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Centralised and Localised Hydrogen Generation by Ammonia Decomposition

A technical review of the ammonia cracking process

Julie Ashcroft*, Helen Goddin

Johnson Matthey, Orchard Road, Royston, Hertfordshire, SG8 5HE, UK

*Email: julie.ashcroft@matthey.com

Ammonia is a strong candidate as a hydrogen vector and has the flexibility to be used directly as a fuel or decomposed to form pure hydrogen. The format of an ammonia decomposition plant is only starting to emerge, with two types becoming significant: centralised locations feeding into the national gas network and decentralised units to supply fuelling stations, the chemical industry or remote applications. In this paper, we review the aspects critical to decompose ammonia in both cases. While the centralised cracking flowsheet can use equipment standard to current hydrogen production methods, the localised cracking unit requires a more innovative design. Energy and safety considerations may favour low temperature operation for decentralised applications, requiring high activity catalysts, while centralised industrial sites may operate at higher temperatures and use a base metal catalyst. Purification to deliver hydrogen suitable for fuel cells is one of the biggest challenges in developing the flowsheet.

1. Introduction

1.1 The Hydrogen Economy

The hydrogen economy is gathering momentum with many pilot studies underway and governments publishing updated roadmaps to demonstrate a route to implementation (1–3). While the benefits of a carbon-free fuel are large, there are many technical challenges to enable the transition, spanning production, storage, transport and use. While hydrogen could be produced locally, there are some countries (such as Japan) who will need to import hydrogen to meet their needs. Hydrogen gas has a relatively low energy density, making it difficult to transport long distances, and several alternatives offering a higher hydrogen density, as illustrated in **Figure 1**, are now being explored.

Liquefied hydrogen has a higher energy density than gaseous hydrogen but the process of liquefaction is inefficient and expensive (4, 5). Liquid organic hydrogen carriers could be used to transport hydrogen without the cooling penalties, but there are other disadvantages including the energy required for the dehydrogenation step and the logistics involved in returning used material to a hydrogenation source (6). Methanol can be used as a fuel and a hydrogen carrier and is easy to transport but requires a source of sustainable carbon to achieve carbon neutrality (7). Ammonia is a carbon-free hydrogen carrier which is manufactured and transported at scale but has challenges with the large amounts of energy required to decompose it (8).

