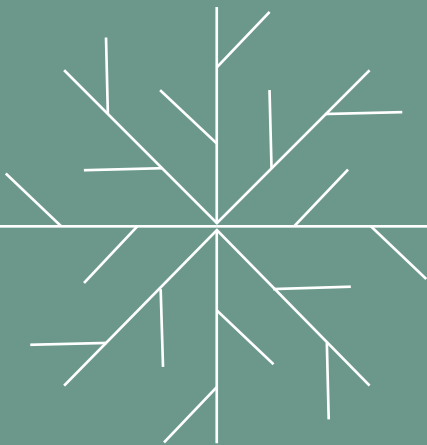


CO₂ as refrigerant in Cooling and Heating systems

Fundamentals & Applications

PART 1: CO₂ as refrigerant



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The transition towards low GWP refrigerants

The transition towards low GWP refrigerants represents a significant shift in the world of cooling and refrigeration systems. Historically, synthetic refrigerants, such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs) have been widely used due to their non-flammable and non-toxic properties. However, the adverse environmental impacts of these synthetic substances, particularly their role in depleting the ozone layer (CFC and HCFC) and contributing to global warming, have led to a pressing need for more sustainable alternatives.

Natural refrigerants, on the other hand, offer a promising solution to mitigate the environmental concerns associated with synthetic refrigerants. These substances occur naturally in the environment and have minimal impact on global warming. Examples of natural refrigerants include carbon dioxide (CO₂), hydrocarbons (such as propane and isobutane), and ammonia.

The usage of natural refrigerants has gained momentum in recent years, driven by increasing awareness of climate change and the need for sustainable solutions. A majority of research and development efforts are directed to identify and optimize the use of natural refrigerants in various applications.

Natural refrigerants which are flammable or toxic have their limitations in their application range. One of the key advantages of natural

refrigerants is their low global warming potential (GWP) and zero ozone depletion potential (ODP). These characteristics make them environmentally friendly alternatives, aligning with the goals of reducing greenhouse gas emissions and protecting the ozone layer. Moreover, natural refrigerants can offer splendid energy efficiency in specific applications and contribute to lower operating costs over the long term.

Natural refrigerants often require system modifications and upgrades to ensure safe and efficient operation. Natural refrigerants which are flammable or toxic have their limitations in their application range. Training and education are crucial to equip technicians and engineers with the knowledge and skills necessary for working with natural refrigerants. Additionally, regulations and standards must be updated to accommodate the use of natural refrigerants, ensuring proper handling, storage, and disposal practices.

In conclusion, the application of natural refrigerants represents a pivotal moment in the refrigeration industry's journey toward sustainability. With their lower environmental impact and improved energy efficiency, natural refrigerants offer a viable and eco-friendly alternative. As the world continues to prioritize environmental-friendly solutions, the adoption of natural refrigerants is set to reshape the cooling and refrigeration landscape, contributing to a greener and more sustainable future.

CO₂ as refrigerant

Carbon dioxide, also known as R744, had been utilized as a refrigerant in vapor compression refrigeration cycles since 1880s. However, with the introduction of synthetic refrigerants in the 1930s, CO₂ gradually lost its market share due to issues related to energy efficiency, system design complexity, and technological limitations. Cheap, safe, and easy to use CFCs and HCFCs systems dominated the commercial and residential refrigeration/AC market, while

NH₃ has been the main refrigerant for industrial refrigeration.

However, in the 1980s, when the detrimental environmental effects of synthetic refrigerants became apparent, CO₂ experienced a revival as a viable solution (Lorentzen, 1994). This revival was made possible by advancements in system and component design, as well as improvements in manufacturing processes.





CO₂ is a unique refrigerant. Some of the key properties of CO₂ as a refrigerant include:



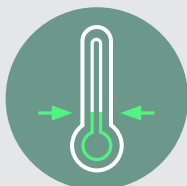
LOW GLOBAL WARMING POTENTIAL (GWP): CO₂ has a GWP of 1, which means it has a minimal impact on global warming compared to other commonly used refrigerants. This makes it environmentally friendly and aligns with sustainability goals.



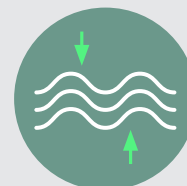
LOW OZONE DEPLETION POTENTIAL (ODP): CO₂ has an ODP of 0, meaning it does not deplete the ozone layer.



NON-FLAMMABLE AND NON-TOXIC: CO₂ is non-flammable, classified in A1 group, eliminating fire hazards in case of leakage. It is also non-toxic, posing no direct risk to human health. These properties make CO₂ a safe refrigerant option.



LOW CRITICAL TEMPERATURE: CO₂ has a critical temperature of 31°C (87.98°F) and a critical pressure of 73.8 bar (1,070 psi). This critical temperature is lower than all other type of conventional refrigerants. This low critical temperature forces the system to operate in the supercritical phase in warm ambient conditions. There is a challenge to maintain an acceptable energy efficiency level under these conditions. The methods to improve this energy efficiency are discussed in part 2 of this report series.



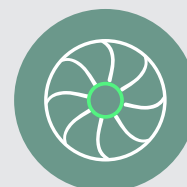
HEAT TRANSFER PROPERTIES: CO₂ has excellent heat transfer properties, allowing for efficient heat exchange. It has a higher volumetric cooling capacity compared to some other refrigerants, enabling compact system designs. Its characteristics while rejecting the heat to a liquid coolant substance (water, ...) are also unique, make it an excellent choice, for example, under certain heat recovery strategies and boundary conditions. The shape of isothermal lines in transcritical mode can provide an efficient match with the coolant temperature profile.



