



ALL FACTS:
CO₂ AS A REFRIGERANT

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NEW-OLD REFRIGERANT

Carbon Dioxide for Industrial Refrigeration

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Carbon dioxide (CO₂) is an old refrigerant, first patented in the United Kingdom in 1850 by Alexander Twining, where it was subsequently used in air-conditioning and marine applications. With the development of the CFC, HCFC, and HFC synthetic refrigerants beginning around 1930, CO₂ decreased in popularity, all but disappearing by 1960. Over the next two decades or so, it was experimentally determined that CFC and HCFC refrigerants were depleting the earth's upper atmospheric ozone layer at a rate that would likely cause its disappearance.¹

In response to these findings, many countries agreed to halt the production of these CFC and HCFC refrigerants within an appropriate time frame, allowing the ozone layer to replenish. This agreement is called the Montreal Protocol where its second and fourth amendments concern CFCs and HCFCs.^{2,3} At this same time, Lorentzen^{4,5} proposed CO₂ as an alternative refrigerant for the CFC and HCFC refrigerants. After CO₂'s reintroduction, applications first appeared with mobile air conditioning and heat pump water heaters. Other applications soon followed, which include CO₂ as a heat transfer fluid, low-temperature refrigerant in a cascade refrigeration system, or as the sole refrigerant. In North America, more than 150 supermarket transcritical and other CO₂ systems are in operation,⁶ and over 70 NH₃-CO₂ industrial subcritical cascade systems operating with many being planned.⁷

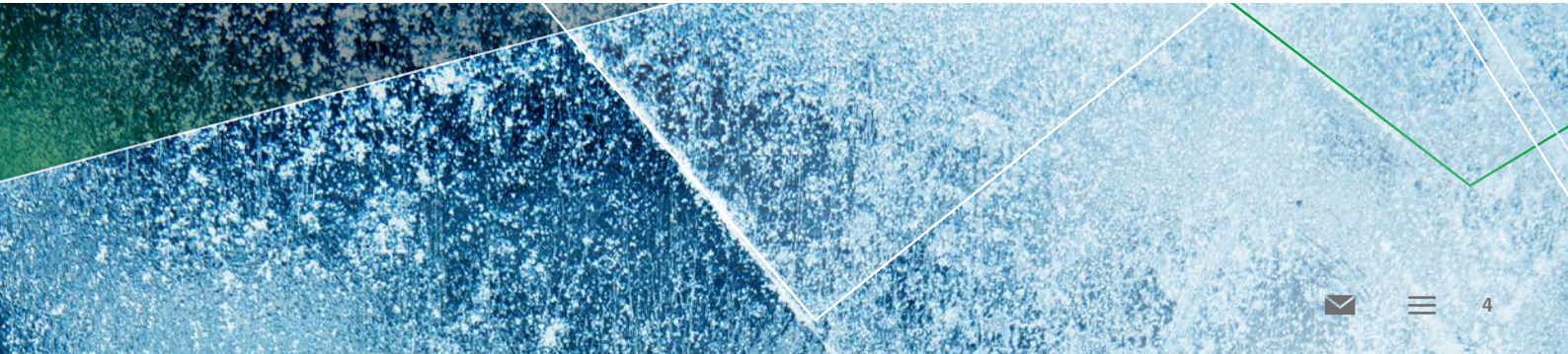


Transcritical refrigeration cycles involve CO₂ gas cooling (rather than condensation for heat rejection) at conditions above the refrigerant's critical point where the refrigerant is called a "supercritical fluid" and behaves as a dense gas.⁸ In contrast, subcritical refrigeration systems operate at conditions below the critical point where phase change, condensation, occurs. The focus of this article is industrial refrigeration where CO₂ is used as a refrigerant.

CO₂ is a naturally occurring substance because it is present in the earth's atmosphere at a concentration of about 404 ppm (v/v). The other substances classified as natural refrigerants are ammonia, water, air, and hydrocarbons, all of which are naturally occurring.

Scientific study of the atmosphere has revealed that the CO₂ in the earth's atmosphere is a significant contributor to global warming. The important sources of atmospheric CO₂ are emissions from fossil fuel electrical power generating plants and from combustion engines powering vehicles of all types. Currently, regulations do not limit CO₂ quantities that may be vented from a refrigeration system.

The ozone depletion potential for all the natural refrigerants is zero. The global warming potential for these refrigerants is either zero, or very small. The global warming potential of CO₂ is 1.0 (set to this value by definition), where in contrast the CFC and HCFC refrigerants have values generally exceeding 1,000.



CO₂'s Physical Characteristics

The physical characteristics of CO₂ are unique. The thermodynamic vapor compression refrigeration cycle, component design, system design, and operation are constrained by the characteristics of CO₂, which are shown in Table 1. Note that the freezing point (triple point) of CO₂ is -56.6 °C (-69.8 °F), and NH₃'s freezing point is -77.7 °C (-107.8 °F), both in the same neighborhood.

