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New shades of synthesis

How developments in green and blue ammonia synthesis and ammonia cracking could support the growth of both the fertilizer and hydrogen markets.

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An increased global focus on reducing greenhouse gas (GHG) emissions, principally carbon dioxide (CO₂), has resulted in increasing interest in ammonia as a potential solution for producing carbon-free hydrogen.

In addition to current applications within the fertilizer industry, ammonia can be used as a hydrogen transport vector and has the flexibility to be used directly as a fuel, or decomposed and purified to form hydrogen.

As current methods of ammonia production have significant associated carbon emissions, there is ongoing development of green and blue ammonia processes to meet the projected demand for ammonia whilst minimising associated GHG emissions as much as possible. Using ammonia as a transport vector for hydrogen requires the development of an efficient ammonia cracking process, which, after transport of green ammonia, will increase the ease of conversion to green hydrogen.

The development of these processes requires innovative process technology in combination with optimised catalysts to maximise the recovery of hydrogen at each step within the supply chain.

Green and blue ammonia synthesis

Most of the ammonia produced today is classified as grey ammonia, manufactured using a hydrocarbon feedstock that undergoes steam methane reforming (SMR) to produce hydrogen to feed into an ammonia synthesis loop.

A consequence of SMR is the formation of carbon monoxide (CO), and eventual release of CO₂ into the atmosphere. Currently, the production of ammonia is responsible for 1.8% of global CO₂ emissions.

The demand within the fertilizer market for ammonia production will continue to grow, and there will be additional demand for ammonia as a carbon-free fuel, either as a fuel itself or as a transport vector for hydrogen. As a result, there is a drive to reduce the emissions associated with ammonia production, with growing interest in blue and green ammonia. Table 1 summarises the different colours of hydrogen and ammonia, with their associated emissions.

The production of blue ammonia is similar to that of grey ammonia, with the addition of carbon capture and storage (CCS) and with changes to the reforming step, i.e. replacing the standard primary and secondary reforming stages with either an autothermal reformer (ATR) or both a gas-heated reformer (GHR) and an ATR to remove the fuel stream present in the primary reformer and ensure that the CO₂ generated in the process is at a high pressure

and thus easily removed and sequestered. The ammonia synthesis loop is likely to operate at similar conditions in both blue and grey plants. As a result, only minor optimisation of current catalyst products will be required for blue ammonia production.

Green ammonia production differs significantly from that of blue and grey ammonia. Hydrogen is generated by a hydrolysis stage, powered with renewable electricity. Consequently, this process has the potential to achieve zero GHG emissions. The green hydrogen is then combined with nitrogen, sourced from air via a renewable-powered air separation unit via the Haber-Bosch process, generating green ammonia.

There is ongoing discussion regarding the scale and location of green ammonia synthesis units, and both centralised and decentralised processes are being developed.

A centralised ammonia synthesis unit would operate at a similar scale to current ammonia synthesis loops, and hydrogen would be generated by an array of smaller scale electrolyser units before being compressed and fed to an ammonia synthesis loop operating at similar pressures to current grey ammonia loops. In this case, currently available ammonia synthesis catalysts – including the **KATALCO™** 74 series and 35 series – could be used to achieve the required performance.

A modular, decentralised design would operate with one electrolyser to generate hydrogen that would be fed into a dedicated ammonia synthesis reactor, with each unit generating ammonia at a significantly smaller scale in the order of magnitude of 10 tpd, with multiple modules required to achieve the necessary production. The operating pressure of the synthesis loop would likely match that of the electrolyser, in order to remove the costly compressor step within the process. Given the performance of recently-developed electrolysers, this would require an ammonia synthesis catalyst capable of performing in the region of 30 barg. This is significantly lower than existing ammonia synthesis loop pressures: >80 barg, with the majority >120 barg.

The development of high-activity ammonia synthesis catalysts to increase activity at lower pressure has been ongoing, and **KATALCO** 74-1 GREEN will achieve high activity at lower pressures, rendering it suitable to support low-pressure green ammonia synthesis applications.

Ammonia cracking

With growing interest in the use of ammonia as a transport vector for green or blue hydrogen, there is an increased focus on the ammonia cracking process that will be used to generate hydrogen at the intended destination. A potential route to increasing the use of green hydrogen across the globe is the generation of green ammonia in areas with large amounts of renewable electricity, which is then shipped and cracked in areas with limited renewable resources.

The basic flowsheet requirements for ammonia cracking, shown in Figure 1, include a vaporisation and pre-heating stage to convert liquid ammonia to gas at the desired operating temperature. Ammonia gas is then passed through a catalyst bed within a reactor, with an external energy source providing sufficient energy to maintain the required temperatures for the reaction to occur. As ammonia cracking is an equilibrium-limited reaction, there will be residual ammonia in the cracked gas feed, and the level will depend on the operating temperature and pressure. The cracked gas will undergo a separation stage – removing nitrogen, ammonia and likely some hydrogen – to generate a hydrogen stream of the required purity that can be compressed to the required pressure. The separation stage will generate a tail gas that has the potential to be used as a fuel source.

