867 the American inventor Lowe described how carbon dioxide could be used in refrigeration: Franz Windhausen from Brunswick in Germany, in 1886 patented a compressor for a carbon dioxide refrigerating machine. The following year the British Company J&E Hall bought a licence to build a CO_2 compressor from Windhausen himself. The same Company built the first two-stage CO_2 compressor as well (Cavallini and Steimle 1998).

This can be considered the starting point of the extended use of carbon dioxide as a working fluid in mechanical refrigeration. Some previous attempt is also known, as for example by Carl Von Linde, who had designed a refrigerating machine working with CO_2 for the Company F. Krupp of Essen, in Germany.

It is commonly believed that carbon dioxide was exclusively used as a refrigerant aboard ships. It is certainly true that, of the three sectors which drove the rapid expansion of mechanical refrigeration at the beginning of the twentieth century, that is ice manufacturing, beer brewing and meat transportation from Australia and Latin America to Great Britain, this last one mainly involved the general use of equipment working with CO_2 as a refrigerant starting from 1890; before this date air-cycle machines were mainly employed. By 1910 J&E Hall had already installed 1800 refrigerating machines aboard ships.

But there are also numerous examples of use of CO_2 refrigerating machines in different sectors. Examples are cooling of the ammunition magazine in warships, in breweries, in wine or liquor cellars, in slaughterhouses, in dairy industries, in artificial ice factories and also in all civil application where the safety issue was considered of prominent importance. The number of CO_2 compressor manufacturers rapidly increased in the first decade of the twentieth century, in particular in the Central and North European Countries. A German manual of 1915 lists 29 CO_2 compressor manufacturers in North Europe, 24 of them in Germany, a number hard to believe nowadays.

The entrance into the market, starting from 1931, of the new synthesised halogenated refrigerants marked the rapid and inexorable decline in the use of carbon dioxide as a refrigerant, which though withstood in the field for long. In 1946, 88 percent of the British Fleet still used CO_2 as the refrigerant, and in 1963, 22 percent of the ships recorded in the French Register of Shipping was equipped with CO_2 refrigerating machines.

The reasons for this rapid decline lay certainly in the low energy efficiency of this equipment, and in the drastic reduction in refrigerating power when ambient temperature increases (problem soon evidenced in ships crossing the warm equatorial seas). But certainly also in the failure of CO_2 compressor manufacturers to conform their production to modern technological developments (more compact and faster equipment, and therefore less costly).

2. PROPERTIES OF CARBON DIOXIDE AS A REFRIGERANT

Quite a few general properties of CO_2 (official designation R-744 (ASHRAE 1997)) are absolutely ideal for the use of this product as a working fluid in vapour compression refrigerating machines and heat pumps (Lorentzen 1994):

- carbon dioxide is very abundant in the environment, waste of many technological processes; its cost is thus extremely low, easily available anywhere, and its recovery from dismissed equipment or in maintenance is not required;

- being a natural fluid, its harmlessness to the biosphere is demonstrated, both as far as known actions are concerned in the immediate (as the depletion of stratospheric ozone), and with reference to possible still unknown harmful actions (an always possible danger in the use of new synthesised products foreign to nature, as the happenings with CFCs and DDT have shown). CO_2 is certainly a greenhouse gas, but for its possible use as a refrigerant one recurs to recovery from industrial waste. For this application therefore the added greenhouse impact is to be considered nil, as nil is of course its impact on the stratospheric ozone depletion;

- it is a product that displays no special local safety problem, as it is non-flammable and non-toxic. Gas heavier than air, it can accumulate in the lower part of a non-ventilated ambient, especially in a basement, causing suffocation for lack of oxygen. Holds of ships may be prone to this kind of events;

- it is an inert product, compatible with all common materials encountered in a refrigerating circuit, both metals and plastics or elastomers;

- special synthetic lubricants have been developed and are now tentatively available for CO_2. They seem suitable and are under close scrutiny, with good results so far. The three most interesting candidates are at the moment POE, Alkyl Naftenic (AN) and PVE products.

As far as thermodynamic properties of carbon dioxide are concerned, the state diagram *p* – *h* (pressure, in a logarithmic scale – specific enthalpy) is reproduced in Fig. 1. Table 1 gives values for some fundamental properties of carbon dioxide, together with those for R-22, and some other in-kind refrigerants. R-22 will constitute a comparison synthesised refrigerant in the following of this discussion.

Table 1. *Characteristic properties of Carbon Dioxide and some other traditional refrigerants*

Fluid	Critical Temperature [°C]	Critical Pressure [bar]	Saturation Pressure [bar]		Volumetric Latent Heat at –20 °C [kJ/m^3] (1)	Molecular Mass [kg/kmol]
			at –20°C	at + 30°C		
CO_2	31.06	73.84	19.67	72.05	14592	44.01
R-22	96.15	49.90	2.453	11.92	2371	86.47
R-134a	101.06	40.59	1.327	7.702	1444	102.03
R-410A	71.36	49.03	4.007(2)	18.89(2)	3756	72.59
NH_3	132.25	113.33	1.901	11.672	2131	17.03

(1) latent heat divided by the specific volume of dry saturated vapour. (2) refers to the liquid phase.

The diagram and data in the Table evidence the peculiarities of CO_2 when used as a working fluid in the traditional refrigeration processes. The main difference, as compared to traditional refrigerants such as R-22, is the very low value of the critical temperature, 31 °C for R-744, that is around the maximum summer ambient temperature in Countries with tempered climate. As a consequence, in the traditional vapour compression refrigerating cycle, the process of heat rejection to the environment does not usually imply condensation of the working fluid carbon dioxide, but a dense gas progressive cooling at (ideally) a constant pressure higher than the critical pressure. This of course happens unless a heat sink (cooling water from a natural source, for example) is available at temperature around 20 °C or less, a more and more unusual circumstance in today’s world.