However, the critical temperature of CO₂ is 31.0 °C (87.8 °F) and 132.3 °C (270.1 °F) for NH₃, much less than NH₃'s. While the freezing point (triple point) for CO₂ is not much different than NH₃'s, the CO₂ critical temperature is significantly less than that of NH₃.

R-22, an HCFC whose production is now curtailed, was once a popular refrigerant for industrial systems. Refrigerants R-507A and R-404A are an azeotrope and blend, respectively, and both are HFCs. Their high GWP makes their future as refrigerants uncertain. NH₃, despite its good thermodynamic characteristics, has disadvantages including toxicity and moderate flammability. These reasons now make CO₂ a refrigerant worthy of consideration for many applications in industrial refrigeration systems.

Table 1: CO₂ and other refrigerant physical properties.⁹

	R-22	R-507A	R-404A	NH ₃	CO ₂
Natural Substance	No	No	No	Yes	Yes
Chemical Formula	CHClF ₂	R-125/143a (50.0/50.0)	R-125/142a/134a (44.0/52.0/4.0)	NH ₃	CO ₂
Molecular Mass	86.5	98.9	97.6	17.0	44.0
ODP	0.04	0	0	0	0
GWP	1,790	4,000	3,700	<1	1
Critical Pressure (psia)	723.7	537.4	540.8	1,643.7	1,070.0
Critical Temperature (°F)	205.1	159.1	161.7	270.1	87.8
Boiling Point (°F)^a	-41.5	-52.1	-51.2	-28.0	-109.1 ^b
Freezing Point (°F)	-251.4	-	-	-107.8	-69.8
Flammable	No	No	No	Yes	No
Toxic	No	No	No	Yes	No
Ashrae Safety Group	A1	A1	A1	B2L	A1

^a At 14.696 psia; ^b Sublimes



Figure 1 is a plot of saturation pressure versus saturation temperature for several refrigerants including CO₂ and NH₃, which shows:

- The absolute CO₂ triple-point pressure 5.18 bar (75.1 psi) is above atmospheric pressure.
- The CO₂ critical-point temperature is less than typical design condensing temperature.

Note that CO₂ is a low-temperature refrigerant (above atmospheric pressure at low temperatures) where in contrast, NH₃ is an intermediate-temperature refrigerant. The CO₂ phase diagram is shown in [Figure 2](#) where only essential features are shown. Here the latent heat of CO₂ is indicated by the horizontal distance between the saturated liquid and vapor lines. Comparison to R-22 reveals that the latent heat of CO₂ is considerably higher than, but not as high as, NH₃'s latent heat. Also, the CO₂ pressure-enthalpy diagram shows that CO₂ exists with high pressures and low temperatures – the top of the dome (critical point) is only 31.0 °C (87.8 °F).

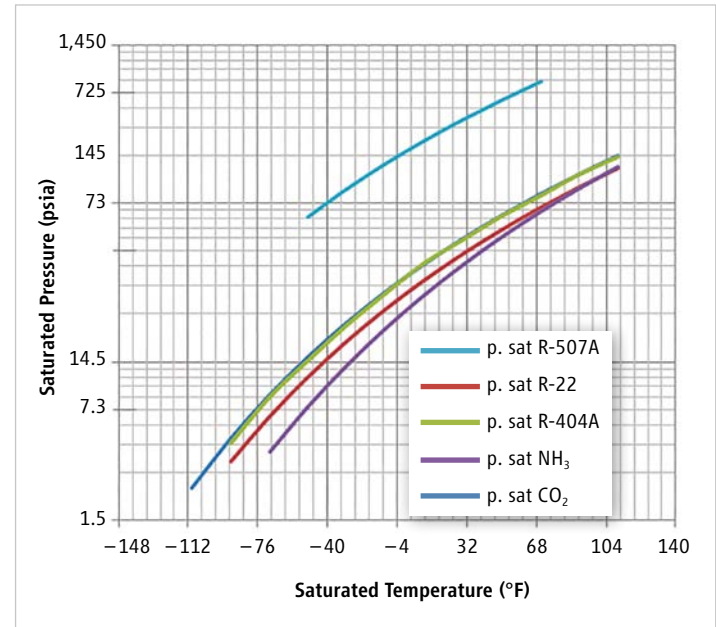


Figure 1: Saturated pressures and temperatures for several refrigerants.



Figures 3 and 4 show the saturated liquid and saturated vapor lines for CO₂ and NH₃ on p-h (pressure-enthalpy) axes, respectively. These two charts and the characteristics mentioned above result in important and practical consequences when applying CO₂ to industrial refrigeration.

