

How to manage cryogenic boil-off

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LPG Tanker

Cryogenic liquefaction of a gas consumes mechanical energy which is generally provided from an electrical motor through a compressor. Once liquefied, the gas is colder than the ambient surroundings.

Regardless of how good the insulation around the cryogenic liquid storage vessel is, it will not be perfect. So, over time, it is inevitable that heat will 'leak' into the liquefied gas and it will progressively 'boil-off' to become a vapour, known as boil-off gas (BOG).

When a liquefied cryogenic gas boils-off, the pressure inside the storage vessel increases. To protect the vessel, it must be fitted with a pressure relief vent valve and potentially also a bursting disc. If boil-off is not controlled, BOG will be vented and lost from the system.

The BOG will certainly have a financial value both from the chemical itself and the energy that has been used to liquefy it. Additionally, it may be toxic (ammonia), flammable (hydrogen), asphyxiant (carbon dioxide) or a highly potent greenhouse gas (methane). Therefore, it is essential to mitigate boil-off to prevent monetary loss, and to protect people, assets and the environment.

Liquid hydrogen and super insulation

The temperature difference between cryogenic liquid hydrogen, when

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stored at circa 5 bar, and normal ambient temperature is about 270°C. That is more than the temperature difference between your hand and a pan of boiling frying oil. In this most severe case, super insulation using a combination of vacuum and multi-layer insulation (MLI) is essential to avoid rapid boil-off and loss of liquid hydrogen.

Cryogenic vacuum insulation is achieved by using two steel, or stainless steel tanks. One is placed inside the other and a support structure links the two. Between the two tanks there is a gap of circa 100mm. A vacuum is pulled between the two tanks to minimise conductive heat transfer. The presence of the vacuum means that the outer tank is exposed to "under-pressure" so it must be strong to avoid crumpling inwards.

Also, inside the space between the two tanks, there are multiple layers of a reflective material MLI which prevents radiative heat ingress to the cryogenic liquid. MLI is made of alternating layers of Mylar film, coated with a microscopic layer of aluminium, and a fine mesh, generally made of polyester

or nylon. This MLI is like the coating used on satellites, where the film is often coated with a microscopic layer of gold for even better radiation protection.

Closed loop cryogenic reliquefaction

Liquid helium and liquid hydrogen are used in superconductivity and deep space research where ultra-low temperatures are required. Deliveries of liquid or gaseous helium and hydrogen incur cost and, in space-constrained research centres, they can be logistically inconvenient. The solution is to charge the system with the require gas or liquid during startup, and then perpetually reliquefy the boil-off gas over the years of operation.

At small-scale, the Stirling Cycle is an ideal process for reliquefaction of BOG at the ultra-low cryogenic temperatures encountered with liquid helium and hydrogen. The cycle compresses the helium or hydrogen in a piston in the cryogenerator. The heat of compression is removed, and the gas is expanded. The process repeats this cycle to create a sufficiently cold environment in the machine to liquefy the gas.

A single cryogenerator can be used during startup to liquefy the initial supply of gaseous hydrogen or helium and then to reliquefy BOG that is produced during normal operation. During BOG reliquefaction, less electrical power is required than during the high-intensity startup phase because the gas entering the Stirling cryogenerator is cold.

Liquid CO₂ and foam insulation

The temperature of liquid carbon dioxide (CO₂) at the pressure under which it is normally stored (circa 15 bar) is around -30°C. Much warmer than the liquid hydrogen, which is around -250°C. This means the temperature difference, which is the driving force for heat to leak into the storage tank, is around 50°C: substantially less than in ▶

Liquid hydrogen sphere
Kennedy Space Centre
Cape Canaveral



▶ the case of liquid hydrogen.

Cryogenic liquid CO₂ can be stored in a vacuum insulated vessel. However, due to the smaller temperature difference to ambient conditions, it is also possible to use a foam insulation layer. The converse does not apply for very cold cryogenic liquids such as nitrogen, hydrogen or LNG. They must be stored in vacuum insulated tanks. In a foam-insulated tank, they would boil off within hours due to the high amount of heat ingress caused by the large temperature difference between

LNG delivery, Revithoussa Greece



will need 10 cryogenic road tanks to support liquid nitrogen logistics, and 10 to support their CO₂ distribution requirements, the lowest capital solution would be to purchase 10 super insulated vacuum tanks for the liquid nitrogen and 10 foam insulated tanks for the CO₂.

On the other hand, if the demand for either of these two liquefied gas distribution tanks changes due to distribution distances increasing, or the balance of the two products shifting in the market then there is no possibility to use the foam-insulated tanks for liquid nitrogen. Additional assets must either be purchased or leased.