HIGH OPERATING PRESSURES: CO₂ operates at higher pressures compared to conventional refrigerants. This requires the use of specialized components and systems capable of handling these elevated pressures.



WIDE TEMPERATURE RANGE: CO₂ can be used as a refrigerant for both low-temperature applications (such as freezing, deep freezing, industrial refrigeration, ...) and medium-temperature applications (such as commercial refrigeration and air conditioning).



ADDITIONAL APPLICATIONS: CO₂ can also be used for heat pumps, supercritical power cycles, and other high-efficiency systems, making it versatile in various industrial and commercial applications.

➤ It's important to note that due to its unique properties, the use of CO₂ as a refrigerant often requires system modifications and specialized equipment to accommodate its high pressures and operating characteristics. This will be explored in this report series.

Phase diagram of CO₂

Figure 1 shows a phase diagram of CO₂. The three well-known phases: solid, liquid and vapour are shown as coloured areas. A phase change occurs when a process crosses a boundary between areas - like evaporation or condensation for a process crossing the boundary between liquid and vapour phases. At the boundaries, the two phases exist in equilibrium, and properties, such as temperature and pressure, become dependent. The boundary line between liquid and vapour are often referred to as the vapour pressure curve.

Two important state points are marked in the figure: the triple point and the critical point. For most of the substances used as refrigerants, the triple point and critical point are found for conditions that lie outside the region where they are normally used. CO₂ is the only exception that can reach these conditions.

The triple point represents the condition where all three phases can co-exist in equilibrium. CO₂ reaches the triple point at 5.2 bar [75.1 psi] and -56.6°C [-69.9°F]. At temperatures below the triple point temperature, liquid cannot exist - in other words the triple point temperature sets the lower temperature limit for any heat transfer process based on evaporation or condensation.

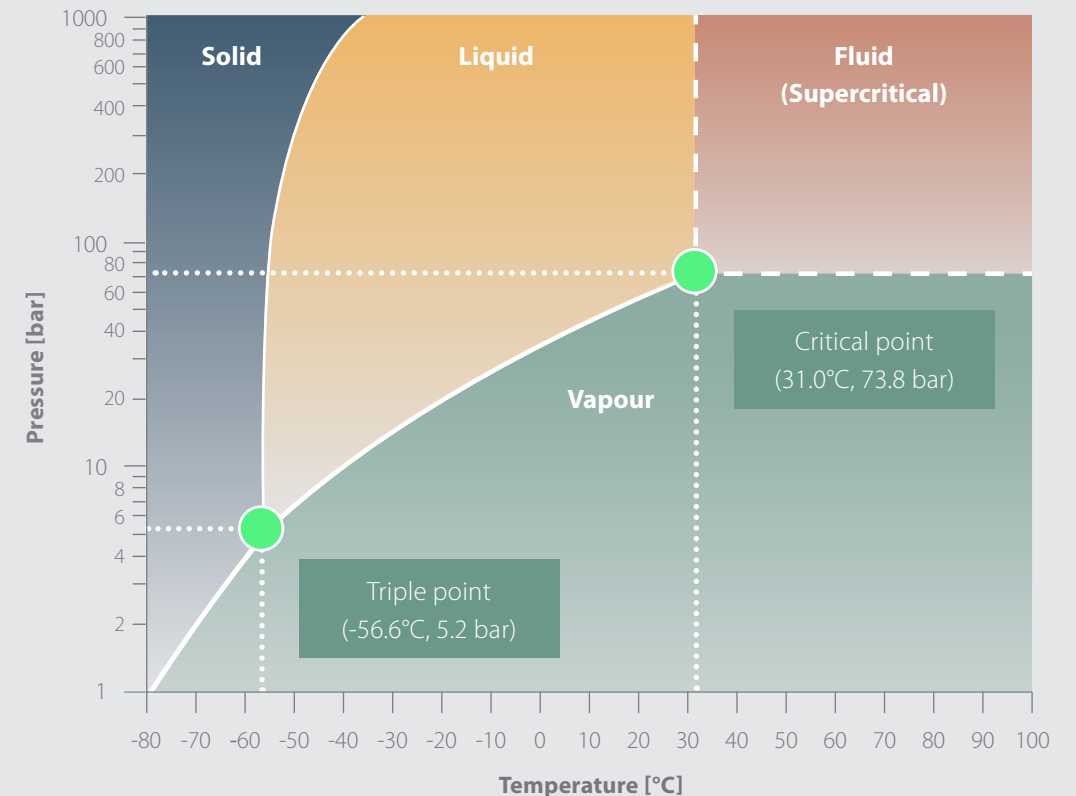
At atmospheric pressure CO₂ can exist only as a solid or a vapour. At this pressure, it has no ability to form a liquid: below -78.4°C [-109.1°F], it is a solid "dry ice"; above this temperature, it sublimates directly to a vapour phase.

At the other end of the vapour pressure curve, the critical point marks the upper limit for heat transfer processes based on evaporation or condensation.

At temperatures and pressures higher than those at the critical point, no clear distinction can be drawn between what is called liquid and what is called vapour. Thus, there is a region extending indefinitely upward from, and indefinitely to the right of, the critical point – and this region is called the fluid region. The fluid region is bounded by dashed lines that do not represent phase changes, but which conform to arbitrary definitions of what is considered a liquid and what is considered vapour. A condition in the fluid region is referred to as a supercritical condition – or very often also as a gas condition.



