CO₂ refrigerant for Industrial Refrigeration
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Introduction

The application of carbon dioxide (CO₂) in refrigeration systems is not new. Carbon dioxide was first proposed as a refrigerant by Alexander Twining (ref. [1]), who mentioned it in his British patent in 1850. Thaddeus S.C. Lowe experimented with CO₂ military balloons, but he also designed an ice machine with CO₂ in 1867. Lowe also developed a machine onboard a ship for transportation of frozen meat.

From reading the literature it can be seen that CO₂ refrigerant systems were developed during the following years and they were at their peak in the 1920s and early 1930s. CO₂ was generally the preferred choice for use in the shipping industries because it was neither toxic nor flammable, whilst ammonia (NH₃) or R717 was more common in industrial applications (ref. [2]). CO₂ disappeared from the market, mainly because the new “wonder working refrigerant” “Freon” had come on the market, and was very successful in marketing this.

Ammonia has continued to be the dominant refrigerant for industrial refrigeration applications over the years. In the 1990s there was renewed focus of the advantages offered by using CO₂ due to ODP (Ozone Depletion Potential) and GWP (Global Warming Potential), which has restricted the use of CFC’s and HFC’s and restrictions on the refrigerant charge in large ammonia systems.

CO₂ belongs to the so-called “Natural” refrigerants, together with e.g. ammonia, hydrocarbons such as propane and butane, and water. All of these refrigerants have their respective disadvantages.

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>R 134a</th>
<th>NH₃</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural substance</td>
<td>NO</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td>Ozone Depletion Potential (ODP)*</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Global Warming Potential (GWP)*</td>
<td>1300</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Critical point</td>
<td>bar [psi]</td>
<td>40.7 [590]</td>
<td>113 [1640]</td>
</tr>
<tr>
<td>°C</td>
<td>101.2 [214]</td>
<td>132.4 [270]</td>
<td>31.1 [87.9]</td>
</tr>
<tr>
<td>Triple point</td>
<td>bar [psi]</td>
<td>0.004 [0.06]</td>
<td>0.06 [0.87]</td>
</tr>
<tr>
<td>°C</td>
<td>-103 [-153]</td>
<td>-77.7 [-108]</td>
<td>-56.6 [-69.9]</td>
</tr>
<tr>
<td>Flammable or explosive</td>
<td>NO (YES)</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>Toxic</td>
<td>NO</td>
<td>YES</td>
<td>NO</td>
</tr>
</tbody>
</table>

Figure 2 shows the temperature-pressure phase diagram of pure CO₂. The areas between the curves define the limits of temperature and pressure at which different phases can exist: solid, liquid, vapor and supercritical. Points on these curves indicate the pressure and corresponding temperatures under which two different phases can exist in equilibrium, e.g., solid and vapor, liquid and vapor, solid and liquid. At atmospheric pressure CO₂ can exist only as a solid or vapor. At this pressure, it has no ability to form a liquid; below −78.4°C [−109.1°F], it is a solid "dry ice"; above this temperature, it sublimates directly to a vapor phase.

At 5.2 bar [75.1 psi] and −56.6°C [−69.9°F], CO₂ reaches a unique state called the triple point. At this point all 3 phases i.e., solid, liquid and vapor, exist simultaneously in equilibrium.

CO₂ reaches its critical point at 31.1°C [88.0°F]. At this temperature, the density of liquid and vapor states is equal (figure 3). Consequently, the distinction between the two phases disappears, and this new phase, the supercritical phase, exists. Pressure-enthalpy diagrams are commonly used for refrigeration purposes. The diagram is extended to show the solid and supercritical phases (figure 4). The marked areas indicate the different phases.
**CO₂ as a refrigerant**

CO₂ may be employed as a refrigerant in a number of different system types, including both subcritical and supercritical. For any type of CO₂ system, both the critical point and the triple point must be considered.

The classic refrigeration cycle we are all familiar with is subcritical, i.e., the entire range of temperatures and pressures are below the critical point and above the triple point.

A single stage subcritical CO₂ system is simple, but it also has disadvantages because of its limited temperature range and high pressure (figure 5).

Transcritical CO₂ systems are at present only of interest for small and commercial applications, e.g., mobile air conditioning, small heat pumps, and supermarket refrigeration, not for industrial systems (figure 6). Transcritical systems will not be described further in this handbook.

Operating pressures for subcritical cycles are usually in the range 5.7 to 35 bar [8 to 507 psi] corresponding to –55 to 0°C [–67 to 2°F]. If the evaporators are defrosted using hot gas, then the operating pressure is approximately 10 bar [145 psi] higher.

---

**Figure 4**

Log p,h-Diagram of CO₂

- Critical point: 31°C [87.8°F] 73.6 bar [1067 psi]
- Triple point (line): –56.6°C [–69.9°F] 5.2 bar [75.1 psi]

**Figure 5**

Subcritical refrigeration process

- –5.5°C [22°F]
- –40°C [–40°F]
**CO₂ as a refrigerant**

(Continued)

**CO₂ as a refrigerant in industrial systems**

CO₂ is most commonly applied in cascade or hybrid system designs in industrial refrigeration, because its pressure can be limited to such extent that commercially available components like compressors, controls and valves can be used.

