CO2 in closed loop
Christophe Marvillet

To cite this version:

HAL Id: hal-02358587
https://hal.science/hal-02358587
Submitted on 6 Jan 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Carbon dioxide is used in closed circuits mainly for energy use in food processing applications and especially for cold applications that is to say at temperatures below ambient and can go down to temperatures close to -40 °C.

The two major functions provided by this fluid CO2 in refrigeration systems are:

- Use as a secondary coolant that is to say the transport of thermal energy from a point of use (heat source) to a point of cold production (heat sink) at temperatures, according to applications, between 10 °C and -40 °C

- Use as a refrigerant which flows in the circuit of the refrigeration equipment, is compressed in the compressor in vapour phase, evaporates in the evaporator in liquid/vapour phase and allows in this equipment the effective production of cold that is to say the absorption of heat at low temperature from the medium or fluid to be cooled.

The increased use of CO2 in refrigeration systems in recent years is due not only to the specific characteristics of this fluid - in particular its low impact on the environment - but above all to the new regulatory constraints that apply to HFC refrigerants (hydrofluorocarbons) which have major impacts on the environment and on secondary fluids based on alcohol, synthetic or silicone oils also concerned by environmental constraints but also by their unsuitability for agro-food uses.

In this chapter, we will discuss the following points:

- The specific properties of CO2 as a coolant and refrigerant and the advantages / limitations of this fluid in the intended applications,

- The use of CO2 as a secondary coolant by recalling the architecture of energy systems, the main design rules of these systems and the precautions to be taken when using this fluid in these uses.

- The use of CO2 as a refrigerant by recalling the main refrigeration cycles in which it can be valued, the main design rules of these systems.

1/ The Carbon dioxide thermo-dynamical and thermo-physical properties

Carbon dioxide is an inorganic compound whose chemical formula is CO2, the molecule having a linear structure of the form O = C = O. Under normal conditions of temperature and pressure, it presents itself as a colourless, odourless gas with a pungent flavour.
At atmospheric pressure, it sublimes at -78.5 °C (passage from the solid state to the gaseous state), but does not melt (passage from the solid state to the liquid state). The liquid phase can only exist at pressure above the minimum pressure of 519 kPa, and in a temperature range of -56.6 °C (triple point) to 31.1 °C maximum at 7.38 MPa (critical point). The figure 1 shows the diagram Pressure/temperature of two-phase CO2 equilibrium data (gas/solid, liquid/solid and liquid/gas). The latent heat values are the following:

- Vaporization: at 0°C the latent heat is equal to 234.5 kJ/kg, at -16.7°C to 276.8 kJ/kg, at -28.9 °C to 301.7 kJ/kg
- Fusion: at -56.6°C the latent heat is equal to 199 kJ/kg

It will be noted that one of the particular points of CO2 lies, whether for secondary coolant or refrigerant uses, by the high pressure values encountered with this fluid in the temperature range of -10°C to 80°C, range of temperature of use in refrigerating equipment. In comparison, with traditional fluids, we note:

- For secondary coolant use, glycol mixtures in liquid form, for example, only require pressures not exceeding 300 kPa, whereas a CO2 circuit can reach values of several MPa depending on the temperatures reached.

- For refrigerant uses, Table 1 shows the comparison of CO2 saturation pressures with the refrigerants commonly used and highlights the very important values achieved with this fluid.

![Figure 1: Diagram Pressure-Temperature for Carbon dioxide](image-url)
The CO2 thermo dynamical properties of CO2 has important impact on fluid manipulation: prior to charging the system must be evacuated first and it’s important to never brake the vacuum with liquid CO2 because the spontaneous evaporation have severe cooling effect and generate risk of brittleness and thermal shock of the materials. To avoid the formation of solid CO2, it is strongly recommended to charge the plant with gaseous CO2 up to approx 10 up to 20 bars.