Since all carriers have their advantages and disadvantages, it is difficult to forecast which will hold a majority segment. Ammonia is currently considered a front runner by many due to its carbon-free nature and the existing standards for safe bulk transportation and storage associated with its maturity within the fertiliser market (9, 10). However, if ammonia decomposition is required at the destination, the final technology solution will be very dependent on the location
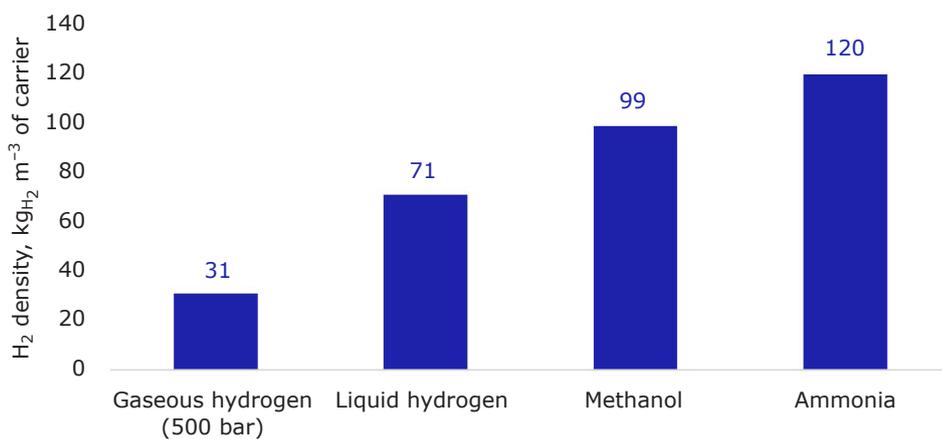
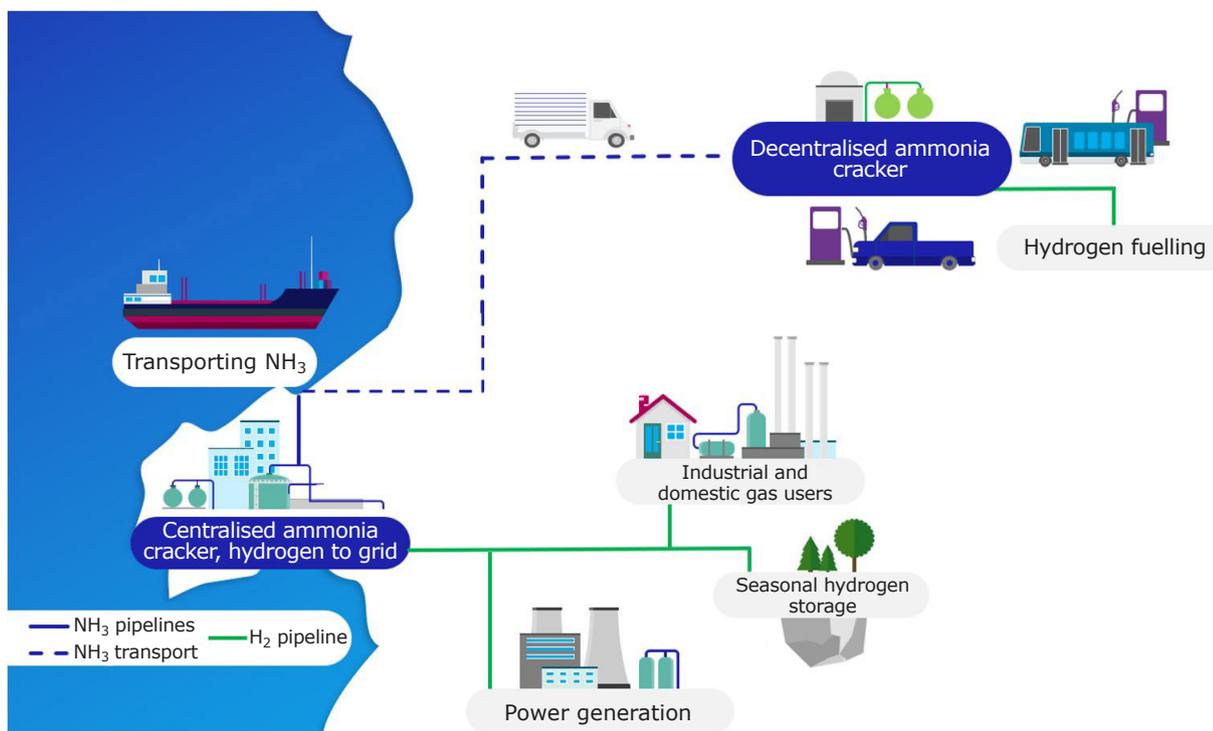Fig. 1. Hydrogen densities of different carriers demonstrating the high density associated with ammonia

Fig. 2. Production of hydrogen from ammonia *via* centralised and decentralised ammonia flowsheets and potential hydrogen applications

of the site. The aim of this paper is to review the technologies required to decompose ammonia in: (a) large centralised locations; and (b) decentralised locations, such as hydrogen refuelling stations, as illustrated in **Figure 2**.

1.2 Ammonia as a Hydrogen Carrier

To minimise environmental impact, ammonia must first be produced either with conventional processes using carbon capture and storage technology ('blue' ammonia) or using hydrogen generated by electrolysis, which is powered by renewable

sources ('green' ammonia). Ammonia has a high hydrogen storage capacity by volume (123 kg m^{-3} at 10 bar) and by mass (17.7 wt%) which result in low investment costs (11). While it is toxic, it has a strong odour which can be detected at low levels. It has a high ignition temperature, which makes it safe to transport, but more challenging to use as a fuel.

Ammonia can be cracked over a catalyst to produce hydrogen and nitrogen or burned directly to produce energy without carbon dioxide (12, 13). Combustion directly is made more efficient by having a small amount of precracking, as hydrogen

within the mix improves ignition (14). Combustion of ammonia could be a large opportunity in the shipping industry which generates large amounts of carbon emissions (15, 16). Ammonia may also be combusted in gas turbines to generate power and this is a subject of ongoing research (12). While CO_2 is not produced during combustion, burning in air can produce nitrogen oxides (NO_x) and nitrous oxide, which would need to be abated to minimise environmental impact.

1.3 Centralised *vs.* Local Approach for Cracking

In the centralised scenario, ammonia is transported to a large cracking plant and then hydrogen is distributed to point of use. Existing pipelines can often be repurposed and gas companies are currently receiving governmental funding to demonstrate this (17). The primary applications in this case would be gas for domestic heating and cooking but the hydrogen could also be sent to fuel stations to be further purified for fuel cell vehicles. In the decentralised scenario, ammonia is transported to point of use and cracked onsite to produce either high purity hydrogen for vehicles or lower grade hydrogen on industrial sites.