CO₂ cascade systems can be designed in different ways, e.g., direct expansion systems, pump circulating systems, or CO₂ in volatile secondary “brine” systems, or combinations of these.

Figure 7 shows a low temperature refrigerating system –40°C [–40°F] using CO₂ as a phase change refrigerant in a cascade system with ammonia on the high-pressure side.

**CO₂ as a refrigerant**

(Continued)
The CO₂ system is a pump circulating system where the liquid CO₂ is pumped from the receiver to the evaporator, where it is partly evaporated, before it returns to the receiver. The evaporated CO₂ is then compressed in a CO₂ compressor and condensed in the CO₂-NH₃ heat exchanger. The heat exchanger acts as an evaporator in the NH₃ system. Compared to a traditional ammonia system, the ammonia charge in the above mentioned cascade system can be reduced to approx. 1/10.

Figure 8 shows the same system as in figure 9, but includes a CO₂ hot gas defrosting system.

**Figure 8**

**Figure 9**
When determining the design pressure for CO₂ systems, the two most important factors to consider are:

- Pressure during stand still
- Pressure required during defrosting

Importantly, without any pressure control, at stand still, i.e., when the system is turned off, the system pressure will increase due to heat gain from the ambient air. If the temperature were to reach 0°C (32°F), the pressure would be 34.9 bar (505 psi) or 57.2 bar (830 psi) at 20°C (68°F). For industrial refrigeration systems, it would be quite expensive to design a system that can withstand the equalizing pressure (i.e., saturation pressure corresponding to the ambient temperature) during stand still. Therefore, installing a small auxiliary condensing unit is a common way to limit the maximum pressure during stand still to a reasonable level, e.g., 30 bar (435 psi).

With CO₂, many different ways of defrosting can be applied (e.g., natural, water, electrical, hot gas). Hot gas defrosting is the most efficient, especially at low temperatures, but also demands the highest pressure. With a design pressure of 52 bar-g (754 psig), it is possible to reach a defrosting temperature of approx. 10°C (50°F).

The saturated pressure at 10°C (50°F) is 45 bar (652 psi). By adding 10% for the safety valves and approximately 5% for pressure peaks, the indicated maximum allowable working pressure would be ~ 52 barg (~754 psig) (figure 11 & 12).
**Design pressure** (Continued)

![Design pressure / temperature for CO\textsubscript{2}](image)

**Practical limit:** \( PS \geq P_{\text{saturated}} + 15\% \)

**Pressure peaks**

**Safety valve**

![Saturated pressure](image)

---

**Safety**

\( \text{CO}_2 \) is an odourless, colourless substance classified as a non-flammable and non-toxic refrigerant, but even though all the properties seem very positive, \( \text{CO}_2 \) also has some disadvantages.

Due to the fact that \( \text{CO}_2 \) is odourless, it is not self-alarming, if leaks occur, (ref. [6]).

\( \text{CO}_2 \) is heavier than air, which means that it falls to the floor. This can create dangerous situations, especially in pits or confined spaces. \( \text{CO}_2 \) can displace oxygen to a point when it is fatal. The relative density of \( \text{CO}_2 \) is 1.529 (air=1 @ 0°C [32°F]). This risk requires special attention during design and operation. Leak detection and / or emergency ventilation are obvious equipment.

Compared to ammonia, \( \text{CO}_2 \) is a safer refrigerant. The TLV (threshold limit value) is the maximum concentration of vapour \( \text{CO}_2 \) in air, which can be tolerated over an eight-hour shift for 40 hours a week. The TLV safety limit is for Ammonia 25 [ppm] and for \( \text{CO}_2 \) 5000 [ppm] (0.5%).

Approx. 0.04% \( \text{CO}_2 \) is present in the Air.

With higher concentration, some adverse reactions are reported:

- 2% 50% increase in breath rate
- 3% 100% increase in breath rate
- 5% 300% increase in breath rate
- 8-10% The natural body’s respiration is disrupted, and breathing becomes almost impossible. Headache, dizziness, sweating and disorientation.
  - > 10% Can lead to loss of consciousness and death.
  - > 30% Quickly leads to death.
Efficiency

In CO\textsubscript{2} - NH\textsubscript{3} cascade systems it is necessary to use a heat exchanger. Introducing exchangers creates a loss in the system efficiency, due to the necessity of having a temperature difference between the fluids. However, compressors running with CO\textsubscript{2} have a better efficiency and heat transfer is greater. The overall efficiency of a CO\textsubscript{2} - NH\textsubscript{3} cascade system is not reduced when compared to a traditional NH\textsubscript{3} system (figure 13 & ref. [3]).