CO₂ reaches its critical point at 31.1°C [88.0°F]. At this temperature, the density of the liquid and vapour states is equal. Consequently, the distinction between the two phases disappears and this new phase, the *supercritical* phase, exists. An illustration of CO₂ phase change can be found on Youtube: [CO₂ Phase Changes | Danfoss Cool | Video english - YouTube](#)



> **Figure 1:** CO₂ phase diagram

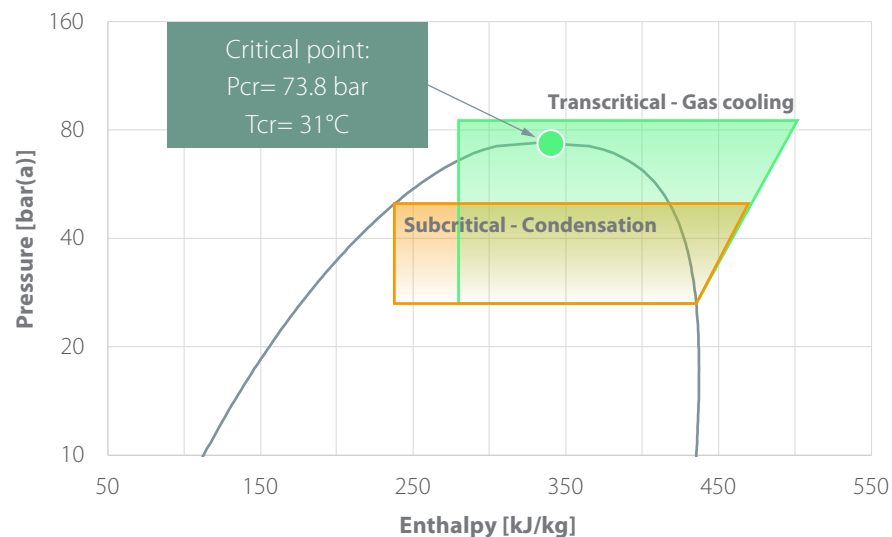
Subcritical and Transcritical cycles

The refrigeration vapor compression cycle typically operates in a *subcritical* mode, meaning that the operating pressures fall below the critical point but remain above the triple point. This can be observed in Figure 2, which depicts a pressure-enthalpy (P-h) diagram. In vapor compression cycles, refrigerants operate usually within subcritical conditions.

Beyond the critical point on the P-h diagram lies the supercritical phase. A *transcritical* cycle is capable of operating in both subcritical and supercritical regions. Among refrigerants, CO₂ stands out as the only one able to operate in transcritical mode in refrigeration, heat pump, and air conditioning applications. The ability to operate transcritically depends on high-pressure control and thermal boundaries.

By rejecting waste heat into the atmosphere during warm ambient conditions or recovering it for heat reclaim, the cycle can operate in the supercritical phase using transcritical mode. The advantages of heat recovery in the supercritical phase will be explored in subsequent chapters. Figure 3 illustrates an example of a transcritical cycle.

In the subcritical mode, heat rejection is accomplished through condensation, while in the transcritical mode, it is achieved through gas cooling. To fulfill this purpose, CO₂ refrigeration systems employ a specific heat exchanger called a gas cooler. The gas cooler plays a vital role in the CO₂ refrigeration system by facilitating efficient heat transfer during the gas cooling process.

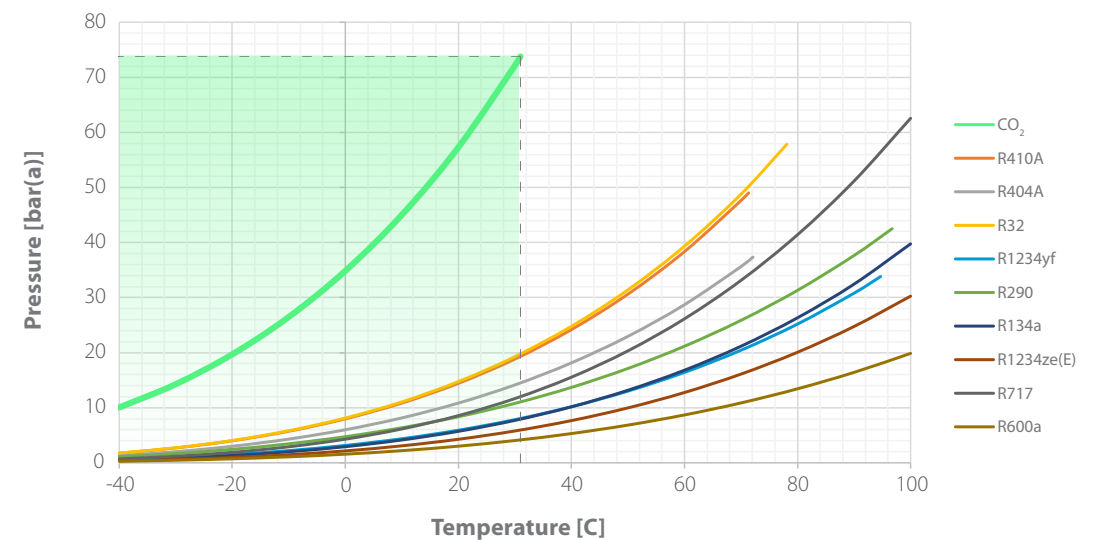


> Figure 2: CO₂ Subcritical and Transcritical cycles

Vapour compression and the cooling effect

Figure 3 illustrates the saturation lines of CO₂ and several conventional refrigerants. A clear distinction can be observed: CO₂ operates at significantly higher pressures compared to other refrigerants at identical

saturation temperatures. For instance, while the evaporating pressure of all the refrigerants shown at 0°C is less than 10 bar, it reaches 35 bar for CO₂.