**The thermo-physical properties** that must be analyzed are those that condition the design of the technical equipment of refrigerant fluid circuits or refrigerating machines. These properties are:

- The densities of the liquid and vapour phases which determine the size of pipes and active elements such as pumps and compressors,

- The thermal capacities and thermal conductivity of the liquid and vapour phases which determine the size of the exchangers (evaporator, condenser),

- The viscosity of the liquid and vapour phases which condition the pressure losses in the fluid circuits and the dimensions of the pumps and other technical equipment.

Here again we distinguish two distinct uses:

- As a coolant, a comparison (Table 2a) of properties of CO2 and a water-MEG (mono ethylene glycol) mixture is made.

- As a refrigerant, a comparison (Table 2b) of the properties of CO2 and a "traditional" fluid HFC404a is realized.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Density (kg/m³)</th>
<th>Heat Capacity (kJ/kg.K)</th>
<th>Thermal conductivity (W/m.K)</th>
<th>Dynamic viscosity (kg/m.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water+MEG</td>
<td>Liquid</td>
<td>1047</td>
<td>3627</td>
<td>0,43</td>
</tr>
<tr>
<td>CO2</td>
<td>Liquid+vapour*</td>
<td>981 (71)</td>
<td>2,3(1,5)</td>
<td>0,12 (0,016)</td>
</tr>
</tbody>
</table>

*(values for vapour are in bracket)

**a/ Properties of secondary fluid: CO2 vs Water+MEG at -10°C**

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Density (kg/m³)</th>
<th>Heat Capacity (kJ/kg.K)</th>
<th>Thermal conductivity (W/m.K)</th>
<th>Dynamic viscosity (kg/m.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFC507</td>
<td>Liquid+vapour*</td>
<td>1193 (23,2)</td>
<td>1,34 (0,93)</td>
<td>0,078 (0,011)</td>
</tr>
<tr>
<td>CO2</td>
<td>Liquid+vapour*</td>
<td>981 (71)</td>
<td>2,3(1,5)</td>
<td>0,12 (0,016)</td>
</tr>
</tbody>
</table>

*(values for vapour are in bracket)

**b/ Properties of refrigerant: HFC507 vs CO2 at -10°C**
Carbon dioxide has undeniable qualities as a secondary coolant especially due to its application conditions of +15 to -50 °C with interesting thermo-physical properties: low viscosity in the liquid phase, high thermal capacity and conductivity in liquid phase as shown in table 2. These real qualities can moreover be valorised by a use in the form of a liquid-vapor mixture which makes it possible to use the evaporation enthalpy and to very significantly reduce the flow rate of circulating fluid. The advantage of such a device lies in the very high heat-carrying power of the fluid due to the use of the latent heat of the coolant fluid (CO2): thus, the thermal power transported per unit volume (of the liquid phase) of CO2 is more than 20 higher than that transported, with a temperature difference of 5 °C, by a performing monophasic secondary coolant, that is to say water/MEG. This results in substantial gains in terms of piping and pump dimensions, pumping energy and the elimination of the temperature variation on the exchangers which makes it possible to raise the evaporation temperature of the primary fluid by 4 at 6 K, a reduction in the size of the compressors and an improvement in system performance of about 15%.

Carbon dioxide shows also good qualities as refrigerant because of high latent heat of evaporation and high vapour density which allows a strong reduction of circuit and compressor size. The thermal conductivity of liquid CO2 are significantly higher that of HFC507A, a traditional refrigerant in low temperature refrigeration machine. The refrigeration cycle with CO2, due to low value of critical temperature, may show supercritical conditions: in these conditions, as can be seen on figure 2, supercritical CO2 shows a typical evolution of thermo physical properties:

- Dramatically increase of isobaric heat capacity and thermal conductivity at pressure between 74 to 86 bars: this has to be taken into account for high pressure gas cooler design.
- Strong change of viscosity and density for temperature between 31°C to 41°C; this has also great impact in the heat exchangers design.
2/ The Carbon dioxide environmental impacts