Example:

![COP-coefficient of refrigerant system performance](image)

Source: IAIR - Albuquerque, New Mexico 2003, P.S Nielsen & T.Lund
Introducing a New Ammonia/CO\textsubscript{2} Cascade Concept for Large Fishing Vessels

Oil in CO\textsubscript{2} systems

In CO\textsubscript{2} systems with traditional refrigeration compressors, both miscible and immiscible oil types are used (table 2).

For immiscible lubricants, such as polyalphaolefin (PAO), the lubricant management system is relatively complicated. The density of PAO is lower than the density of the liquid CO\textsubscript{2}. Thus the lubricant floats on top of the refrigerant, making it more difficult to remove than in ammonia systems. Also, to avoid fouling evaporators, the compressor oil separation with non-miscible oils must be highly effective; basically, a virtually oil-free system is desirable.

With miscible lubricants, such as polyl ester (POE), the oil management system can be much simpler. POE oils have high affinity with water, so the challenge when using POE is to ensure the stability of the lubricant.

In volatile brine systems using CO\textsubscript{2} as a secondary refrigerant, and in recirculating systems with oil free compressors, no oil is present in the circulated CO\textsubscript{2}. From an efficiency point of view, this is optimum because it results in good heat transfer coefficients in the evaporators. However, it requires that all valves, controls and other components can operate dry.

CO\textsubscript{2} and oil

<table>
<thead>
<tr>
<th>Oil type</th>
<th>PAO Poly-alpha-olefin oil (Synthetic Mineral oil)</th>
<th>POE Polyol-ester oil (Ester oil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility</td>
<td>Low (immiscible)</td>
<td>High (miscible)</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>Low</td>
<td>High affinity to water</td>
</tr>
<tr>
<td>Oil separation system</td>
<td>Special demand:</td>
<td>No special requirements</td>
</tr>
<tr>
<td></td>
<td>High filtration demanded</td>
<td>(System requirements like HCFC/HFC)</td>
</tr>
<tr>
<td></td>
<td>Multistage coalescing filters</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Active carbon filter</td>
<td></td>
</tr>
<tr>
<td>Oil return system</td>
<td>Special demand:</td>
<td>Simple</td>
</tr>
<tr>
<td></td>
<td>Oil drain from low temperature receiver (oil density lower than CO\textsubscript{2}-opposite NH\textsubscript{3})</td>
<td>(System requirements like HCFC/HFC)</td>
</tr>
<tr>
<td>Challenge</td>
<td>Oil separation and return system</td>
<td>High affinity to water</td>
</tr>
<tr>
<td></td>
<td>Long term oil accumulation in e.g. evaporators</td>
<td>Long term stability of oil</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&quot;Clean&quot; refrigerant system required</td>
</tr>
</tbody>
</table>

Table 2
Comparison of component requirements in CO₂, ammonia and R134a systems

Compared to ammonia and R134a, CO₂ differs in many respects. The following comparison illustrates this fact; to allow an "true" comparison, operational conditions, i.e., evaporating temperature, condensing temperature, are kept constant.

### Table 3

#### Comparison of pipe cross section area

**Wet return / Liquid lines**

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>R 134a</th>
<th>R 717</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity kW [TR]</td>
<td>250 [71]</td>
<td>250 [71]</td>
<td>250 [71]</td>
</tr>
<tr>
<td>&quot;Wet return&quot; line</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔT K [°F]</td>
<td>0.8 [1.4]</td>
<td>0.8 [1.4]</td>
<td>0.8 [1.4]</td>
</tr>
<tr>
<td>Δp bar [psi]</td>
<td>0.0212 [0.0308]</td>
<td>0.0303 [0.439]</td>
<td><strong>0.2930 [4.249]</strong></td>
</tr>
<tr>
<td>Velocity m/s [ft/s]</td>
<td>11.0 [36.2]</td>
<td>20.2 [66.2]</td>
<td><strong>8.2 [26.9]</strong></td>
</tr>
<tr>
<td>Area &quot;Wet return&quot; mm² [inch²]</td>
<td>36385 [56.40]</td>
<td>13894 [21.54]</td>
<td><strong>3774 [5.85]</strong></td>
</tr>
</tbody>
</table>

#### "Liquid" line

| Velocity m/s [ft/s] | 0.8 [2.6] | 0.8 [2.6] | 0.8 [2.6] |

#### Total pipe cross section area

| Area "Wet return" mm² [inch²] | 39353 [61.0] | 14892 [23.08] | 6382 [9.89] |
| Liquid cross section area % | 8 | 7 | 41 |

\[ \text{L}_{\text{eqv}} = 50 \text{ [m]} / 194 \text{ [ft]} \]  -  Pump circ.: \( n_{\text{circ}} = 3 \)  -  Evaporating temp.: TE = –40[°C] / –40[°F]

