Making and breaking NH_3 – Ammonia and its place in the low carbon economy

Tom Davison, Julie Ashcroft
Johnson Matthey

Reprinted from Nitrogen + Syngas Conference 2022, Berlin, Germany

Introduction

As part of the drive towards reducing global greenhouse gas emissions ammonia has come to the fore, both as a means of energy storage or transport vector for decarbonised energy systems and, in a cracked form towards hydrogen, as a replacement fuel. This interest has driven a number of development projects in this area, along with green and blue ammonia projects for the sustained demand for fertiliser production. Ammonia cracking will play a key role in allowing ease of transport of green hydrogen, as green ammonia, around the globe from regions with sufficient renewable energy to manufacture green hydrogen.

This paper covers both the catalyst duties of ammonia synthesis in green ammonia production and ammonia cracking, firstly looking at catalyst selection and optimisation for the conditions found in emerging green ammonia production flowsheets, particularly focusing on the testing and performance of **KATALCO**™ 74 -1 GREEN catalyst at the range of ammonia synthesis pressures that may be encountered in some of these flowsheets.

In addition, the paper discusses Johnson Matthey's ammonia cracking process technology offer, cracking catalysts, including **KATALCO** 27-2, a catalyst for high temperature applications and **KATALCO** 27-612, which targets lower temperature applications, and considers the different technical requirements for large scale centralised cracking, generating hydrogen for the energy grid, and smaller decentralised units for consumer fuel usage.

Introduction

As part of a global focus on reducing greenhouse gas (GHG) emissions, there is significant interest in the use of hydrogen as a carbon-free fuel. Green hydrogen can be manufactured through electrolysis and transported from areas with excess renewable electricity to areas with less abundant renewable electricity. However, there are significant challenges associated with the transport of hydrogen; compressed hydrogen gas has a relatively low energy density (42 kgH_2 per m^3 at 700 bar), resulting in a reduction in energy density per shipment, and liquefied hydrogen, while having a higher energy density at 72 kgH_2 per m^3, must undergo inefficient and expensive liquefaction prior to transport.

As a result, the feasibility of using other compounds as hydrogen transport vectors has become a topic of discussion. Ammonia is currently considered a front-runner as a hydrogen transport vector due to a high hydrogen density (108 kgH_2 per m^3) and existing infrastructure for storage and transportation associated with the mature fertiliser and chemicals industry. Ammonia can also be used as a fuel itself, either as pure ammonia or partially decomposed ammonia along with the option to fully decompose to hydrogen. However, a large amount of energy is required to decompose ammonia, and the efficiency of the ammonia cracking process is critical to the success of ammonia as a hydrogen carrier.

There is also the question of where ammonia will be sourced. Currently, the dominant demand for ammonia is within the fertiliser industry - this demand will continue to steadily grow, whereas much more rapid growth in demand is predicted for low-carbon ammonia within the energy sector. There are significant carbon emissions associated with current methods of ammonia production, often labelled 'grey ammonia'. As a result, there is development work on-going into green ammonia (manufactured from green hydrogen) and blue ammonia (utilising CCS technology) to meet this increased demand whilst minimising the associated greenhouse gas emissions. Projections of the market show that the ammonia merchant market will triple from 2020 to 2035 (from ~20 Mt to ~60 Mt) with this increase coming from blue and green ammonia and driven by this new demand in clean energy generation, both for power production and marine fuels. In conjunction with this it is likely that much of the existing ammonia production capacity will look to retrofit their plants to reduce carbon emissions as legislation changes and limits on emissions are reduced.

The development of green ammonia synthesis and ammonia cracking flowsheets requires novel process technology combined with optimised catalysts to maximise the hydrogen recovery and energy efficiency for each unit operation within the supply chain.