Because of CO₂'s high pressures, atmospheric air and water are not likely to enter the system. And, because CO₂'s suction vapor density is high, compressors are small and evaporators operate with good performance. Further, observe (Figure 1) that the slope of the pressure-temperature curve for CO₂ shows a much greater pressure change for the same temperature change. In other words, pressure drops in CO₂ result in much smaller temperature drops. For example, saturated CO₂ vapor at -42.8 °C (-45 °F) with a 0.07 bar (1.0 psi) pressure drop has a corresponding 0.22 °C (0.4 °F) temperature drop.

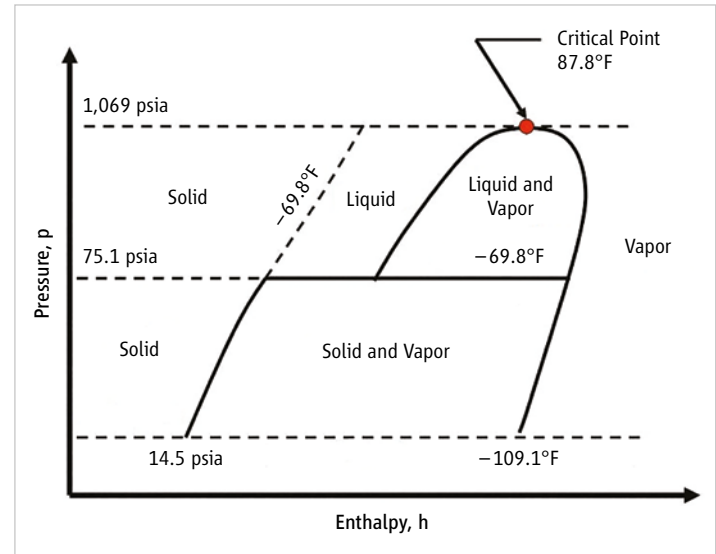


Figure 2: Pressure-enthalpy diagram for CO₂.⁹

In contrast, saturated NH_3 vapor at -42.8°C (-45°F) with 0.07 bar (1.0 psi) pressure drop has a corresponding 2.0°C (3.6°F) temperature drop that is larger by a factor of about 9 or 10. These consequences add together, giving CO_2 excellent characteristics for subcritical vapor compression refrigeration cycles.

A concern with CO_2 is the possible formation of solid CO_2 (dry ice) in the outlet piping from a pressure safety relief valve blocking the vapor flow. Observe from [Figure 2](#) that CO_2 back pressures less than the triple-point absolute 5.2 bar (75.1 psi) will result in the formation of dry ice.

For relief valves connected to a compressor's discharge or protecting a liquid separator, the risk of solidification is minimized when the CO_2 discharge is piped to an outlet header. Relief valves protecting components or vessels containing saturated liquid CO_2 should be located outdoors and have no outlet piping to avoid solidification.



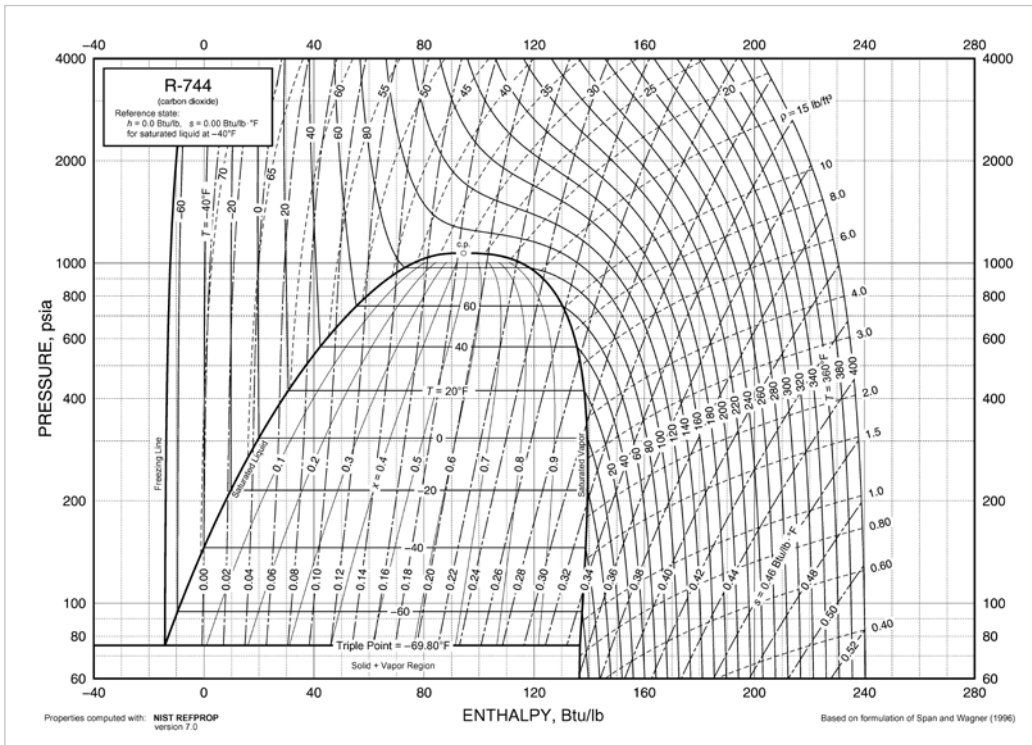


Figure 3: Pressure-enthalpy diagram for CO₂.¹⁰

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CAMh and CAMhk series with PN52 design for handling CO₂