### Table 4

#### Comparison of pipe cross section area

**Dry suction / Liquid lines**

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>R 134a</th>
<th>R 717</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity kW [TR]</td>
<td>250 [71]</td>
<td>250 [71]</td>
<td>250 [71]</td>
</tr>
<tr>
<td>&quot;Dry suction&quot; line</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔT K [°F]</td>
<td>0.8 [1.4]</td>
<td>0.8 [1.4]</td>
<td>0.8 [1.4]</td>
</tr>
<tr>
<td>Δp bar [psi]</td>
<td>0.0212 [0.0308]</td>
<td>0.0303 [0.439]</td>
<td><strong>0.2930 [4.249]</strong></td>
</tr>
<tr>
<td>Velocity m/s [ft/s]</td>
<td>20.4 [67]</td>
<td>37.5 [123]</td>
<td><strong>15.4 [51]</strong></td>
</tr>
<tr>
<td>Area “Dry suction” mm² [inch²]</td>
<td>22134 [34.31]</td>
<td>8097 [12.55]</td>
<td><strong>2242 [3.48]</strong></td>
</tr>
</tbody>
</table>

#### "Liquid" line

| Velocity m/s [ft/s] | 0.8 [2.6] | 0.8 [2.6] | 0.8 [2.6] |
| Diameter mm [inch] | 37 [1.5] | 21 [0.8] | 35 [1.4] |
| Area “liquid” mm² [inch²] | 1089 [16.9] | 353 [0.55] | 975 [1.51] |

#### Total pipe cross section area

| Liquid cross section area % | 5 | 4 | 30 |

Comparison of component requirements in CO₂, ammonia and R134a systems

(Continued)

Comparison of pipe cross section area
Dry suction / Liquid lines

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>R 134a</th>
<th>R 717</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity kW [TR]</td>
<td>250 [71]</td>
<td>250 [71]</td>
<td>250 [71]</td>
</tr>
<tr>
<td>&quot;Dry suction&quot; line Area &quot;Dry suction&quot; mm² [inch²]</td>
<td>22134 [34.31]</td>
<td>8097 [12.55]</td>
<td>2242 [3.48]</td>
</tr>
<tr>
<td>&quot;Liquid&quot; line Area &quot;liquid&quot; mm² [inch²]</td>
<td>1089 [1.69]</td>
<td>353 [0.55]</td>
<td>975 [1.51]</td>
</tr>
<tr>
<td>Total pipe cross section area Area &quot;Dry suction + liquid&quot; mm² [inch²]</td>
<td>23223 [36.00]</td>
<td>8450 [13.10]</td>
<td>3217 [4.99]</td>
</tr>
<tr>
<td>Relative cross section area</td>
<td>-</td>
<td>7.2</td>
<td>2.6</td>
</tr>
<tr>
<td>Liquid section area %</td>
<td>5</td>
<td>4</td>
<td>30</td>
</tr>
<tr>
<td>Vapour section area %</td>
<td>95</td>
<td>96</td>
<td>70</td>
</tr>
</tbody>
</table>

Table 5

Comparison of compressor displacement

Comparison of pressure / subcooling produced in liquid risers

Table 6

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>R 134a</th>
<th>R 717</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refrigerant capacity kW [TR]</td>
<td>250 [71]</td>
<td>250 [71]</td>
<td>250 [71]</td>
</tr>
<tr>
<td>Required compressor displacement m³/h [ft³/h]</td>
<td>1628 [57489]</td>
<td>1092 [38578]</td>
<td>124 [4387]</td>
</tr>
<tr>
<td>Relative displacement</td>
<td>-</td>
<td>13.1</td>
<td>8.8</td>
</tr>
</tbody>
</table>

Table 7
A comparison of pump circulating systems shows that for "wet return" lines, CO₂ systems require much smaller pipes than ammonia or R134a (table 3). In CO₂ “wet return” lines, the allowable pressure drop for an equivalent temperature drop is approximately 10 times higher than for ammonia or R134a wet return lines. This phenomenon is a result of the relatively high density of the CO₂ vapor. The above comparison is based on a circulating rate of 3. The result would be slightly different if the circulating rate is optimized for each refrigerant.

In the comparison of “dry suction” lines, the results are very nearly the same as in the previous comparison, in terms of both pressure drop and line size (table 4).

For both recirculating and dry expansion systems, calculated sizes for CO₂ liquid lines are much larger than those for ammonia, but only slightly larger than those for R134a (table 3 and 4). This can be explained by ammonia’s much larger latent heat relative to CO₂ and R134a. Refer to the tables showing the relative liquid and vapor cross-sectional areas for the three refrigerants (table 5). The total cross-section area for the CO₂ system is approximately 2.5 times smaller than that of an ammonia system and approximately seven times smaller than that of R134a. This result has interesting implications for the relative installation costs for the three refrigerants. Due to the relative small vapor volume of the CO₂ system and large volumetric refrigeration capacity, the CO₂ system is relatively sensitive to capacity fluctuations. It is therefore important to design the liquid separator with sufficient volume to compensate for the small vapor volume in the pipes.