> Figure 3: Saturation lines of refrigerants

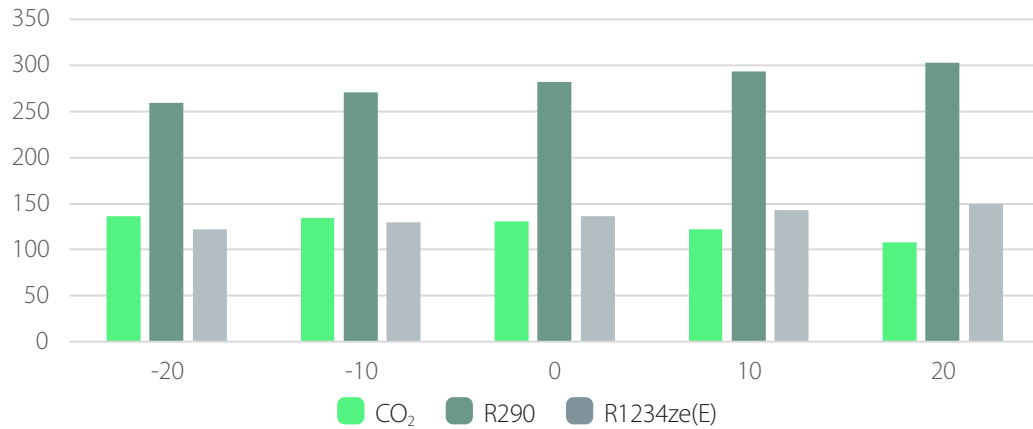


The high operating pressure of CO₂, particularly at the compressor suction, translates to a higher volumetric cooling capacity VCC. The volumetric cooling capacity (expressed in kJ/m³) is calculated by multiplying the latent heat of vaporization (in kJ/kg) by the suction density (in kg/m³).

$$VCC \left[\frac{kJ}{m^3} \right] = Latent\ heat \left[\frac{kJ}{kg} \right] * \rho_{suction} \left[\frac{kg}{m^3} \right]$$

The latent heat of vaporization represents the enthalpy difference over the evaporator between saturated vapor and inlet liquid refrigerant at a specific saturated pressure/temperature. It indicates the refrigerant's

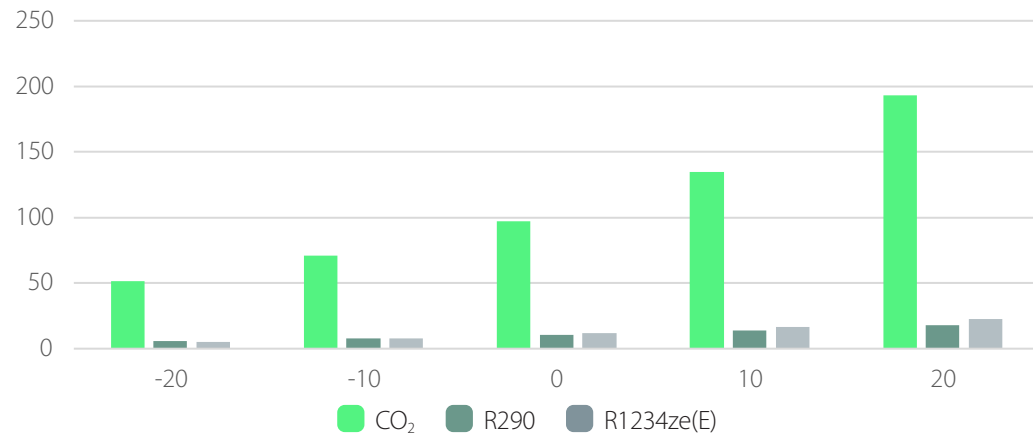
ability to absorb heat in the evaporator while undergoing the two-phase condition. Figure 4 provides an example comparing the heat of vaporization of CO₂ with two other refrigerants, R290 and R1234ze(E).



> **Figure 4:** Latent heat of vaporization [kJ/kg] at five evaporation temperatures. The high pressures assumed for similar condenser/gas cooler exit temperature of 35°C.

Another important parameter for evaluating refrigerant performance is its density at the compressor suction. Higher density implies a lower required volumetric flow rate. Figure 5

illustrates the saturated vapor density of CO₂ in comparison to the two refrigerants at various evaporation temperatures. CO₂ exhibits considerably higher density.

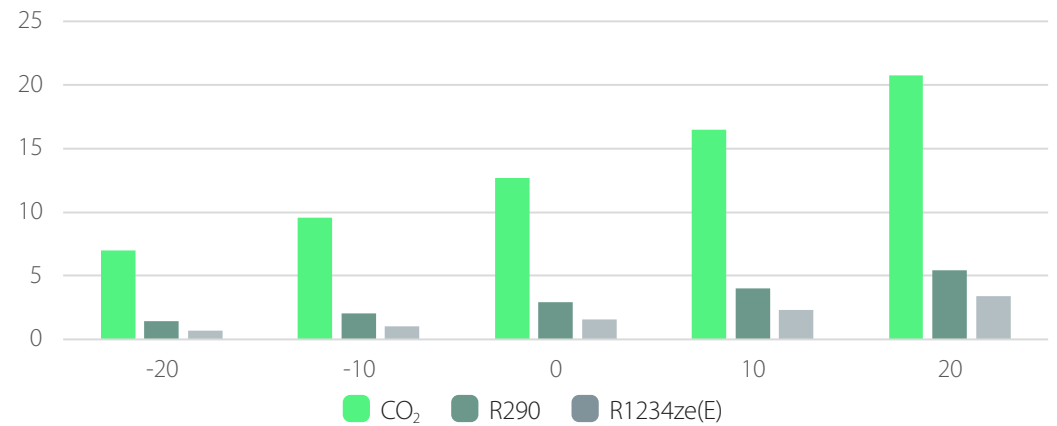


> **Figure 5:** Suction vapour density at five evaporation temperatures [kg/m³]

