Cryogenic gas purification for ammonia production

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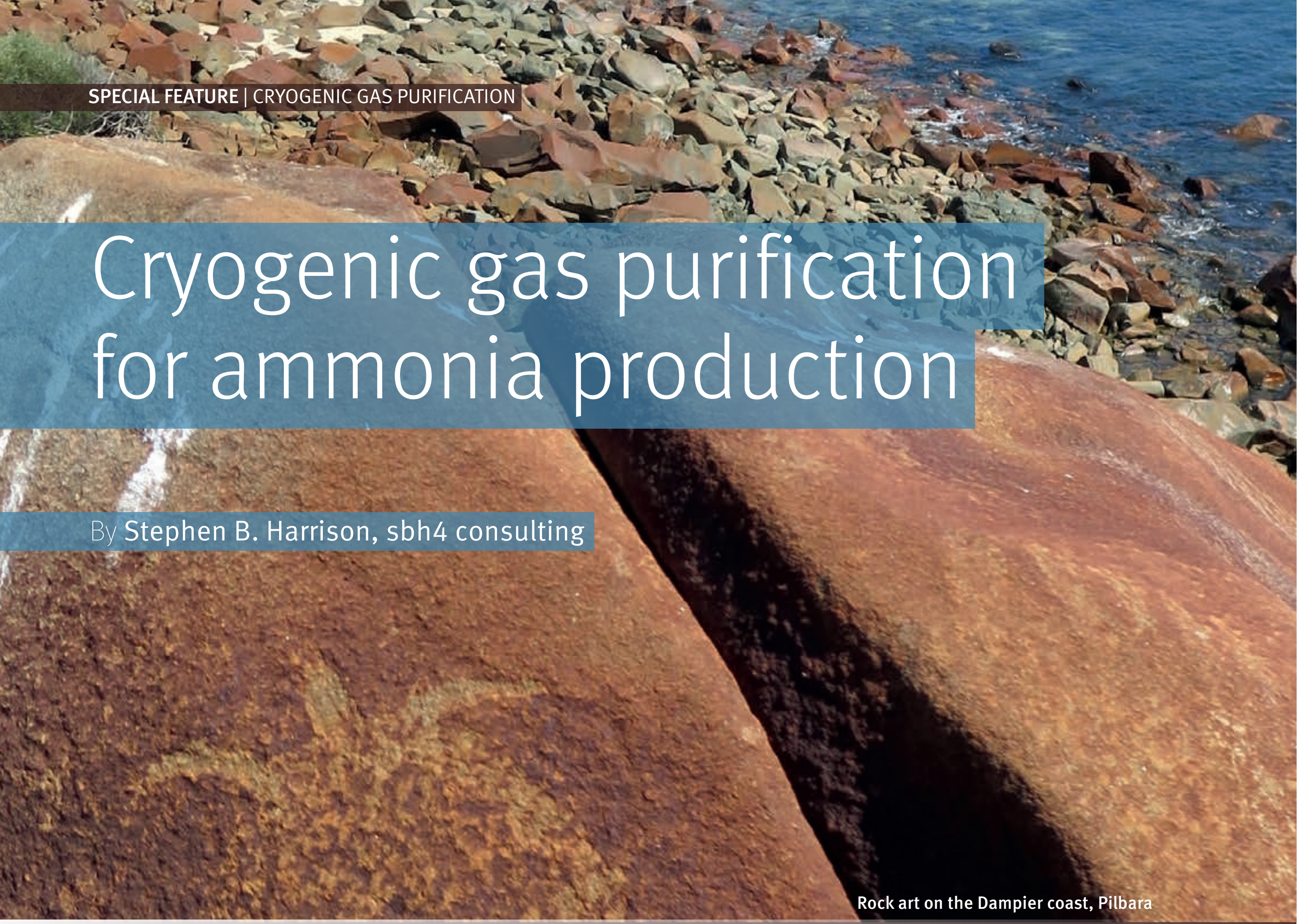

Rock art on the Dampier coast, Pilbara

Ammonia is produced from hydrogen, which is generated through reforming of natural gas or gasification of coal. The reforming process often introduces air, which brings in the nitrogen that reacts with hydrogen to make ammonia.