The development of an infrastructure which is based on centralised or decentralised generation of hydrogen is dependent on country-specific factors such as distribution of population, renewable energy availability and geographic factors (18). Centralised systems have the advantage of traditional economy of scale; reactors can be run continuously at high temperatures and pressures and achieve large efficiencies and automation of machine operations can be used to minimise the labour per unit output (19). Decentralised systems have the advantage of a lower upfront cost and independence from a hydrogen gas network.

Application of centralised or decentralised units could vary as the hydrogen becomes established as a viable fuel. In the early years of technology adoption, hydrogen generation could focus on a decentralised infrastructure to avoid high costs of new pipelines and upfront capital expenditure (capex). As hydrogen becomes more established, a centralised system becomes more cost effective and lower risk for investors but may still be supported by onsite hydrogen production in remote areas (18).

Several authors have modelled the technoeconomic viability of using ammonia as a hydrogen carrier, extrapolating capex and operational expenditure (opex) costs based on their designs and estimating a cost of hydrogen and payback period for the investment (20–23). In one study, centralised and decentralised scenarios for ammonia cracking were compared and decentralised was found to be more economic as the distribution radius increased, due to the lower cost of transporting ammonia compared to hydrogen gas (22). In another, a centralised scenario was compared to a decentralised scenario for use in fuel cells and the cost of hydrogen resulted in an unviable 30-year payback period for the decentralised solution (23). The economic viability of ammonia cracking is sensitive to the technology solution selected (such as the catalyst and plant design) and also the price of hydrogen and ammonia which are susceptible to external driving factors.

2. Ammonia Cracking Flowsheet

2.1 Existing Ammonia Cracking Applications

Ammonia decomposition has been used historically to produce forming gas, which has widespread applications including welding, soldering and brazing. To produce the gas mixture, ammonia is vapourised and then passed through an electrically heated cracker at high temperatures to achieve a high conversion and low ammonia slip (24). These applications do not require the separation of hydrogen from the mixture and the cracking process operates at high temperatures to minimise the residual ammonia within the product (24). Base metal catalysts, which are highly active at these high temperatures, have been used in these applications for over 50 years (25, 26). These applications are small scale, with typical ammonia flowrates lower than 250 m^3 h^{-1} (27). The units typically consist of a single catalyst bed heated by surrounding electrical elements. **Figure 3** shows two reactor configurations as described by Hogg (24) for consumption of up to 8.5 Nm^3 h^{-1} ammonia.

Ammonia crackers have also been used in petrochemical plants to generate nitrogen as an inert, removing the hydrogen by combustion, or to generate a hydrogen mixture for use in the reduction of certain catalysts (28). These reactors
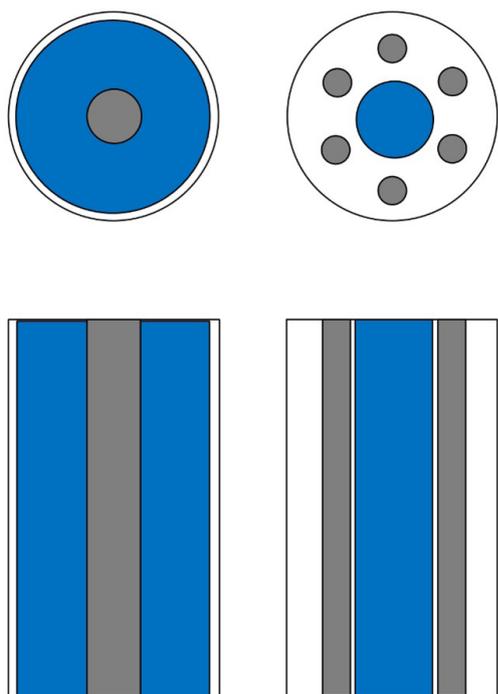
Fig. 3. Schematic showing typical reactor layout for small scale existing ammonia crackers, with electrical elements (grey) providing heat to the catalyst bed (blue). This schematic is based on reactor layout described by Hogg (24)
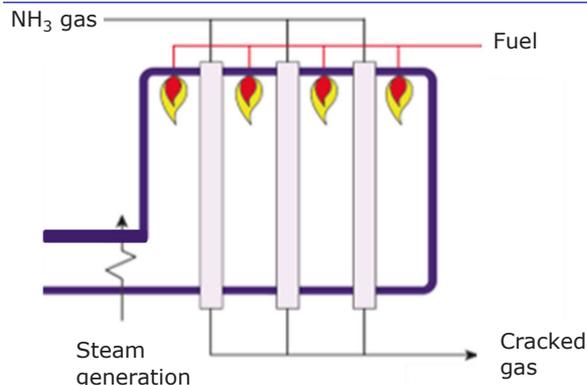

Fig. 4. The endothermic nature of the cracking reaction results in a reactor design similar to steam-methane reforming applications to enable efficient delivery of heat into the catalyst bed

resemble small scale steam-methane reformers, as shown in **Figure 4**.