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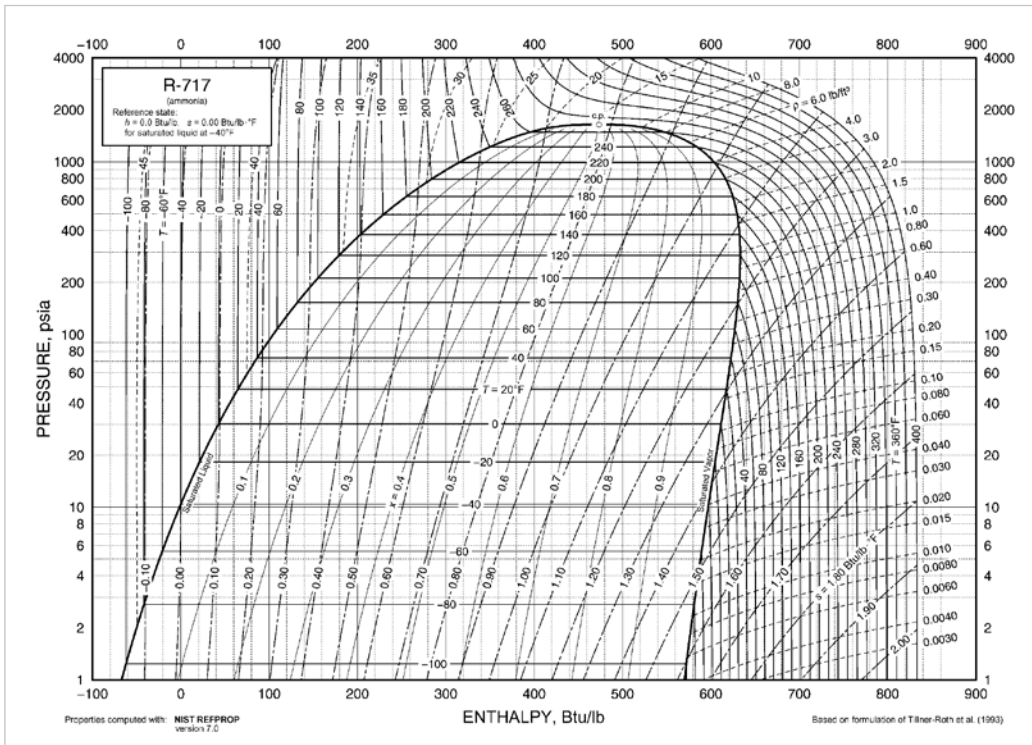


Figure 4: Pressure-enthalpy diagram for NH₃.¹⁰

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CO₂ Vapor Compression Cycles

CO₂ Transcritical Cycle

The basic vapor compression refrigeration cycle consists of four components where the refrigerant is conveyed to and from the components by the interconnecting piping. Figure 5 is a schematic showing these components and how they are connected to each other. Figure 6 is a p-h diagram of CO₂ where the cycle state points are shown. The cycle shown is a transcritical vapor compression cycle because the heat rejection process occurs above CO₂'s critical pressure and consists of "gas cooling" rather than ordinary condensation. Presently, this cycle is being applied to commercial refrigeration systems such as supermarkets.

The fadeout vessel shown in Figure 5 limits the CO₂ pressure during a shutdown. Located on the low-side of the system and oriented so liquid may drain during operation, its volume is such that as liquid flashes into vapor upon warming, the pressure increase is maintained at a modest level. Other methods include relieving the pressure by safety relief valves and subsequent recharge or by a small recondensation unit.

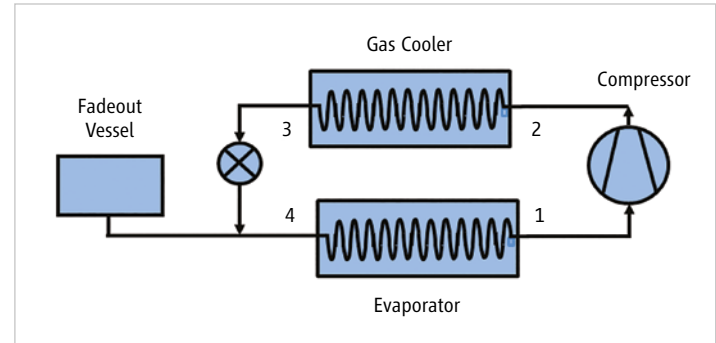


Figure 5: Transcritical vapor compression refrigeration cycle components.

