MAKING MODERN LIVING POSSIBLE

CO$_2$ refrigerant for Industrial Refrigeration

REFRIGERATION &
AIR CONDITIONING DIVISION

Article

Contents

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Introduction

The application of carbon dioxide (CO_2) 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 CO_2 military balloons, but he also designed an ice machine with CO_2 in 1867. Lowe also developed a machine onboard a ship for transportation of frozen meat.

From reading the literature it can be seen that CO_2 refrigerant systems were developed during the following years and they were at their peak in the 1920's and early 1930's. CO_2 was generally the preferred choice for use in the shipping industries because it was neither toxic nor flammable, whilst ammonia (NH_3 or R717) was more common in industrial applications (ref. [2]). CO_2 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 1990's there was renewed focus of the advantages offered by using CO_2, 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.

CO_2 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 Ammonia is toxic, hydrocarbons are flammable, and water has limited application possibilities. In comparison, CO_2 is non-toxic and non-flammable.

CO_2 differs from other common refrigerants in many aspects, and has some unique properties. Technical developments since 1920 have removed many of the barriers to using CO_2, but users must still be highly aware of its unique properties, and take the necessary precautions to avoid problems in their refrigeration systems.

The chart in figure 1 shows the pressure/temperature relationship for CO_2, R134a and ammonia. Highlights of CO_2's properties relative to the other refrigerants include:

- Higher operating pressure for a given temperature
- Narrower range of operating temperatures
- Triple point at a much higher pressure
- Critical point at a very low temperature.

While the triple point and critical point are normally not important for common refrigerants, CO_2 is different. The triple point is high: 5.2 bar [75.1 psi], but more importantly, it is higher than the normal atmospheric pressure.
This circumstance can create some problems, unless the proper precautions are taken. Also, CO_2's critical point for is very low: 31.1°C [88.0°F], which greatly affects the design requirements.

In table 1, the different properties of CO_2 are compared with R134a and ammonia.

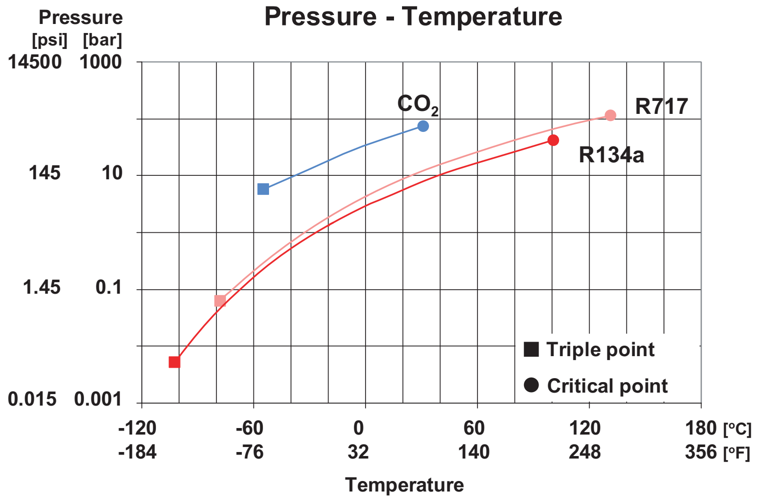


Figure 1

CO_2 properties compared with various refrigerants

Refrigerant			R 134a		NH₃		CO₂	
Natural substance			NO		YES		YES	
Ozone Depletion Potential (ODP)*			0		0		0	
Global Warming Potential (GWP)*			1300		-		1	
Critical point	bar	[psi]	40.7	[590]	113	[1640]	73.6	[1067]
	°C	[°F]	101.2	[214]	132.4	[270]	31.1	[87.9]
Triple point	bar	[psi]	0.004	[0.06]	0.06	[0.87]	5.18	[75.1]
	°C	[°F]	–103	[–153]	–77.7	[–108]	–56.6	[–69.9]
Flammable or explosive			NO		(YES)		NO	
Toxic			NO		YES		NO	

Table 1

* prEN 378-1 (2003)

Characteristics of CO$_2$

Figure 2 shows the temperature-pressure phase diagram of pure CO$_2$.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 CO$_2$ 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], CO$_2$ reaches a unique state called the triple point. At this point all 3 phases i.e., solid, liquid and vapor, exist simultaneously in equilibrium.

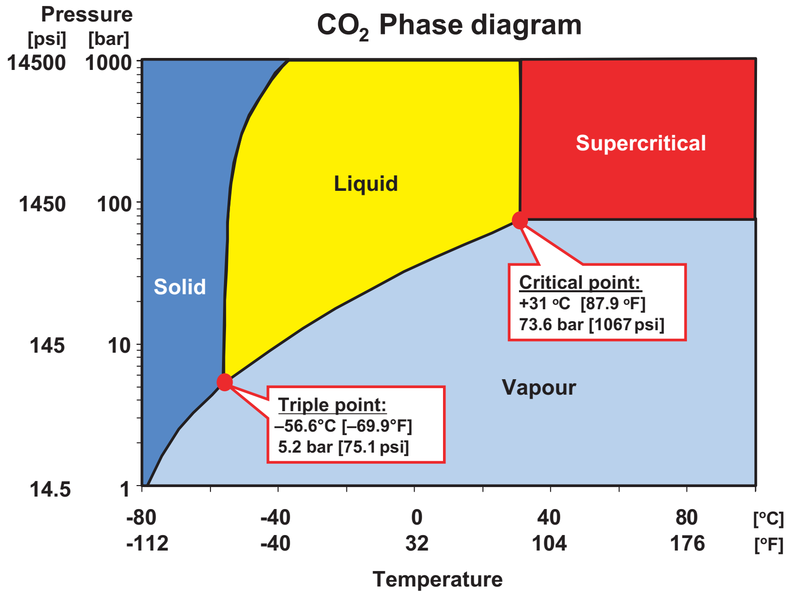


Figure 2

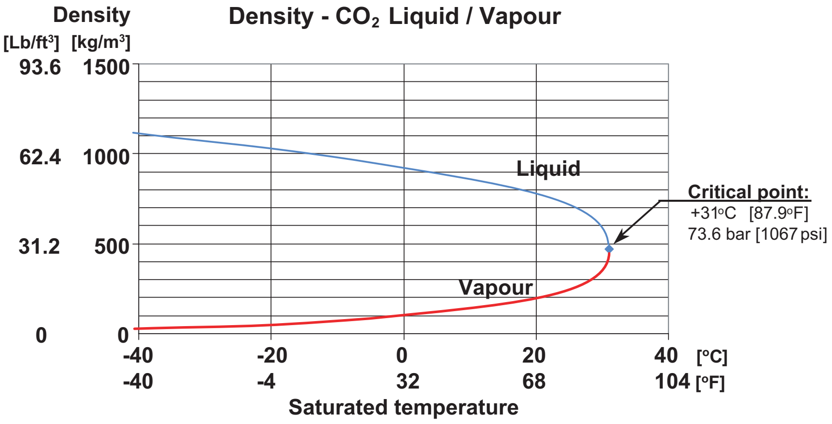


Figure 3

CO$_2$ 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.

CO_2 as a refrigerant

CO_2 may be employed as a refrigerant in a number of different system types, including both subcritical and supercritical. For any type of CO_2 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 CO_2 system is simple, but it also has disadvantages because of its limited temperature range and high pressure (figure 5).

Transcritical CO_2 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 [83 to 507 psi] corresponding to –55 to 0°C [–67 to 32°F]. If the evaporators are defrosted using hot gas, then the operating pressure is approximately 10 bar [145 psi] higher.