The required compressor capacity for identical refrigeration loads is calculated for the three refrigerants (table 6). As illustrated, the CO₂ system requires a much smaller compressor than the ammonia or R134a systems.

For compressors of identical displacements, the capacity of the compressor using CO₂ is 8.8 times higher than using ammonia, and 13 times higher than that using R134a.

The subcooling produced in a liquid riser of a given height “H” is calculated for the three refrigerants (table 7). The subcooling for the CO₂ liquid riser is much smaller than that for ammonia and R134a. This characteristic must be noted when designing CO₂ systems to prevent cavitations and other problems with liquid CO₂ pumps.

In ammonia systems, oil is changed and non-condensables are purged frequently to minimize the oil, oxygen, water and solid contaminants that can cause problems.

Compared to ammonia systems, CO₂ is less sensitive, but if water is present, problems may occur. Some early CO₂ installations reported problems with control equipment, among other components. Investigations revealed that many of these problems are caused by water freezing in the system. Modern systems use filter driers to maintain water content in the system at an acceptable level.

The acceptable level of water in CO₂ systems is much lower than with other common refrigerants. The diagram in figure 14 is showing the solubility of water in both liquid and vapor phases of the CO₂ liquid and vapor as function of temperature. The solubility in the liquid phase is much higher than in the vapor phase. The solubility in the vapor phase is also known as the dew point.

---

**Water in CO₂ Systems**

In ammonia systems, oil is changed and non-condensables are purged frequently to minimize the oil, oxygen, water and solid contaminants that can cause problems.

Compared to ammonia systems, CO₂ is less sensitive, but if water is present, problems may occur. Some early CO₂ installations reported problems with control equipment, among other components. Investigations revealed that many of these problems are caused by water freezing in the system. Modern systems use filter driers to maintain water content in the system at an acceptable level.

The acceptable level of water in CO₂ systems is much lower than with other common refrigerants. The diagram in figure 14 is showing the solubility of water in both liquid and vapor phases of the CO₂ liquid and vapor as function of temperature. The solubility in the liquid phase is much higher than in the vapor phase. The solubility in the vapor phase is also known as the dew point.

---

**Figure 14**

*Water solubility in liquid / vapour CO₂*

- Liquid CO₂
- Vapour CO₂

**Table 1**

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Weight *10^-3 of water / weight of refrigerant [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-40</td>
<td>0</td>
</tr>
<tr>
<td>-30</td>
<td>200</td>
</tr>
<tr>
<td>-20</td>
<td>400</td>
</tr>
<tr>
<td>0</td>
<td>600</td>
</tr>
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<td>20</td>
<td>800</td>
</tr>
<tr>
<td>40</td>
<td>1000</td>
</tr>
<tr>
<td>60</td>
<td>1200</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Temperature [°F]</th>
<th>Weight *10^-3 of water / weight of refrigerant [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-40</td>
<td>0</td>
</tr>
<tr>
<td>-30</td>
<td>200</td>
</tr>
<tr>
<td>-20</td>
<td>400</td>
</tr>
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<td>0</td>
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<td>800</td>
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<tr>
<td>40</td>
<td>1000</td>
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<tr>
<td>60</td>
<td>1200</td>
</tr>
</tbody>
</table>

---

**Table 3**

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>Wet return lines in recirculation systems:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A comparison of pump circulating systems shows that for “wet return” lines, CO₂ systems require much smaller pipes than ammonia or R134a (table 3). In CO₂ “wet return” lines, the allowable pressure drop for an equivalent temperature drop is approximately 10 times higher than for ammonia or R134a wet return lines. This phenomenon is a result of the relatively high density of the CO₂ vapor. The above comparison is based on a circulating rate of 3. The result would be slightly different if the circulating rate is optimized for each refrigerant.</td>
</tr>
</tbody>
</table>

---

**Table 4**

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>Suction lines in dry expansion systems:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In the comparison of “dry suction” lines, the results are very nearly the same as in the previous comparison, in terms of both pressure drop and line size (table 4).</td>
</tr>
</tbody>
</table>

---

**Table 5**

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>Liquid lines:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>For both recirculating and dry expansion systems, calculated sizes for CO₂ liquid lines are much larger than those for ammonia, but only slightly larger than those for R134a (table 3 and 4). This can be explained by ammonia’s much larger latent heat relative to CO₂ and R134a. Refer to the tables showing the relative liquid and vapor cross-sectional areas for the three refrigerants (table 5). The total cross-section area for the CO₂ system is approximately 2.5 times smaller than that of an ammonia system and approximately seven times smaller than that of R134a. This result has interesting implications for the relative installation costs for the three refrigerants. Due to the relative small vapor volume of the CO₂ system and large volumetric refrigeration capacity, the CO₂ system is relatively sensitive to capacity fluctuations. It is therefore important to design the liquid separator with sufficient volume to compensate for the small vapor volume in the pipes.</td>
</tr>
</tbody>
</table>