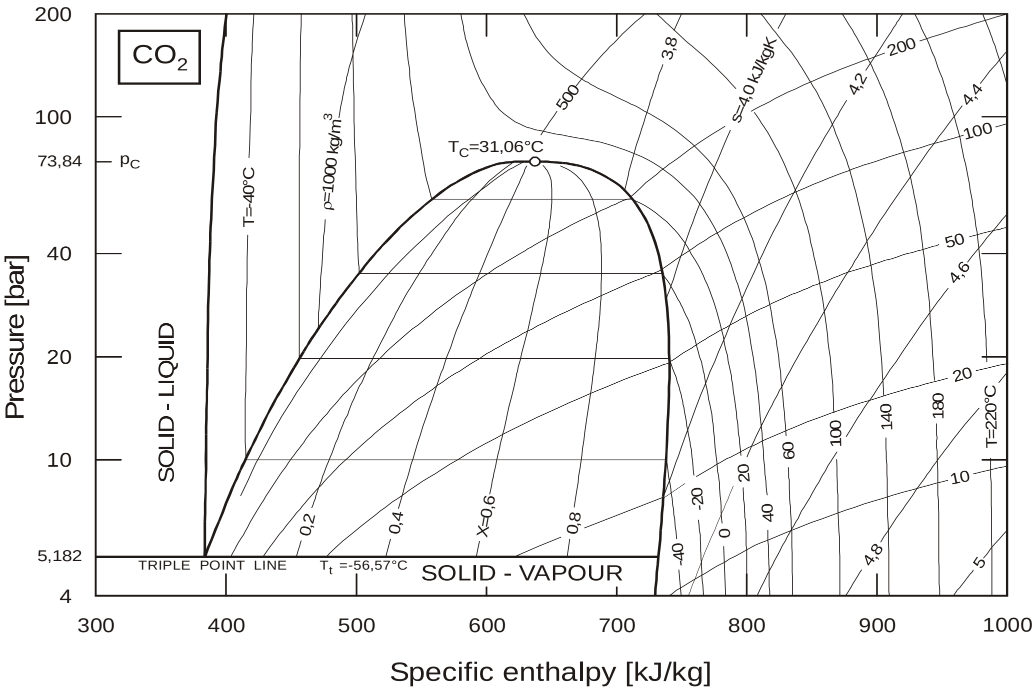


Figure 1 – Thermodynamic diagram *specific enthalpy – pressure* for Carbon Dioxide.

At design conditions a CO_2 refrigerating machine therefore does not usually work with a condenser, but rather with a high pressure gas cooler. The corresponding refrigerating cycle is dubbed *transcritical*, inasmuch as it takes place between two isobars, the former at a pressure value lower than the critical one (evaporator), and the latter at a pressure above the critical one (gas cooler).

Figure 2 shows, in a pressure – enthalpy diagram, two ideal transcritical CO_2 cycles, at two different values for the gas cooler pressure. A peculiar feature of the transcritical cycle, as it appears in Fig. 2, is the existence of an optimum value for the gas cooler pressure, that brings about the maximum value for the cycle *COP*, once the other operating conditions have been fixed. In fact one can see in Fig. 2 how, by moving from cycle 1-2-3-4, with 90 bar gas cooler pressure, to cycle 1-2'-3'-4', with 100 bar gas cooler pressure, both the refrigerating effect and the compression work increase (by ΔQ_0 and ΔW_c respectively). It depends on the relative increases of these two quantities whether the *COP* increases or decreases. To be noted that a constant value for the gas cooler exit temperature $t_3 = t_{3'}$ =40 °C was kept.

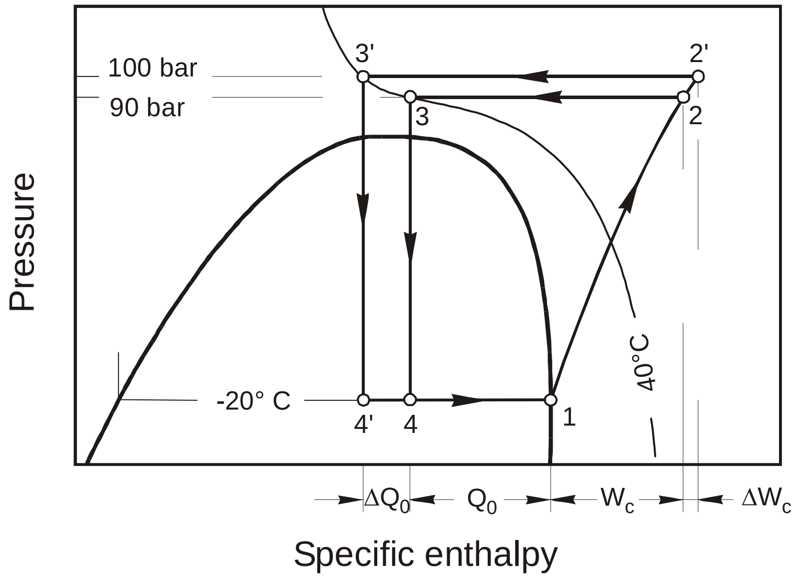


Figure 2 – Two transcritical refrigerating cycles (with different values for the gas cooler pressure) depicted in the *h-p* diagram for CO_2.

The shape of the constant-temperature lines (the isotherm at 40 °C is plotted in the figure) explains why an optimum gas cooler pressure exists. This evidently depends on all specific conditions defining the cycle considered (evaporation temperature, possible superheat of the compressor suction gas, isoentropic compression efficiency, gas temperature at gas cooler exit, etc.). For an ideal simple transcritical cycle, such as the one depicted in Fig. 2, the value of the optimum pressure p_{opt} of the gas cooler can be estimated, as a function of evaporation temperature t_e and gas temperature at gas cooler exit t_{gce}, by the equation (Liao and Jakobsen 1998):

$$
\begin{aligned}
&p_{opt} = (2.778 - 0.0157 \cdot t_e) \cdot t_{gce} + (0.381 \cdot t_e - 9.34) \\
&\text{with } t_e \text{ and } t_{gce} \text{ in } [°C] \text{, and } p_{opt} \text{ in } [\text{bar}] \qquad (1) \\
&-40°C < t_e < +5°C \; ; \; 31°C < t_{gce} < 50°C
\end{aligned}
$$

The above equation is valid for isoentropic compression and dry saturated vapour at compressor suction.