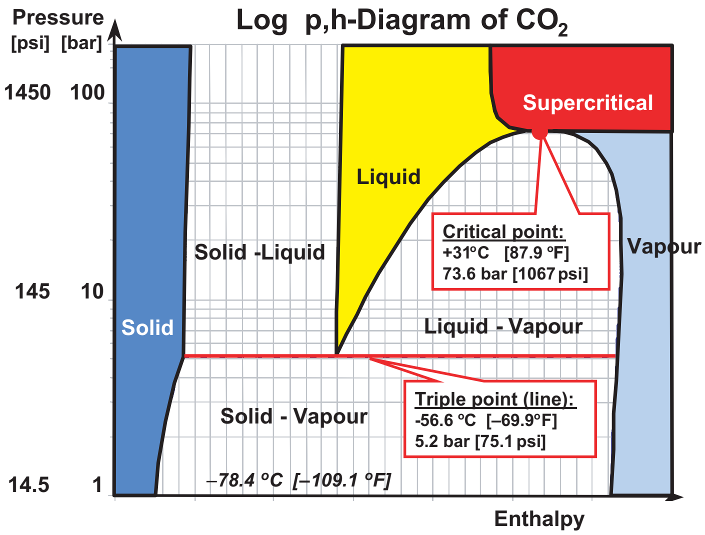


Figure 4

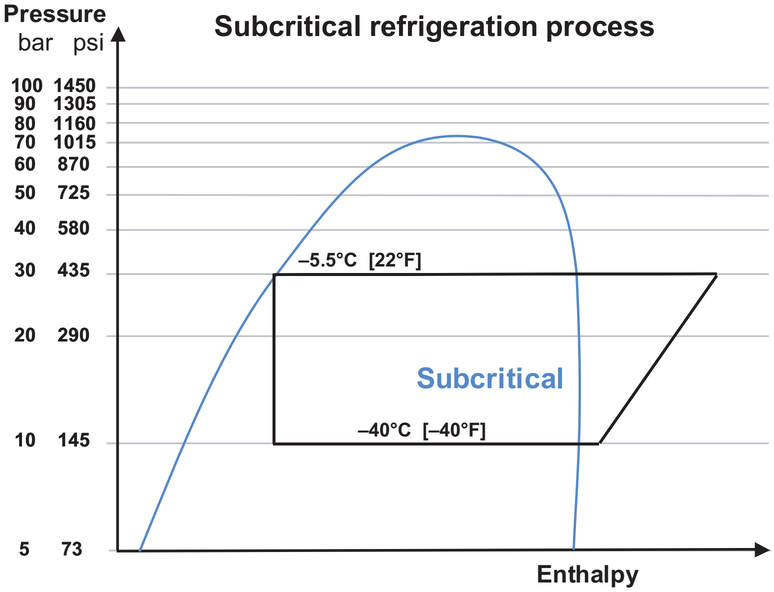


Figure 5

CO_2 as a refrigerant
(Continued)

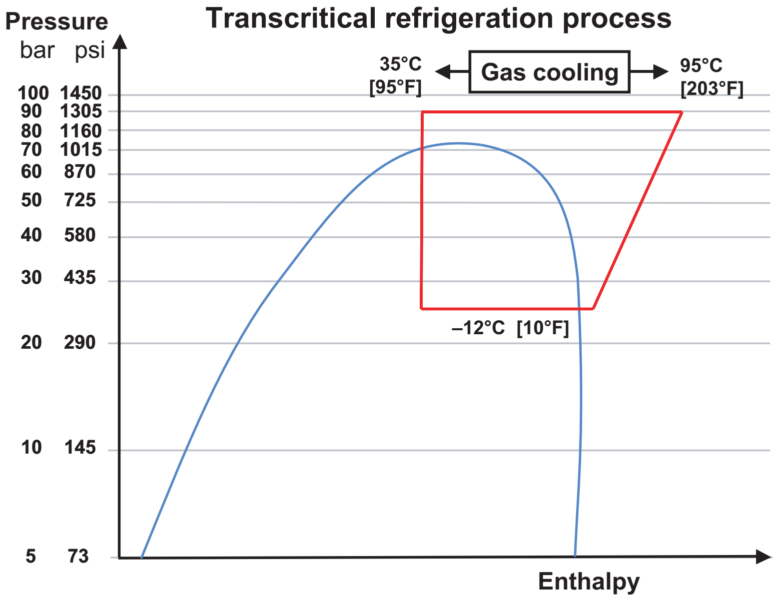


Figure 6

CO_2 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.

CO_2 cascade systems can be designed in different ways, e.g., direct expansion systems, pump circulating systems, or CO_2 in volatile secondary "brine" systems, or combinations of these.

CO_2 as a refrigerant in industrial systems

Figure 7 shows a low temperature refrigerating system –40°C [–40ºF] using CO_2 as a phase change refrigerant in a cascade system with ammonia on the high-pressure side.

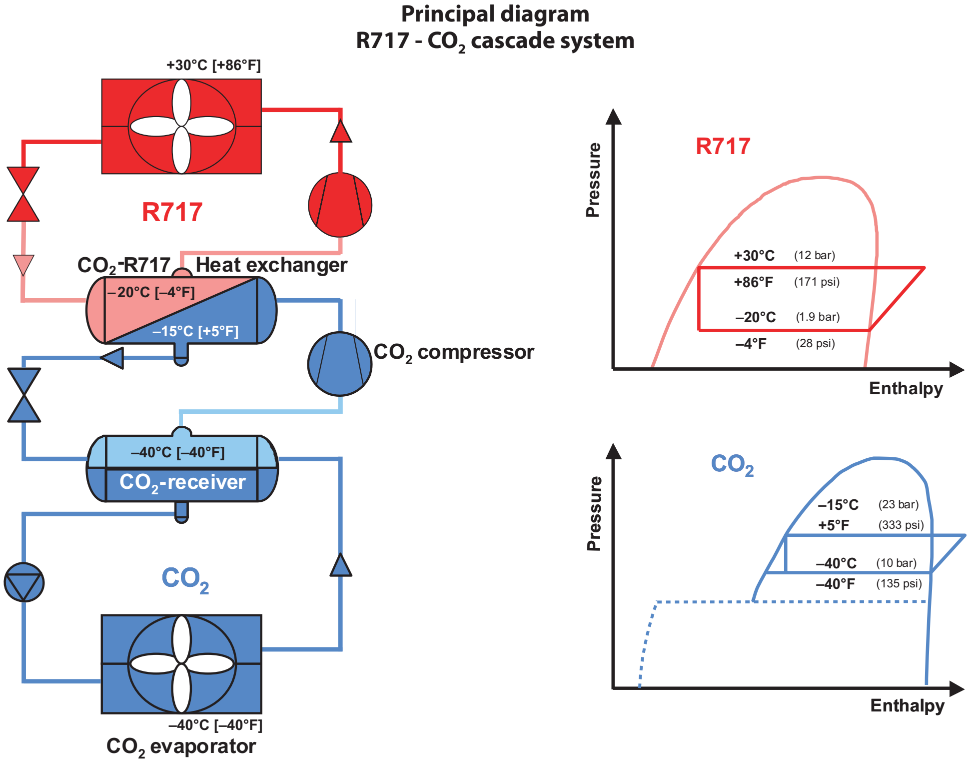


Figure 7

CO_2 as a refrigerant in industrial systems
(Continued)

