

# Air gases for commodity chemicals

Their important role in ammonium nitrate and nitric acid production

By **Stephen B. Harrison, sbh4 consulting**

**A**mmonium nitrate (AN) and urea are the two main nitrogen-containing fertilisers used worldwide. AN has an advantage over urea because it can be top-dressed onto the soil and left uncovered, without the release of nitrogen gas to the atmosphere.

As the catastrophic and tragic explosion in Beirut harbour demonstrated in August of 2020, AN can explode if it is stored incorrectly or

exposed to fire. So, as a fertiliser, urea is generally considered easier to handle. However, the explosive properties of AN mean that it can be blended with fuel oil to create ANFO, an explosive in the mining industry.

The medical gas nitrous oxide ( $N_2O$ ) is produced by heating AN to 240 °C. The AN decomposes to form water vapour and  $N_2O$ . AIGA Doc 080/16 describes 'Safe practices for the production of

nitrous oxide from ammonium nitrate'. It refers to the importance of storing AN in a dry location, separated from other products.

AN is produced by reacting nitric acid and ammonia. The nitric acid is derived from the oxidation of ammonia to form nitrogen dioxide, which is dissolved in water. Ammonia production is at the heart of this commodity chemical value chain. The main air gases, nitrogen, and

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oxygen, play a major role in ammonia and nitric acid production.

### Classical air-fed ammonia production

For many years, large-scale ammonia production introduced air in the secondary reformer. This is an autothermal reformer (ATR) that is used after the primary reformer, which is generally a steam methane reformer (SMR). The oxygen was consumed by partial oxidation reactions in the ATR. The nitrogen that enters with the air remains in the process to be reacted with hydrogen from the reformers.

After the reformers, high temperature shift and low temperature shift reactors convert carbon monoxide and steam to hydrogen and CO<sub>2</sub>. Subsequently, the CO<sub>2</sub> is removed using absorption and desorption in a solvent. Hot potassium carbonate (HPC) is commonly used for this purpose.

The equipment to capture CO<sub>2</sub> is generally a twin tower system. Luigi Tomasi, General Manager at Giammarco-Vetrocoke in Venice says that “we have improved the traditional

two-tower HPC process with our HPC-EcoEnergi™ technology. It uses one absorber tower followed by two stripping towers which operate at different pressures.” As the CO<sub>2</sub> laden solvent flashes from the high-pressure tower to the low-pressure tower steam is released. This strips CO<sub>2</sub> out of the HPC solvent with no additional energy input required.

Giammarco-Vetrocoke has deployed their HPC-EcoEnergi™ configuration on multiple reference plants, achieving improvements in energy efficiency of more than 30%. “We are the international leader for re-vamping CO<sub>2</sub> capture equipment on older ammonia plants. Often, our modifications can help to increase ammonia production capacity by 30% and simultaneously reduce CO<sub>2</sub> capture energy requirements by 30%.”

Older ammonia plant CO<sub>2</sub> absorption systems used two towers in parallel due to size and weight limitations of transporting process equipment on roads and rail systems. Tomasi explains that “when we re-vamp these plants, we implement our HPC-EcoEnergi™ configuration so that the two strippers run in series at different pressures.”

“As a further innovation”, he adds, “we can include an additional flash separation in our HPC-NovaFlash™ configuration to achieve an extra efficiency improvement of up to 10%”.

After removing most of the CO<sub>2</sub> from the syngas, there are drying and methanation stages. Methanation converts any residual CO and CO<sub>2</sub> to methane through reaction with hydrogen, which is present in the gas mixture.

After methanation, the process gas contains nitrogen and hydrogen, which are required to yield ammonia. It also contains methane and argon, which was entrained with the air. These two gases are removed in a cryogenic nitrogen wash stage and purged from the system.

In such an ammonia production process configuration, neither an air separation unit, nor nitrogen generator is required. Oxygen for the ATR and nitrogen for the cryogenic nitrogen wash and ammonia synthesis are drawn into the process from air.

### Green ammonia synthesis

An alternative pathway for ammonia synthesis is to react pure nitrogen and ▶

Ammonium nitrate loading



Beirut, ammonium nitrate explosion on 4 August 2020



Ammonia, ammonium nitrate and nitric acid plant



► pure hydrogen together. In this pathway, hydrogen can be produced on an SMR with water gas shift reactors. After the SMR, hydrogen can be separated from unreacted methane, residual CO and CO<sub>2</sub> using a pressure swing adsorption (PSA) system. Alternatively, green hydrogen can be produced from electrolysis of water using renewable power.

Christoph Krinninger, Global Business Development Manager Power-to-X at Clariant Catalysts says that “the catalyst for green ammonia synthesis is like the one that has been used for more than a century to make ammonia from reformed natural gas.”

Clariant’s ammonia catalysts are called ‘AmoMax®’. “Wustite, which is an oxide of iron with the formula FeO is the main component in AmoMax”, confirms Krinninger. “The trick is to selectively mix promoters with the Wustite to increase its activity, porosity, and resilience”.

One of the challenges of green ammonia production is that the process may need to be flexible to turn down by more than 50% from the peak operating load. The process design must be adapted to ensure reliable operation with the reduced throughput. Adjusting the ammonia synthesis loop pressure is one possible mitigation. As the production load decreases, the gas flow over the catalyst can be maintained at a suitably high velocity by reducing the pressure.

“Avoiding channelling and hot spots in the reactor is key to maintaining the activity of the ammonia catalyst over many years of operation,” explains Krinninger. “Changes in the process and equipment design are essential. In addition to that, with the goal of supporting efficient green hydrogen production, we have innovated the AmoMax® range to ensure that it both effective and resilient across a wide range of operating pressures.”