This substantial difference in density leads to a significantly higher volumetric cooling capacity for CO₂, as depicted in Figure 6. This pattern is not limited to this particular example but holds true when comparing CO₂ with many other refrigerants.

the required volumetric flow rate of a CO₂ compressor is much smaller compared to other refrigerants. This means a more compact compression volume within a specific compressor. This also means smaller pipe diameters transmitting the refrigerant.

Essentially, this means that in order to transfer a specific amount of heat in the evaporator,



> **Figure 6:** Volumetric cooling capacity [MJ/m³]

Heat rejection: condenser vs gas cooler

A significant difference between CO₂ and other refrigerants becomes apparent when considering the heat rejection on the high pressure side. In a refrigeration system, the heat exchanger dedicated for heat rejection is typically referred to as a condenser since it facilitates the condensation of the refrigerant from vapor to liquid. However, in a CO₂ system operating in transcritical mode, this heat exchanger is known as a gas cooler. This distinction arises because there is no condensation process or phase change involved in transcritical mode.

To gain a better understanding of this distinction, let's compare CO₂ with Propane R290 (representing hydrocarbon refrigerants) and R1234ze(E) (representing synthetic refrigerants). The evaporation temperature in this example is -10°C.

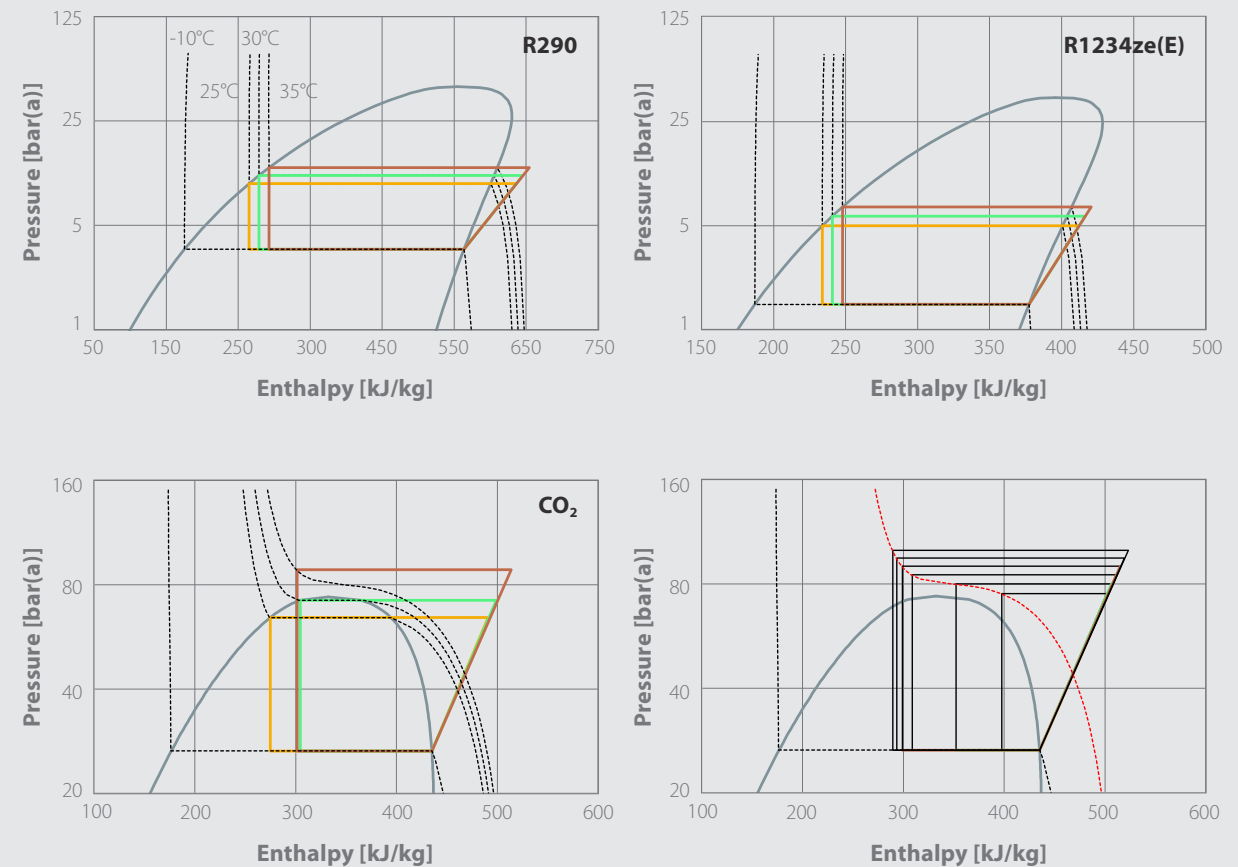
Isothermal lines play a crucial role in this analysis, and Figure 7 showcases the heat rejection at three different temperatures: 25°C, 30°C, and 35°C, with dotted lines representing the isothermal lines. The three cycles appear relatively similar for R290 and R1234ze(E). The condensation pressures for these refrigerants are dependent on the condensation temperature.