Principal diagram
R717 - CO_2 cascade system with CO_2 hot gas defrosting

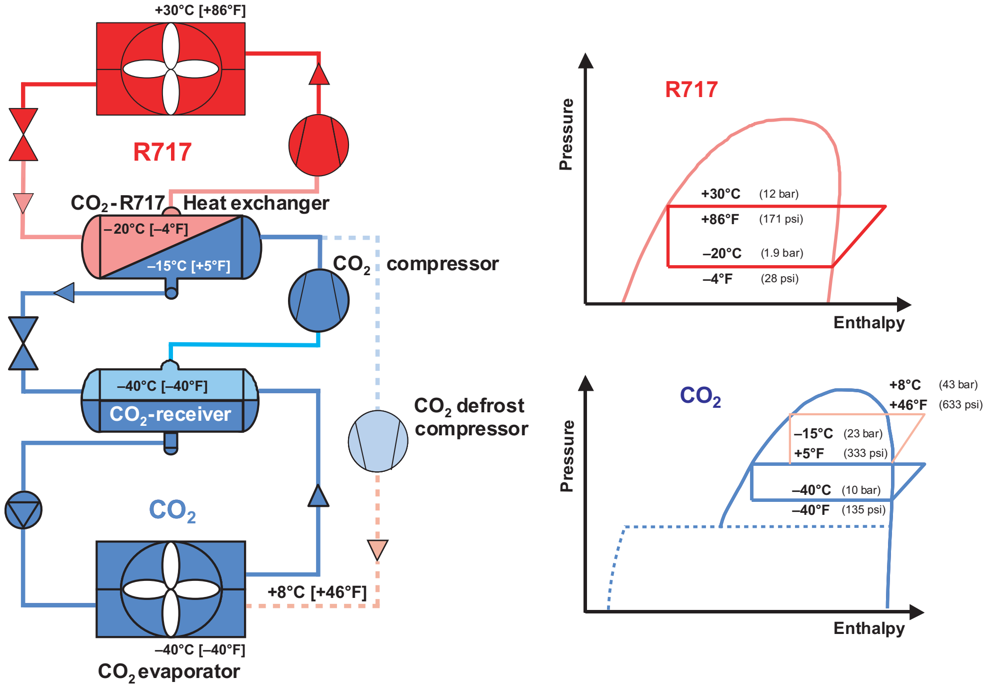


Figure 8

The CO_2 system is a pump circulating system where the liquid CO_2 is pumped from the receiver to the evaporator, where it is partly evaporated, before it returns to the receiver. The evaporated CO_2 is then compressed in a CO_2 compressor, and condensed in the CO_2-NH_3 heat exchanger. The heat exchanger acts as an evaporator in the NH_3 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 CO_2 hot gas defrosting system.

Principal diagram
R717 - CO_2 brine system

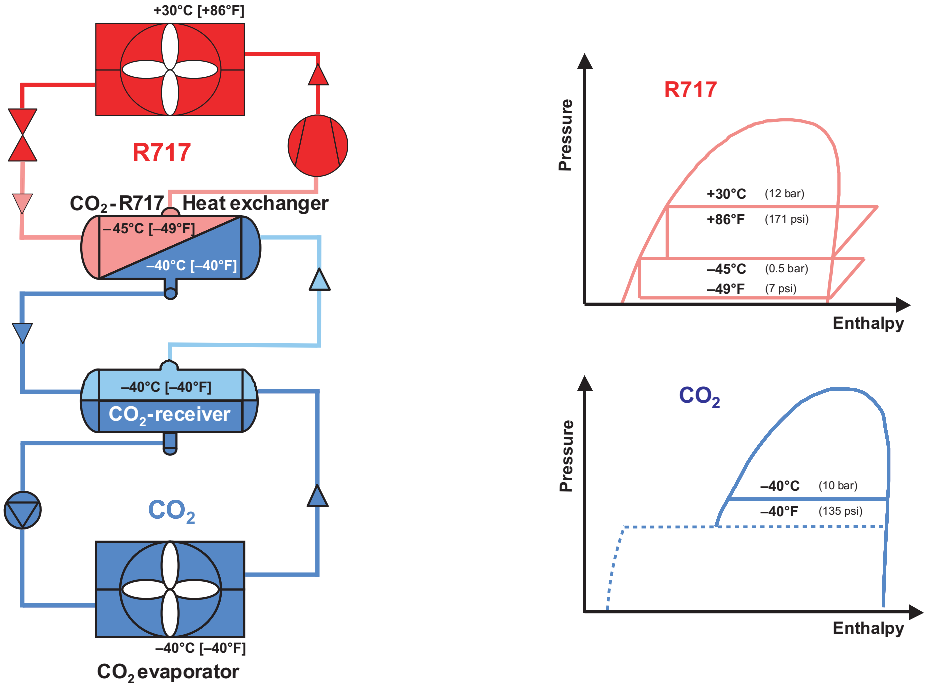


Figure 9

CO_2 as a refrigerant in industrial systems

(Continued)

Principal diagram
CO_2 cascade system with 2 temperature levels
(e.g. supermarket refrigeration)

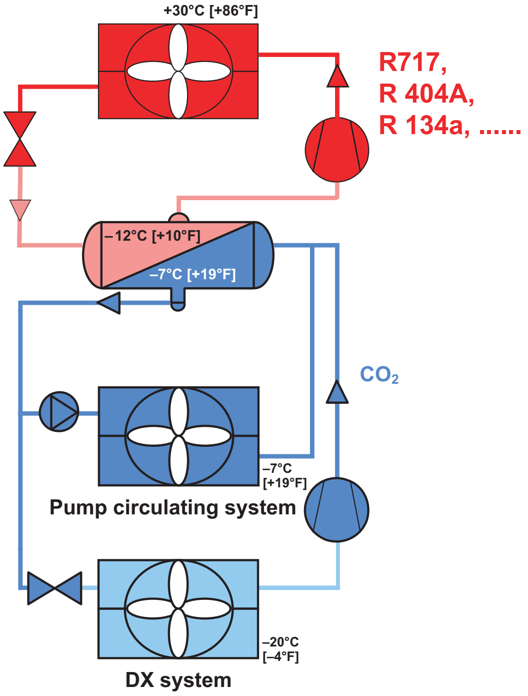


Figure 10

Figure 9 shows a low temperature refrigerating system –40°C [–40°F] using CO_2 as a "brine" system with ammonia on the high-pressure side. The CO_2 system is a pump circulating system, where the liquid CO_2 is pumped from the receiver to the evaporator. Here it is partly evaporated, before it returns to the receiver.

The evaporated CO_2 is then condensed in the CO_2- NH_3 heat exchanger. The heat exchanger acts as an evaporator in the NH_3 system. Figure 10 shows a mixed system with flooded and DX-system, e.g. for a refrigeration system in a supermarket, where 2 temperature levels are required

Design pressure

When determining the design pressure for CO_2 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] @ 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 CO_2, 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)

