



Advanced ammonia cracking

Priyan Mistry, Johnson Matthey, UK, explaining how an innovative ammonia cracking process approach enables efficient, low-emission hydrogen transport.

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A low-angle photograph of an industrial ammonia cracking plant. The image shows several large, vertical, cylindrical vessels with multiple levels of metal walkways and railings. A large, curved pipe runs across the foreground, leading towards the background. The sky is a clear, bright blue. The overall scene conveys a sense of large-scale industrial engineering.

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As the world focuses on reducing greenhouse gas (GHG) emissions, hydrogen is gaining attention as a carbon-free fuel alternative. Green hydrogen, produced through electrolysis, and 'blue' hydrogen, produced from natural gas by combining reforming technologies with carbon capture, utilisation and storage (CCUS), can be transported from regions with surplus renewable electricity to areas with less renewable energy availability. However, transporting hydrogen presents significant challenges. Consequently, the feasibility of using other compounds such as ammonia as hydrogen transport vectors has gained attention.

Ammonia's crucial role as an energy carrier

In global decarbonisation, there is a critical need to transition from traditional feedstocks like oil, natural gas, and coal to more sustainable alternatives such as renewable energy, captured CO₂, biomass, and waste. Ammonia cracking plays a vital role within this ecosystem by enabling the transportation of hydrogen as an energy vector over long distances.

Through the ammonia cracking reaction, hydrogen can be extracted efficiently. This process is essential for expanding the hydrogen value chain, allowing hydrogen to be transported as ammonia, therefore addressing the global supply-demand imbalance. While renewable electricity can be produced cheaply in certain regions, demand often resides elsewhere. Directly transporting electricity via long-distance high-voltage DC cables, such as from North America to

Europe, is challenging and costly. Consequently, converting electricity into hydrogen facilitates more straightforward and economical long-distance transportation, similar to the current global transport of LNG or oil.

Another transport option is liquid hydrogen, but its transportation presents significant challenges due to the need to liquefy it at -253°C. This process is both technically demanding and energy-intensive, resulting in high costs.

Ammonia, on the other hand, is a more favourable molecule for long-distance hydrogen transport for several reasons. Firstly, it contains no carbon, allowing it to be reconverted into hydrogen without managing CO₂. Secondly, qualifying CO₂ molecules for hydrogen transport are scarce and are expected to be prioritised for sustainable aviation fuel (SAF) production.

Additionally, ammonia is a globally traded commodity with approximately 20 million t transported annually. This existing infrastructure, including industry standards, container vessels, and export/import terminals, supports the efficient transport of ammonia.

To facilitate economical transportation from low-cost production regions to areas of high demand, large-scale ammonia cracking is expected to be implemented at portside locations such as Rotterdam (the Netherlands), Antwerp (Belgium), Wilhelmshaven and Rostock (Germany) and Ulsan (South Korea), where the necessary infrastructure for ammonia storage will be available. The resulting hydrogen will be transported to end users via the hydrogen pipelines currently under construction across Europe.