While CO₂ cycle operates in the subcritical region, the heat rejection at 25°C condensing temperature is similar to other refrigerants. At 30°C, the operation remains subcritical, but the heat of condensation—representing the enthalpy difference between saturated vapor and saturated liquid at 30°C—is relatively small. Consequently, the condensation process is not energy-efficient. Thus, it is common to avoid operating near the critical temperature, and control mechanisms enforce higher pressures above the critical point.

Moving along the isothermal lines at 35°C, the system operates in the transcritical mode. In the supercritical region, pressure and temperature become independent variables. This means the pressure can be controlled while keeping the temperature fixed at 35°C. This can be seen in Figure 7, bottom-right. The optimum control of the pressure for max energy efficiency is discussed in subsequent chapters.



Overall, these observations highlight the unique behaviour of CO₂ compared to other refrigerants, especially when it comes to heat rejection. The transcritical operation mode of CO₂ introduces distinct pressure and temperature dynamics, necessitating specific control strategies to optimize system performance.



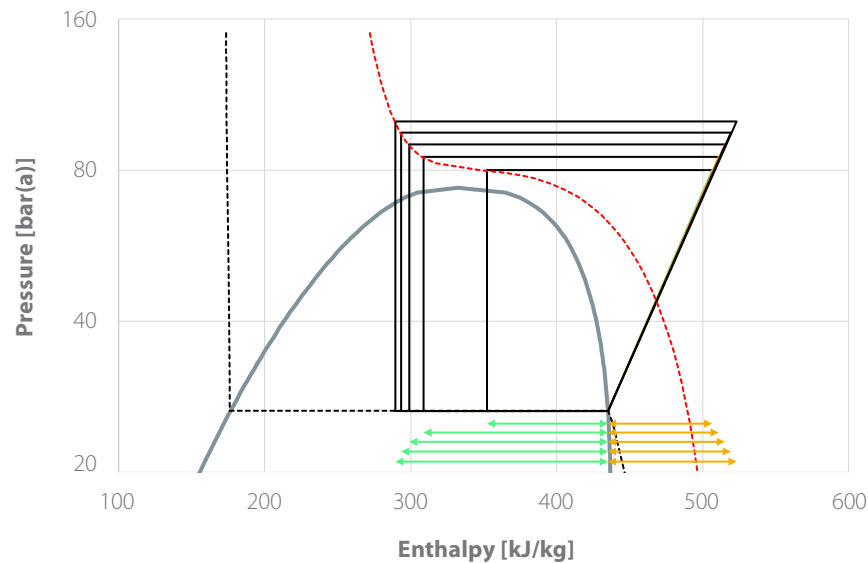
> **Figure 7:** Thermodynamics cycles and heat rejection isothermal lines of R290, R1234ze(E) and CO₂ @ temperatures 25, 30 & 35°C. Evaporation temperature = -10 °C. Bottom-right: heat rejection at variable supercritical pressures and fixed gas cooler exit temperature of 35°C.

Discharge pressure control

Effective control of the gas cooling pressure plays a vital role in optimizing the energy efficiency of the system. An optimization algorithm is required to achieve the highest possible coefficient of performance (COP) at every gas cooler outlet temperature. Figure 8 shows an example of various cycles operating at 80, 85, 90, 95 and 100 bar discharge pressure while gas cooler outlet temperature is constant at 35°C.

While conventional refrigerants benefit from lowering the condensation pressures to enhance energy efficiency, the optimal pressure for a CO₂ system operating in transcritical mode must be regulated by the control

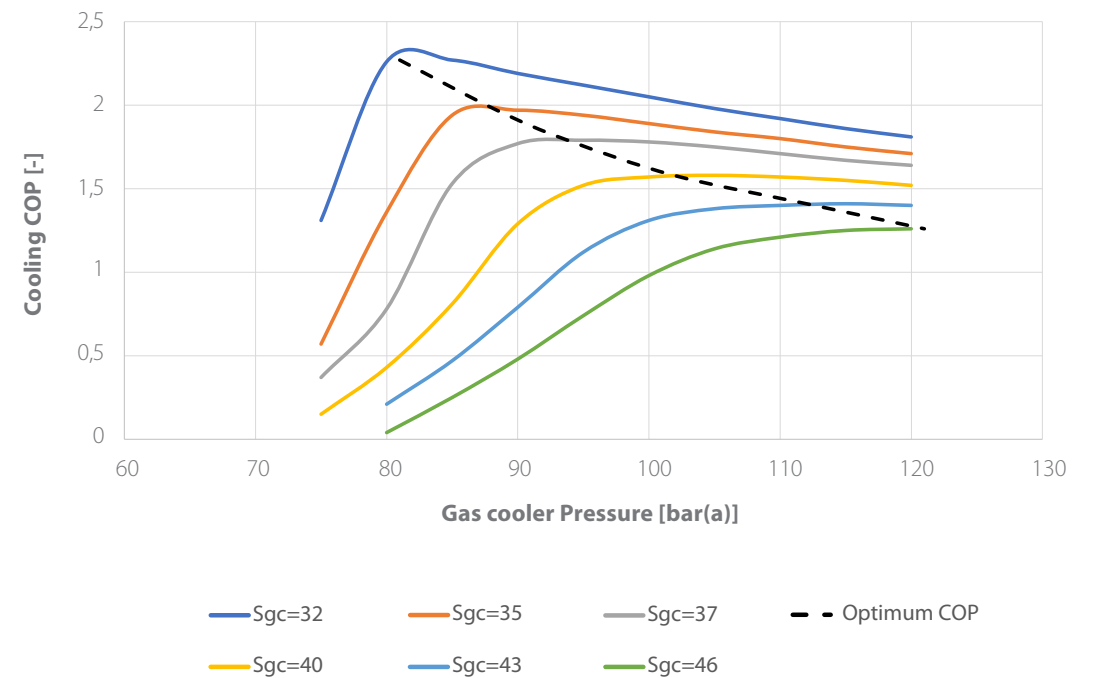
system to maximize energy efficiency. The lowest pressure in the example, 80 bar, is not the optimum pressure as there is not enough enthalpy difference over the evaporator (short blue line). The pressure should be raised to higher values to achieve better performance of the system. This behavior differs from that of other refrigerants and highlights the unique characteristics of CO₂ systems. In transcritical mode a marginal increase in pressure will result in an increase in enthalpy of compression. If this increase results in even larger enthalpy gain in the heat exchangers, it results in a COP increase. When the enthalpy net gain reaches zero the optimum has been found.