For all refrigeration systems using CO₂, the level of water contamination must be kept low. The water that may be present could be liquid, ice, and/or hydrates (crystalline solids that appear as ice). The ice and hydrates form in the low-temperature side of the system, particularly behind expansion devices and inside receivers, pumps, and evaporators. Currently, it is recommended that the water content be maintained at a concentration of 10 ppm (v/v) or less, preventing formation of hydrates.⁸

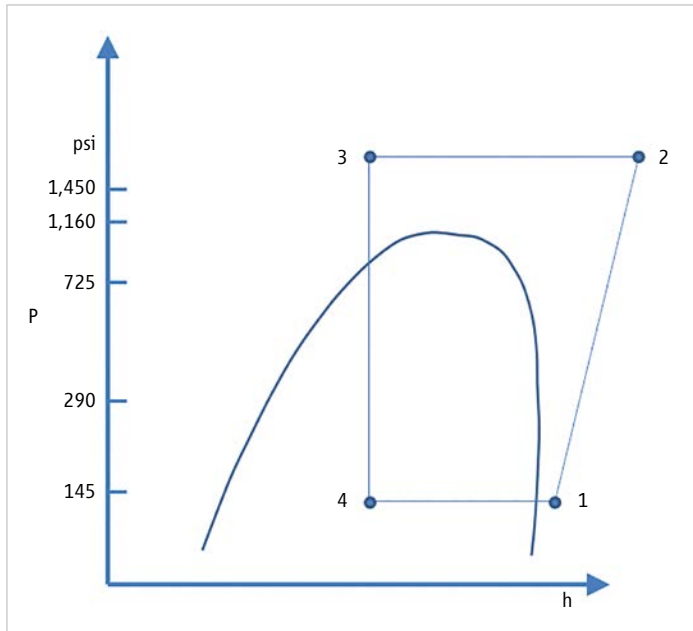


Figure 6: p-h diagram for the transcritical compression refrigeration cycle.

CO₂–NH₃ Cascade Cycle

Industrial refrigeration systems operate with significantly larger capacities, resulting in larger component sizes for evaporators, compressors, condensers, control valves, vessels, and piping, among others. Due to the high pressures of CO₂ when above the critical point, industrial refrigeration systems are currently designed as subcritical cycles in which the CO₂ pressure remains below the critical pressure where manufactured components are generally available at the working design pressure. With subcritical cycles, the heat rejection process involves the phase change from vapor to liquid, which is actual condensation. The focus of the remainder of this article is CO₂ subcritical vapor compression refrigeration cycles as they are applied in the field of industrial refrigeration. General references regarding CO₂ refrigerant in industrial refrigeration systems include the ASHRAE Handbook – Refrigeration⁹ and the IIAR (International Institute of Ammonia Refrigeration) CO₂ Handbook.⁸

CO₂ when used in subcritical vapor compression cycles appears on the low-temperature circuit of a cascade system or as a secondary coolant where the highest CO₂ pressure is modest. In either situation, NH₃ is confined to the machinery room with a much reduced charge. A schematic of a CO₂–NH₃ cascade system is shown in Figure 7 where the high-temperature circuit (5-6-7-8) uses NH₃ and the low-temperature circuit uses CO₂ (1-2-3-4).

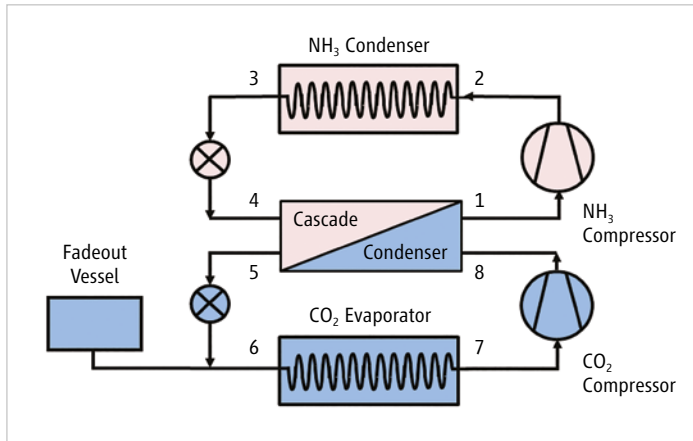


Figure 7: Cascade vapor compression refrigeration system.

A cascade heat exchanger transfers the heat from the low-temperature circuit to the high-temperature circuit; it serves as both an evaporator and as a condenser. A favorable temperature difference in the cascade condenser is needed to transfer heat from the CO₂ to the NH₃ and is typically designed between 13.3 °C (23.9 °F) and 12.2 °C (21.96 °F), balancing equipment and operating costs as shown in [Figure 8](#).

The cascade heat exchanger is crucial in the operation of the CO₂–NH₃ cascade system. It must prevent leakage of CO₂ to the NH₃ side which, if it occurs, would likely shut down the system. Approaches to avoid shutdown of the system include: redundant heat exchangers that may be isolated and alarming systems detecting leaks before the system shuts down. The design pressure on the CO₂ side of the cascade heat exchanger is high – about absolute 41.4 bar (600 psi). Three types of heat exchangers are suitable for the cascade heat exchanger: shell-and-tube, plate-and-frame, and shell-and-plate.