2.2 Transitioning to Low Carbon Ammonia

The ammonia cracking flowsheet for generation of hydrogen as a pure fuel source is more complex than the applications discussed above due to the focus on a low carbon impact and the separation and purity requirements for the hydrogen product. Energy efficiency is more of a focus due to market uncertainty in fuel prices.

Figure 5 shows the main processes for an ammonia cracking flowsheet. Ammonia is transported as a compressed liquid and must be vapourised and preheated to a suitable temperature prior to the cracking stage. Commercial grade ammonia contains up to 0.5 wt% water and 5 ppm oil (29) and a water-oil effluent will be generated in the vaporisation stage. The gaseous ammonia may be cracked within a reactor bed containing a pelleted catalyst typically comprising a base metal or platinum group metal (pgm). Depending on the reactor size, this may comprise one bed or multiple

tubes of catalyst that may be heated either by electrical elements or combustion of a fuel. The cracked gas contains nitrogen and hydrogen in a molar ratio of 1:3 and ammonia, the composition of which is limited by the equilibrium position, as shown in **Figure 6**, and determined by the conversion achieved in the reactor. Heat recovery is necessary to maximise energy efficiency. The cracked gases are separated and purified to enable market grade hydrogen to be produced. There is an opportunity for utilising the waste stream containing residual ammonia and unrecovered hydrogen as a fuel. The composition of the waste stream is dependent on the ammonia slip and separation hydrogen recovery rate: cracked gas containing 0.5 mol% ammonia being separated with 90% hydrogen recovery would generate a tails gas containing 75.7% nitrogen, 22.7% hydrogen and 1.6% ammonia, whereas with 60% recovery would yield 45.0% nitrogen, 54.1% hydrogen and 0.9% ammonia.

Hydrogen can be separated using several technologies including pressure swing adsorption, cryogenic distillation and membranes. The purity of hydrogen gas required is dependent on the application, with a much higher purity placed on fuel cells than for domestic cooking appliances and boilers.

Depending on the recovery rate of the separation technology, there can be significant levels of hydrogen in the waste stream. A unique challenge for modern ammonia cracking applications is the utilisation of the waste stream to maximise process efficiency. Pressure swing adsorption, a large-scale separation process, can achieve 60–90% recovery of hydrogen to the purity required
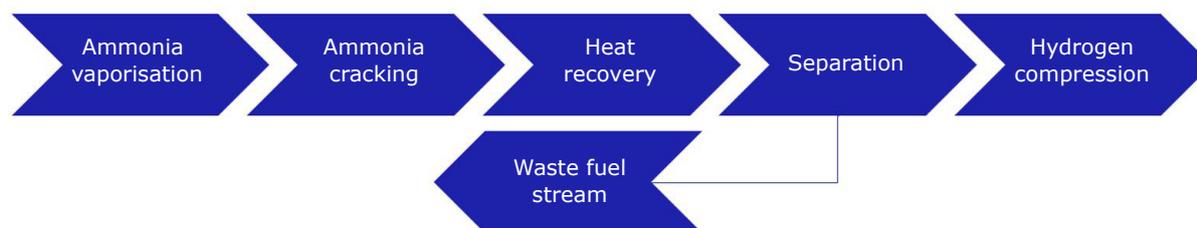
Fig. 5. Schematic showing the main processes with the ammonia decomposition flowsheet
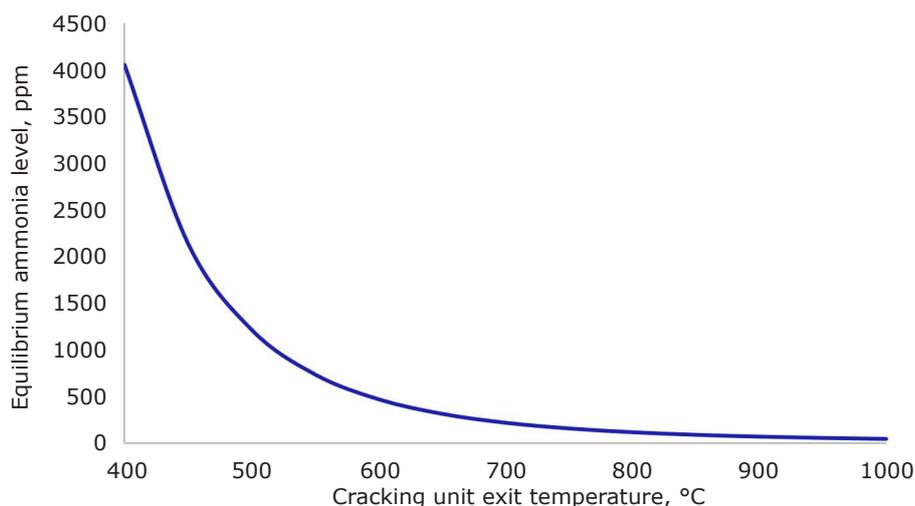