> **Figure 8:** Transcritical cycles at fixed gas cooler outlet temperature 35°C, @ Gas cooler pressures 80, 85, 90, 95, 100 bar

What is shown in Figure 8 means that high pressure can be controlled as a function of gas cooler outlet temperature since these two parameters are independent in supercritical region. So let's have a practice, calculating the COP of a system as a function of different gas cooler outlet temperatures.

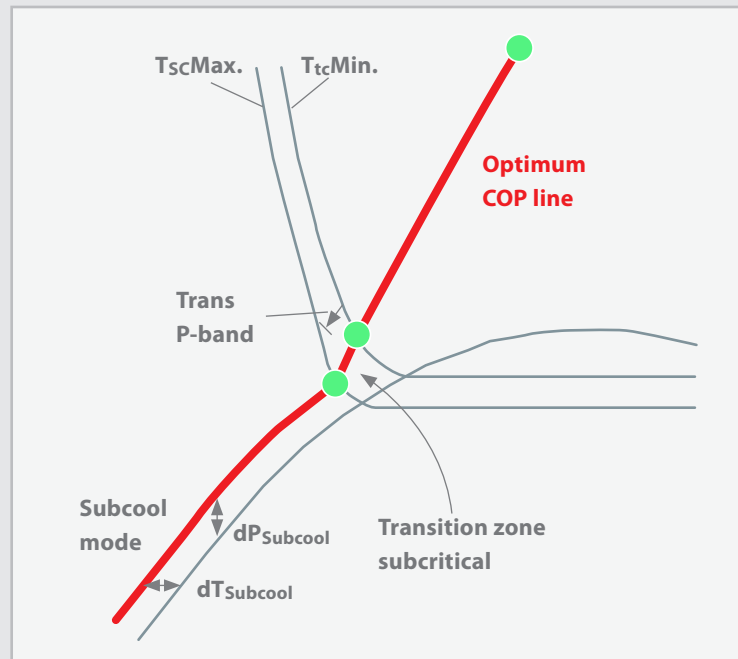
Figure 9 shows the calculation of cooling COP as a function of gas cooler pressure and 6 outlet temperatures, marked as Sgc. Cooling COP is defined as the ration of cooling capacity to the electricity use. If max cooling COPs of the sets are connected, an optimization algorithm can be generated (the dotted line).



> **Figure 9:** Cooling COP as a function of gas cooler pressure and outlet temperature - Optimum pressure control line



This was a simple example of optimum pressure control. Danfoss uses the same fundamentals but applies more advanced algorithms on how to control the discharge pressure in supercritical, subcritical, and transition zone between this two, as shown in Figure 10.



> **Figure 10:** Optimum pressure control

At subcritical temperatures the system is controlled as a conventional refrigeration system where the subcooling is the control parameter on high pressure side (normally, control is not necessary with condensing refrigerants).

At temperatures approaching the critical point the algorithm changes, gradually increasing the subcooling to bridge the gap between conventional control and transcritical control. The system operates in transition mode to avoid the losses in efficiency and stability happening close

to the critical point. To have a smooth change, set subcooling increases when the condensation temperature reaches "max subcritical temperature" T_{scMax} . When the condensation temperature reaches "min transcritical temperature" T_{tcMin} , the system starts to follow an optimum COP algorithm in transcritical mode.

At transcritical conditions, the pressure is a function of the temperature out of the gas cooler. The goal is to obtain as high a COP as possible at the given temperature, shown as optimum COP line.

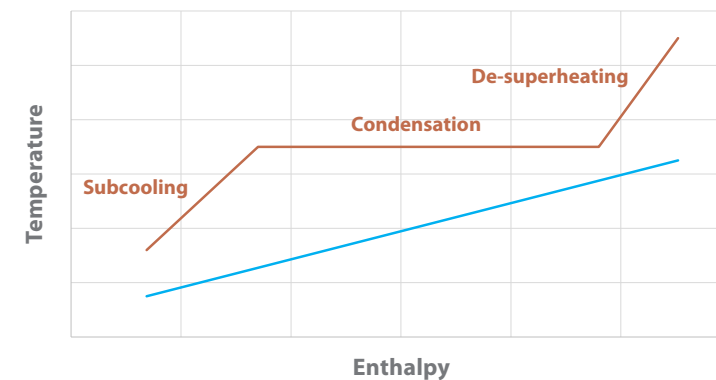
The gas cooler fans are controlled by the CO_2 temperature out of the gas cooler. If the temperature is lower than the set point, the fans slow down. When no compressors are running, the fans stop as well.