From a great number of years, halogenated hydrocarbons (CFC, HCFC, HFC) are used as refrigerant in the refrigeration systems. We know that stratospheric ozone is destroyed by chlorine transported at these altitudes by halogenated hydrocarbons which have a long life in the atmosphere, mainly by CFCs but also, to a much lesser extent measured by HCFCs. We also know that it is this criterion that has decided the international community to ban these compounds chlorinated. The action of each compound on stratospheric ozone is characterized by the ODP (Ozone Depletion Potential), the potential for destroying ozone. The values of the ODP are generally given with reference to R-11, (CCl₃F) one of the CFCs the most aggressive from this point of view. Only refrigerants having a zero ODP should continue. Table 3 gives ODP values reported in CO₂ and HFC, HCFC.

Greenhouse gases are essential for people living in our planet which, in their absence, would have a temperature much too low to be habitable (-18 °C). However, the excess of these gases, hindering the exit (towards the cosmos) of the radiation terrestrial, can, in the long run, cause a slow warming, dangerous for our world. At aside from the well-known greenhouse gases (water vapour, CO₂, methane, nitrogen oxides, etc.), the halocarbon refrigerants have a very significant action. Although unfortunately not widespread in the atmosphere, their influence is much greater than, for example, that of CO₂ whose greenhouse effect is the best known. The greenhouse effect of a compound is characterized by the global warming potential GWP (Global Warming Potential). Table 3 gives GWP values reported in CO₂ and CFC, HFC, HCFC; these relationships change with the time period envisaged because CO₂ molecules and those of gaseous refrigerants considered do not disappear from our atmosphere to the same speed. For comparisons with CO₂, we generally adopt a reference
period of 100 years. The GWP translates the effect greenhouse effect (consequence of leakage or non-recovery). The compression refrigeration systems generate a greenhouse effect indirect, linked to their electricity consumption (CO2 emission during electricity production).

Many of the proposed neo-refrigerants, such as HFCs, who have GWP considered by some to be too important, which leads to the wish for the exclusive use of natural fluids: CO2, water, ammonia, propane, butane, etc.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Fluid composition and designation</th>
<th>Normal boiling temperature (°C)</th>
<th>Critical Temperature (°C)</th>
<th>ODP (1 for R11)</th>
<th>GWP (100 years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>NH3 (R717)</td>
<td>-33,35</td>
<td>132,4</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO2 (R744)</td>
<td>-31</td>
<td>0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>H20 (R718)</td>
<td>100</td>
<td>374</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>C3H8 (R290)</td>
<td>-42,1</td>
<td>96,7</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>Isobutane</td>
<td>C4H10 (R600a)</td>
<td>-11,7</td>
<td>134,7</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>Trichlorofluoromethane</td>
<td>CFCl3 (R11)</td>
<td>23,7</td>
<td>198</td>
<td>1</td>
<td>4750</td>
</tr>
<tr>
<td>Chlorodifluoromethane</td>
<td>CCIF2CF3 (R115)</td>
<td>-39,2</td>
<td>80</td>
<td>0,04</td>
<td>1790</td>
</tr>
<tr>
<td>R502</td>
<td>R22/R115 (48,8/51,2)</td>
<td>-45,3</td>
<td>81,5</td>
<td>0,3</td>
<td>4600</td>
</tr>
<tr>
<td>R507A</td>
<td>R125/R43a (50/50)</td>
<td>-46,7</td>
<td>70,6</td>
<td>0</td>
<td>3800</td>
</tr>
<tr>
<td>R404A</td>
<td>R125/R143a/R134a (44/52/4)</td>
<td>-46,2</td>
<td>72</td>
<td>0</td>
<td>3700</td>
</tr>
<tr>
<td>R407C</td>
<td>R32/R125/R134a (23/25/52)</td>
<td>-43,6</td>
<td>86</td>
<td>0</td>
<td>1700</td>
</tr>
</tbody>
</table>

