Froya liquid CO_2 tanker on the Kiel Canal

Transportation enabler: using 'zero, zero' ammonia refrigerant gas for CO_2 liquefaction

Connecting CO_2 sources to sinks is often forgotten in CCS terminology. The full supply chain could be called 'CCTUS' or CO_2 capture, transportation and utilisation or storage. The mid-stream CO_2 transportation segment is either done using supercritical CO_2 through high pressure pipelines, or with liquid CO_2. CO_2 liquefaction can be achieved using chillers that are charged with F-Gases or ammonia. However, an outright ban on the use of F-Gases and other fluoropolymers is being debated in the EU. Ammonia offers high efficiency CO_2 liquefaction and eliminates the global warming risks of inadvertent F-Gas emissions. Ammonia also has zero ozone depletion potential.

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CO_2 transmission is super-critical

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. CCS and EOR schemes around the world have used this method for several decades.

Pipelines are efficient, but inflexible. They can link points A and B, but 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 commercial operations in the next 10 years.

CO_2 utilisation to produce electro-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 cars. Efficient CO_2

liquefaction will be at the heart of this value chain.

Use of ammonia as a refrigerant gas to provide the low temperatures for CO_2 liquefaction has been widely deployed in recent decades, due to it being a highly efficient way to liquefy CO_2 at scale.

Ammonia - a cost-effective refrigerant gas

Ammonia has been used as a refrigerant gas for CO_2 liquefiers for more than 50 years and is ideally suited to the CO_2 liquefaction cycle. 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 between €7 and €10 per Kg.

Industrial or commercial grade ammonia at 99.8% purity is normally used for refrigeration applications. In some countries, a low-moisture, oil free grade of ammonia for refrigeration is available.

A two-stage screw, or reciprocating, compressor with interstage and second stage cooling is the ideal ammonia compressor configuration. For a 50 tonne per day liquefier, an ammonia compressor of approximately 350 kW would be required. This increases to around 530 kW for a 150 tonne per day CO_2 liquefier.

Petra-Nova CO_2 supercritical pipeline. Copyright NRG Energy.

Normally the ammonia compressor suction pressure is just above atmospheric pressure at around 0.01 bar(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.

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 down to the wet bulb temperature of water.

Alternative F-Gas liquefier systems

In the CO_2 liquefier, the CO_2 gas is compressed to around 20 bar to enable its liquefaction at a moderate temperature by the chilled liquid ammonia. There is a trade-off between the size and cost of the CO_2 compressor and the size of the refrigerant gas compressor and the type of refrigerant gas that must be used.

Use of R12 as a refrigerant could achieve -29 °C, close to the temperature achieved with ammonia. Other F-Gases can achieve lower temperatures. R22 can operate at -40 °C, R404A down to -45 °C and R410A down to -51 °C. Chilling to these lower temperatures means the CO_2 would need to be compressed to a pressure less than 20 bar. However, the refrigerant gas compressor would need to operate at a higher pressure and therefore consume more power. A larger and more expensive refrigerant gas 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 1/7th 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.

Of the above F-Gases gases, R404A has a global-warming potential (GWP) of 3,920. R410A has a lower GWP of 2,088. R22 is slightly less at 1,810, however, unlike R404A and R410 it does not have zero ozone depletion potential (ODP). Due to the presence of chlorine in the R22 molecule, its ODP is 0.05. R12 is the most environmentally damaging of these gases, with an ODP of 1 and GWP of 10,800.

The GWP of ammonia is zero. It also has zero ODP. There is no

Cryogenic liquid CO_2 distribution by road

other refrigerant gas suitable for CO_2 liquefaction that has these ‘zero, zero’ environmental credentials.

Safety around ammonia refrigeration

The ammonia refrigeration system vessels and piping are generally designed for 18 bar(g) pressure operation and hydraulicly tested for 27 bar(g) pressure. In extremely warm locations, where peak summer temperature may rise to around 50 °C, the system must be designed for a higher pressure of 24 bar(g).

Safety valves are fitted to each vessel, but they should never need to open, because their set pressure is never achieved. This is because the automated process control system ensures that the ammonia compressor will trip at about 2 bars below the relief value set pressure.

For safety, 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 will absorb into the water to avoid a toxic gas cloud being formed.

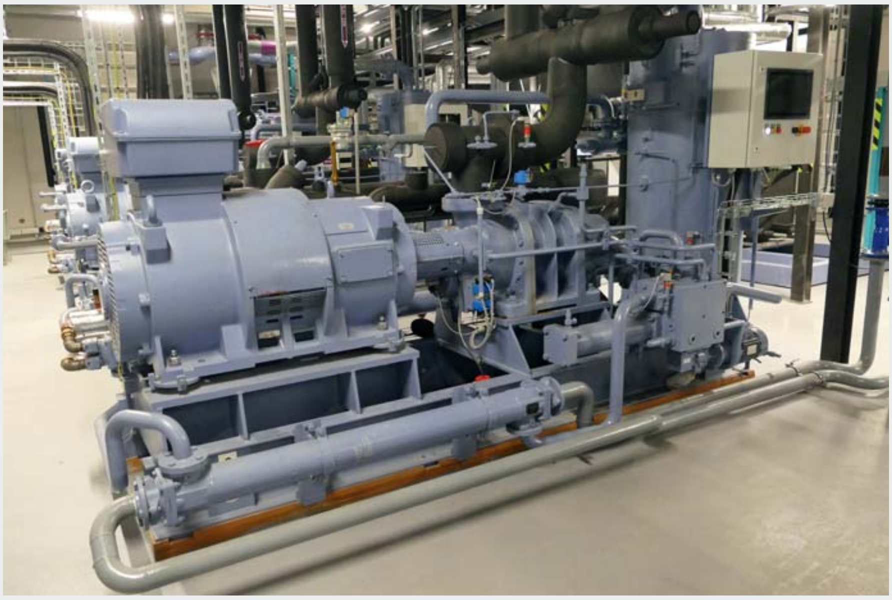
Suitable gas and flame detection equipment can be installed around the ammonia refrigeration system. The EN378 standard advocates detection and alarms at 500 and 30,000 ppm of ammonia to protect the plant from an ammonia explosion.

Whilst these high levels are appropriate to protect the equipment, employees must be protected at lower levels. For toxic detection the COSHH regulation specifies a limit of 25ppm over 8 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. 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.

Installation and maintenance precautions

Ammonia system will breathe air (and atmospheric dew) from the atmosphere. Air can be removed using an automatic air purger to remove air from the ammonia. Ammonia is highly soluble in water. So, a water and ammonia mixture will convert to an aqueous solution.



Screw compressors are ideal for ammonia refrigeration circuits.

An ammonia purifier is also located in the refrigeration gas circuit to remove water. Compressor crank case oil will carry forward along with discharge ammonia gas from compressor. This oil carry over is also removed in the ammonia purifier.

If the ammonia refrigeration system requires maintenance, the entire ammonia charge in the system must be pumped down to a receiver and condenser. Normally when system is not in working condition, system pressure will be 10 bar(g). At this pressure the density of ammonia is 8.25 kg/m^3. So, the residual volume of ammonia to be diluted in water / vented will be small.

After installation or maintenance, leak testing on the high-pressure CO_2 side of the equipment can be performed using a traditional soapy bubble leak test. However, leak testing on the ammonia circuit is 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 an ammonia leak is present, even at a ppm level, the cloth will immediately turn pink. Any minor leakage detected through this procedure can be attended to prior to operating the system after maintenance.

Sustainable methanol shipping will require CO_2 utilization.