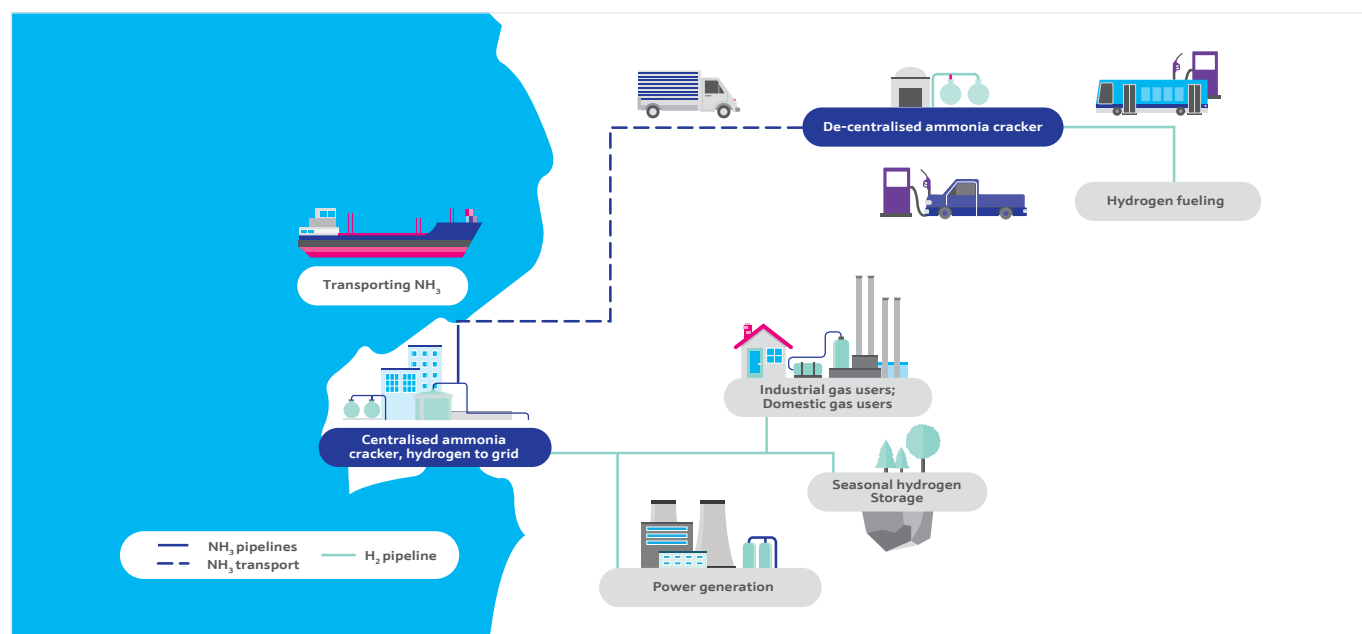


Figure 1. Import green ammonia to generate hydrogen via ammonia cracker.

Efficient ammonia cracking at large-scale

Ammonia cracking is an endothermic reaction that requires an energy input of 35 MJ per kilomole of ammonia, with high temperatures and low pressures favouring hydrogen production. The process is energy-intensive, necessitating substantial heat integration and the optimal design of high-temperature equipment to minimise external energy input.

Johnson Matthey (JM) has developed an ammonia cracking process suitable for large-scale hydrogen or cracked gas production. Leveraging JM's expertise in catalyst design, process design, and chemical plant scale-up, this technology has been refined to minimise risk and ensure reliability.

The basic flowsheet for ammonia cracking involves several stages. First, liquid ammonia is vaporised and preheated to convert it into gas and bring it to the required operating temperature. The ammonia gas then enters a catalyst bed within a reactor, where a fuel source provides the high temperature necessary for the endothermic reaction. Since ammonia cracking is an equilibrium-limited reaction, the resulting cracked gas will contain residual ammonia, with its concentration depending on the operating temperature and pressure. This gas then undergoes a separation process to remove nitrogen, ammonia, and some hydrogen, yielding a hydrogen stream of the required purity that can be compressed to the necessary pressure.

The separation stage also produces tail gas, which can be used as a fuel source, enhancing the process's overall energy efficiency.

A virtuous cycle with ammonia as a fuel

Historically, small-scale ammonia crackers have been deployed which have been fuelled using natural gas or electric heating. With the development of ammonia cracking to transport blue or green hydrogen, large-scale crackers will need a low-emission fuel source.

Due to the similarity in catalysts and endothermic nature with steam methane reformers, large-scale ammonia cracking units may resemble primary reformers found in ammonia and methanol production plants. However, while a centralised ammonia cracking unit might look like a primary reformer, its fuel requirements will differ. The four main fuel sources to consider are ammonia, cracked gas, the separation waste gas stream, and electrical power.

JM's ammonia cracker represents a significant innovation that uses a fuel blend of ammonia and separation waste gas streams. This method eliminates the need for external fuel or energy sources by utilising fuel derived from the pressure swing adsorption (PSA) tail gas and a portion of the ammonia fed into the plant. These novel fuel blends have been extensively tested, gaining valuable insights into their flame properties and emissions, and facilitating the move away from natural gas combustion.

The primary reason for adopting this pathway is to reduce carbon intensity. Although natural gas is an inexpensive external fuel that could leverage existing combustion systems from steam methane reforming (SMR), it produces CO₂ emissions. Using fossil fuels to extract hydrogen from clean ammonia or other vectors contradicts the goal of importing clean energy, bringing its long-term viability into question.