Clean ammonia synthesis

Blue ammonia

Blue ammonia will be a key technology in the drive to low carbon ammonia and energy, whilst carbon dioxide is still produced by the process, it is produced in a form which can be captured and sequestered. This technology is closer to a conventional 'grey' ammonia plant and as such in the short term is more viable for the bulk of the large scale new ammonia plants, whereas green ammonia technology at this scale will likely become more prominent in the mid to long term. As the major differences between existing 'grey' ammonia plants and blue ammonia flowsheets are around the reforming section, the conditions within the synthesis loop will be within the bounds of currently operating plants. Both **KATALCO** 35 series and the high activity **KATALCO** 74 series catalysts

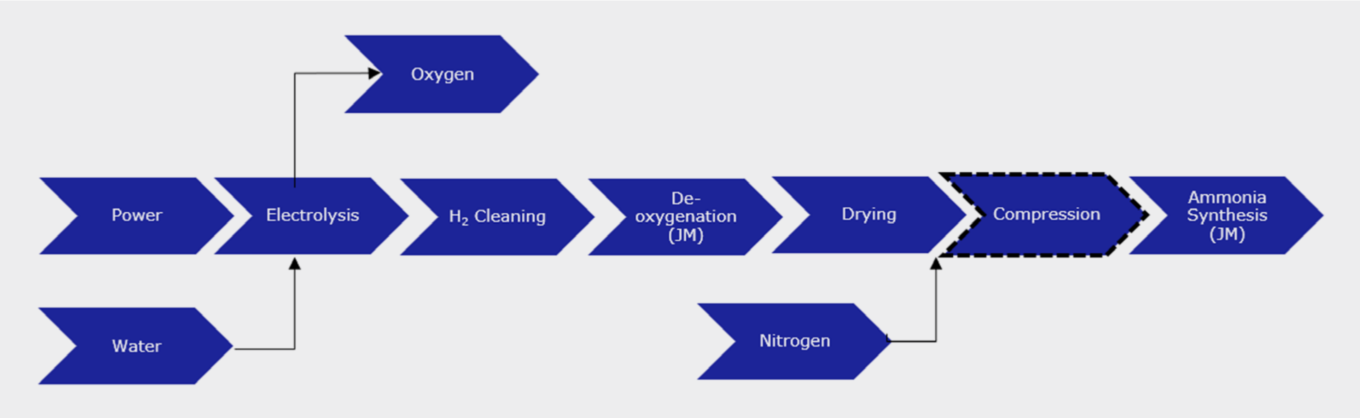

Fig 1: Typical schematic of a green ammonia process

have proven strong performance at these conditions – in particular the **KATALCO** 74 series catalysts can be used to maximise activity within the ammonia synthesis reactor and optimise loop performance.

Green ammonia

The production of ammonia using hydrogen derived from electrolysis is not actually a new technology. During the 1950's for example, AWE (Alkaline Water Electrolysis) was used until cheap natural gas made it uncompetitive against SMR technology (steam methane reforming) and it fell out of use. With improved electrolyser technology, falling renewable energy costs and the drive to reduce carbon emissions green ammonia is looking increasingly favourable as a viable alternative to SMR based production. The majority of projects in development are based on updated AWE or PEM (Proton Exchange Membrane) type electrolysers, with a general configuration similar to that shown in Figure 1, a process schematic showing the building blocks of a typical green ammonia process.

One of the big considerations for these plants is how best to match the input power to the desired ammonia production rates. To effectively decarbonise the system the power generated must come from renewable or decarbonised energy production, but most renewable energy production methods have large fluctuations in output, for example wind and solar energy both fluctuate greatly depending on the weather. To minimise this effect many of the large scale projects are targeting geographic locations that have significant wind resources along with high levels of solar radiation as the presence of one mitigates against the lack of the other. Other schemes look to use nuclear power to 'top up'/stabilise power output to minimise the variations in the synthesis loop. Despite this compared to a conventional 'grey' ammonia plant there will be more fluctuation in the flow of syngas to the synthesis loop so this will need to be factored into the design of the equipment in the loop to ensure that it is robust and adaptable to these conditions.

The green ammonia technologies in development fall into two major categories – designs with high pressure synthesis loops and those that have low pressure ammonia synthesis at the electrolyser operating pressure. The low pressure plants tend to be at a smaller scale or modular in design, with multiple modules to achieve the desired capacity. The high pressure plants may also have a modular approach in terms of the electrolysis section, with the potential to add more capacity over time but they have a large ammonia synthesis loop operating at high pressures (in the range of 130 to 300+ barg). Some of the projects focussing on the smaller/modular plants are designing for ammonia production at the operating pressure of the PEM electrolyser to reduce the need for compression. These projects are looking at ammonia synthesis at significantly lower pressures than existing large scale ammonia production, from some as low as 20 barg to around 45 barg, with relatively low conversion per pass of ammonia in the synthesis reactor due to the less favourable equilibrium conditions. The pressure ranges of proposed projects in the public domain are shown in Figure 2, along with ranges for existing and historic plants. When comparing the two scales of green ammonia projects there are significant efficiencies that are gained when scaling up power requirements/production – intensification at scale means that the power requirements per unit ammonia are significantly reduced and is closer to the grey and blue ammonia processes in terms of cost per tonne of ammonia.