---

**Table 6**

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>The required compressor capacity for identical refrigeration loads is calculated for the three refrigerants (table 6). As illustrated, the CO₂ system requires a much smaller compressor than the ammonia or R134a systems.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>For compressors of identical displacements, the capacity of the compressor using CO₂ is 8.8 times higher than using ammonia, and 13 times higher than that using R134a.</td>
</tr>
</tbody>
</table>

---

**Table 7**

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>The subcooling produced in a liquid riser of a given height “H” is calculated for the three refrigerants (table 7). The subcooling for the CO₂ liquid riser is much smaller than that for ammonia and R134a. This characteristic must be noted when designing CO₂ systems to prevent cavitations and other problems with liquid CO₂ pumps.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>The subcooling produced in a liquid riser of a given height “H” is calculated for the three refrigerants (table 7). The subcooling for the CO₂ liquid riser is much smaller than that for ammonia and R134a. This characteristic must be noted when designing CO₂ systems to prevent cavitations and other problems with liquid CO₂ pumps.</td>
</tr>
</tbody>
</table>

---

**Figure 14**

*Water solubility in liquid / vapour CO₂*

- Liquid CO₂
- Vapour CO₂

**Table 8**

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Weight *10^-3 of water / weight of refrigerant [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-40</td>
<td>0</td>
</tr>
<tr>
<td>-30</td>
<td>200</td>
</tr>
<tr>
<td>-20</td>
<td>400</td>
</tr>
<tr>
<td>0</td>
<td>600</td>
</tr>
<tr>
<td>20</td>
<td>800</td>
</tr>
<tr>
<td>40</td>
<td>1000</td>
</tr>
<tr>
<td>60</td>
<td>1200</td>
</tr>
</tbody>
</table>

**Table 9**

<table>
<thead>
<tr>
<th>Temperature [°F]</th>
<th>Weight *10^-3 of water / weight of refrigerant [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-40</td>
<td>0</td>
</tr>
<tr>
<td>-30</td>
<td>200</td>
</tr>
<tr>
<td>-20</td>
<td>400</td>
</tr>
<tr>
<td>0</td>
<td>600</td>
</tr>
<tr>
<td>20</td>
<td>800</td>
</tr>
<tr>
<td>40</td>
<td>1000</td>
</tr>
<tr>
<td>60</td>
<td>1200</td>
</tr>
</tbody>
</table>
Water in CO₂ Systems
(Continued)

Water solubility in various refrigerants in vapour phase

Figure 15

Water solubility in CO₂

Figure 15.1

Water solubility in CO₂

Figure 16
Water in CO₂ Systems
(Continued)

The diagram in figure 14 is showing that the water solubility in CO₂ is much lower than for R134a or ammonia. At –20°C [-4°F], water solubility in the liquid phase is:
- CO₂, 20.8 ppm
- R134a, 158 ppm
- Ammonia, 672 ppm

Below these levels, water remains dissolved in the refrigerant and does not harm the system. Figure 16 illustrates how water (H₂O) molecules are dissolved if the concentration is lower than the maximum solubility limit, and how the H₂O molecules precipitate out of solution into droplets if the water concentration is higher than the maximum solubility limit.

Chemical reactions

It is important to notice, that the below mentioned reactions with water don’t take place in a well-maintained CO₂ system, where the water contents is below the maximum solubility limit.

In a closed system such as a refrigeration system, CO₂ can react with oil, oxygen, and water, especially at elevated temperatures and pressures. For example, if the water content is allowed to rise above the maximum solubility limit, CO₂ can form carbonic acid, as follows (ref. [4] and [5]).

In CO₂ production systems, where water concentrations can rise to high levels, it is well known that carbonic acid can be quite corrosive to several kinds of metals, but this reaction does not take place in a well-maintained CO₂ system, because the water content in the system is kept below the maximum solubility limit.

Water in Vapor Phase

If the water concentration is relatively high, CO₂ and water in vapor phase can react to form a CO₂ gas hydrate.

\[ \text{CO}_2 + 8 \text{H}_2\text{O} \rightarrow \text{CO}_2(\text{H}_2\text{O})_8 \]

(CO₂ + water → hydrated CO₂)

The CO₂ gas hydrate is a large molecule and can exist above 0°C (32°F). It can create problems in control equipment and filters, similar to the problems that ice can make.

POE lubricant

Generally, esters such as POE react with water as follows:

\[ \text{RCOO' + H}_2\text{O} \rightarrow \text{R'O} + \text{RCOOH} \]

(esteralcohol + organic acid)

As shown, if water is present, POE will react with water to form alcohol and an organic acid (carboxylic acid), which is relatively strong and may corrode the metals in the system. Thus, it is very important to limit the water concentration in CO₂ systems if POE lubricants are used.

PAO lubricant

\[ 2\text{RCH}_2 + 3 \text{O}_2 \rightarrow 2\text{H}_2\text{O}_2 + 2\text{RCOOH} \]

(oil + oxygen → water + acid)

As shown, if water is present, POE will react with water to form alcohol and an organic acid (carboxylic acid), which is relatively strong and may corrode the metals in the system. Thus, it is very important to limit the water concentration in CO₂ systems if POE lubricants are used.
Removing water

Controlling the water content in a refrigeration system is a very efficient method to prevent the above-mentioned chemical reactions.