However, the air also contains the inert gas argon. Some methane from the natural gas also slips through the reformer without being converted to hydrogen. The methane and argon can be separated from the hydrogen and nitrogen using a cryogenic nitrogen wash to ensure cost-effective ammonia production.

Ammonia production using cryogenics

KBR has innovated ammonia production over several decades. Their plant designs have catered for ever increasing capacities on a single train and have focused on low capital cost and high efficiency. The KBP Purifier™ design was first implemented in 1966. It uses a cryogenic nitrogen wash gas separation process to recycle methane as a fuel gas to the SMR and remove inert argon from the reactor recycle gas.

The Burrup Fertilizers Ammonia Plant was commissioned in April 2006 and was, at that time, the largest implementation of the KBR Purifier™ process. The maximum ammonia production capacity is 950,000 tonnes per annum which equates to 2,600 tonnes per day. Yara Pilbara Fertilisers Pty Ltd, part of Yara International ASA, acquired the controlling stake of the Burrup plant in 2012.

The plant is located approximately 11km from the town of Karratha in the Burrup Peninsula, which is a rocky headland on the West Pilbara coast. The Burrup Peninsula has been identified as having cultural significance due to the abundance of Aboriginal rock art. In 2013, the area was proclaimed as the Murujuga National Park.

In 2016, KBR completed handover of a 2,190 tonne per day ammonia plant to Dyno Nobel at Waggaman, Louisiana. Dyno Nobel Louisiana Ammonia LLC is a subsidiary of Australia's Incitec Pivot Ltd. The project was the first to use KBR's Purifier™ ammonia technology along with KBR's engineering, procurement, and construction (EPC) services. The combination proved to be very successful and the time from contract award to handover was only 42 months. Linde Engineering provided the cryogenic nitrogen wash system for this project.

In 2019, EuroChem Group AG started up a new 2,890 tonne per day ammonia plant based on KBR's Purifier™ ammonia technology. At an annual capacity of more than 1 million tonnes, the facility is the largest ammonia plant in Europe. In this project, KBR was the technology licensor and provided basic engineering design for the $1 billion project.

The KBR Purifier™ Ammonia Process

There are several key attributes of the KBP Purifier™ process. Firstly, the ammonia synthesis reactor, filled with a magnetite catalyst is horizontal, whereas many other ammonia plants use a vertical reactor configuration. Secondly, the process uses a large, unified ammonia chiller heat exchanger.

As with many other ammonia production technologies, the KBR Purifier™ introduces air to the secondary reformer. This is an autothermal reformer (ATR) located after the primary reformer, which is a steam methane reformer (SMR). The oxygen is required to complete the autothermal reforming reactions.

Since air is used, both nitrogen and argon are entrained into process. The nitrogen is required to react with hydrogen to produce ammonia. However, argon is inert and would accumulate in and ammonia synthesis recycle loop. The KBR Purifier™ is a cryogenic nitrogen wash which avoid this argon accumulation. In recent years, several ammonia technology licensors have incorporated a similar nitrogen wash concept.

The nitrogen wash removes argon and un-reacted methane by cooling the process gas to a cryogenic temperature less than -182 °C, followed by distillation. The methane and argon are recovered from the bottom of the cryogenic distillation column to form the so-called 'purge gas' stream. The cryogenic liquids and cold gases leaving the distillation column enter a heat exchanger where they cool the incoming gases. At a temperature of around 2 °C, the hydrogen and nitrogen gas mixture flows to the ammonia synthesis reactor.