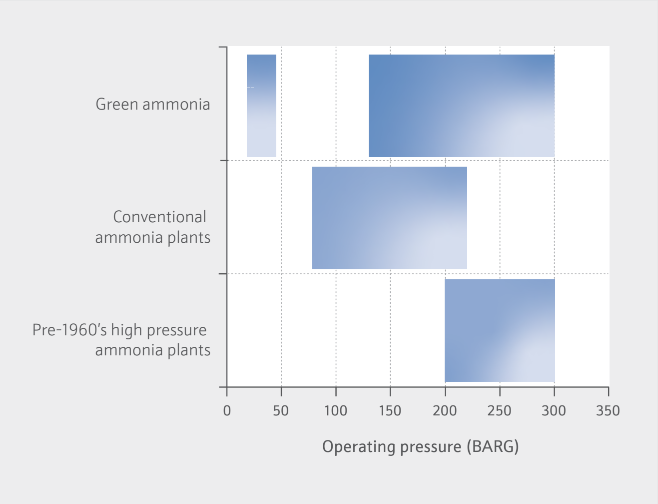

Fig 2: Operating pressure ranges of ammonia synthesis

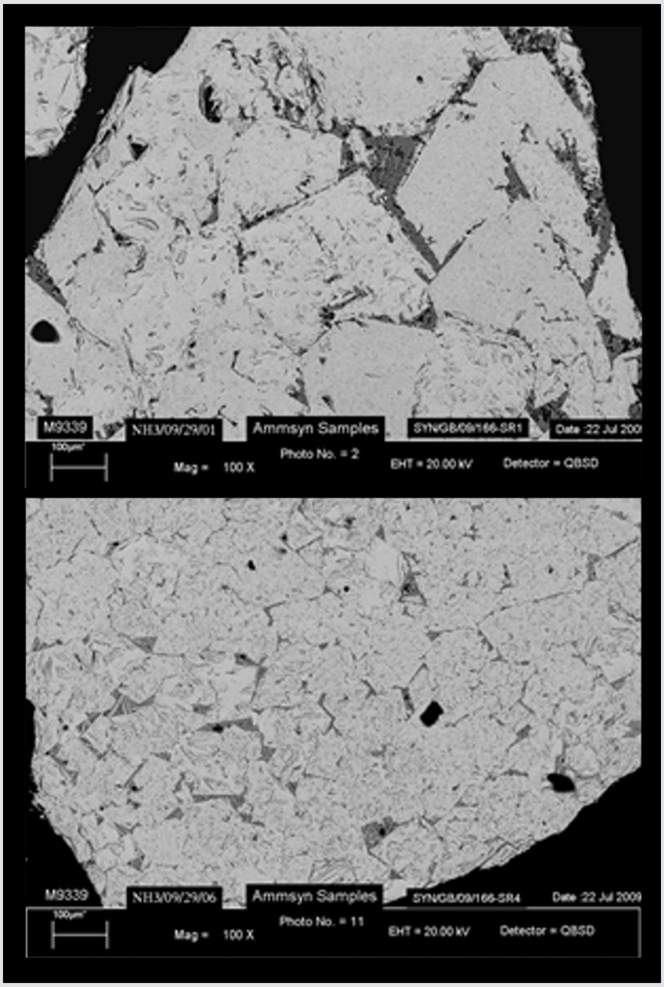

Figure 3: Microscopy images of standard and cobalt promoted magnetite

Oxygen removal

Rather than some of the poisons that would typically be seen in conventional "grey" ammonia plants (CO and CO_2), with electrolysis based green ammonia plants the major poison for the ammonia synthesis catalyst is oxygen. Oxygen, and also CO, CO_2 and water, locally oxidise the ammonia synthesis catalyst, forming localised hot spots and resulting in sintering and associated loss of activity over time. To remove the residual oxygen in the hydrogen stream a de-oxogenation stage can be included, using a catalyst to react the oxygen with a portion of the hydrogen to form water that can subsequently be removed in a drying step (Figure 1). Johnson Matthey offer a range of precious metal combustion catalysts in both pellet and monolith forms that reduce the oxygen concentration down to the stringent levels required at the inlet to the ammonia synthesis converter.