In Freon systems, filter driers are commonly used to remove water, usually the type with a zeolite core. The zeolite has extremely small pores, and acts like a molecular sieve (figure 18).

Water molecules are small enough to penetrate the sieve, and being very polar, are adsorbed inside the zeolite molecules. R134a molecules are too large to penetrate the sieve. When the replaceable core is removed, the water goes with it.

![Figure 18](image-url)

**Refrigerant molecules and Molecular Sieves**

Micropore size in Zeolite LTA

1×10⁻⁶ mm [39×10⁻⁹ inch]

Example:

-40° to 10°C - CO₂ pump circulating system with 20 [ppm] water

<table>
<thead>
<tr>
<th>20 ppm</th>
<th>1 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH = 15.4%</td>
<td>RH = 0.25%</td>
</tr>
</tbody>
</table>

Max solubility in liquid CO₂:

- @ -40°C: 130 [ppm]
- @ -10°C: 405 [ppm]

Max solubility in vapour CO₂:

- @ -40°C: 7 [ppm]
- @ 10°C: 33 [ppm]

![Figure 18.1](image-url)
Removing water  
(Continued)

**Figure 18.2**

CO₂ is a non-polar molecule, so the removal process is different. Like water molecules, CO₂ molecules are small enough to penetrate the molecular sieve. However, the water molecules adsorbed onto the molecular sieve act in such a way as to “kick out” the CO₂ molecule, due to the difference in polarity. Zeolite filter driers cannot be used in ammonia systems, because both water and ammonia are very polar. Even though the driers function differently in this respect in CO₂ systems, the efficiency is fairly good. The water retention capacity is approximately the same as in R134a systems.

The most effective location to detect and remove water is where the concentration is high. The solubility of vapor-phase water in CO₂ is much lower than in the liquid phase. Therefore, a greater amount of water can be transported in liquid lines.

**Example:**
-40/-10°C - CO₂
DX system
with 20 [ppm] water

**Max. solubility in liquid CO₂**
@ -40°C: 130 [ppm]  
@ -10°C: 405 [ppm]

**Max solubility in vapour CO₂**
@ -40°C: 7 [ppm]  
@ -10°C: 33 [ppm]

**Fig. 18.1** illustrates the variation of the relative humidity in a pump circulation system operating at -40°C. The illustration shows that the relative humidity is highest in the wet return line, and that it is depending on the circulating rate. In a DX system the variation of the relative humidity differs, but also in this case the highest concentration is located in the suction line (fig. 18.2).

Taking advantage of this principle, moisture indicators and filter driers are typically installed in a liquid line or liquid bypass line from the receiver (figure 19). The moisture level indicated by these devices varies according to temperature and also by type of indicator. In figure 20, the indication level of a Danfoss SGN indicator is shown for liquid CO₂.

**Principle diagram: CO₂-NH₃ cascade system**

**Example:**
-40/-10°C - CO₂
DX system
with 20 [ppm] water

**Max. solubility in liquid CO₂**
@ -40°C: 130 [ppm]  
@ -10°C: 405 [ppm]

**Max solubility in vapour CO₂**
@ -40°C: 7 [ppm]  
@ -10°C: 33 [ppm]

**RH > 100%**

**RH = 66.7%**

**RH = 4.9%**
Removing water
(Continued)

Unlikely in some ammonia systems, the pressure in CO₂ systems is always above atmospheric. However, water can still find its way into CO₂ systems.

Water may contaminate a CO₂ system through five different mechanisms:

1. Diffusion
2. Maintenance and repair practices
3. Incomplete water removal during installation/commissioning
4. Water-contaminated lubricant charged into the system
5. Water-contaminated CO₂ charged into the system

Obviously, all these mechanisms should be avoided/minimized.

How does water enter a CO₂ system?

To illustrate a scenario in which water may contaminate a system, think of a contractor, who, believing CO₂ is a very safe refrigerant, thinks that it may be handled without following the normal ammonia safety requirements. He might open up the system to perform a repair. Once the system is opened up, air enters, and the moisture in the air condenses inside the piping. If he does not evacuate the system very thoroughly, some water may well be retained.

In another scenario, our contractor forgets that the lubricant used in the system, POE, has a high affinity for water, and leaves the cap off the container. After charging the POE into the system, the water may begin to cause mischief within the system.
Article  
CO₂ refrigerant for industrial refrigeration

Miscellaneous features to be taking into consideration in CO₂ refrigeration systems

Safety valve
CO₂’s particularly high triple point can cause solid CO₂ to form under certain conditions. Figure 21 shows the expansion processes occurring in pressure relief valves starting at three different conditions. If the set pressure of a pressure relief valve in the vapor phase is 50 bar [725 psi] or less, e.g., the centerline, the pressure in the relief line will pass through the triple point at 5.2 bar [75.1 psi]. Once below the triple point, the CO₂ will be pure vapor.