The same equation holds good for cycles with isoentropic efficiency less than 1, provided that it can be considered constant (that is, independent of the compression pressure ratio).

In all cases, not only with reference to an ideal simple cycle, the trend of the cycle coefficient of performance as a function of the gas cooler pressure for $p>p_{opt}$ is rather flat. Therefore a slight overpressure in the gas cooler with respect to the optimum, does not penalise too much the cycle efficiency. On the other hand, a gas cooler pressure below the optimum value can sometimes drastically penalise the cycle efficiency. A proper control of the high-pressure level is indispensable to take best advantage of CO_2 refrigeration technology.

A further important difference of CO_2 transcritical cycles, as compared to traditional refrigerating cycles, is given by the much higher pressure levels (see data reported in Tab. 1), at equivalent working conditions as far as temperatures of the external source and sink are concerned.

It is no doubt that high pressure levels penalise the structural design of components of a refrigerating circuit, and in particular of the compressor; nevertheless their reduced sizes counterbalance this drawback. As compared to traditional refrigerants, the reduced volume flow rate of CO_2 necessary to yield a certain refrigerating power is evidenced by the value of the volumetric latent heat reported in Tab. 1. This is six times larger for CO_2 than for R-22, even if one must also take into account the high vapour quality of CO_2 at the evaporator inlet, as compared to that of R-22 in comparable situations, proper to the transcritical cycle.

The high pressure level with CO_2 also brings about a reduced penalty due to the fluid pressure loss when designing the refrigerating circuit appropriately.

From what said above it can be concluded that equipment with CO_2 as the refrigerant, in spite of the higher working pressure, is not necessarily heavier or bulkier or potentially more dangerous as compared to equivalent equipment operated with the traditional working fluids. This is due to the smaller flow cross sections of the components, consequent on the reduced refrigerant volume flow rate.

Moreover, at equivalent working conditions, the compressor pressure ratio with CO_2 is notably lower than with traditional refrigerants. Together with a higher pressure level, this fact makes it possible to get higher compression isoentropic efficiencies, with advantages in energy consumption. On the other hand, CO_2 compressors work with much higher differential pressures than traditional refrigerating compressors, and this fact may enhance backflow losses.

Another peculiarity of carbon dioxide is evident in the diagram of Fig. 1: the triple point pressure (p_t=5.18 bar) is above that of the natural environment. At atmospheric pressure the transition from solid to gas (sublimation process) takes place at temperature t_t=-78.9 °C, and the cooling effect is exploited in the so-called dry ice. In mechanical refrigeration this means that, in the event of collapse of a circuit, residual CO_2 solidifies in the plant at around –79 °C, sublimating successively into the atmosphere.

3. THE CO_2 TRANSCRITICAL REFRIGERATING CYCLE

Energy performance of a CO_2 transcritical cycle is now discussed and compared with that of a traditional refrigerating cycle operated with conventional working fluids. To make the discussion concrete and to be able to argue about definite numerical values, two refrigerating cycles are directly analysed: a transcritical one operating with CO_2, and a traditional one operated with R-22; this last refrigerant is in fact often taken as a bench-mark. The operative conditions for the two cycles, illustrated in Tab. 2, are fixed in such a way that they can be considered approximately equivalent with respect to external constraints.

The situation considered refers to an outside air temperature t_a=28 °C, with an air temperature increase in the R-22 condenser equal to 10 °C, and condensation of the refrigerant 5 °C above the condenser air exit temperature. For the CO_2 transcritical cycle, a 3

°C temperature approach at the counter-current gas cooler cold end has been assumed; further, the optimum gas cooler pressure p_{opt}=78 bar (refer to relationship (1)) is assumed.

Table 2. *Vapour compression refrigerating cycles*

Point(s)	Description	Refrigerants	
		CO_2	R-22
$4 \rightarrow 1$	Temperature of isobaric evaporation	t_e=-10 °C	t_e=-10 °C
$1 \rightarrow 2$	Isoentropic efficiency of adiabatic compression	η_{ic}=0.80	η_{ic}=0.80
$\rightarrow 3$	Temperature of isobaric condensation (R-22)		t_c=43 °C
$2 \rightarrow 3$	Pressure (constant) in the gas cooler (CO_2)	p_{gc}=78 bar	
3	Outlet gas cooler temperature (CO_2)	t_{gce}=31 °C	
1	Vapour superheat at compressor inlet	0 °C	0 °C
3	Liquid sub-cooling at condenser outlet (R-22)		0 °C
	Temperature (constant) of the cooled source	t_r=-5 °C	t_r=-5 °C
	CYCLE COEFFICIENT OF PERFORMANCE COP	**2.52**	**3.04**

It can be noticed that for the theoretical cycles compared in the Table, in spite of the fact that a close temperature approach has been assumed for the CO_2 gas cooler, carbon dioxide *COP* is penalised by 20% as compared to the benchmark refrigerant R -22.

To examine the reasons for the lower energy efficiency of the CO_2 transcritical cycle (at least at the considered working conditions), one can find, for any single process making up the cycle, the *thermodynamic loss*. This is defined as the individual contribution to the increase of the needed compression work, with respect to the one strictly necessary, with ideal thermodynamic processes, to obtain the same cooling effect, still complying with the external constraints.