Air-cooled gas coolers are often used in refrigeration systems where there is no heat reclaim or only partial heat reclaim. Typically fin and tube gas coolers are used for CO_2 . The refrigerant charge in the gas cooler varies greatly with pressure and temperature, magnifying the need for a heat exchanger with small internal volume.

Water cooled gas coolers are usually used in CO_2 systems for heat recovery or heat pump functions. Understanding the temperature profiles is vital to operate this heating system in the optimum way. These profiles can be compared for a conventional and CO_2 refrigerants.

Figure 11 shows the heat transfer process in a condenser while heating a water stream, the blue line. This heat transfer is usually composed of three sections: de-superheating, condensation, and subcooling of the refrigerant.

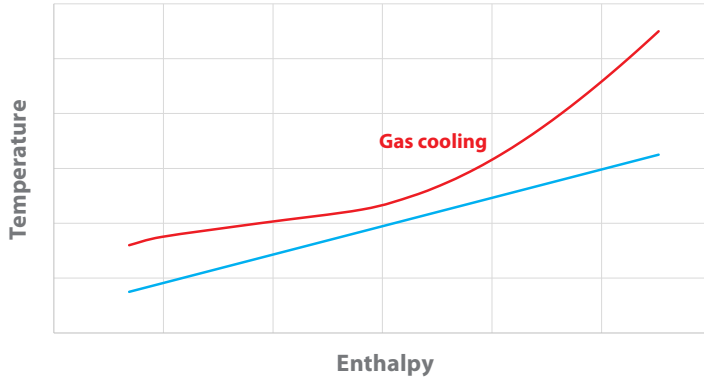
The closest point between the two lines is called the pinch point. It is desired to have the pinch point as small as possible: closer refrigerant-water temperature profiles means more efficient heat transfer. And a more compact heat exchanger can be used. Pinch point of the conventional refrigerant cycles usually occurs close to the de-superheating section at the inlet of the refrigerant side. This means water outlet temperature (forward temperature) dictates the refrigerant condensation temperature and pressure.



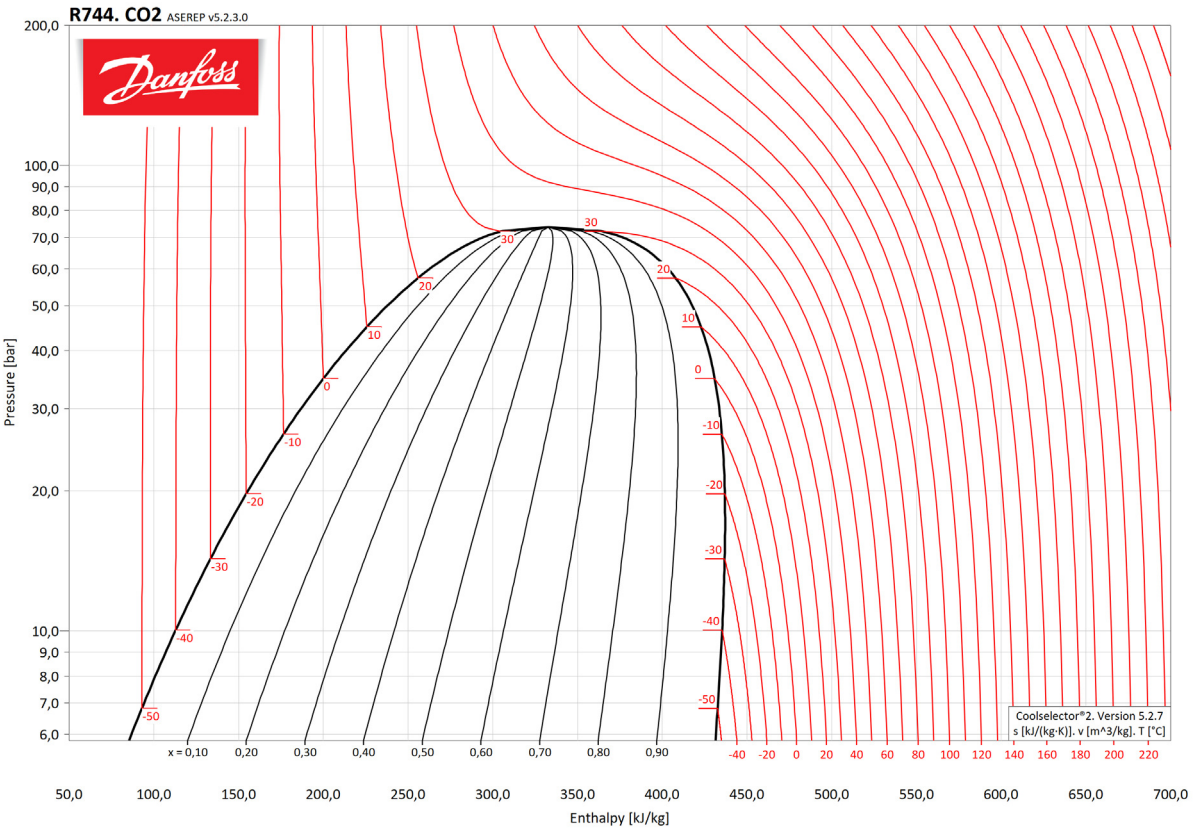
> **Figure 11:** Heat transfer in the conventional refrigerants' condensers

CO₂-water temperature profiles can be seen in Figure 12. As shown here, the pinch point occurs in the middle or the outlet section of the gas cooler. This means the gas cooling pressure is strongly governed by the water inlet

temperature, called water return temperature. This is an important difference compared to other refrigerants and will be discussed in details in the subsequent chapters.



> **Figure 12:** Heat transfer in CO₂ gas coolers





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