Ammonia as a refrigerant

CO_2 liquefaction in focus

By Stephen B. Harrison, sbh4 consulting

© SICGIL | Bulk liquid CO_2 tanker, India

Compression of carbon dioxide (CO_2) to a supercritical state and transmission by pipeline can be a cost-effective way to move large quantities of carbon dioxide from sources to sinks. Carbon capture and storage (CCS) and enhanced oil recovery (EOR) schemes in North America have used this method for several decades.

Pipelines are efficient, but inflexible. They can link points A and B at a very low long-term cost, but they do not offer the flexibility of a road, rail or shipping logistics network. Furthermore, the planning and construction of pipeline infrastructure can be prohibitively expensive and too slow for project developers who wish to commence operations in the next 10 years.

CO_2 utilisation to produce e-fuels such as e-methanol and synthetic aviation fuel (eSAF) is destined to ramp up during this decade. This will pull for a flexible liquid CO_2 distribution network enabled by new CO_2 tanker ships and rail waggons. Efficient CO_2 liquefaction will be at the heart of this value chain. Use of ammonia as a refrigerant gas (R717) combined with a pressurised CO_2 system has been deployed in many cases in recent decades and is now widely accepted as the most efficient way to liquefy CO_2 at scale.

Ammonia for CO_2 liquefiers

"In India, ammonia has been used as a refrigerant gas for CO_2 liquefiers for about 50 years," says Pulin Modi, Safety & Technical Director at SICGIL Industrial Gases Limited in India.

"SICGIL operates more than 20 CO_2 liquefiers and not a single one uses F-Gas."

Industrial or commercial-grade ammonia at 99.8% purity is normally used in India. In some other countries, a refrigerant grade of ammonia is available.

Ammonia is ideal as a refrigerant gas to use in the CO_2 liquefaction cycle for several reasons. Firstly, it is readily available with a low cost of around €1 per kg. This is a significant saving versus suitable alternative F-Gas refrigerants which typically cost in the range of €7 to €10 per kg.

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Ammonia cylinders and PPE

Ammonia refrigeration piston compressor

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Process design for high efficiency

In the liquefier, CO_2 gas is compressed to around 18 to 20 bar to enable its liquefaction at a moderate temperature. With fewer inert gas impurities in the CO_2 feed, the lower pressure of 18 bar can be used. There is a trade-off between the outlet pressure, size and cost of the CO_2 compressor, and the type of refrigerant gas that can be used and the required refrigerant gas compressor.

A two-stage screw, or reciprocating, compressor with interstage and second stage cooling is the ideal compressor configuration. "In our four tonne per hour liquefiers, we use 355 kW frame size ammonia compressors. This increases to 550 kW for our 6.7 tonne per hour CO_2 liquefier unit," Modi adds.

Normally the ammonia compressor suction pressure is just above atmospheric pressure at around 0.1 psi(g). This avoids the risk of air ingress into the system. Allowing for the pressure drop of gaseous ammonia between the CO_2 liquefier and the ammonia compressor suction, the corresponding liquid ammonia temperature in the CO_2 liquefier will be close to -33°C.

Performance advantages of ammonia

Like ammonia, R12 could achieve -29°C. Other F-Gases can achieve lower temperatures (R22 down to -40°C, R404A down to -45°C and R410A down to -51°C), but the compressor must operate at a higher pressure and therefore consumes more power. A larger and more expensive compressor would also be required.

Ammonia has a higher latent heat of evaporation compared to F-Gases such as R12 and R404A. The implication is that only $1/7^{th}$ of the refrigerant gas inventory is required. Compared to these F-Gas alternatives, ammonia has a lower condensation pressure and temperature – which means a higher co-efficient of performance (CoP) and less electrical power consumption is required to achieve the same cooling effect.

Ammonia allows for a flooded condenser design, which generates a higher efficiency for heat transfer than gas-to-gas heat exchangers that would be required when using other refrigerant gases. The flooded system also allows for smaller pipe sizes, which helps to keep capital costs low.

Heat is removed from the ammonia through heat exchange with cooling water, through an evaporative condenser. Ammonia flows through the tubes of the condenser, and these are immersed in the cooling water to cool the ammonia as close as possible to the wet bulb temperature of water.

Safety around ammonia systems

"Ammonia is a toxic gas, so designing the equipment with safety in mind is essential," says Modi. "Our ammonia vessels and piping are designed for 18 bar(g) pressure operation and hydraulicly tested for 27 bar(g) pressure."

Safety relief valves are fitted to each vessel, but they should not need to open. The set pressure of the relief valves should never be achieved due to the function of the automated process control system, which ensures that the ammonia compressor will trip if its outlet pressure reaches 16 bar (g).

Ammonia can be used in most parts of the world for CO_2 liquefiers. In extremely warm locations, where peak summer temperature may rise to around 50°C, the system must be designed for a higher operating pressure of 24 bar(g) and a commensurately higher test pressure must be used.

Each vessel containing ammonia can be covered with a water sprinkler. If there is an accidental ammonia gas leakage, the water sprinklers can be activated, and ammonia gas will absorb into the water to avoid a toxic ammonia gas cloud being formed.

Ammonia gas and flame detection

Suitable gas and flame detection equipment can be installed around the ammonia refrigeration system. The Refrigeration Standard EN 378-1:2016 Annex C advocates alarm points at 500 as an early warning and a high level alarm at 30,000 ppm (parts-per-million) of ammonia to protect the plant from an ammonia explosion.

Whilst these high levels are appropriate to protect the equipment, employees must be protected at lower concentrations of ammonia. For toxic detection the COSHH regulation specifies a limit of 25 ppm over eight hours and 35 ppm over 15 minutes. These are the levels that are generally built into portable gas detectors that operators wear as part of their personal protective equipment.