The computation of the thermodynamic losses of the individual cycle processes (referred to the unit mass of refrigerant) can be easily performed by recurring to the thermodynamic function exergy, once a suitable value for the ambient temperature t_a is recognised. In this example, this is clearly the temperature at which the external cooling agent (air, in this case) is available for rejecting the condenser (R-22 cycle) or gas cooler (R-744 transcritical cycle) heat, that is t_a=28 °C (that is, T_a=301.15 K).

Without going into the details of the theory of exergy (to be found in any *Basic Applied Thermodynamics* textbook), here below the expressions of the *specific thermodynamic losses* π (that is, referred to a unit mass of refrigerant) are reported. Reference is made to the four processes of the CO_2 transcritical cycle represented in Fig. 3, conforming to operative conditions given in Tab. 2:

- *Adiabatic compression loss* $$\pi_{com} = T_a\left(s_2 - s_1\right) \quad (2)$$
- *Gas cooler loss* $$\pi_{gc} = h_2 - h_3 - T_a\left(s_2 - s_3\right) \quad (3)$$
- *Adiabatic throttling loss* $$\pi_t = T_a\left(s_4 - s_3\right) \quad (4)$$
- *Evaporator loss* $$\pi_{ev} = T_a\left(s_1 - s_4 - \frac{\left|Q_0\right|}{T_r}\right) \quad (5)$$

In the expressions above, h and s are specific enthalpy and specific entropy of refrigerant respectively, while $Q_0=h_1-h_4$ is the cycle refrigerating effect. Capital T is temperature in absolute units.

The necessary input to perform the cycle is the compression work $|W_c| = h_2 - h_1$, while the desired output of the cycle is the removal of heat $Q_0 = h_1 - h_4$ from the refrigerated heat source at temperature t_r. In terms of exergy, the effect is evaluated as $E_{Q0} = |Q_0|\left(\frac{T_a}{T_r} - 1\right)$, that is the exergy received, per unit mass of refrigerant, by the refrigerated heat source. This last quantity also coincides with the minimum exergy ideally required to obtain the very same effect, that is the minimum work required in an ideal (Carnot) refrigerating cycle.

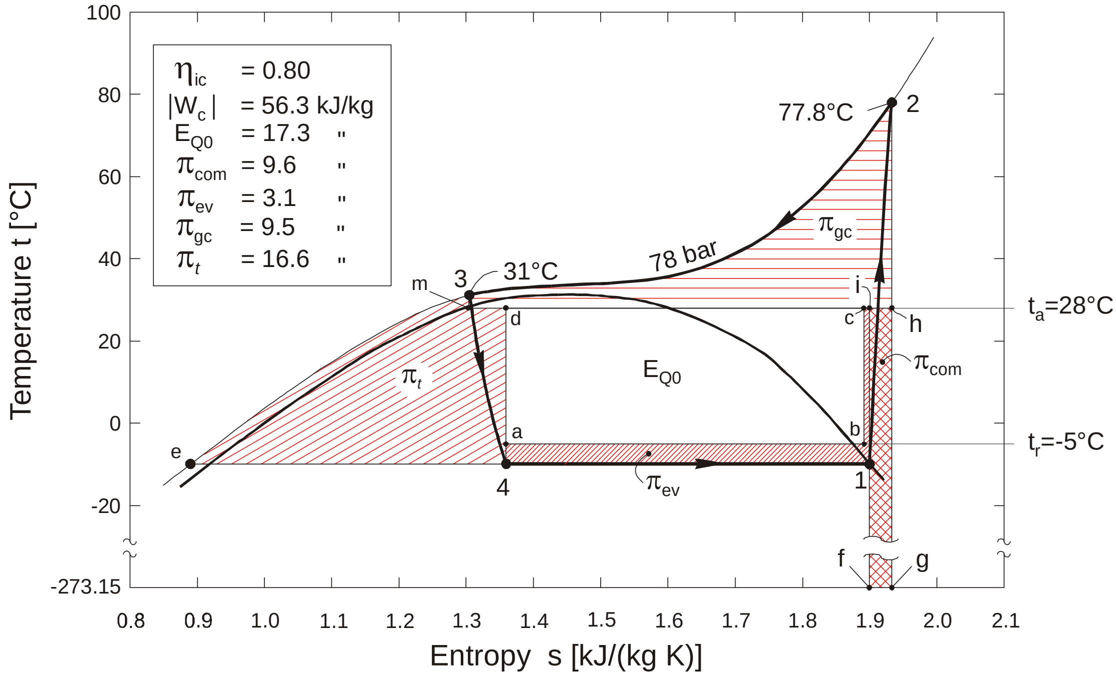


Figure 3 – Exergy losses π depicted in a *T-s* diagram for CO_2, relative to a simple transcritical refrigerating cycle.

The actual compression work, relative to the real cycle considered above, can be computed as the sum of the minimum ideal work plus the various thermodynamic losses of the four processes making up the actual cycle, that is:

$$|W_c| = E_{Q0} + \pi_{com} + \pi_{gc} + \pi_t + \pi_{ev} \tag{6}$$

All the different terms appearing in expression (6) can be represented as single surfaces in a *T-s* diagram. This is done in Fig. 3, where the transcritical CO_2 cycle at conditions reported in Tab. 2 is plotted. The location of the different points defining the areas in Fig. 3 is immediate, except perhaps point *b*. It is to be located, in the constant temperature line at t_r, so as to meet the condition $\overline{ab} = \overline{41} \cdot T_{ev}/T_r$, where T_{ev} is the refrigerant evaporating absolute temperature. To be noted that, for the throttling loss π_t, the representation as the indicated area is only an approximation, although within narrow limits.