Figure 21

If the set pressure of a safety valve in the vapor phase is 50 bar [725 psi], e.g., the centerline, the relief line pressure will pass the triple point and 3% of the CO₂ will change into solid as it continues to relieve. In a worst-case scenario (e.g., a long relief line with many bends), solid CO₂ may block this line. The most efficient solution to this problem would be to mount the safety valve without an outlet line, and relieve the system directly to the atmosphere. The phase change of the CO₂ does not take place in the valve, but just after the valve, in this case, in the atmosphere.

If a pressure relief valve is set to relieve liquid at 20 bar [290 psi], the relief products would pass through the triple point, whereupon 50% of the CO₂ would change into solid upon further relief, subjecting the relief line to a high risk of blockage. Thus, to safely protect liquid lines against formation of dry ice, connect safety relief valves to a point in the system at a pressure higher than the triple point pressure of 5.2 bar [75.1 psi].

Figure 22

CO₂ expansion - phase changes
Safety valves

Cleaning filers / charging CO₂
Charging CO₂

It is important to start up with CO₂ in the vapor phase, and continue, until the pressure has reached 5.2 bar (75.1 psi). Thus, it is strongly recommended to write a procedure for charging a CO₂ system. One must be aware when charging a refrigerant system that until the pressure reaches the triple point, the CO₂ can only exist as a solid or vapor inside the refrigeration system. Also, the system will exhibit very low temperatures until the pressure is sufficiently raised (figure 22). For example, at 1 bar (14.5 psi), the sublimation temperature will be −78.4°C (−109°F).

Filter cleaning

The same phenomenon applies also when cleaning liquid strainers/filters. Even though CO₂ is non-toxic, one cannot just drain the liquid outside the system. Once the liquid CO₂ contacts the atmosphere, the liquid phase will partly change into the solid phase, and the temperature will drop dramatically, as in the example described above. Thus sudden temperature drop is a thermal shock to the system materials, and can cause mechanical defects in the materials. Such a procedure would be considered to be a code violation because this equipment is not normally designed for such low temperatures.

Trapped liquid

Trapped liquid is a potential safety risk in refrigerant systems, and must always be avoided. This risk is even higher for CO₂ systems than for ammonia or R134a systems. The diagram in figure 23 are showing the relative liquid volume change for the three refrigerants. As shown, liquid CO₂ expands much more than ammonia and R134a, especially when the temperature approaches CO₂’s critical point.

<table>
<thead>
<tr>
<th>Relative liquid volume</th>
<th>Reference: −40 °C / °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td></td>
</tr>
<tr>
<td>R134a</td>
<td></td>
</tr>
<tr>
<td>R717</td>
<td></td>
</tr>
</tbody>
</table>

Figure 23

Leaks in CO₂ - NH₃ cascade systems

The most critical leak in a CO₂ - NH₃ cascade system is in the heat exchangers between CO₂ and NH₃. The pressure of the CO₂ will be higher than the NH₃, so the leak will occur into the NH₃ system, which will become contaminated.

\[ \text{CO}_2 + 2 \text{NH}_3 \rightarrow \text{H}_{2}\text{NCOONH}_4 \]

Ammonium carbamate is formed immediately when CO₂ is in contact with NH₃. Ammonium carbamate is corrosive (ref. [5]).
**Article**

CO₂ refrigerant for industrial refrigeration

**Material compatibility**

CO₂ is compatible with almost all common metallic materials, unlike NH₃. There are no restrictions from a compatibility point of view, when using copper or brass. The compatibility of CO₂ and polymers is much more complex. Because CO₂ is a very inert and stable substance, the chemical reaction with polymers is not critical. The main concern with CO₂ is the physiochemical effects, such as permeation, swelling and the generation of cavities and internal fractures. These effects are connected with the solubility and diffusivity of CO₂ in the actual material.

Danfoss has carried out a number of tests to ensure that components released for use with CO₂ can withstand the impact of CO₂ in all aspects.

**Conclusion**

CO₂ has good properties, in particular at low temperature, but it is not a substitution for ammonia. The most common industrial CO₂ refrigeration systems, is hybrid systems with ammonia on the high temperature side of the system.

CO₂ is in many aspects a very uncomplicated refrigerant, but it is important to realize that CO₂ has some unique features compared with other common refrigerants. Knowing the differences, and taking these into account during design, installation, commissioning and operation, will help avoid problems.

**References**

2. Lorentzen, Gustav, Reprint from IIR Conference 1994 Proceedings “New Applications of Natural Working Fluids in Refrigeration and Air Condition”
| Article | CO₂ refrigerant for industrial refrigeration |
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Controls for Industrial Refrigeration
Electronic Controls & Sensors
Industrial Automation
Household Compressors
Commercial Compressors
Sub-Assemblies
Thermostats

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