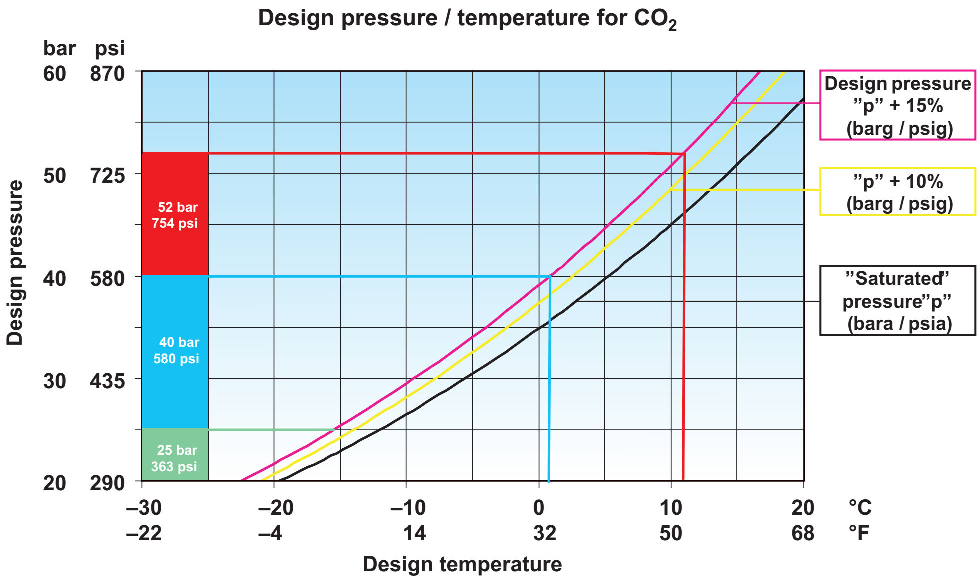


Figure 11

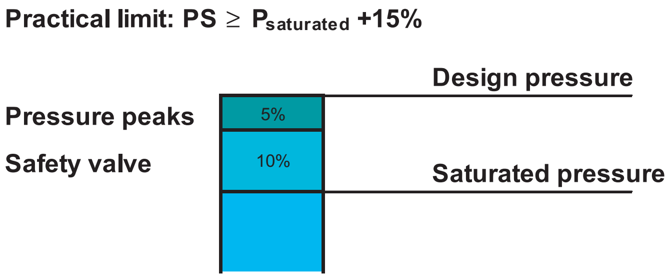


Figure 12

Safety

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, CO_2 also has some disadvantages.

Due to the fact that CO_2 is odourless, it is not self-alarming, if leaks occur, (ref. [6]).

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. CO_2 can displace oxygen to a point when it is fatal. The relative density of 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, CO_2 is a safer refrigerant. The TLV (threshold limit value) is the maximum concentration of vapour 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 CO_2 5000 [ppm] (0.5%).

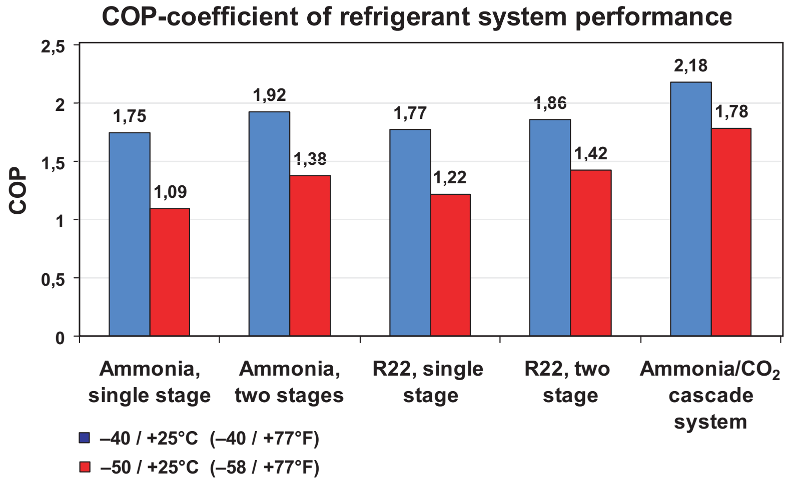
Approx. 0.04% CO_2 is present in the Air. With higher concentration, some adverse reactions are reported:

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_2- NH_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_2 have a better efficiency and heat transfer is greater. The overall efficiency of a CO_2- NH_3 cascade system is not reduced when compared to a traditional NH_3 system (figure 13 & ref. [3]).

Example:



Source: IIAR - Albuquerque, New Mexico 2003, P.S Nielsen & T.Lund
Introducing a New Ammonia/CO_2 Cascade Concept for Large Fishing Vessels

Figure 13

Oil in CO_2 systems

In CO_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_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 polyol 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_2 as a secondary refrigerant, and in recirculating systems with oil free compressors, no oil is present in the circulated CO_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_2 and oil

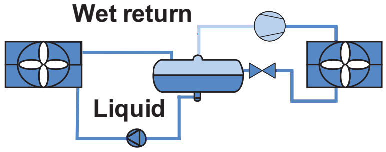
Oil type	**PAO** **Poly-alpha-olefin oil** *(Synthetic Mineral oil)*	**POE** **Polyol-ester oil** *(Ester oil)*
Solobility	Low (immiscible)	High (miscible)
Hydrolysis	Low	High affinity to water
Oil separation system	**Special demand:** ● High filtration demanded ● Multistage coalescing filters ● Active carbon filter	**No special requirements** (System requirements like HCFC/HFC)
Oil return system	**Special demand:** ● Oil drain from low temperature receiver (oil density lower than CO_2 - opposite NH_3)	**Simple** (System requirements like HCFC/HFC)
Challenge	● Oil separation and return system ● Long term oil accumulation in e.g. evaporators	● High affinity to water ● Long term stability of oil ● "Clean" refrigerant system required

Table 2

Comparison of component requirements in CO$_2$, ammonia and R134a systems

Compared to ammonia and R134a, CO$_2$ 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.

Comparison of pipe cross section area
Wet return / Liquid lines



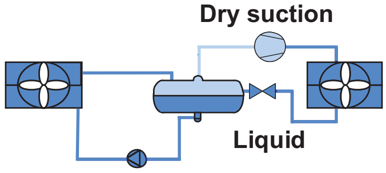
	Refrigerant			R 134a		R 717		CO_2	
	Capacity	kW	[TR]	250	[71]	250	[71]	250	[71]
"Wet return" line	ΔT	K	[F]	0.8	[1.4]	0.8	[1.4]	0.8	[1.4]
	Δp	bar	[psi]	0.0212	[0.308]	0.0303	[0.439]	0.2930	[4.249]
	Velocity	m/s	[ft/s]	11.0	[36.2]	20.2	[66.2]	8.2	[26.9]
				●		●		●	
	Diameter	mm	[inch]	215	[8.5]	133	[5.2]	69	[2.7]
	Area "Wet return"	mm^2	[inch^2]	36385	[56.40]	13894	[21.54]	3774	[5.85]

"Liquid" line	Velocity	m/s	[ft/s]	0.8	[2.6]	0.8	[2.6]	0.8	[2.6]
				●		●		●	
	Diameter	mm	[inch]	61	[2.4]	36	[1.4]	58	[2.3]
	Area "liquid"	mm^2	[inch^2]	2968	[4.6]	998	[1.55]	2609	[4.04]
Total pipe cross section area	Area "Wet return"	mm^2	[inch^2]	39353	[61.0]	14892	[23.08]	6382	[9.89]
Liquid cross section area		%		8		7		41	

L_{eqv} = 50 [m] / 194 [ft] - Pump circ.: n_{circ} = 3 - Evaporating temp.: TE = –40[°C] / –40[°F]

Table 3

Comparison of pipe cross section area
Dry suction / Liquid lines



	Refrigerant			R 134a		R 717		CO_2	
	Capacity	kW	[TR]	250	[71]	250	[71]	250	[71]
"Dry suction" line	ΔT	K	[F]	0.8	[1.4]	0.8	[1.4]	0.8	[1.4]
	Δp	bar	[psi]	0.0212	[0.308]	0.0303	[0.439]	0.2930	[4.249]
	Velocity	m/s	[ft/s]	20.4	[67]	37.5	[123]	15.4	[51]
				●		●		●	
	Diameter	mm	[inch]	168	[6.6]	102	[4.0]	53	[2.1]
	Area "Dry suction"	mm^2	[inch^2]	22134	[34.31]	8097	[12.55]	2242	[3.48]

"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"	mm^2	[inch^2]	1089	[1.69]	353	[0.55]	975	[1.51]
Total pipe cross section area	Area "Dry suction + liquid"	mm^2	[inch^2]	23223	[36.00]	8450	[13.10]	3217	[4.99]
Liquid cross section area		%		5		4		30	