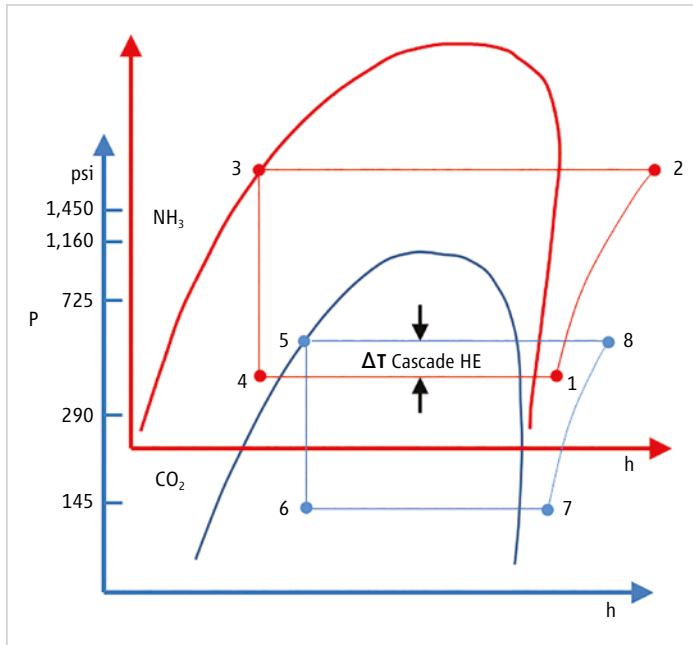


Figure 8: Pressure-enthalpy diagram for the NH_3 - CO_2 cascade refrigeration system.

Shell-and-tube: This configuration is an acceptable choice, but suffers the disadvantage of a relatively high NH_3 charge and large footprint. To reduce the risk of leakage in the tube and tube-sheet joints, shell-and-tube heat exchangers are available with double-tubes (concentric), providing an additional barrier to leakage.

Plate-and-frame: These heat exchangers are relatively small and need only small NH_3 charges. Additionally, their configuration is such that if a weld fails, the CO_2 will not leak into the NH_3 . Because of the high CO_2 design pressure, fully welded construction is required.

Shell-and-plate: A moderately low NH_3 charge, small footprint, and lower cost than plate-and-frame heat exchangers characterize these units. The plate-stack (inside of which the CO_2 condenses) is submerged in NH_3 , so any leak that may occur will allow CO_2 to enter the NH_3 side.

If a leak were to occur on the high CO₂ pressure side of the cascade condenser, the CO₂ would leak into the NH₃ and chemically react to form ammonium carbamate (H₂NCO₂NH₄), which is corrosive to steel and appears as a white powder precipitate. If ammonium carbamate forms, it clogs the system, especially filters and valves. Therefore, detectors are used to instantly sense the presence of ammonium carbamate, closing automatic isolating valves and alerting plant personnel, so the contamination does not spread throughout the system. Fortunately, ammonium carbamate can be washed out with hot water.

Figure 9 shows the predicted performance of an ideal CO₂–NH₃ cascade cycle compared to that of an ideal two-stage NH₃ refrigeration system. “Ideal” refers to the following conditions: saturated liquid at exit of condenser, saturated vapor at exit of evaporator, no pressure losses and no heat transfer in piping, and 0°C (0°F) approach temperature for the cascade condenser. The NH₃ two-stage has a greater COP compared to the CO₂–NH₃ cascade system for evaporating temperatures varying from –28.9°C (–20°F) to –51.1°C (–60°F) for cascade condenser temperatures –23.2°C (–10°F), –17.8°C (0°F), and –12.2°C (10°F), for 0°C (0°F) approach temperature.