Green ammonia plant synthesis catalyst

KATALCO 74 series catalysts were originally developed for low pressure applications in the ICI AMV and LCA ammonia processes, which required the higher activity of these cobalt promoted magnetite catalysts to provide high performance down at operating pressures of approximately 80 bar. The cobalt oxide, along with re-optimised levels of the conventional promotors also present in magnetite catalysts such as **KATALCO** 35-4 catalyst enables this high activity, with the addition of cobalt having the effect of increasing the rates of nitrogen adsorption and ammonia desorption from the surface of the catalyst, hence increasing the rate of the overall synthesis reaction. This is achieved as the cobalt is incorporated into the magnetite iron lattice, which distorts the crystalline structure of the catalyst and the generated cobalt spinels result in smaller iron crystallites once the catalyst is reduced, increasing available surface area for reaction. This effect can be seen in Figure 3, which shows the crystalline structure of both a standard and cobalt promoted magnetite based catalyst.

KATALCO 74-1 is installed in some of the lowest pressure synthesis loops in operation at ~85 bar and has been historically used at pressures down to 80 bar in the AMV and LCA processes, so already has strong performing references down at lower than usual synthesis pressures, where its high activity has enabled installed catalyst lifetimes double than normally seen in the industry.
It has also operated in a commercial plant at pressures as low as 60 bar whilst the plant was operating at turndown rates. Future potential projects are looking at pushing the operating envelope with ammonia synthesis pressures below 80 bar and to support this testing of the **KATALCO** 74-1 catalyst down to 60 bar was performed,

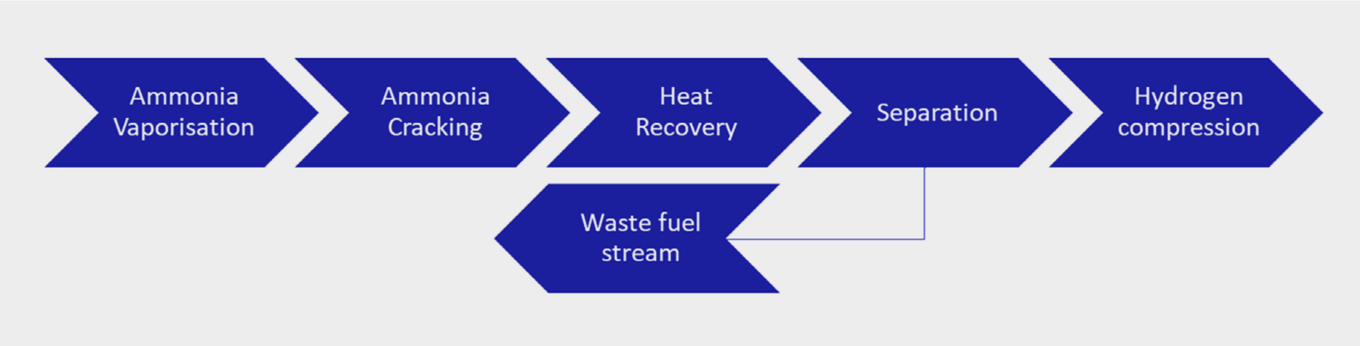

Figure 4: Schematic showing the main unit operations with the ammonia decomposition flowsheet

to ensure that the catalyst activity is maintained at these pressures and the reaction remains in the same kinetic regime as the JM kinetics derived for higher pressures.

KATALCO 74-1 also has proven high performance at high synthesis loop pressures and is installed in the main synthesis loop in world scale 2,200 mtpd and 3,300 mtpd ammonia plants where it operates at pressures of approximately 200 bar. The extra activity relative to standard magnetite catalysts enables either a relative reduction of catalyst volume or optimisation of the loop by maximising make or increasing efficiency depending on the priorities of the operator. These same benefits can be realised on large green ammonia projects where the pressures would be similar or up to ~300 bar, as this high relative activity is maintained across the range of pressures and can give increased performance or reduced converter sizes and corresponding CAPEX reduction for these green ammonia projects.