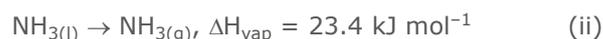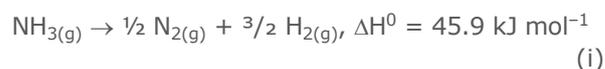Fig. 6. Equilibrium residual ammonia during operation at 1 bara

for hydrogen being used in the grid (30), which results in a waste stream containing 23–55 mol% hydrogen. Utilising this energy within the process is desirable, including as a direct energy source for the endothermic cracking reactor or to drive a gas turbine to generate electrical energy. The high nitrogen content within the fuel is a challenge associated with the development of ammonia cracking flowsheets. The impact on burner design and heat transfer of a fuel with a high level of inert must be considered, and the NOx generated must be reduced to low levels using emission control systems.

2.3 Centralised Crackers

Historically, large scale ammonia crackers would have been fuelled using natural gas and small-scale crackers electrically heated. Given the development of ammonia cracking as a method of transportation for blue or green hydrogen, large scale crackers will require a low emission fuel source. While the development of larger scale electrical crackers

is ongoing (22), there are no units in operation currently.

Ammonia decomposition is a highly endothermic reaction, as illustrated in Equation (i), and in conjunction with the energy requirements for ammonia vaporisation, as shown in Equation (ii), the process consumes a significant amount of energy. In addition to these energy intensive steps the ammonia gas must be preheated from the vaporisation temperature to the reaction temperature, which can be in the range of 400–900°C and can consume in the region of 50 J mol^{-1} K^{-1}.

$$NH_{3(g)} \rightarrow \tfrac{1}{2} N_{2(g)} + \tfrac{3}{2} H_{2(g)}, \Delta H^0 = 45.9 \text{ kJ mol}^{-1} \tag{i}$$

$$NH_{3(l)} \rightarrow NH_{3(g)}, \Delta H_{vap} = 23.4 \text{ kJ mol}^{-1} \tag{ii}$$

Due to the similarity in catalyst and endotherm with the steam-methane reformers, large scale ammonia cracking units may look similar to primary reformers currently installed in ammonia and methanol production plants (22).

Specifications for feeding hydrogen into the mains gas network are still in draft form but may be around 98 mol% in the UK (31). Pressure swing adsorption is already widely used for purifying hydrogen commercially at the large scale and can deliver hydrogen purities of 98–99.999 mol% hydrogen (32). Cryogenic separation is also used commercially but delivers a lower purity than pressure swing adsorption (33).

While a centralised ammonia cracking unit is likely to look like a primary reformer, as illustrated in **Figure 4**, the fuel requirements will be different. There are four main sources of fuel to consider: ammonia, hydrogen, separation waste gas stream and electrical power.

The shortfall in energy from combusting the waste stream can be met by the addition of ammonia, hydrogen or a mixture of these gases to the waste gas for combustion. To maximise energy efficiency, pure ammonia mixed with the separate waste gas stream is a logical choice of fuel, as the addition of hydrogen product reduces both hydrogen recovery and energy efficiency of the process. Depending on the composition of the fuel stream, the addition of hydrogen may be required to improve the properties of the flame as pure ammonia burns with low flame stability and low flame speed (34).

Experiments have shown a partially cracked ammonia stream containing 70 mol% ammonia and 30 mol% cracked ammonia burns with similar properties, including NO_x emissions, to natural gas (35) which allows the opportunity for retrofitting existing natural gas burners. NO_x generation is expected during the combustion of ammonia-hydrogen fuel mixture when combusted at near stochiometric conditions and the generation of N_2O, a potent greenhouse gas, is significant in very lean conditions (34). Downstream abatement units will be required to reduce emissions to an acceptable and safe level prior to emission to atmosphere.