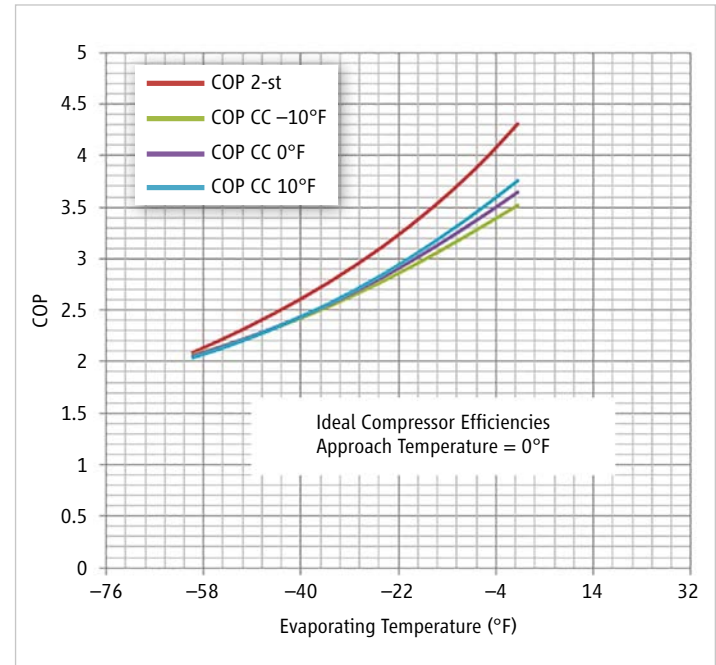


Figure 9: Variation of ideal NH₃ two-stage cycle COP with ideal CO₂–NH₃ cascade cycle COP with evaporating temperature at 0°F approach temperature and different cascade temperatures.

The influence of the cascade temperature is observed to be small. At about -0.6°C (31°F), the NH_3 two-stage COP is approximately 10% greater than that of the $\text{CO}_2\text{-NH}_3$ cascade and decreases to about 1% greater at -51.1°C (-60°F). Figure 10 uses realistic compressor efficiency for the NH_3 two-stage and $\text{CO}_2\text{-NH}_3$ cascade systems to predict COP where the cascade temperature and cascade approach temperatures are fixed at -6.7°C (20°F) and -4.4°C (8.0°F), respectively.

Figure 10 predicts that the $\text{CO}_2\text{-NH}_3$ cascade COP overtakes the NH_3 two-stage at roughly -42.8°C (-45°F) evaporating temperature. Operating experience reported by Toogood¹¹ for one $\text{CO}_2\text{-NH}_3$ cascade system used in a cold storage warehouse -28.9°C (-20°F) freezer, -6.7°C ($+20^{\circ}\text{F}$) cooler and dock with blast freezing -50°C (-58°F) demonstrated reduced electrical power consumption for refrigeration by 5.8% compared to a two-stage NH_3 system. Lynch¹² has subsequently reported similar results for eleven $\text{CO}_2\text{-NH}_3$ cascade systems operating throughout the United States.

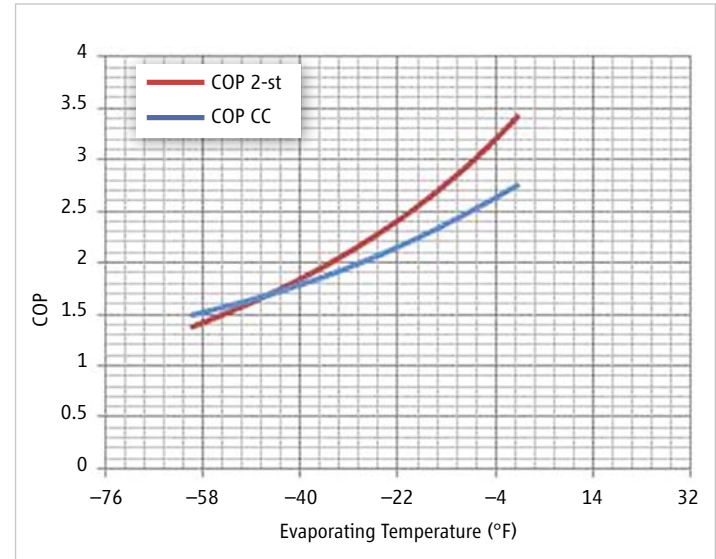


Figure 10: Comparison of cycle COP for NH_3 two-stage with cycle COP for $\text{CO}_2\text{-NH}_3$ cascade using realistic compressor efficiencies where the cascade temperature is 20°F and the approach temperature is 8.0°F .

CO₂ as a Secondary Coolant

CO₂ used as a secondary coolant in conjunction with a vapor compression system is shown schematically in Figure 11. In this instance, the entire refrigeration capacity is developed by the two-stage NH₃ refrigeration system, which cools the CO₂ secondary coolant in an NH₃ evaporator (liquid chiller).

The two-stage NH₃ charge is significantly reduced because it is only needed by the evaporator, condenser, piping, and the vessels in the machinery room, except for the outside evaporative condenser. However, if the evaporative condenser were replaced with a cooling tower and heat exchanger, all the NH₃ charge could reside in the machinery room. Specifically, Figure 11 shows a pumped recirculating liquid coolant CO₂ system where liquid is both supplied to the CO₂ process heat exchanger and returned.