#### Nitrogen supply options

Nitrogen can be supplied to the process in a variety of ways, depending on the scale required. In an industrial scale, cylinder gas deliveries would be impractical. The purity would be ideal, but the volume of nitrogen required is far more than can economically be delivered through this supply mode. Liquid nitrogen deliveries would also offer a suitably high purity but may also fall short of the economic threshold for merchant liquid nitrogen deliveries.

On-site nitrogen generation using a membrane may be able to provide the required volumes for a typical ammonia process. However, membranes do not achieve a very high nitrogen purity and the argon and oxygen impurities would need to be purged from the ammonia synthesis loop, resulting in energy losses.

Nitrogen generation using an air-fed PSA system may be appropriate to

yield the desired purity and flowrate. However, there is no option to generate liquid nitrogen from the PSA unit to store as a backup if the PSA is not operating.

The ideal choice may be an on-site cryogenic nitrogen generator. It can provide a high volume of high purity gaseous nitrogen to the ammonia synthesis process and may simultaneously produce liquid nitrogen which can be stored in a cryogenic vessel on-site. If required as a backup to the cryogenic nitrogen generator, liquid nitrogen from this storage can be vaporised and fed to the ammonia synthesis loop.

#### Oxygen for process intensification

Nitric acid is produced by the Ostwald Process. The first stage of this process is to oxidise ammonia over a 95% platinum and 5% rhodium catalyst at over 900 °C and at 6.5 bar pressure to form nitric oxide and superheated steam. Oxygen for the reaction is generally from air. The steam is used to drive the gas compression train to bring air into the reactor.

The cooled gases from the reactor are passed into a sequence of absorption columns where additional oxygen is added to further oxidise the nitric oxide to nitrogen dioxide. At this point, the oxygen can be introduced from air and enriched with pure oxygen.

In 1997, Praxair (EP 0 808 797 B1) and Air Liquide (EP 0 799 794 A1) both filed patents related to oxygen enrichment of the gas stream after the oxidation reactor and prior to the absorber. Later, in 2014 Messer filed a similar patent (EP 2 953 894 B1).

The absorber is also referred to as the bleacher. At this point, nitrogen oxides are absorbed into water and dilute nitric acid to yield nitric acid at about 60% concentration. Oxygen enrichment in the absorber leads to process intensification. This can reduce the required size of the equipment for new plant build. Alternatively, oxygen supply can be retrofitted to an existing plant to increase its capacity or reduce NOx emissions.

In an integrated ammonia and nitric acid facility, an air separation unit can provide oxygen to the nitric acid process and nitrogen to the ammonia process. Alternatively, oxygen enriched vent gas from a nitrogen generator, which contains around 35% oxygen, can be

Ammonium nitrate big bags

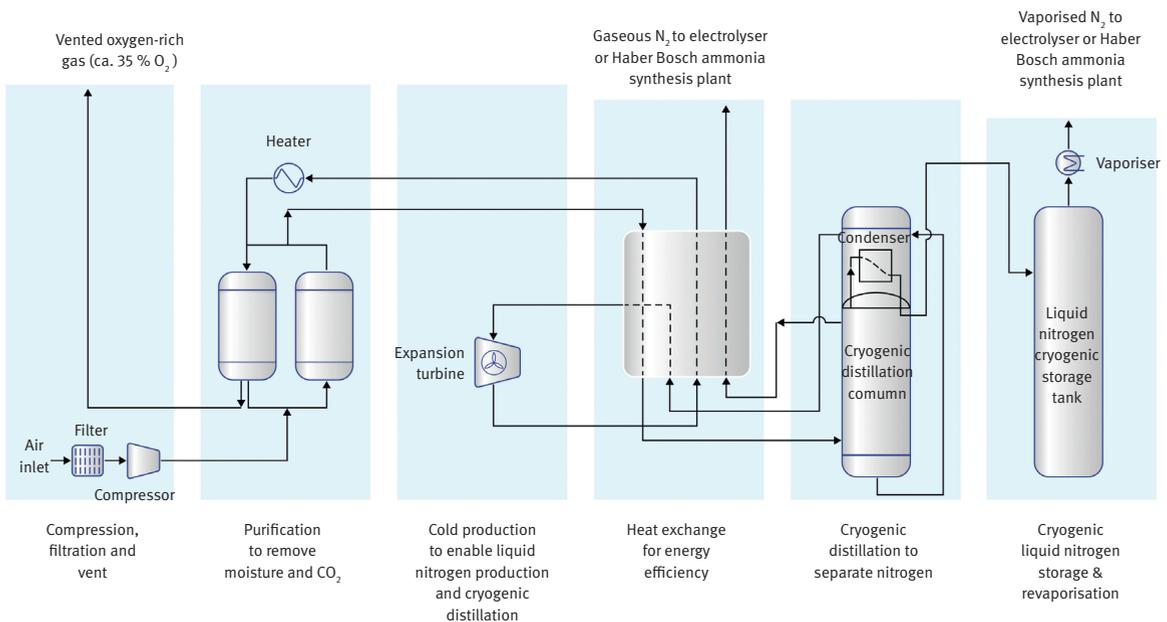


used to feed the nitric acid absorption column to achieve process intensification and integration.

In future, it is possible that hydrogen for ammonia production will be

produced by the electrolysis of water. Oxygen is produced as a co-product during electrolysis. In such a scheme, the oxygen can be used to enhance the nitric acid production. [-GW](#)

Cryogenic nitrogen generator to produce nitrogen for electrolysis and ammonia synthesis



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