Flame detectors for ammonia are specialised and differ from those used with hydrocarbon flames such as gasoline or natural gas. Ammonia burns with an inorganic flame and detection of the infrared signature associated with methane or carbon dioxide is therefore not possible. Detection in the UV spectrum is used for ammonia and hydrogen to overcome this issue.

Top up and system maintenance

The ammonia refrigeration circuit will breathe air (and atmospheric moisture) from the atmosphere. After a long period of usage, this air needs to be removed.

"SICGIL uses an automatic air purger to remove air from the ammonia," confirms Modi. "We also use an ammonia purifier to remove oil and water from the ammonia refrigerant gas."

Ammonia is highly soluble in water. So, a water and ammonia mixture will convert to an aqueous solution. Compressor crank case oil will carry forward along with discharge ammonia gas from compressor. This oil carry over would also be the case when using F-Gases. Using the air purger and ammonia purifier, if there is no leakage from the system, there is no need to top up or replace the ammonia charge during normal operation.

If the ammonia refrigeration system requires maintenance, the entire ammonia charge in the system must be pumped down to a receiver and condenser. After pump down, only gaseous ammonia will remain in the piping system. Normally, when the system is not in a ▸

working condition, the system pressure will be 10 bar(g). At this pressure the density of gaseous ammonia is 8.25 kg/m³. So, the residual volume of ammonia to be diluted in water or vented will be small.

During system recommissioning after maintenance, leak testing with ammonia can be done using phenolphthalein. One drop of this liquid chemical is applied to a cotton cloth, which is held close to flanges and valve glands. If ammonia leakage is present, even at a ppm level, the cloth will immediately turn pink. Any minor leakage detected through this procedure can be attended to with appropriate maintenance.

Global ambitions

SICGIL operates CO_2 liquefiers in several countries in Asia. The quality of the CO_2 produced has been acknowledged by major soft drinks brands as ideal for beverage carbonation.

In addition to industrial gas operations, SICGIL offers CO_2 liquefier design and EPC services internationally. "Our experience operating CO_2 liquefiers positions us as the ideal partner to design systems – we know exactly what will work in the real world," says Modi. He adds that "recently, we were excited to have had the opportunity to quote a leading German specialty chemicals operator for a CO_2 liquefier."

"Their requirements were highly specific, with a relatively high nitrogen content in the CO_2 feedgas to be liquefied. They also specified a low turn-down ratio with the need for efficient operation over the annual duty cycle. Our solution was to offer a multi-train CO_2 liquefier with ammonia refrigeration."

"We are highly optimistic that we will be supplying many of our CO_2 liquefier and ammonia chiller systems internationally this decade." gw

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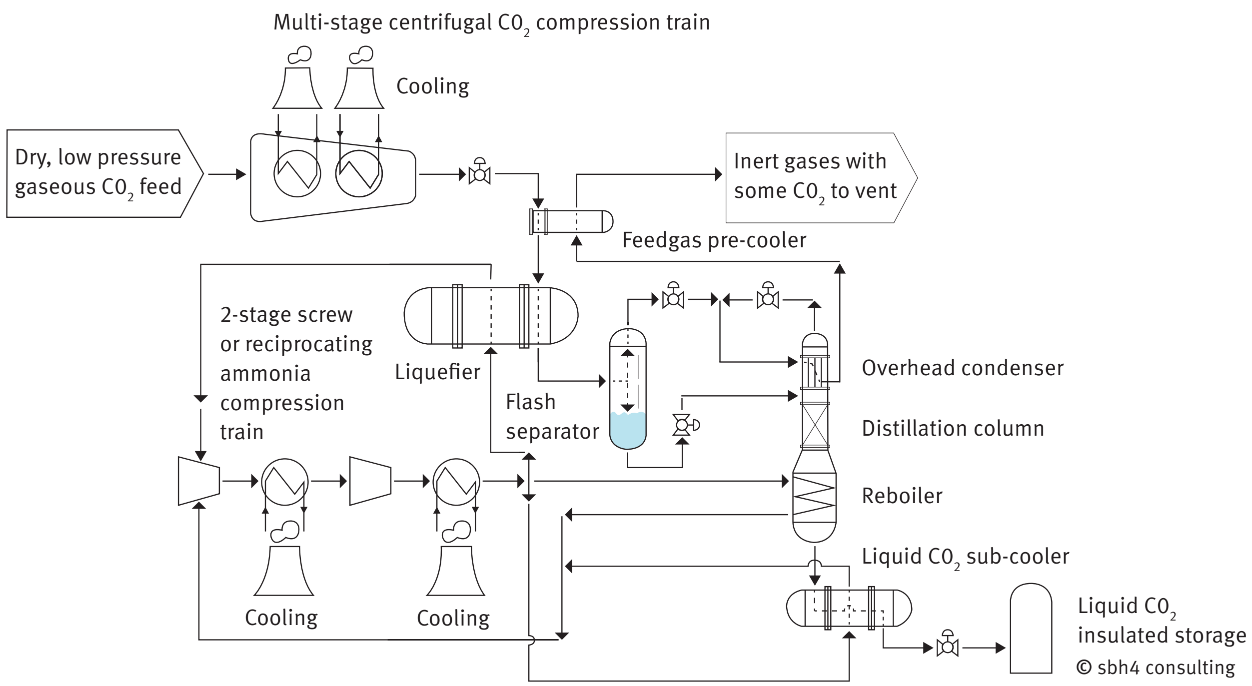
C02 Liquefier with Ammonia Refrigeration Cycle



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