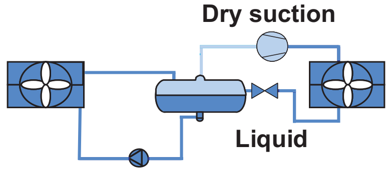
L_{eqv} = 50 [m] / 194 [ft] - Evaporating temp.: TE = –40[°C] / –40[°F] - Condensing temp.: TE = –15[°C] / –5[°F]

Table 4

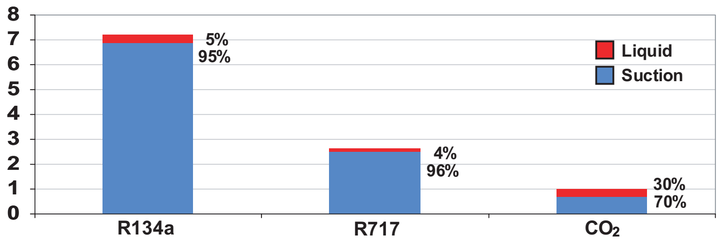
Comparison of component requirements in CO$_2$, ammonia and R134a systems

(Continued)

Comparison of pipe cross section area
Dry suction / Liquid lines



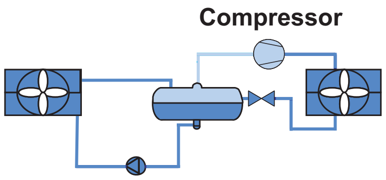
Refrigerant				R 134a		R 717		CO$_2$	
	Capacity	kW	[TR]	250	[71]	250	[71]	250	[71]
"Dry suction" line	Area "Dry suction"	mm^2	[inch^2]	22134	[34.31]	8097	[12.55]	2242	[3.48]
"Liquid" line	Area "liquid"	mm^2	[inch^2]	1089	[1.69]	353	[0.55]	975	[1.51]
Total pipe cross section area	Area "Dry suction + liquid	mm^2	[inch^2]	23223	[36.00]	8450	[13.10]	3217	[4.99]
Relative cross section area		-		7.2		2.6		1.0	
Liquid cross section area		%		5		4		30	
Vapour cross section area		%		95		96		70	



L_{eqv} = 50 [m] / 194 [ft] - Evaporating temp.: TE = –40[°C] / –40[°F] - Condensing temp.: TE = –15[°C] / –5[°F]

Table 5

Comparison of compressor displacement

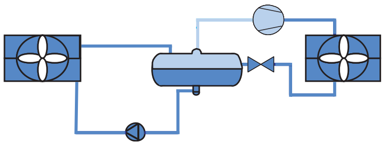


Refrigerant			R 134a		R 717		CO$_2$	
Refrigerant capacity	kW	[TR]	250	[71]	250	[71]	250	[71]
Required compressor displacement	m^3/h	[ft^3/h]	1628	[57489]	1092	[38578]	124	[4387]
Relative displacement	-	-	13.1		8.8		1.0	

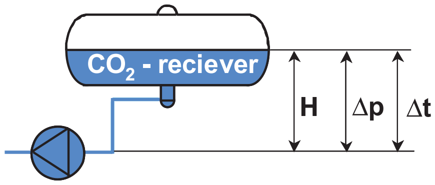
Evaporating temp.: TE = –40[°C] / –40[°F] - Condensing temp.: TE = –15[°C] / –5[°F]

Table 6

Comparison of pressure / subcooling produced in liquid risers



Refrigerant			R 134a		R 717		CO$_2$	
Hight of liquid riser "H"	m	[ft]	3	[9.8]	3	[9.8]	3	[9.8]
Pressure produced in liquid riser "Δp"	bar	[psi]	0.418	[6.06]	0.213	[2.95]	0.329	[4.77]
Subcooling produced in liquid riser "Δt"	K	[°F]	14.91	[26.8]	5.21	[9.4]	0.88	[1.6]



Evaporating temp.: TE = –40[°C] / –40[°F]

Table 7

Wet return lines in recirculation systems:

A comparison of pump circulating systems shows that for "wet return" lines, CO_2 systems require much smaller pipes than ammonia or R134a (table 3). In CO_2 "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 CO_2 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.

Suction lines in dry expansion systems:

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).

Liquid lines:

For both recirculating and dry expansion systems, calculated sizes for CO_2 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 CO_2 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 CO_2 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 CO_2 system and large volumetric refrigeration capacity, the CO_2 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 CO_2 system requires a much smaller compressor than the ammonia or R134a systems.

For compressors of identical displacements, the capacity of the compressor using CO_2 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 CO_2 liquid riser is much smaller than that for ammonia and R134a. This characteristic must be noted when designing CO_2 systems to prevent cavitations and other problems with liquid CO_2 pumps.

Water in CO_2 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, CO_2 is less sensitive, but if water is present, problems may occur. Some early CO_2 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 CO_2 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 CO_2 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*.

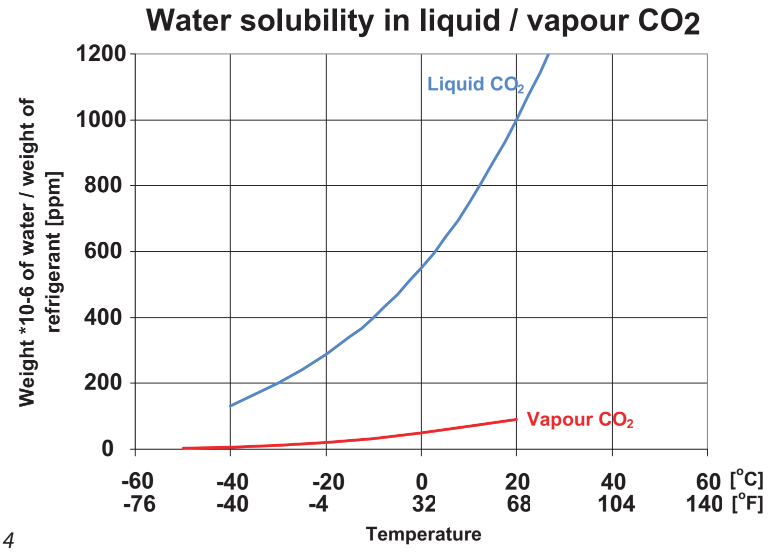


Figure 14

Water in CO_2 Systems
(Continued)