Cryogenic purge gas processing

After syngas is produced in the SMR, most of the CO_2 is captured using a twin-tower absorption system. However, the syngas still contains around 0.3% by volume of CO_2 and around 0.1%. of carbon monoxide (CO). These carbon oxides are poisons for the ammonia synthesis catalyst and their concentrations must be reduced to around 5 parts per million.

CO_2 and CO are removed from the syngas through methanation over a nickel-based catalyst. This reacts the CO_2 with some hydrogen in the synthesis gas to make CO. The CO then reacts with additional hydrogen to form methane. The hydrogen concentration in the syngas is reduced by only circa 0.5% and the methane concentration increases from around 0.3% to 0.8%.

Methane is not consumed during

"The maximum ammonia production capacity is 950,000 tonnes per annum which equates to 2,600 tonnes per day"

© OQ SAOC | OQ Salalah ammonia plant using the Linde Ammonia Concept LAC.L3

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Figure 1: Air-fed Ammonia Production Process

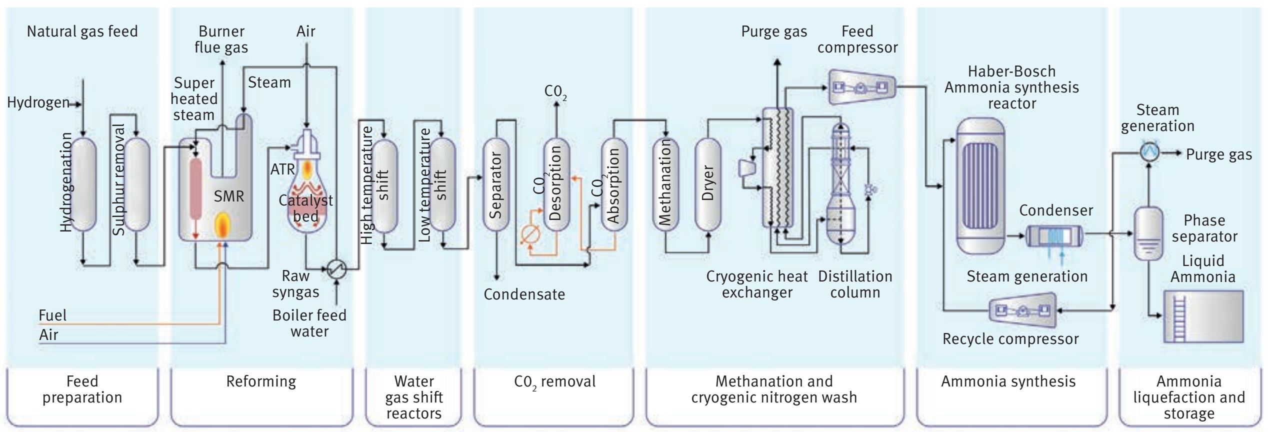

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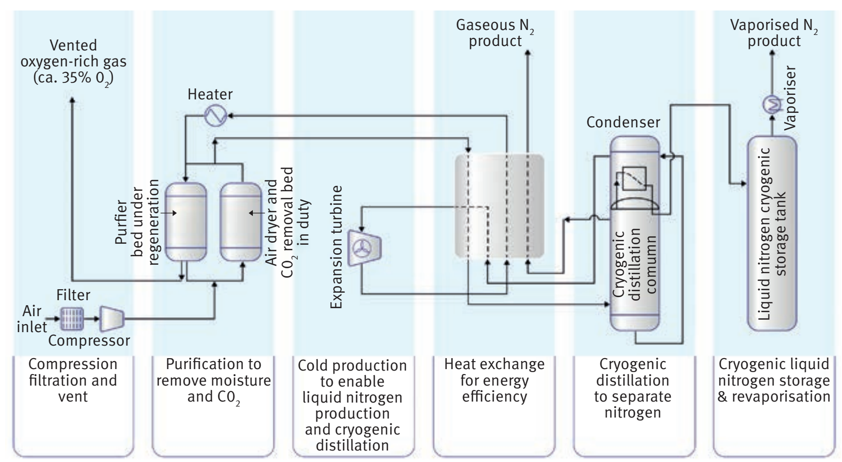
Figure 2: Cryogenic Nitrogen Generator to Produce Geseous and Liquid Nitrogen



ammonia synthesis. So, the methane that enters the ammonia synthesis loop builds up over time due to the recycling of gases around the ammonia synthesis loop. Methane must be purged to avoid their concentration building up to levels that would damage the ammonia synthesis catalyst.