To assess the viability of ammonia synthesis at the low pressures associated with the small, modular green ammonia units in development, testing of **KATALCO** 74-1 GREEN catalyst was undertaken down to pressures of 25 barg. This testing and associated modelling confirmed that **KATALCO** 74-1 GREEN still shows high activity at these low pressures and Johnson Matthey's in house models provide a good measure of the reaction dynamics even at these low pressures. Due to the low pressures the equilibrium conversion is significantly lower than in conventional ammonia synthesis reactors so the outlet ammonia concentration from the reactor is lower (likely <10 %mol NH_3). This does mean that the exotherm over the catalyst beds is smaller than for conventional reactor, which enables the use of mechanically simpler reactor designs which combined with the smaller exotherms would potentially be more easily controlled to cope with fluctuations in power/syngas flow.

Ammonia cracking

Chemistry

Following transportation of green or blue ammonia to the desired location, the ammonia must be converted back to hydrogen. The cracking reaction (equation 1) is endothermic, requiring an input of 46 kJ per mole of ammonia, and the equilibrium position favours hydrogen production at high temperatures and low pressures.

$$NH_3 \Longleftrightarrow \tfrac{3}{2}H_2 + \tfrac{1}{2}N_2 \qquad (1)$$

The combination of an endothermic reaction and operation at relatively high temperatures results in an energy intensive process. To minimise the external energy input required to maintain the cracking reaction, there will be a requirement for significant heat integration and for optimal design of high temperature equipment within the flowsheet.

Flowsheet

The basic flowsheet requirements for ammonia cracking, shown in Figure 4, include a vaporisation and pre-heating stage, to convert liquid ammonia to gas and heat to the required operating temperature. Ammonia gas enters a catalyst bed within a reactor, with an external energy source providing energy to maintain the operating temperature as the endothermic reaction progresses. As ammonia cracking is an equilibrium-limited reaction, there will be residual ammonia in the cracked gas feed, with the level dependent of the operating temperature and pressure. The cracked gas will undergo a separation stage, removing nitrogen, ammonia and likely some hydrogen, producing a hydrogen stream at the required purity that can be compressed to the required pressure. The separation stage will generate a tails gas that has the potential to be used as a fuel source.

Industrial ammonia cracking

It is likely that a portion of ammonia decomposition will occur close to the import location with hydrogen being fed into a gas grid, whilst some ammonia will be transported further inland and undergo decomposition at the location where hydrogen is required. These two scenarios, illustrated in Figure 5, will have distinct benefits, drawbacks, and challenges, as summarised in Table 1.

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, with a cracker 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. The hydrogen purity specification for this application can be achieved using well-established separation technology, with pressure swing absorption able to deliver high recovery rates at the required purity.

In the decentralised scenario, ammonia is transported to point of use, and cracked onsite to produce hydrogen. Hydrogen generation at fuel stations for fuel cell electric vehicles and localised hydrogen generation for off-grid users would benefit from this type of application. The purity requirement for hydrogen within fuel cell applications is extremely high; ammonia levels over 0.1 ppmv and nitrogen levels over 300 ppmv are not acceptable. As a result, the purification stage for this application may need to utilise technologies such as palladium membrane separation, which while technically proven are not operating on a significant scale within any markets today.

	Centralised ammonia cracking	De-centralised/point of use ammonia cracking
Application	Hydrogen generation for distribution into hydrogen grid	Local hydrogen generation to provide fuel for hydrogen filling stations or for remote users
Scale	Large scale production (>1000 MTPD NH_3)	Small scale production (>100kg/hr NH_3)
Location	Industrial plant near port site using imported ammonia	Urban location, filling station forecourt; Remote location with accessibility challenges
Energy requirements	Can benefit from heat integration & efficiency of large-scale high temperature applications	Energy requirement will be minimised by low temperature operation; May favour electrical heating.
Product specification (separation)	Feeding H_2 into grid – purity requirements similar to current large scale hydrogen production	Stringent H_2 purity requirements requiring specialised separation step
Catalyst requirements	High temperature catalyst, scale requires high GHSV	Low temperature catalyst, scale can economically support low GHSV