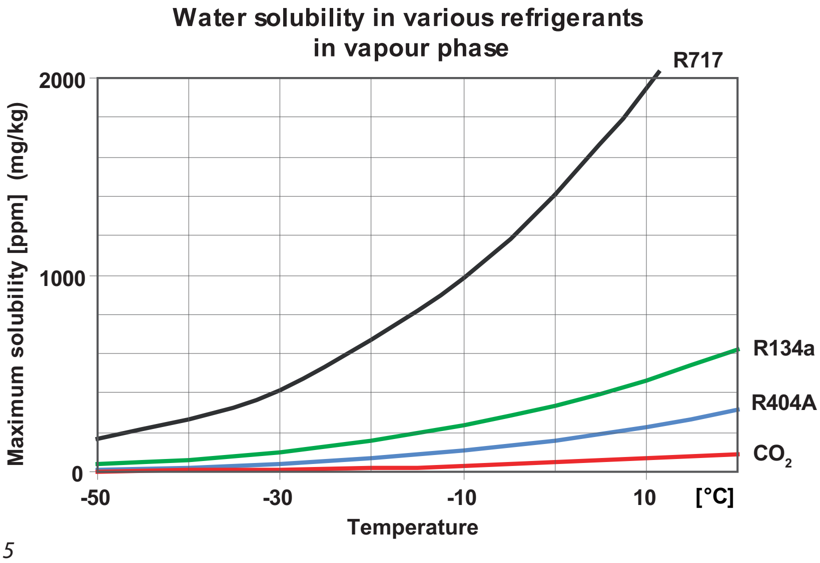


Figure 15

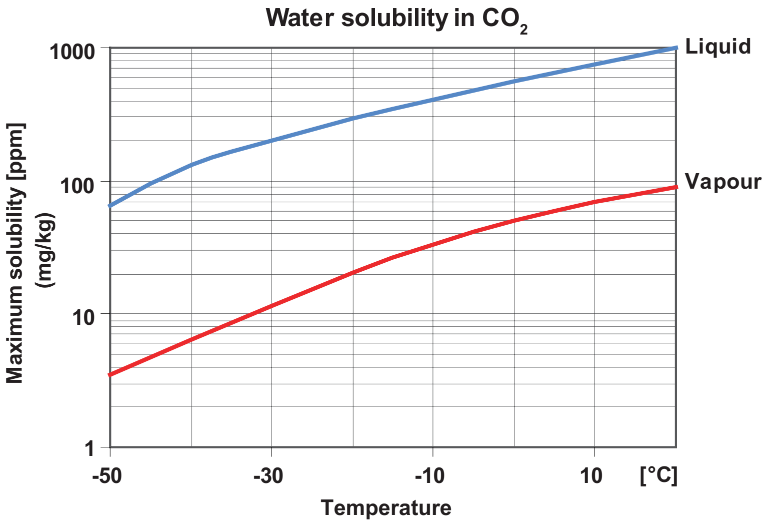


Figure 15.1

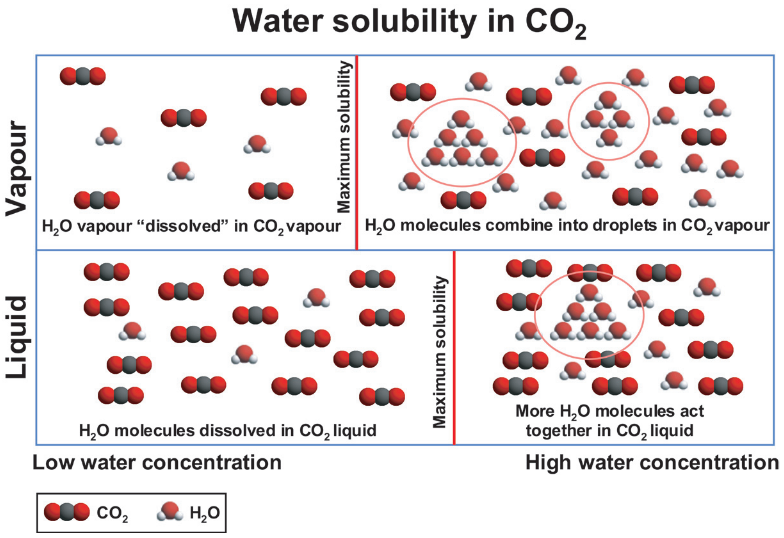


Figure 16

Water in CO_2 Systems
(Continued)

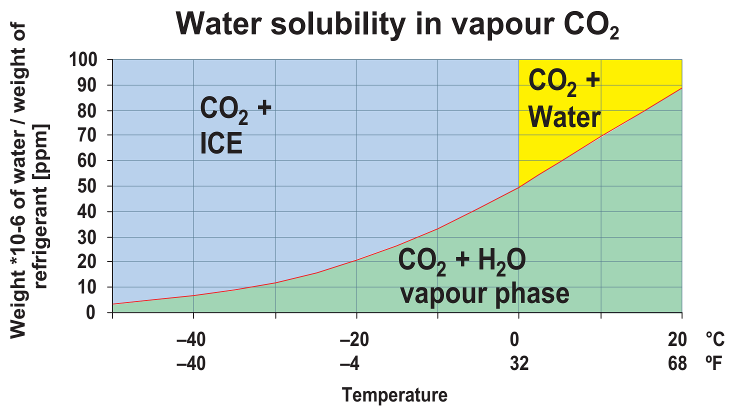


Figure 17

The diagram in figure 14 is showing that the water solubility in CO_2 is much lower than for R134a or ammonia. At –20°C [–4°F], water solubility in the liquid phase is:

- CO_2, 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 (H_2O) molecules are dissolved if the concentration is lower than the maximum solubility limit, and how the H_2O molecules precipitate out of solution into droplets if the water concentration is higher than the maximum solubility limit.
If the water is allowed to exceed this limit in a CO_2 system, problems may occur, especially if the temperature is below 0°C. In this case, the water will freeze, and the ice crystals can block control valves, solenoid valves, filters and other equipment (figure 17). This problem is in particular critical in flooded and direct expansion CO_2 systems, but not so much in volatile secondary systems because less sensitive equipment is used.

Chemical reactions

It is important to notice, that the below mentioned reactions with water don't take place in a well-maintained CO_2 system, where the water contents is below the maximum solubility limit.

In a closed system such as a refrigeration system, CO_2 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, CO_2 can form carbonic acid, as follows (ref. [4] and [5]).

$CO_2 + H_2O \rightarrow H_2CO_3$
(CO_2 + water → carbonic acid)

In CO_2 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 CO_2 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, CO_2 and water in vapor phase can react to form a CO_2 gas hydrate.

$CO_2 + 8\,H_2 0 \rightarrow CO_2(H_2 0)_8$
(CO_2 + water → hydrated CO_2)

The CO_2 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:

$RCOOR' + H_2O \rightarrow R'OH + RCOOH$
(ester + water → alcohol + 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 CO_2 systems if POE lubricants are used.

PAO lubricant

$2RCH_3 + 3\,O_2 \rightarrow 2\,H_2 0_2 + 2RCOOH$
(oil + oxygen → water + acid)

PAO lubricant is also called synthetic mineral oil. Ordinarily, PAO is very stable. However, if sufficient free oxygen is present, such as might be available from corrosion in pipes, the oxygen will react with the lubricant, and form carboxylic acid.

Removing water

Controlling the water content in a refrigeration system is a very efficient methode 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.