The case for an electrical cracker must be considered as this allows all ammonia to go to product and does not consume any product hydrogen as fuel, maximising the hydrogen recovery of the process. The feasibility of such a system will largely be driven by the cost, and availability, of green electricity. It is likely that ammonia crackers will be situated in locations where there is a lower availability of renewable energy and hence this could be a limiting factor. Energy from the waste gas stream would have to be extracted through separate combustion and integration with a gas turbine in purely electrical ammonia crackers.

2.4 Localised Ammonia Cracking

Electrically heated crackers are more likely to be a feasible solution for smaller, localised cracking systems, where efficiency and safety aspects of design would be negatively impacted using a fired heater. These localised systems are envisaged to provide fuel cell grade hydrogen for remote communities or transportation requirements and as a result could be situated in populated areas. The use of a fully electrically heated cracking unit has an inherent disadvantage of not utilising the waste gas stream to provide energy for the cracking reaction, however the energy could be alternatively utilised to generate electrical energy for use within the wider site.

A specification for polymer electrolyte membrane (PEM) fuel cells for vehicles is given by ISO 14687-2, where the purity of hydrogen is stipulated as 99.97 mol%, and there are set limits for other contaminants, in particular nitrogen 300 ppm and ammonia <0.1 ppm (36). For transport applications, the hydrogen must be delivered at the pressure of the hydrogen storage tank (300–1000 barg), necessitating a compression stage as well as a separation stage (37, 38).

At fuel station locations, pressure swing adsorption becomes less attractive due to the high energy requirements to deliver high purity hydrogen (39). Technoeconomic analysis of a pressure swing adsorption scenario for a decentralised location has been assessed and found to give an unviable cost of hydrogen production and payback period (23).

Membranes are a more compact solution but few have been commercialised. Several types of membrane for separating hydrogen from other gases have been investigated in the literature, including palladium, metal, polymer, carbon and metal organic frameworks (40). Palladium-silver membranes are used today to generate ultra-pure hydrogen in applications such as semiconductor manufacturing. While very effective, they are costly and a non-precious metal alternative would be attractive to the market. Recently a palladium-coated vanadium membrane was investigated and found to be suitable providing operating controls are put into place to reduce the risk of hydrogen embrittlement (41). Polymer membranes are cost efficient and make up a large percentage of

the market. Key commercial examples include polysulfone, cellulose acetate, polyimide and polyamide (33). Polymer membranes suffer from a trade-off between permeability and selectivity and so work in this area is focused on polymer blending and mixed matrix membranes including components such as zeolite and silicon dioxide (42). Molecular sieving carbon membranes have received interest as they are able to give good selectivity and fluxes (43, 44). However, they can be brittle and expensive and can degrade when ammonia is present (40). Proton-electron conducting ceramic membranes, formed using metal-ceramic materials (typically nickel or palladium and perovskites), are also a possibility for hydrogen separation (45). If the structure is both proton and electron conducting, then hydrogen can be separated with high selectivity, low cost and at high flux, without an electrical driving force. The technology is not yet commercially available due to challenges with achieving the necessary selectivity and flux as well as lifetime.

When considering purification of hydrogen from an ammonia cracked gas stream there is a particular challenge with the large amount of nitrogen present. Hydrogen must be separated from a dilute stream and impurities removed to meet the required specification. Multistep processes have been proposed to meet the PEM fuel cell standard, for instance using an absorbent to remove the ammonia immediately after the cracking process and then a second stage to remove the other gases (46). Challenges exist with ensuring these steps are compatible and cost effective within the cost constraints of a localised design.

Electrochemical compression could be an opportunity to combine the purification and pressurisation step. These devices comprise of an anode, a cathode and a proton exchange membrane between the electrodes. Hydrogen gas is catalytically dissociated at an anode into protons and electrons. Electrons are transported by an external current *via* an external circuit which provides the driving force for the diffusion of the protons through the membrane against a pressure gradient. The protons and electrons then recombine at the cathode. Current levels of purification achieved with this method are not sufficient to meet the demand for fuel cell applications (47), however could form part of a multistage purification solution. A significant challenge with generating hydrogen for fuel cell electric vehicle (FCEV) applications is the high-pressure requirements of up to 1000 bar. Electrochemical compression has been demonstrated to achieve compression to 1028 bar in a single stage at laboratory scale (48), showing that progress is being made in development of this application. This would allow ammonia cracking to occur at a lower pressure which favours equilibrium before purifying and compressing the hydrogen stream to the required specifications.