The composition of the purge gas varies according to the ammonia production technology being used. As an example, it can contain 60% hydrogen with 20% nitrogen, 10% methane, 5% argon and 5% ammonia.

Flaring the purge gas is possible, but wasteful. As an alternative, recovery of hydrogen, nitrogen, argon, and methane from the purge gas is possible. The first stage in purge gas processing is to absorb the small amount of ammonia in a water was system to make aqueous ammonia, which is a marketable product.

The purge gas can then be dried, and hydrogen can be separated using a cryogenic technique that condenses the methane, nitrogen, and argon from the cold gaseous hydrogen stream. Alternatively, a selective membrane can be used to recover the hydrogen. Hydrogen can be used in the ammonia synthesis loop. The methane, nitrogen and argon are returned to the SMR as fuel gas for the burners.

In 2013, Linde Engineering implemented this process at the Morón Ammonia Plant, operated by Pequiven Petroquimica de Venezuela. The process yields more than 40,000 Nm3/hr of high pressure and medium pressure hydrogen.

A more advanced cryogenic technique enables recovery of high purity gaseous nitrogen and liquid argon from the purge gas, in addition to recovery of the hydrogen and methane. In this case, nitrogen can be recycled to the ammonia synthesis loop or used on site as a utility gas. Argon is produced as a liquid, which can be sold to the local merchant market.

Linde Engineering implemented this technology in 2017 at the ammonia plant operated by Krishak Bharati Cooperative Limited (KRIBHCO) in Hazira, the port area of Surat in Gujarat, India. The plant can produce more than 950 Nm3/hr of liquid argon at 99.9995% purity. KRIBHCO is the second largest producer of urea on a single location in India.

The Linde Ammonia Concept

Cryogenic air separation or nitrogen generation is integral the Linde Ammonia Concept, known as the LAC™. Four versions of the LAC have been proposed, of which three have been implemented. The most common is the LAC.L1 which uses natural gas as a feedstock and has been deployed six times.

In the LAC.L1 process, hydrogen is produced on a steam methane reformer (SMR) without the use of an air-fed secondary autothermal reformer (ATR). This avoids the introduction of nitrogen during the reforming stages, which reduces the size of the equipment downstream of the reformer since no nitrogen ballast gas is being carried through the process.

Another key aspect of the LAC™ is that hydrogen is removed from the syngas produced by the SMR on a pressure swing adsorption unit (PSA). The carbon monoxide (CO), methane and carbon dioxide that are present in the syngas are separated from the hydrogen in the PSA unit and these gases are used to generate the heat required by the SMR.

The use of the PSA to selectively pull hydrogen from the syngas eliminates the need for a cryogenic nitrogen wash stage to purify the syngas. It also eliminates the need for a CO_2 capture unit.

Since the LAC.L1 process does not introduce air into the ATR, nitrogen must be blended with the pure hydrogen just prior to the Haber Bosch ammonia synthesis loop. The LAC.L1 process relies on a cryogenic nitrogen generator to produce nitrogen gas. A cryogenic nitrogen generator is a simplified air separation unit which does not produce pure oxygen as a co-product.

The LAC.L3 is like the LAC.L1 but uses an external hydrogen-rich stream as the feed. The LAC.L3 was implemented by OQ at Salalah in Oman at a facility that started up in September of 2022. Purge gas from an adjacent methanol production plant is purified to yield the hydrogen required to produce 1,000 tonnes per day of ammonia. gw

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Salalah port, Oman