The location and scale of ammonia cracking plants is likely to depend on the end use of the hydrogen generated. Two scenarios are envisioned: centralised large-scale cracking units and decentralised small-scale cracking units, which are summarised in Table 2 and illustrated in Figure 2.

For centralised ammonia cracking, ammonia would be transported to a large cracking plant, situated close to a port, and would be processed through a cracker similar in

scale to current ammonia industrial processes and similar in design to a steam methane reformer. The hydrogen would be distributed through new or repurposed pipelines, with this hydrogen grid replacing the conventional natural gas grid.

Grey	Blue	Green
Natural gas	Natural gas	Renewable electricity
SMR, no CCS	Advanced gas reforming, CCS	Electrolysis
High GHG emissions (11 t CO ₂ /t hydrogen)	Low GHG emissions (0.2 t CO ₂ /t hydrogen)	Potential for zero GHG emissions

Table 1. Routes to hydrogen and ammonia production and associated emissions

In the decentralised scenario, ammonia is transported to the point of use and cracked onsite to produce hydrogen. Hydrogen generation at fuel stations for fuel cell electric vehicles (EVs) and localised hydrogen generation for off-grid users would benefit from this type of application.

Due to the large endothermic nature of ammonia cracking, the source of energy supplied to the process is a key consideration. For large-scale cracking applications, renewable fuels could offer a cost-efficient way to maintain the high temperatures required for cracking, potentially making use of the separation stage off-gas – containing ammonia, hydrogen and nitrogen – to maximise energy efficiency. For lower temperature and smaller scale applications that are likely to be located in more urban environments, electrical heat generation appears to be an attractive route.

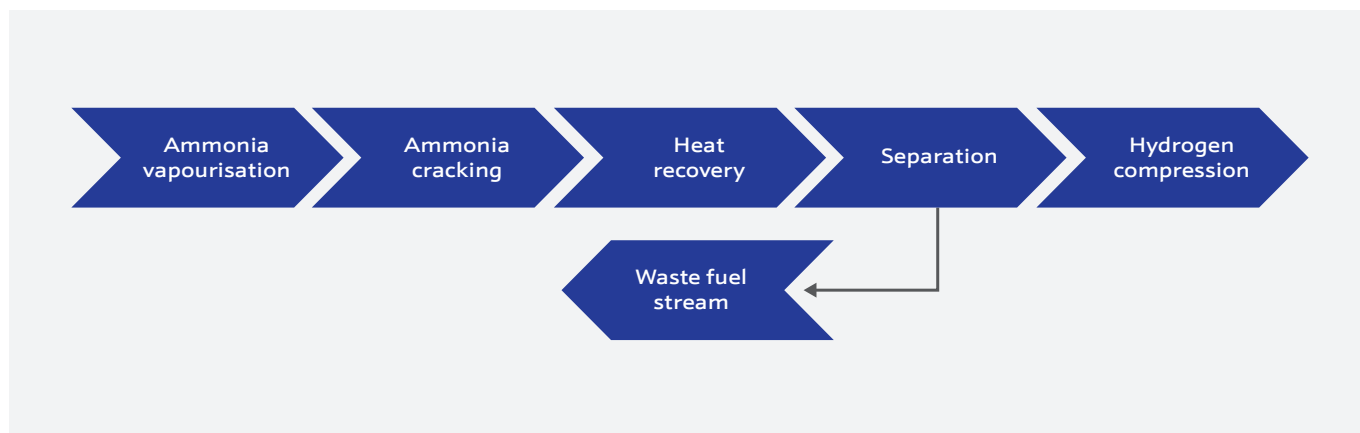


Figure 1. Schematic showing the main unit operations with the ammonia decomposition flowsheet.

	Ammonia cracker for hydrogen utility grid	Ammonia cracker for hydrogen at point of use
Description	Centralised cracker at industrial site	Decentralised cracker at garage
Application	Large plant, near port site to convert ammonia to hydrogen for distribution in hydrogen grid	Local cracker to provide hydrogen to hydrogen filling stations
Catalyst	Different forms of catalyst to operate at differing conditions likely to be required by the different processes	

Table 2. Centralised and decentralised ammonia cracking options

Ammonia cracking applications have been around for over 50 years, historically supporting the welding industry through the generation of forming gas with small-scale cracking units, and operating at high temperatures of 800 – 950 °C to ensure a low equilibrium position of ammonia in the product gas.

Base metal catalysts are well-suited to these applications, and **KATALCO 27-2**, a nickel-based ammonia cracking catalyst, has been used in these applications over the last few decades. When operated at high temperatures, this catalyst can achieve near-equilibrium conversion. However, nickel catalysts do not show significant activity below 600 °C.

Due to their high activity at high temperatures, near-equilibrium conversion can be achieved at relatively high space velocities. The lower volume requirements, combined with the inherently lower cost of raw materials when compared to precious metal catalysts, results in a catalyst that is suitable and cost-effective for large-scale applications.