3. Ammonia Cracking Catalysts

3.1 Materials Selection

Several metals are active catalysts for ammonia cracking, including ruthenium, iron, copper, nickel, iridium, molybdenum, cobalt, platinum, palladium and rhodium and these have been investigated across a range of oxide and carbon supports (49). The material used as the supports can have a significant impact on the overall activity due to the influence on particle size and shape, electronic structure of the active material and ability to bond with intermediates (such as hydrogen and nitrogen) during the cracking process (49).

Of these catalyst candidates, ruthenium and nickel are of particular interest due to the former's high activity at low temperatures and experience of the latter in other high-temperature applications. Nickel catalysts have an extensive history in steam-methane reforming applications. The first nickel catalyst for reforming was patented by BASF in 1913 (50) with steam-methane reforming having similar heat delivery demands as ammonia cracking. Other pgm candidates have lower activity than ruthenium (51) in addition currently being traded at a higher price (52). Iron has been used historically as an ammonia cracking catalyst as part of the deuterium production process (53), however in addition to showing lower activity than nickel (54), it is poisoned by low levels of water (55), making it unsuitable for cracking of transported anhydrous ammonia which contains up to 0.5 wt% water (29).

Selection of a catalyst for a particular temperature range requires an acceptable level of activity at the temperature range of interest and stability of both the active metal and support at the temperature of interest. For example, alumina is considered a useful support but is known to go through phase transitions which could remove an initially high surface area (56).

3.2 Nickel Catalysts for High Temperature Applications

Nickel catalysts have been widely investigated across a range of supports such as alumina, lanthanum oxide, silica, magnesium oxide, ceria, titania and zirconia and have been found to give high activity at temperatures greater than 600°C (49, 57, 58). Operational conditions are typically up to 900°C where near-equilibrium conversion can be achieved (24). Concentrations of nickel in ammonia cracking catalysts have ranged from 1–40 wt% in the literature (50). Changes in loading of nickel on alumina have been found to change the particle size and phase present, which can influence the performance of the catalyst. Low loadings weaken the strength of the interaction with the support and increase the catalyst susceptibility to sintering. High nickel loadings require a reduction at high temperature which can result in a reduction of surface area (54).

The relative cost of nickel catalysts, compared with precious metal catalysts, is low, and this is further benefited by the minimum viable space velocity required for near equilibrium conversion being significantly higher than for lower temperature application catalysts. This makes nickel catalysts suitable and cost effective for large scale applications where a significant volume of catalyst would be required.

3.2 Low Temperature Applications

Recent developments in ammonia cracking catalysts have focused on achieving high activity at lower temperatures than conventional catalysts with a focus on operation below 500°C. Ruthenium catalysts have been proven to have high activity, particularly when promoted with alkalis such as lithium (59, 60). Such catalysts are now available commercially with supporting refining processes in place. Alternative catalysts in the literature such as amide-based catalysts have shown promising activities and are still under development (61, 62).

Operation at lower temperatures is of interest for applications within the blue and green hydrogen space, significantly reducing the energy requirements of the ammonia cracker. The drawback of operating at lower temperatures, compounded when also operating at higher pressures, is that a less favourable equilibrium position is achieved, as observed in **Figure 2**. This may have a significant impact on hydrogen recovery depending on the ability to utilise the residual ammonia. Ammonia

as a gaseous waste stream can be combusted to regain some energy, however ammonia trapped in sorbent material will not be usefully realised and sorbent regeneration will incur further operating costs.

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. Due to the high cost of the raw materials, low temperature catalysts are likely to be more economically favourable for applications with low volume requirements, such as distributed small-scale crackers. Ruthenium is shown to be an active catalyst at low temperatures, but even low catalyst loadings can add a significant cost to the catalyst, with ruthenium prices in December 2021 sitting close to US$600 per troy ounce (52), and ruthenium prices having high variability due to the small market size (**Figure 7**).

To ensure the sustainability of using a ruthenium ammonia cracking catalyst, a refining and recovery solution will be required for spent catalyst. The majority of ruthenium is obtained as a byproduct of platinum mining and the small market can be heavily impacted by supply and demand effects, as shown in 2007 when prices rose as a result of advances in hard disk technology (63).

5. Discussion

The use of ammonia as a carrier to support the hydrogen economy will require widespread adoption of ammonia cracking. The two likely hydrogen distribution models, localised and centralised, have differing technical requirements driven by scale and hydrogen purity.