Alternatively, a volatile liquid CO₂ system is possible where CO₂ boils in the CO₂ process heat exchanger now serving as an evaporator, returning vapor (or mixture) back to the NH₃ evaporator for condensing as shown in [Figure 12](#), where the CO₂ state points 10 and 11 reveal the CO₂ liquid-to-vapor conversion. The advantage of the volatile

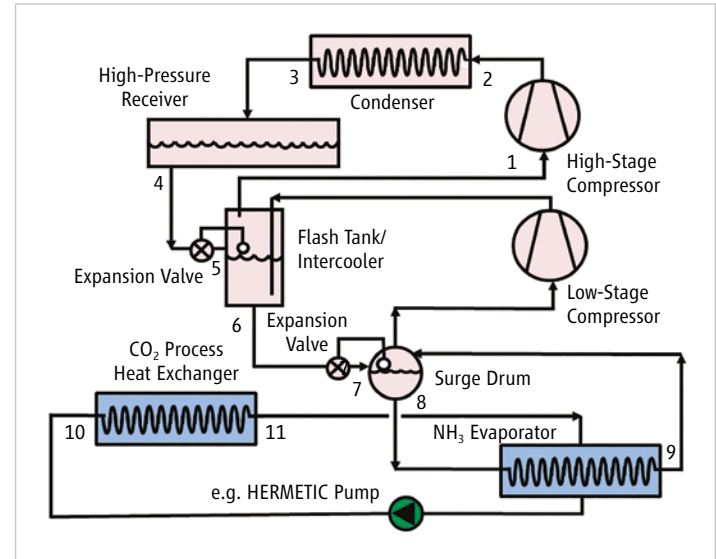


Figure 11: Two-stage NH₃ vapor compression system with CO₂ as a secondary coolant.

fluid is the reduced CO₂ charge. Boiling in the CO₂ evaporator uses CO₂'s latent heat of evaporation (330.3 kJ/kg [142 Btu/lb]) rather than its relatively low liquid specific heat (2.1 kJ/kg·K [0.5 Btu/lb·°F]). Thus, a volatile fluid system delivering one pound of CO₂ provides 142 Btu (149 kJ) of refrigeration, converting to a vapor, while an entirely liquid system with a liquid temperature increase of 5.6 °C (10 °F) merely provides 11.6 kJ/kg CO₂, or 5 Btu/lb CO₂. Another possibility is direct expansion in the CO₂ evaporator and subsequent CO₂ recondensing. Combinations of the CO₂ systems described above are also possible.

Generally, lubricating oil is not present in the CO₂ passing through the evaporators. In this way, the greatest overall heat transfer coefficient is achieved, resulting in very good system performance. Oil-free reciprocating compressors are available for use with CO₂. Lubricated reciprocating or screw compressors may also be used in conjunction with oil separators using both mechanical separation and coalescing elements. One caution is in order: components such as valves and controls must be able to operate oil-free.

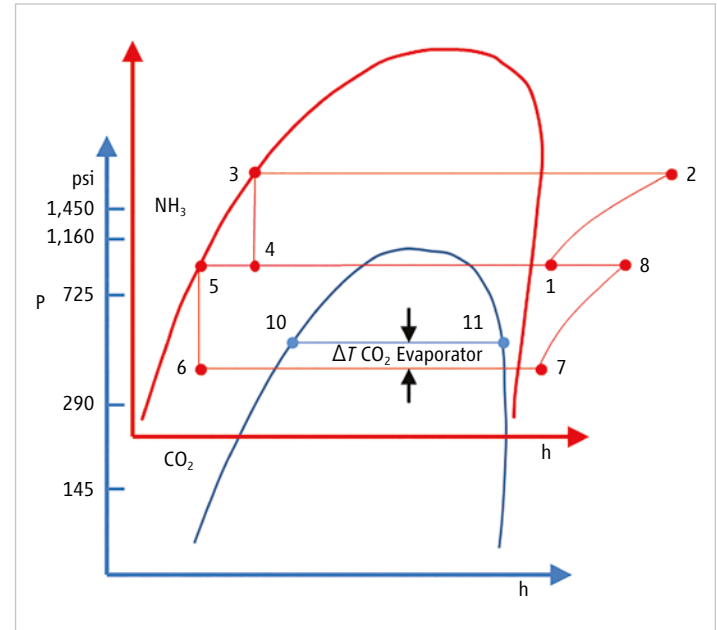


Figure 12: p-h diagram for CO₂ as a volatile secondary fluid.

Conclusions

CO₂ is one of the five natural refrigerants and over the past 20 years has gained popularity, particularly with low-temperature refrigeration for industrial systems. When CO₂ is used in a cascade or a secondary coolant refrigeration system, the ammonia system charge is reduced by about 80% and confined to the machinery room where the consequences of a leak or spill are decreased. However, CO₂ is not

without drawbacks, two of which are high system working pressure and limited useful operating temperature range of -53.9°C (-65°F) to 26.7°C (80°F). Manufacturers are adding high-pressure components to their offerings, supporting the application of refrigerant CO₂. With continued good engineering design and industry support, CO₂ will increase its popularity as an industrial system refrigerant.

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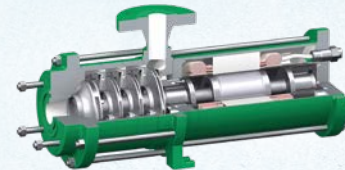
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