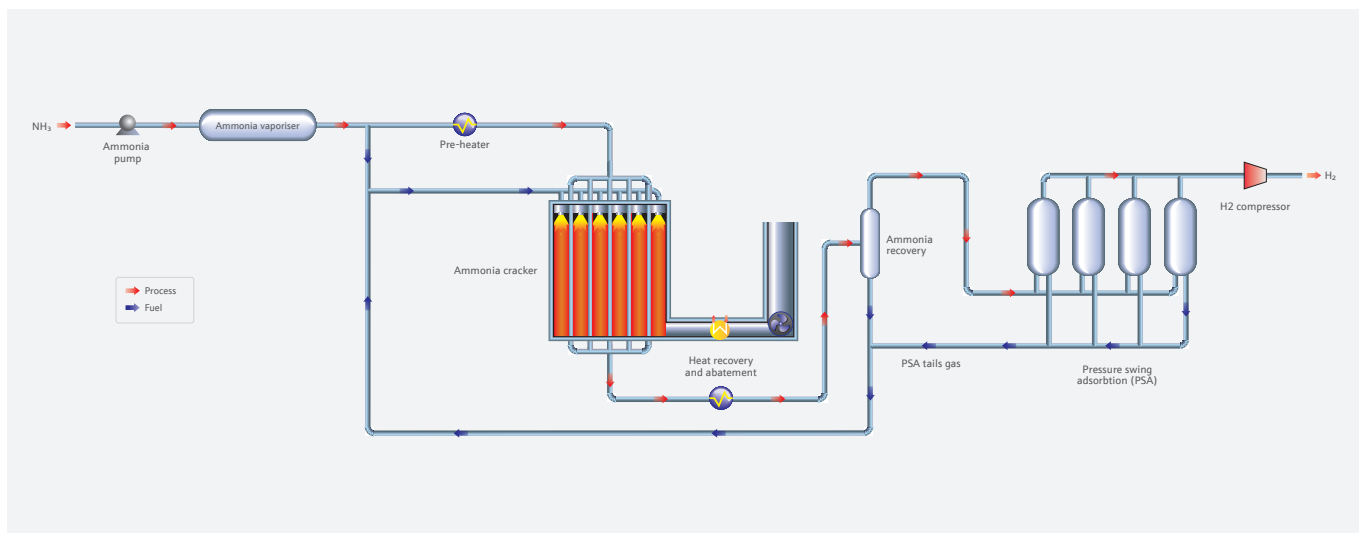


Figure 2. Ammonia cracking flowsheet.

One option to reduce carbon intensity is to use the ammonia cracker to produce both hydrogen product, and fuel for the cracker, the latter of which can be recycled.

However, this approach requires a larger cracker, increasing both **CAPEX** and impacting efficiency. Given that clean ammonia is an expensive feedstock, efficiency is a critical parameter, and **CAPEX** and footprint are important considerations to make projects viable.

The final and most practical option is to use a portion of the virgin ammonia feedstock and recycled gases from the process to fuel the cracker. This method maintains low carbon intensity while reducing the size of the cracker and **CAPEX** requirements, offering an efficient and sustainable solution.

Ammonia has long been considered as a fuel despite its challenges in combustion and high nitrogen oxide emissions. However, it offers significant advantages in ammonia cracking processes. Using ammonia as a fuel provides synergistic benefits: the process tolerates ammonia slip from the cracker, eliminating the need for a high-efficiency PSA unit, and ammonia slip and PSA off-gas can fuel the cracker, saving ammonia for feedstock. Overall, this makes emission levels below 0.1 kg CO₂-e/kg H₂ achievable.

Catalysts at the heart of the system

JM's ammonia cracker utilises the **KATALCO** 27 series catalysts. These nickel-based, high-activity catalysts have been developed to incorporate the **QUADRALOBE** shape to enhance radial heat transfer across the tube and minimise pressure drop growth over time.

In a multi-tubular reactor like an ammonia cracker, burners provide radiant and convective heat to the tubes. The endothermic ammonia cracking reaction creates a radial temperature gradient across the catalyst-filled tubes. The catalyst pellets help mix the bulk gas, promote heat transfer, and minimise the radial heat gradient within the tube. Although a gas film can form at the tube wall and limit heat transfer, the correct catalyst pellet shape and size can manage this by disrupting the gas flow and causing more turbulence. This turbulence reduces the gas film thickness, improving heat transfer into the catalyst, resulting in lower tube wall temperatures and a more efficient process.

Industry concerns about the small amounts of moisture in merchant ammonia have been raised because of their potential to deactivate certain ammonia-cracking catalysts. JM has conducted tests confirming that this issue does not affect the **KATALCO** 27 series. Additionally, it is investing in the extensive characterisation of the ammonia cracking reaction to better understand reaction kinetics, product activation, and chemical inhibition. This research is crucial as small performance variations can significantly impact the economics of large-scale ammonia cracking plants.

A new requirement that leverages tried and tested technology

While cracking on a large scale is new to the market and has not yet been implemented to provide hydrogen to end users, the reaction is well-known and understood, and the chemistry is not new. Solutions in this space are being leveraged in the design of the large-scale ammonia cracking process, making this a new but low-risk process to support a new low-carbon hydrogen economy.

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