Nickel-based catalysts are also routinely used in other high-temperature applications – such as SMR – and are known to be robust under these conditions. While large-scale industrial processes may benefit from operating at high temperatures, the significant energy requirements make high-temperature catalyst operations less attractive for decentralised units, which

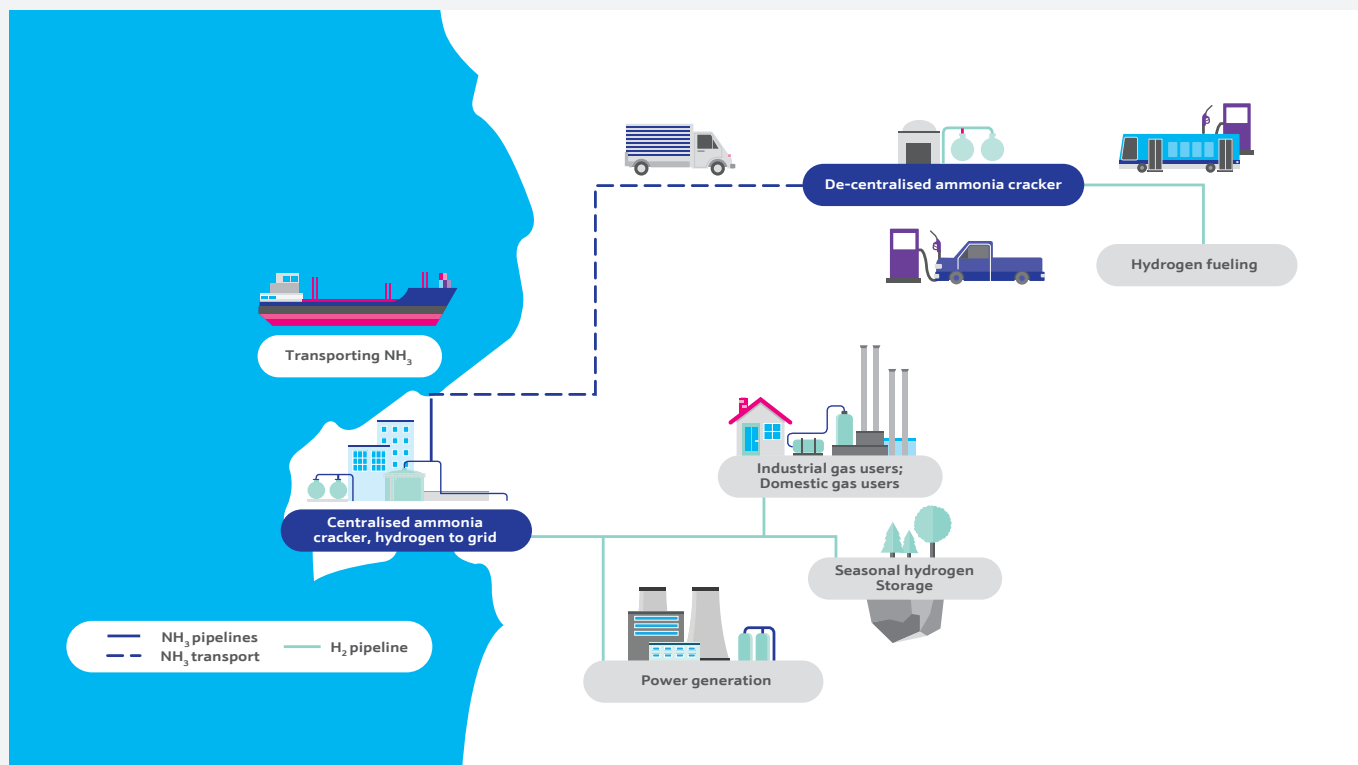


Figure 2. A portion of imported green ammonia is used at point of import to generate hydrogen for the grid in a large, centralised ammonia cracker, whilst the remaining green ammonia is transported to decentralised smaller scale crackers to generate hydrogen for filling stations.

may be utilising electrical energy as the primary heat source. As a result, there has been significant interest in developing a catalyst that is capable of ammonia cracking below 500 °C.

The requirement from industry for a lower temperature ammonia cracking catalyst led to the development of **KATALCO 27-612** by Johnson Matthey. This product is a promoted platinum group metal (pgm) catalyst and achieves high activity when operating between 450 and 500 °C.

Conclusion

Ammonia has a key part to play in the shift towards a green hydrogen economy in the coming years, and green and blue ammonia are likely to become increasingly important in supporting increased demand from the green energy sector, as well as continuing to support the traditional demand from the fertilizer market. In addition to its use as a fuel and within various fertilizer applications, ammonia could play a key role as a transport vector for green hydrogen, and as a result ammonia cracking is an area of growing interest and development.

For both processes, technology and catalyst development are required to meet the technical demands of low-pressure ammonia synthesis and low-temperature ammonia cracking. Ongoing work by Johnson Matthey has resulted in the development of both ammonia synthesis and ammonia cracking catalysts that allow for flexibility in operating temperature range for cracking and pressure range for synthesis. Research is ongoing to further this development.

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