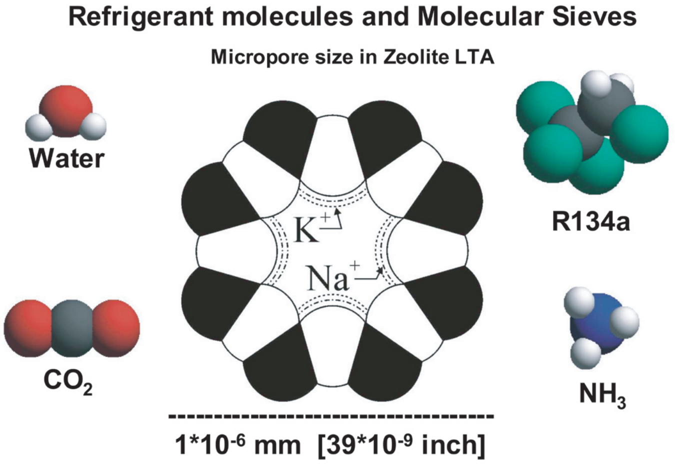


Figure 18

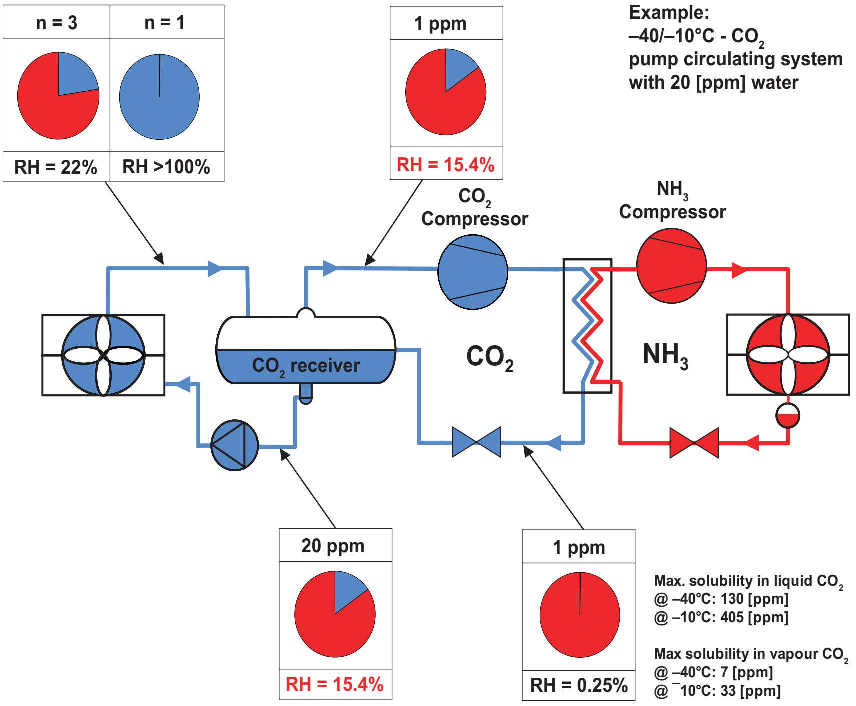


Figure 18.1

Removing water
(Continued)

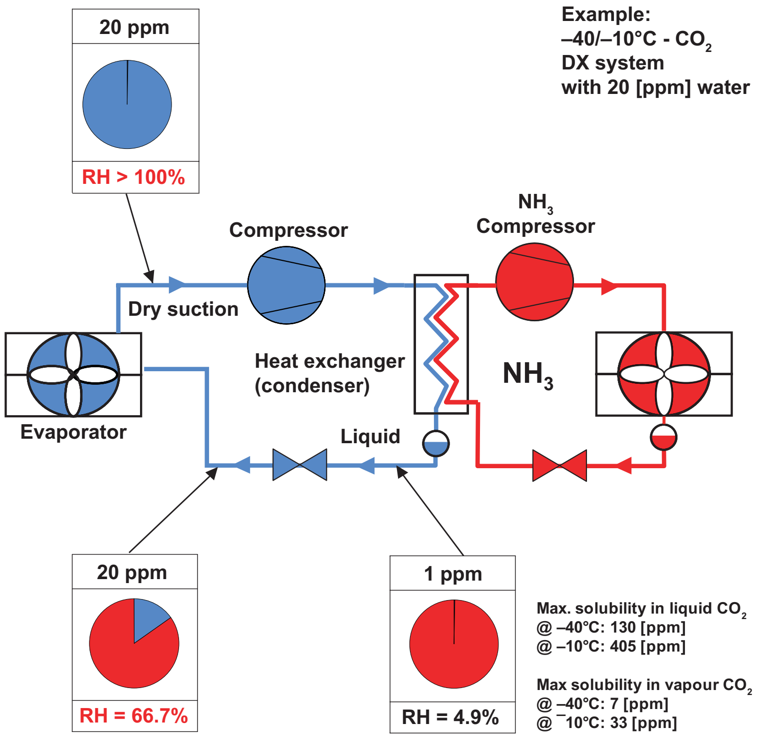


Figure 18.2

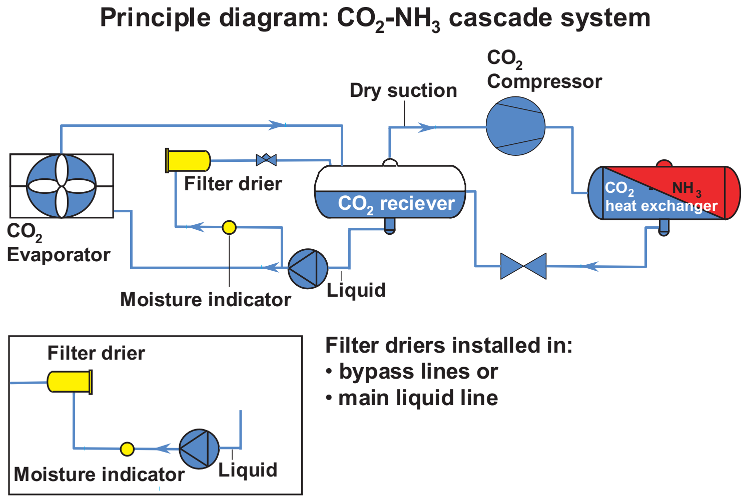


Figure 19

CO$_2$ is a non-polar molecule, so the removal process is different. Like water molecules, CO$_2$ molecules are small enough to penetrate the molecular sieve. However, the water molecules adsorbed onto the molecular sieve act in such as way as to "kick out" the CO$_2$ 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 CO$_2$ 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 CO$_2$ is much lower than in the liquid phase. Therefore, a greater amount of water can be transported in liquid lines.

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 CO$_2$.

Removing water
(Continued)

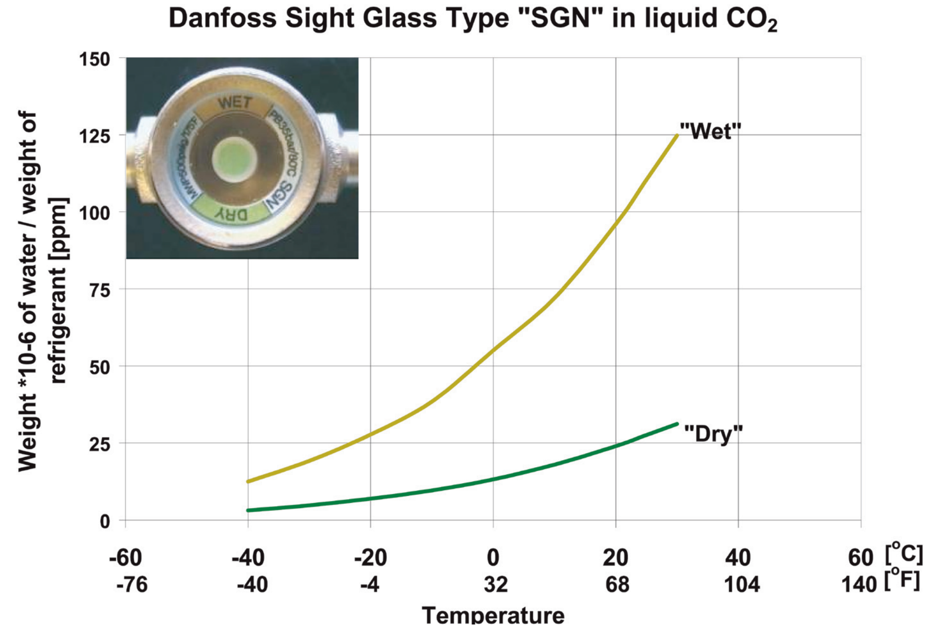


Figure 20

How does water enter a CO$_2$ system?

Unlike in some ammonia systems, the pressure in CO$_2$ systems is always above atmospheric. However, water can still find its way into CO$_2$ systems.

Water may contaminate a CO$_2$ 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 CO$_2$ charged into the system

Obviously, all these mechanisms should be avoided/minimized.

To illustrate a scenario in which water may contaminate a system, think of a contractor, who, believing CO$_2$ 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.

Miscellaneous features to be taking into consideration in CO_2 refrigeration systems

Safety valve

CO_2's particularly high triple point can cause solid CO_2 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 35 bar [507 psi] or less, e.g., the rightmost line, 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 CO_2 will be pure vapor.