Purification of hydrogen was not required in historical ammonia cracking applications but is essential to the concept of using ammonia as a hydrogen carrier. While hydrogen produced for the grid can be separated to desired purity with conventional pressure swing adsorption technology, the high purity requirements demanded by fuel cell applications may require the use of membrane separation, an area of significant ongoing development. The use of multistage separation processes may be appropriate for applications providing hydrogen both to the grid and to fuel cell applications.

The presence of a waste gas stream containing hydrogen and ammonia is also a challenge unique to new ammonia cracking applications. As with any low-carbon application, energy efficiency must be maximised and using the waste gas stream as a
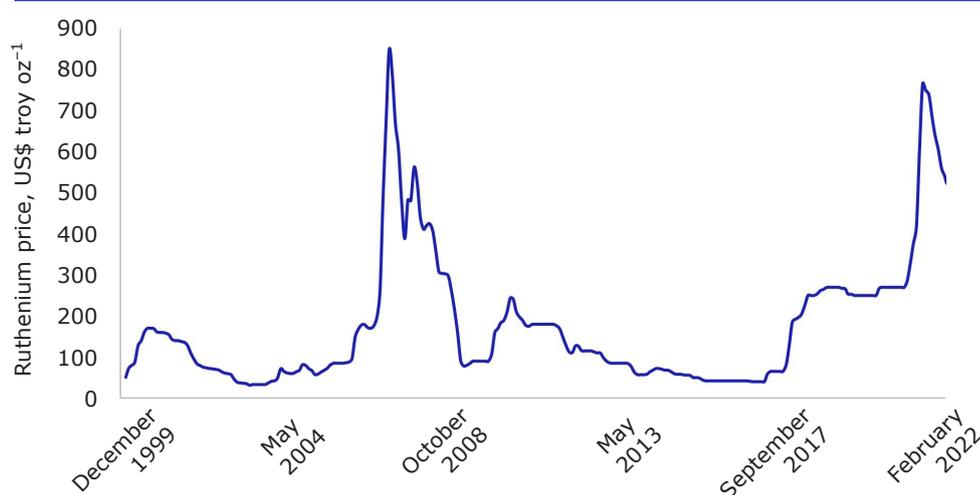
Fig. 7. Variation in ruthenium prices since 2000 (52)

direct energy source to drive the cracking reaction would allow for a high level of energy recovery. For electrical crackers this may not be feasible and while using the waste stream to drive a turbine and extract electrical energy will recover some energy, there will be additional losses associated with a multistep energy recovery system.

Selection of a base metal (high temperature) catalyst or a pgm based (low temperature) catalyst will be dependent on the economics of the flowsheet selected. While pgm prices fluctuate, creating an additional level of uncertainty in an already uncertain market, this type of approach could be cost effective for small volumes. Selection of a pgm or base metal route should be accompanied by an analysis of the lifetime costs.

Ammonia cracking process efficiency can be defined in two ways: the percentage recovery of hydrogen in the product *vs.* the theoretical hydrogen recovery for 100% ammonia conversion and the energy efficiency of the process, which will be influenced by the choice of fuel. Use of combusted ammonia as the fuel source can offer an energy efficient solution as the ammonia has not been processed through the cracker, although a level of product hydrogen may be blended in to improve fuel properties. Electrical energy can be imported to increase the hydrogen recovery at the expense of the energy efficiency of the system and with the caveat that sources of green energy are not likely to be abundant in areas with large ammonia cracking units.

6. Conclusions

Large-scale and small-scale cracking facilities require important design considerations to minimise

costs while achieving a high conversion efficiency and energy efficiency. The waste stream, containing ammonia and hydrogen, can be used as a fuel to drive the cracking reaction to optimise energy recovery. Depending on the constraints of the application, a high- or low-temperature operating regime may be appropriate and a corresponding base metal or precious metal catalyst the most cost-effective solution. Purification of the hydrogen is a challenge where PEM fuel cells are the target end use and if the crackers are to be sited in populated areas.

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The Authors

Julie Ashcroft has worked at Johnson Matthey for over eight years. She graduated from the University of Cambridge, UK, with an MEng in Chemical Engineering. She is currently a Senior Process Engineer in the ammonia and nitric acid engineering team, working in developments within these industries, with a focus on ammonia cracking process development.

Helen Goddin is the Research Group Leader for nitric acid and ammonia decomposition catalysts. She has worked at Johnson Matthey for six years, specialising in metallurgy and catalysis. Prior to that she completed a PhD at the University of Cambridge in Materials Science.