The single thermodynamic losses in the four processes making up the actual cycle, normalised through division by the actual compressor work $|W_c|$, are called efficiency defects δ:

-*Compressor efficiency defect* $\delta_{com} = \pi_{com}/|W_c|$

-*Gas cooler efficiency defect* $\delta_{gc} = \pi_{gc}/|W_c|$

-*Throttling efficiency defect* $\delta_t = \pi_t/|W_c|$

-*Evaporator efficiency defect* $\delta_{ev} = \pi_{ev}/|W_c|$

One can then write:

$$\eta_{ex} = 1 - \delta_{com} - \delta_{gc} - \delta_t - \delta_{ev} = 1 - \sum \delta \qquad (7)$$

The values of the various efficiency defects allow one to single out the contribution of any individual process to the degradation of the cycle thermodynamic efficiency. Comparison among homologous efficiency defects for equivalent refrigerating cycles performed by different working fluids allows one to evidence strengths and weaknesses of a refrigerant in the specific application.

Table 3 reports the values of the above exergetic parameters for the refrigerating cycles considered in Tab. 2. Of course, for the R-22 refrigerating cycles, parameters referred to the condenser are considered, in place of the ones referred to the gas-cooler as is the case for the CO_2 transcritical cycle: definitions are pretty much the same.

Table 3. *Values of some exergetic parameters for the refrigerating cycles of Tab. 2*

Parameter	**Refrigerant**	
	R-744 (CO_2)	**R-22**
Exergetic efficiency η_{ex}	*0.310*	*0.374*
Compressor efficiency defect δ_{com}	*0.171*	*0.173*
Gas cooler efficiency defect δ_{gc}	*0.170*	-
Condenser efficiency defect δ_{cond}	-	*0.224*
Throttling efficiency defect δ_t	*0.294*	*0.161*
Evaporator efficiency defect δ_{ev}	*0.055*	*0.068*
Sum of all efficiency defects $\sum \delta = 1 - \eta_{ex}$	*0.689*	*0.626*

Data reported in Tab. 3 clearly evidence that the process that mostly penalises the CO_2 transcritical cycle, as compared to the R-22 traditional refrigerating cycles, is throttling. Even the cooling of the dense gas in the gas cooler at above critical pressure can penalise the cycle energy efficiency, if a close temperature approach isn't reached. If one is willing to use carbon dioxide as a refrigerant in a compression cycle, he should investigate and exploit all those factors that may curtail the thermodynamic losses (and therefore the efficiency defects) of the throttling and heat rejection processes of the simple refrigerating cycle. This should be done in comparison to what is obtainable with traditional refrigerants. Modifications to the simple refrigerating cycle, aimed at the same goals, are also possible and fruitful (see later on).

When treating the above matter, one cannot disregard the fact that the alteration of one of the processes making up the base cycle usually also brings about variations in the efficiency defects of some other cycle processes; this fact deserves careful and comprehensive consideration. For example, by increasing the isoentropic efficiency of the compression process of the cycle depicted in Fig. 3, the efficiency defects of both the compressor and of the gas cooler are diminished because the compressor discharge temperature T_2 decreases. In this case the exergetic efficiency of the cycle certainly increases; nevertheless the efficiency defects of the throttling process and of the evaporator increase, due to the decrease in the reference compression work. In some cases, consequences of alteration to the basic structure of the cycle are not that immediate.

4. POINTS IN FAVOUR OF THE APPLICATION OF CO_2 AS THE WORKING FLUID FOR REFRIGERATING AND HEAT PUMP EQUIPMENT

The comparison performed above among refrigerating cycles run with CO_2 and R-22 is rather schematic. It does not evidently take in due consideration a series of factors dependent on the peculiar characteristics of CO_2 as compared to the synthesised refrigerants, which can have a strong influence on the actual energy efficiency of equipment working in the field.

According to some sophisticated modelling and preliminary experimentation, these factors in some cases will be able to drastically mitigate, and sometimes even reverse, the indications drawn above about the energy penalisation that goes with the use of CO_2 as the working fluid in vapour compression machines, when this new technology reaches a maturity comparable to what at present exists with the use of traditional working fluids.

The points in favour of the application of CO_2 as a working fluid in the different components of a refrigerating or heat pump circuit are discussed in the following (Pettersen 1997).

Compressors. In CO_2 equipment, compressors work at high levels of effective mean pressure, with large pressure differences, but with pressure ratios considerably smaller than in equivalent machines operated with traditional refrigerants.

Referring to positive displacement reciprocating compressors, it is proved that the adoption of multiple elastic rings in the pistons curtails to a negligible amount the gas throttling leakage between high- and low-pressure cylinder sides, despite the considerable differential pressure. Even leakage through the valves can be avoided (Fagerli 1997).

Whereas the other factors considered favour the production of compact machines with limited stroke, where the negative effect of pressure loss across valves becomes negligible (Süss and Kruse 1997). These effects make possible to obtain higher compression isoentropic efficiencies in CO_2 compressors than in similarly operated machines working with traditional refrigerants. Prototypes of compressors for CO_2 mobile air-conditioners exhibited isoentropic efficiencies up to 10 percentage points higher than machines of present technology operated with R-12 or R-134a (Fagerli 1997).

This fact of course favourably influences the equipment *COP* in the field; to be noted that, in the comparison reported in Tab. 2, equal values for the compression isoentropic efficiencies both for the CO_2 and the R-22 cycles have been assumed.

Heat Exchangers. In the usual operative conditions for the working fluid in refrigerating machines and heat pumps, the thermophysical properties of CO_2 are favourable to produce high heat transfer coefficients in the equipment's heat exchangers (of suitable geometry), often higher than the ones commonly obtained with traditional synthetic refrigerants.

Some favourable properties for CO_2 are the quite high thermal conductivity both of the liquid phase and of the dense gas phase, the large value of the specific heat capacity of the liquid, the pretty low values of the kinematic viscosity and of the surface tension. Further, the low value of the ratio between liquid and vapour densities can favour distribution in evaporators with multi-parallel circuits (more homogeneous two-phase flow).