Table 3: Environmental impact of various refrigerants

3/ Risks and safety instructions for CO2 use

Outside ambient air today contains about 0.04% of CO2. Nevertheless at a certain concentration in the air, this gas is dangerous or even deadly because of the risk of asphyxiation or acidosis, although CO2 is not chemically toxic. The exposure limit value is 3% over a period of fifteen minutes. This value should never be exceeded. Beyond that, the health effects are all the more serious as the CO2 content increases. Thus, at 2% of CO2 in the air, the respiratory rate accelerates. At 10%, visual disturbances, tremor and sweating may occur. At 15%, it’s the sudden loss of consciousness. At 25%, respiratory arrest results in death.

Inhalation of concentrated carbon dioxide causes a blockage of ventilation, sometimes described as a violent feeling of strangulation, a breathlessness, respiratory distress or chest tightness, which can quickly lead to death if exposure is prolonged.

Since carbon dioxide is a colourless, heavy gas accumulating in layers, it is difficult to detect by an inexperienced person.

In high concentrations approaching 50 to 100%, such as those found in artificial carbon dioxide arrays of occupational origin, there may be an effect of nervous breakdown and an immediate loss of
consciousness, followed by fast death in the absence of outside help. These accidents present a high risk of an accident, witnesses can rush to help the victim without thinking about their own safety and become victims of intoxication too.

**Recommendations:** The limit value of exposure to CO2 at the workplace (ELV) corresponds to "Limit values of exposure to workstations" at a concentration of 0.5% by volume. Please note that CO2 not only has an asphyxiating effect but acts directly on the metabolism in our body, even if there is still enough oxygen in the ambient air. The concentration of CO2 must be monitored by taking measurements; a control of the oxygen content gives a false impression of safety.

Another harmful effect of carbon dioxide on the human body is that of cold. If CO2 cooled by detente comes into contact with the skin in the form of ice / dry ice, it can cause frostbite, that is, painful "cold burns". Sensitive skin tissues, such as the cornea, are particularly at risk. Ice formation in pipes and piping or valves may also pose a mechanical hazard to people in the vicinity.

**Recommendations:** Please follow exactly the working instructions for handling CO2. Protect your skin by wearing appropriate protective clothing and gloves. Wearing safety glasses can effectively protect the cornea from cold burns.

The following safety measures are indicated:

- Inform your employees of the special dangers of CO2
- Employees working in the vicinity of applications using CO2 must be trained and instructed accordingly so that they can interpret correctly alarms and their own observations. Develop detailed job descriptions and risk analysis for sectors using carbon dioxide.
- Ensure the tightness of installations using CO2, remedy any leakage without delay. CO2 emissions from technical equipment or safety valves must be vented to the open air. Premises with CO2-based facilities must have efficient ventilation, especially if they are below. This ventilation equipment must be regularly maintained and checked.
- A CO2 monitoring and alarm system must be installed in premises where installations using this gas are located. The surveillance and alarm systems must be checked regularly, periodic maintenance must be carried out by the company that set them up.
- In the event of a sudden escape of CO2, leave the premises immediately, especially if they are located in the basement (pits, cellars), because the risk of CO2 accumulation is particularly high.
- Do not enter rooms where large amounts of CO2 have accumulated with a self-contained breathing apparatus. This also applies when there are injured people in the room who need urgent rescue. Fixed CO2 extinguishing systems must be put into service for control purposes or for necessary intervention only if there is no one in the area where risks exist. If the carbon dioxide can enter other premises through pipes, openings in the wall, ventilation or air conditioning, these premises are also considered risk areas.

**4/ CO2 Cooling and refrigeration loop conception and design.**

**4.1/ Carbon dioxide cooling loop**
Carbon dioxide has undeniable qualities as a secondary coolant especially due to its application conditions of +15 to -50 °C with interesting thermo physical properties: low viscosity in the liquid phase, high thermal capacity also in liquid phase.