Table 1 - Centralised and de-centralised ammonia cracking options

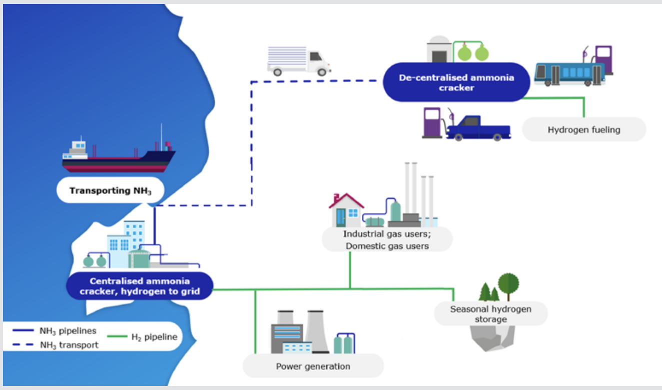

Figure 5: A portion of imported green ammonia is used at point of import to generate hydrogen for the grid in a large, centralised ammonia cracker, whilst the remaining green ammonia is transported to de-centralised smaller scale crackers to generate hydrogen for filling stations.

The common features to both flowsheets are the requirement for efficient heat transfer and recovery from the system, in order to maximise the hydrogen recovery and energy efficiency of the process. Large scale ammonia cracking may be similar to primary steam-methane reforming technologies, with management of heat transfer critical to successful operation of a large-scale ammonia cracking reactor. The design of the reactor and the catalyst plays a part in optimising performance. De-centralised cracking will be on a significantly smaller scale but will benefit when designed with knowledge of heat transfer and high temperature applications.

The separation stage within both large- and small-scale applications generates a waste gas stream containing mostly nitrogen, along with the residual ammonia and unrecovered hydrogen. Within ammonia cracking applications, energy efficiency must be maximised. Within large scale applications, the waste gas can be used as a fuel source to drive the cracking reaction, increasing the

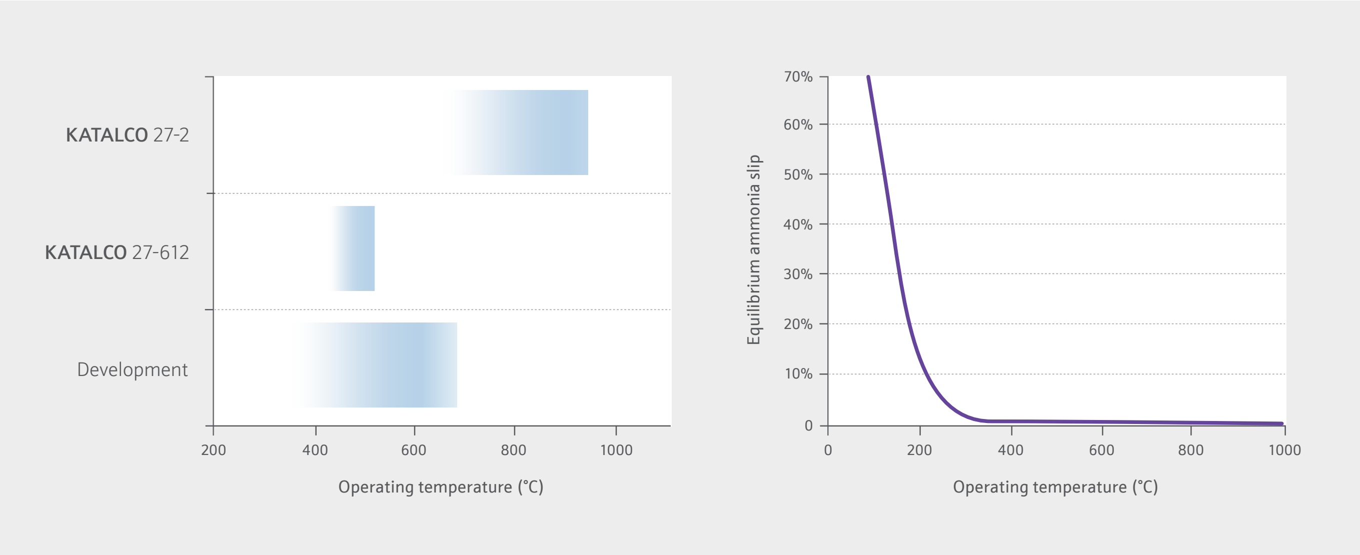

Fig 6: (a) Temperature range of activity for commercially available catalysts, **KATALCO** 27-2 and **KATALCO** 27-612, and temperature range of activity being targeted by catalysts in development, and (b) the equilibrium ammonia slip at atmospheric pressure against operating temperature.

energy efficiency of the process. For electrical crackers, this may not be feasible and other options must be considered, such as using the waste stream to drive a turbine and recover the energy as electricity. However, there are further losses associated with any multi-stage energy recovery system.