Together with favourable thermophysical properties, one should consider that with CO_2 pressure drops in the circuit components at least five times higher than with traditional refrigerants can be allowed, without much penalisation for the *COP* of the equipment, due to the much higher working pressure level. This allows the use of smaller pipes (typical reduction in cross section to around 60% as compared to R-134a), and designing with high values of the mass flow rate. This in turn enhances the heat transfer coefficients, benefiting the energy efficiency of the equipment.

As it is evidenced by the graphical representation in Fig. 3 of the transcritical CO_2 cycle, throttling losses can be drastically reduced by lowering as much as possible the exit supercritical gas cooler temperature. The high values obtainable for the heat transfer coefficients (see, for example, Fig. 4), together with a suitable configuration (close to counter-current), can allow to keep the cool side temperature approach of the gas cooler often within 1-2 degrees Celsius. The effect on the increase of cycle *COP* as a consequence of the decrease in the cool end temperature approach of the gas cooler is remarkable, and must be fully taken advantage of in CO_2 transcritical machines.

Of course even in the evaporator a reduced mean effective temperature difference helps increasing the equipment energy efficiency.

Good heat transfer both in the evaporator and in the gas cooler also contributes to the further reduction of the compression pressure ratio, with an additional advantage in the compression isoentropic efficiency, as discussed above.

It is also to be pointed out that presence of lubricating oil in the working fluid might significantly penalise the heat transfer performance both of the gas cooler and the evaporator; this matter is at present under close research scrutiny.

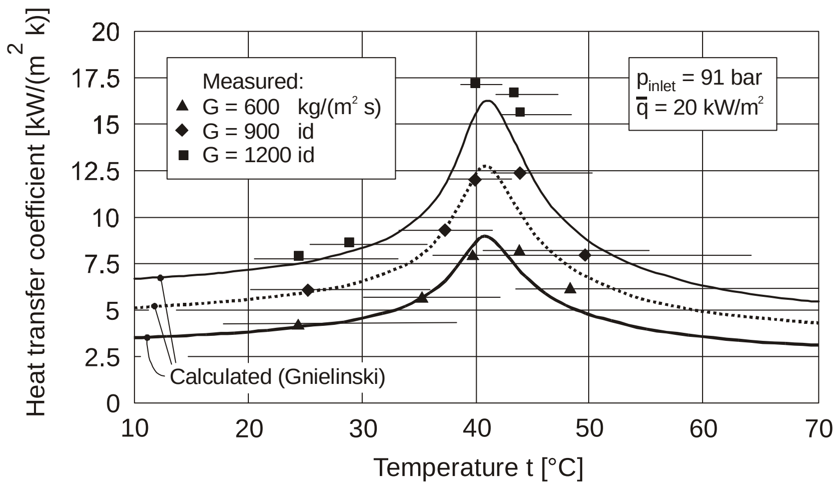


Figure 4 – Influence of varying mass flux on the supercritical pressure heat transfer coefficient, in a microchannel aluminium tube with 25 circular channels with 0.79 mm inner diameter (Pettersen and Vestbøstad 2000).

Ambient Conditions. Often comparisons with alternative refrigerants are done at design conditions, which most often are at the highest ambient temperatures occurring during a year. CO_2 usually compete relatively better at lower ambient temperatures. Lower ambient temperatures will in most climates be dominant during a year. In a seasonal comparison, which is the most important regarding total energy consumption, CO_2 can turn out to be competitive even though the efficiency at the highest ambient temperatures may be lower.

Heat Pumps. In a transcritical CO_2 refrigerating cycle, the considerable amount of exergy made available in cooling the hot dense gas in the gas cooler is completely dissipated by transferring heat to the ambient cooling medium (whether ambient air or water). Whereas, when the transcritical cycle is exploited as a heat pump, part of this same exergy, transferred to the heated medium, makes up just the effect looked forward to. In this case the equipment energy efficiency can be competitive or often higher than the one obtained with machines of the same type operated with traditional refrigerants. The same conclusion can of course be drawn with respect to refrigerating machines with heat recovery at the transcritical gas cooler.

The shape of the constant pressure lines above the critical point for CO_2 makes it clear why transcritical cycles very well lend themselves to heat pumps for sensible heating of a mass flow rate of a fluid through a high temperature change. And the value of *COP* is not much dependent on the maximum temperature of the heated fluid. As an example, Fig. 5 illustrates the excellent matching between temperature profiles of CO_2 at 120 bar and a water flow heated from 15 to 84 °C in the counter-current gas cooler. The same Fig. 5 illustrates also the definitely less favourable temperature profile required in the condenser of a heat pump run with R-134a to accomplish the same duty. Both working fluids processes in the heat pumps are determined with reference to simple vapour compression cycles. The conditions are: suction of dry saturated vapour at 0 °C (evaporation temperature), compression isoentropic efficiency η_{ic}=0.80, with the constraint that in the counter-current heat exchanger (water heater) the local temperature difference between working fluid and water never be less than 5 °C.

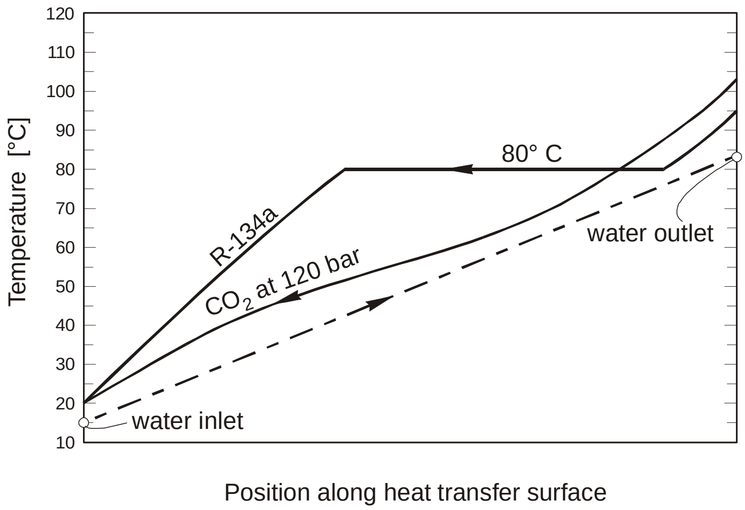


Figure 5 – Temperature profiles in transcritical CO_2 heat pump gas cooler, and in a R-22 heat pump condenser, to heat water from 15 to 84 °C.