These real qualities can moreover be valorized by a use in the form of a liquid-vapour mixture which makes it possible to use the evaporation enthalpy and to very significantly reduce the flow rate of circulating fluid. Under these conditions of use, the figure 3 shows a piping diagram of a technical device in which a CO2 refrigerant circuit is associated with an ammonia, CO2 or HFC cold production unit. Thus, the fluid to be cooled yields thermal energy and thus allows vaporization of the liquid CO2 (for example at -36 °C). The vapour phase produced is sent to the evapo-condenser, exchanger ensuring the heat transfer between the CO2 coolant loop and the cold production unit, and then condensed at a saturation temperature close to that of -36 °C for the example considered: the condensate - substantially sub cooled - is circulated by a pump and sent back to the exchanger in contact with the fluid to be cooled.

**Figure 3: CO2 coolant circuit scheme**

### 4.2/ CO2 refrigeration cycles

Significant developments have been made in the last 10 years for new CO2 systems taking advantage of the low GWP of this fluid and its classification as a safe refrigerant (A1 under EN 378). The drawbacks of CO2 are well known and are mainly related to its low critical temperature of 31°C. This low critical temperature leads to trans-critical cycle when delivering heat at higher temperature. Efficient developments of CO2 are summarized here after.

- Transcritical cycle (figure 4) with intermediate heat exchanger is a basic cycle with a low pressure stage at subcritical conditions. The machine is composed of an evaporator at low pressure, a gas cooler at very high pressure (about 80 to 110 bar), an intermediate
heat exchanger HX. The HP Regulation valve has to regulate the optimum value of high pressure (for a maximum cycle efficiency) in the gas cooler.

- For low temperature applications, a cascading system when condensing CO2 (figure 5) at temperature lower than 31°C, and possibly around –10 to 0°C, CO2 systems show high energy performances due to efficient thermo-physical properties (low viscosity and high thermal conductivity) and the development of cascading systems. Those cascading systems use CO2 at evaporating temperatures varying between –50 and –35°C associated with a high temperature refrigerating system (of the cascade) using either ammonia or HFCs have led to very efficient systems in the food industry.

- In parallel with this effort, a number of laboratories and industries have developed new possible solutions using ejectors in order to improve the energy efficiency. Developments of expansion turbines have also been proposed for the same purpose: limitation of expansion losses. As shown in different publications, high efficiency expansion has to be studied in parallel with heat recovery by a liquid/vapour heat exchanger. The two options are in competition for improvement of energy efficiency.

- The development of heat exchangers is driven by high efficiency heat exchange and the decrease of materials quantities (for mass production components, the mass of the material is a key parameter for the price). The trends are obvious: the thickness of copper tubes has been reduced to 0.3 mm, the thickness of aluminium fins is in the range of 0.1 mm, the diameters have been constantly reduced, and high efficiency fins, groove tubes, have led to improve of a factor 2 to 3 the heat exchange coefficient of air-to-refrigerant heat exchangers in the last 20 years. In parallel with those developments of copper tubes / aluminium fins, fully brazed all aluminium heat exchangers. Condensers have been designed with extruded micro-channel aluminium tubes. Those tubes are brazed with accordion louvered fins, leading to a significantly higher heat transfer coefficient.

![Figure 4: CO2 single stage transcritical cycle](image-url)
5/ Conclusion

In just a few years, CO2 has become a major fluid in refrigeration equipments, particularly in food processing plants, due to future prohibitions on HFC (hydrofluorocarbons) fluids which present an excessive GWP.

The introduction of CO2 as coolant or refrigerant modifies, due to the increased complexity of the systems, strongly the design rules of the installations as well as the modalities of driving and maintenance.

The deployment of these technologies in Europe and more widely on other continents where the prohibition rules are less draconian presupposes a mastery of the rules of design, construction, security, implementation of this fluid through a rigorous respect of the cleanliness and lack of moisture in the CO2 circuits.