If the operator had initially purchased a fleet of 20 vacuum insulated tanks, the initial capex would be higher, but the operational flexibility would be greater. Additionally, owning fewer assets reduces maintenance costs.

the liquid and the ambient conditions.

Use of foam, instead of the vacuum, reduces the cost and weight of the storage tank. Since there is no vacuum, the foam can be covered in a thin, lightweight aluminium shroud which is much lighter, and less costly than the strong outer jacket that is required for the cryogenic vacuum insulation.

Operational considerations

For an industrial gas distribution business which operates with multiple cryogenic liquids, such as nitrogen and CO₂, there is a trade-off between storage tank asset flexibility and capex minimisation.

If a business estimates that they

Product transfer

When a cryogenic liquid is transferred from one tank to another, the receiving tank is likely to be either empty or only partially full with the cryogenic liquid product. The implication is that much of the receiving tank may be a slightly

© Linde Gas | Liquid CO₂ road tanker, Ketzin Germany



higher temperature than the cryogenic liquid that is being introduced. The result is that some of the liquid boils-off.

Also, to transfer the liquid there must be a pressure drop between the source and the receiving tank. This pressure drop also results in cryogenic liquid 'flashing' or boiling off during the product transfer. A good way to visualise this is to observe what happens when a bottle of fizzy water is opened. As the pressure is reduced, gas bubbles emerge as dissolved CO₂ 'flashes' out of the water.

To avoid product loss, with its adverse financial, safety and environmental consequences, the boiled-off vapours are not vented to the atmosphere. Instead they can be used to maintain the pressure in the tank to provide the driving force which transfers the liquid to the receiving tank.

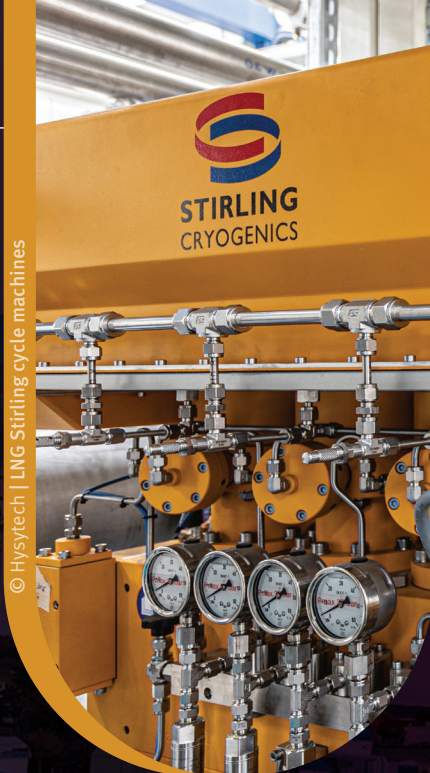
Alternatively, the boil-off during product transfer can be re-liquefied. If the transfer is from port to an liquefied natural gas (LNG) tanker at an LNG terminal, the boiled off methane can be transferred to the inlet of the natural gas liquefaction train.

In modern CO₂ terminals which are being implemented to support CCS value chains, it may be the case that CO₂ is fed to the port as a gas and then liquefied at the port location on a CO₂ liquefier. Here also the CO₂ that boils off during product transfer to the ship can be routed back to the inlet of the CO₂ liquefier.

Shipping LNG

Once LNG is loaded onto the ship, the voyage may be several weeks duration. The short Atlantic crossing from the US Gulf Coast

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to Rotterdam is approximately eight days. From the Gulf through the Straits of Gibraltar and the Mediterranean Sea to the Greek LNG terminal on the Islet of Revithoussa west of Athens is more than 20 days.

Even the best forms of cryogenic insulation cannot prevent boil-off over this timescale.

To prevent methane losses, onboard the LNG tanker there will be a re-liquefaction unit such as the Compact Reliq offered by Wärtsilä. This uses similar technology that is employed in the main LNG liquefaction train, at a smaller scale. It converts the boiled-off natural gas vapour back to LNG which flows back into the storage tanks on the ship.

The required LNG BOG reliquefaction capacity for large tankers means that the thermodynamic cycle and equipment used in the Compact Reliq differs from the Stirling Cycle. Instead of a reciprocating piston, high speed rotating centrifugal compressors and expanders are used to chill nitrogen as a refrigeration gas in a closed-loop Brayton cycle.

The cold nitrogen gas is fed to a cryogenic heat exchanger in which the BOG is also present. This causes the BOG to reliquefy to LNG. The nitrogen returns to the compression and expansion cycle in the Compact Reliq unit to be re-chilled. **SW**

An un-insulated container of liquid hydrogen will liquefy the air around it