In comparison with traditional heat pumps for residential heating, CO_2 transcritical heat pumps, at comparable capacities, lend themselves to heating a smaller air mass flow rate through a larger temperature lift, with fewer problems for cold droughts in the heated rooms.

On the contrary, the application of CO_2 transcritical heat pumps associated with the traditional European radiator heating circuits, with water temperature change of only 20 °C (for example, from 50 to 70 °C), does not prove energy competitive against gas boilers. A reduction in the water flow rate, with a temperature change more than doubled (for example 40-90 °C) might probably make competitive even this application, at least in some circumstances.

Further advantages of transcritical CO_2 heat pumps for ambient heating, as compared to heat pumps working with traditional fluids, can be summarised as follows (Pettersen 1997):

In normal operating conditions, as discussed above, the CO_2 transcritical cycle must be operated at optimum gas cooler pressure. Under extreme outdoor conditions, the cycle can be operated at above-optimum pressure, with an increase in the heat output (or, conversely, keeping the gas cooler pressure constant when the evaporating pressure tends to decrease). In this way, it is less necessary to resort to supplemental heating (often performed with electrical heaters), and therefore without heavily penalising the seasonal energy efficiency of the plant.

The CO_2 transcritical cycle is characterised (even when operated at optimum gas cooler pressure) by a reduced influence of evaporating temperature on heating capacity and coefficient of performance *COP*. At low environmental temperatures, it retains high heating capacities (which can be further increased, as already mentioned, by raising the gas cooler working pressure).

From what discussed above, one can conclude that the seasonal energy efficiency of a CO_2 heat pump, as compared to a standard machine, can turn out to be more favourable throughout the full heating season, even if energy performance at strict design conditions may prove lower. It is always necessary to carry out an extended analysis, taking into account the different operative conditions and the associated working times, considering also energy consumption of system auxiliary components (and in particular, of the different fans), and of the necessity of supplemental heat, to draw really consistent conclusions.

5. MODIFICATIONS TO THE SIMPLE CO_2 TRANSCRITICAL CYCLE

Rather than searching for a fluid suitable for a defined refrigerating cycle, it is more productive to try to adapt the cycle to the favourable characteristics of the natural working fluid CO_2. Following this approach, some possible modifications to the simple transcritical cycle are discussed below, in view to obtain improved energy efficiency with CO_2. The following modifications are limited to a refrigerating cycle; for a transcritical CO_2 heat pump cycle, similar remarks can be considered.

The modifications considered are aimed at reducing exergy losses in the throttling process and/or in the dense gas cooling. This brings about an improvement in the cycle *COP*; the analysis performed above showed in fact that these processes are critical as far as energy efficiency of the full cycle is concerned.

To grant concreteness to this discussion, even from a quantitative point of view, different modifications to the base scheme of the refrigerating machine, together with related *COP* values, are reported in Fig. 6; the operative conditions are reported in the captions to this figure.

The reported *COP*s are those of the related reference cycles, referred to the optimum value for the upper and, if the case, intermediate pressures. All the remarks previously discussed, relative to all factors in favour of CO_2 as compared to traditional refrigerants and not fully evidenced by merely considering cycle performances, hold true also in this circumstance.

Scheme 1. This is the simple basic scheme of a vapour compression refrigerating machine, whose reference cycle is the same one considered in Tab. 2.

Scheme 2. A regenerative heat exchanger is inserted between vapour exiting the evaporator and dense gas / liquid leaving the gas cooler. The consequent reduction in the temperature of the fluid at throttling valve inlet decreases the exergy loss (and therefore the efficiency defect), of throttling. On the other end, the isentropic compression work increases, as does the efficiency defect of heat transfer in the gas cooler, mainly due to the increase in the mean thermodynamic temperature of the gas along the heat rejection process to the environment.

General features of the CO_2 cycles compared

Temperature of isobaric evaporation t_e = -10°C, with dry saturated vapour at evaporator outlet.
Adiabatic compressions with isoentropic efficiencies 0.80.
Adiabatic expansion, with isoentropic efficiency 0.70; expansion work not recovered in schemes 3 and 4.
Regenerative heat exchanger with thermal efficiency 0.70.
CO_2 exit temperature from high-and intermediate-pressure gas coolers 31°C. Optimum pressures.
Negligible pressure losses in heat exchangers and connecting lines.