CO_2 expansion - phase changes
Safety valves

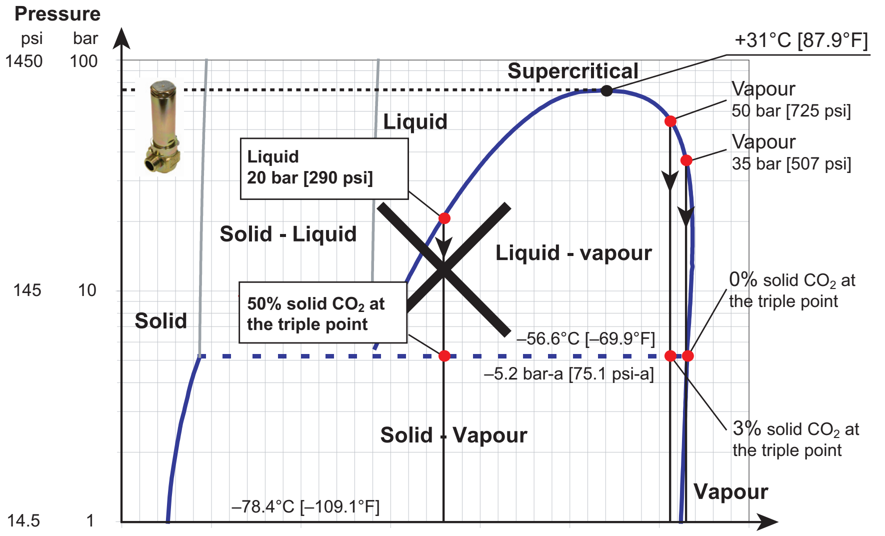


Figure 21

CO_2 expansion - phase changes
Cleaning filers / charging CO_2

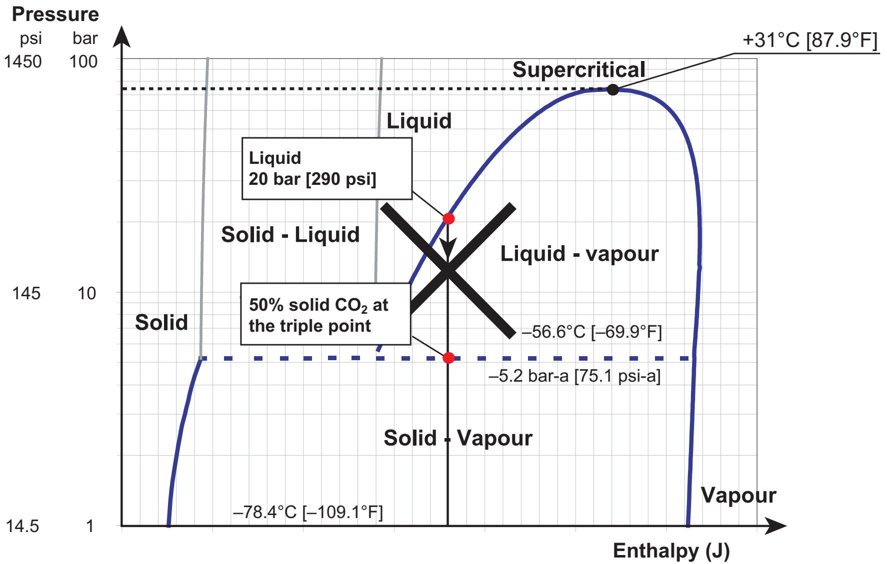


Figure 22

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 CO_2 will change into solid as it continues to relieve. In a worst-case scenario (e.g., a long relief line with many bends), solid CO_2 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 CO_2 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 CO_2 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].

Charging CO_2

It is important to start up with CO_2 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 CO_2 system. One must be aware when charging a refrigerant system that until the pressure reaches the triple point, the CO_2 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 CO_2 is non-toxic, one cannot just drain the liquid outside the system. Once the liquid CO_2 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 CO_2 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 CO_2 expands much more than ammonia and R134a, especially when the temperature approaches CO_2's critical point.

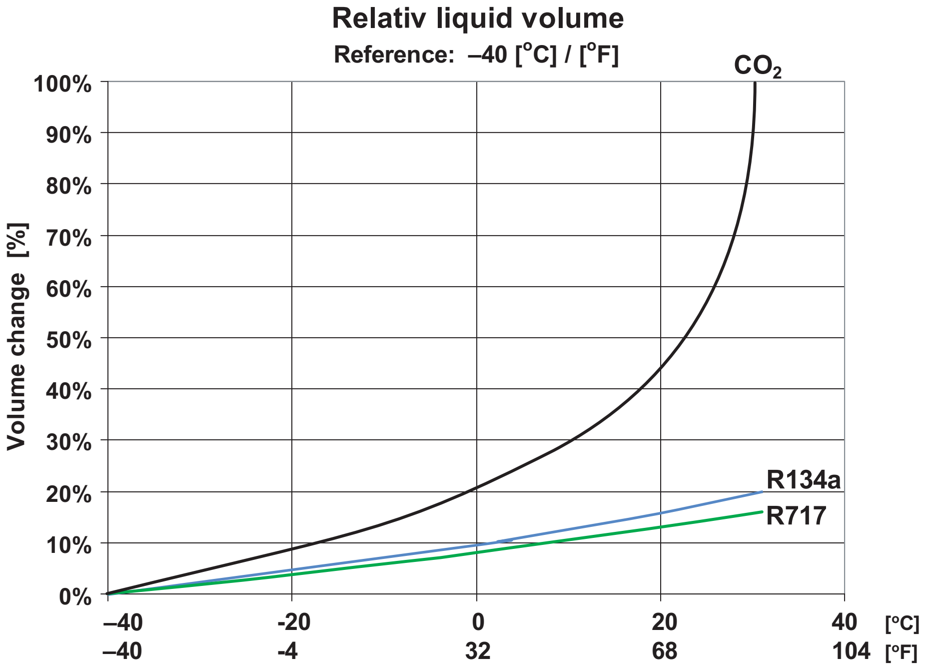


Figure 23

Leaks in CO_2- NH_3 cascade systems

The most critical leak in a CO_2- NH_3 cascade system is in the heat exchangers between CO_2 and NH_3. The pressure of the CO_2 will be higher than the NH_3, so the leak will occur into the NH_3 system, which will become contaminated.

CO_2 + 2 NH_3 → $H_2NCOONH_4$
CO_2 ammonia ammonium carbamate

The solid substance ammonium carbamate is formed immediately when CO_2 is in contact with NH_3. Ammonium carbamate is corrosive (ref. [5]).

Material compatibility

CO_2 is compatible with almost all common metallic materials, unlike NH_3. There are no restrictions from a compatibility point of view, when using copper or brass.
The compatibility of CO_2 and polymers is much more complex. Because CO_2 is a very inert and stable substance, the chemical reaction with polymers is not critical. The main concern with CO_2 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 CO_2 in the actual material.

Danfoss has carried out a number of tests to ensure that components released for use with CO_2 can withstand the impact of CO_2 in all aspects.

The tests have shown that CO_2 is different, and modifications have to be made on some products. The large amount of CO_2, which can dissolve in polymers, has to be taken into consideration. Some commonly used polymers are not compatible with CO_2, and others require different fixing methods e.g. sealing materials. When the pressure is close to the critical pressure and the temperature is high, the impact on polymers is much more extreme. However, those conditions are not important for industrial refrigeration, as pressure and temperatures are lower for these systems.

Conclusion

CO_2 has good properties, in particular at low temperature, but it is not a substitution for ammonia. The most common industrial CO_2 refrigeration systems, is hybrid systems with ammonia on the high temperature side of the system.

CO_2 is in many aspects a very uncomplicated refrigerant, but it is important to realize that CO_2 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.

The availability of components for industrial CO_2 refrigeration systems with pressures up to approximately 40 bar is good. Several manufacturers of equipment for traditional refrigerants can also supply some components for CO_2 systems. The availability of components for the higher pressure industrial CO_2 refrigeration systems is limited, and the availability of critical components is an important factor in the growth rate of CO_2 application.

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