Endothermic reactions such as ammonia cracking benefit from being carried out within a multi-tubular reaction, with an external heat source providing radiant and convective heat to the tubes. Regardless of the energy source there will be heat loss across the tube wall and tube, however this can be minimised through selection of the optimal catalyst pellet. Formation of a gas film at the tube wall limits heat transfer, however this can be managed with the correct catalyst pellet shape and size. A catalyst with good packing can disrupt the gas flow by causing more turbulent flow and by having a smaller gas film more heat is transferred into the catalyst to drive the endothermic reaction which can result in lower tube wall temperatures and a more efficient process.

Johnson Matthey has a long history and significant experience in the development and design of reforming processes and reactors, including pre-reforming, primary reforming and secondary reforming which all have different design requirements. Maximising performance from a reformer-style ammonia cracking reactor requires knowledge of both reactor design and catalyst design, both which are areas Johnson Matthey has significant experience and knowledge.

Ammonia cracking catalysts

Base-metal ammonia cracking catalysts have a long history within industry, with applications including the production of forming gas for welding and generation of nitrogen at chemical plants, through cracking of ammonia and combustion of hydrogen. These catalysts are active at high temperatures, and as a result achieve very low ammonia slip.

Johnson Matthey's **KATALCO** 27-2 is a nickel-based ammonia cracking catalyst that has been supplied to ammonia cracking applications for over 50 years. It is a highly active catalyst that typically operates in the range 700 - 950°C, giving high hydrogen recovery due to the low residual ammonia levels at this temperature range.

Nickel based catalysts are very suitable for use in high temperature applications, providing a robust and stable product that combines good activity with a relatively high tolerance of poisons in the process feed. **KATALCO** 27-2 is robust enough to retain its integrity during the significant thermal cycling exposure that will occur as the plant is operating and shut down. The high GHSV tolerated at higher temperatures minimise the volume of catalyst required, resulting in a smaller reactor. The optimal operating temperature is dependent on the final process design and heat integration requirements.

As the interest in ammonia as an energy vector supporting green hydrogen fuel has growth, there has been a focus on reducing the energy requirements demanded by the cracking process, and subsequent research on the feasibility of ammonia cracking at low temperatures. **KATALCO** 27-612, a commercially available pgm-based ammonia cracking catalyst, was developed in response to this market need. This catalyst typically operates in the range 450 – 500°C, substantially extending the available operating range for ammonia cracking applications. The overall economics of a low temperature application will be a balance between the savings associated with lower temperature operation and the increased catalyst costs for pgm-based catalysts.

In addition to these commercially available catalysts, Johnson Matthey continues to develop and evaluate alternative ammonia cracking catalyst technologies, with a view to further extend the operating range to lower and intermediate temperatures. However, as the reaction is equilibrium limited, there is a limit on the lowest feasible operating temperature. For atmospheric pressure operation, ammonia equilibrium levels increase drastically below 250°C, and this minimum viable temperature increases with operating pressure, reaching 450°C at 35 bar g operation.

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 low carbon energy sector, as well as continuing to support the traditional fertilizer market demand. In addition to its use as a fuel and 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 increasing interest and development.

For both processes, technology and catalyst development is required to meet the technical demands of low-pressure ammonia synthesis and low temperature ammonia cracking. On-going development within Johnson Matthey has resulted in the development of **KATALCO** 74-1 GREEN, an ammonia synthesis catalyst that is optimised for operation at lower pressure, and the development of **KATALCO** 27-612, a low temperature ammonia cracking catalyst. In addition to the established cracking catalyst, **KATALCO** 27-2, this allows for flexibility in operating temperature range for cracking and pressure range for synthesis, and further research is on-going to further this development.

Designed and produced by www.houseoftype.co.uk

For further information on Johnson Matthey, please contact your local sales representative or visit our website. KATALCO is a trademark Johnson Matthey group of companies.

Billingham, UK
Tel +44 (0) 1642 553601
www.matthey.com

JM Johnson Matthey
Inspiring science, enhancing life