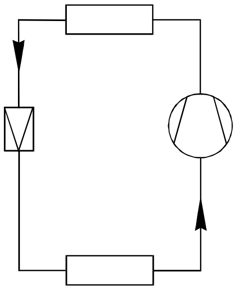
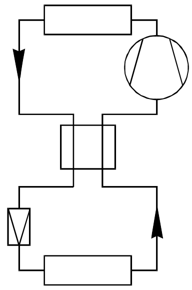
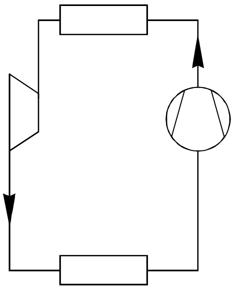
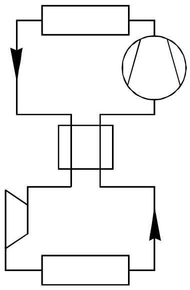
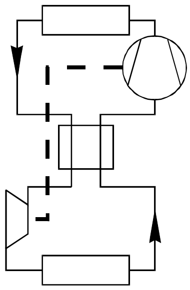
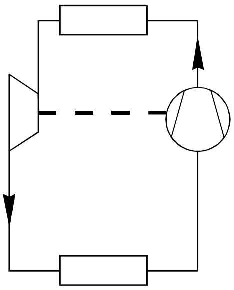
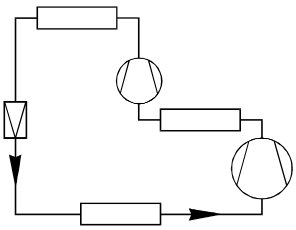
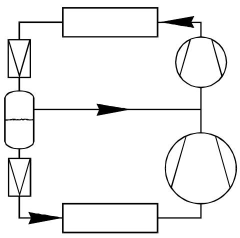
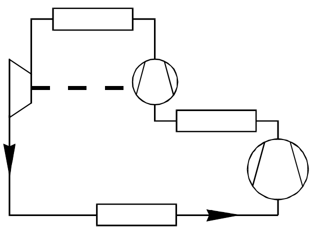
1  *Gas cooler opt. pressure 78 bar* ***COP = 2.52***	2  *Gas cooler opt. pressure 77 bar* ***COP = 2.55***	3  *Gas cooler opt. pressure 77 bar* ***COP = 2.71***
4  *Gas cooler opt. pressure 76 bar* ***COP = 2.66***	5  *Gas cooler opt. pressure 76 bar* ***COP = 2.98***	6  *Gas cooler opt. pressure 77 bar* ***COP = 3.34***
7  *Two-stage cycle* *Optimum pressures 64 & 80 bar* ***COP = 2.67***	8  *Two-stage cycle* *Optimum pressures 46 & 76 bar* ***COP = 3.05***	9  *Two-stage cycle* *Optimum pressures 61 & 77 bar* ***COP = 3.56***

Figure 6 – Possible modifications to the simple transcritical CO_2 refrigerating cycle, in order to increase energy efficiency.

Exergy losses in the regenerative heat exchanger are small, as are the variations in the energy defects of the other plant components. The final result is a very limited increase in the cycle *COP*.

<u>*Scheme 3.*</u> A mechanical expander, without recovering the expansion work released by the fluid replaces the throttling valve. In spite of the dissipation of the expansion work, the exergy loss of the expansion process decreases (as compared to the throttling process), with an increase in the obtained refrigerating effect; the cycle *COP* of course increases.

<u>*Scheme 4.*</u> A regenerative heat exchanger is added to the previous scheme. No benefit is obtained in cycle *COP*; in fact, the cooling of the fluid exiting the gas cooler takes away potential work extractable by the expander.

<u>*Scheme 5.*</u> This scheme is equivalent to the previous one, but in this case the expansion work extracted by the expander is recovered and used in the compression process. Thus, the work supplied by the external source decreases, and consequently the cycle *COP* increases.

<u>*Scheme 6.*</u> This scheme is equivalent to scheme # 3, but even in this case the expansion work extracted by the expander is recovered and used in the compression process. By comparing the *COP* obtainable in this circumstance with the one relative to scheme # 5, one can conclude that the presence of the regenerative heat exchanger is detrimental.

<u>*Scheme 7.*</u> The working-fluid one-stage compression of the basic cycle is replaced by a two-stage compression, with a gas intercooler between the two compression processes. Both compression loss and heat rejection loss are reduced; the compression work decreases, and consequently the cycle *COP* increases.

<u>*Scheme 8.*</u> Two-stage throttling is associated to two-stage compression, and the flash vapour resulting from the first stage throttling is directly sent to the second stage compressor, thanks to the presence of the intermediate pressure separator. Global compression, throttling and heat rejection exergy losses are reduced; small additional exergy losses are added in the gas mixing process between the two compressors. Cycle *COP* drastically increases.

<u>*Scheme 9.*</u> It is equivalent to the previous scheme # 7 (two-stage compression with intercooler), with the replacement of the throttling valve by a mechanical expander, recovering the expansion work for the second-stage compression process. Cycle *COP* impressively increases.

It has been shown how the replacement of throttling devices with mechanical expanders with external work recovery might drastically improve cycle energy efficiency. In particular when the gas outlet temperature from the gas cooler is high, the main effect of a mechanical expander is to curtail the high exergy losses of the throttling process.

In the case of the natural working fluid CO_2, its properties lend themselves in a much better way to the recovery of the expansion work than it may happen with the traditional refrigerants. This work is in fact mainly released in the liquid phase, at high mean pressure and small specific volume, contrary to what happens with the other available natural working fluids, or the synthesised refrigerants (for which, as already evidenced, the energy advantage would anyway be less).

This important issue has activated intense research in the subject of expansion devices, addressed both to expanders working in principle as hydraulic machines, and to volumetric free piston type expander/compressor machines (Heyl *et al*. 1998, Quack *et al*. 2004).

Turbine-compressors are also under scrutiny (Hays and Brasz 2004). This promising matter is still in the research stage.

6. CONCLUSION

The natural fluid Carbon Dioxide displays some excellent properties in the use as a refrigerant in compression-type refrigerating or heat pump systems: it offers unequalled local and ecological safety, widespread availability at low cost, with no need for recycling and containment.

Because of its low critical temperature (around 31 °C), CO_2 does not compare favourably against traditional refrigerants, as far as energy efficiency is concerned, when simple theoretical cycle analyses are carried out.

But this situation can be mitigated, and in some cases completely reversed, by proper design of the system aimed at fully exploiting the unique characteristics of CO_2 and/or the exclusive features of transcritical cycles, which bring about important factors that improve the practical performance of CO_2 systems.

A widespread research activity is underway world-wide for the application of CO_2 in many areas with promising results, including mobile and residential air conditioning, heat pumps, water chillers, commercial and marine applications (Kim *et al.* 2004).

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