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Number 389

May | June 2024

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Merchant ammonia capacity

China's urea exports

Ammonia cracking technology

Improved water gas shift catalysts

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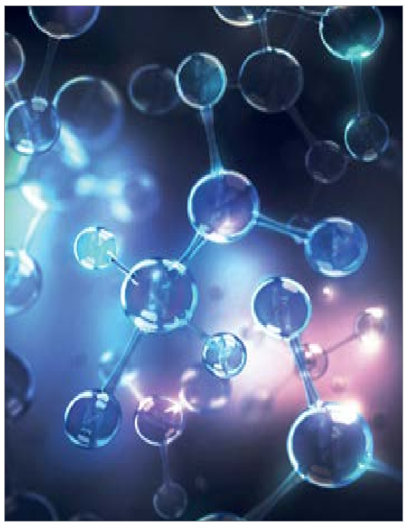

Cover: Energy of molecule or atom.
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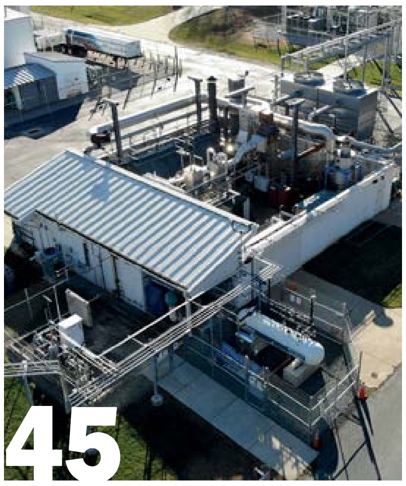

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Published by:
CRU

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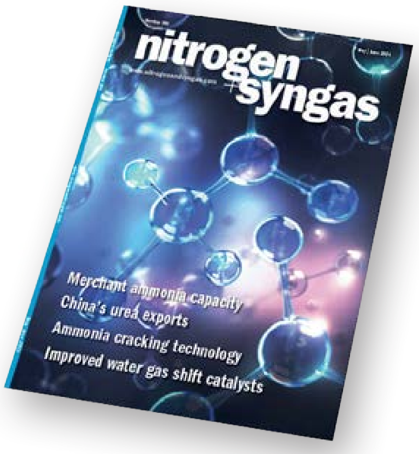
The shipping race



While there has been a lot of talk about decarbonising ammonia and methanol production, for as long as blue and green production is more expensive than conventional production, uptake will be dependent upon markets which are prepared to pay a premium for such chemicals, perhaps because they have no other reasonable choice, given environmental mandates. One sector above all has dominated the prospects for medium term demand for low carbon ammonia and methanol alike, and that is shipping.

> **"By 2027, 270 methanol powered vessels should be in service..."**

The International Maritime Organisation's revised greenhouse gas strategy, adopted at the Marine Environment Protection Committee meeting last year, includes an enhanced common ambition to reach net-zero emissions from international shipping by 2050, a commitment to ensure an uptake of alternative zero and near-zero GHG fuels by 2030, as well as indicative check-points for international shipping to reach net-zero emissions for 2030 (by at least 20%, striving for 30%) and 2040 (by at least 70%, striving for 80%). Several propulsion sources are in the running to be the low carbon shipping fuels of the future, including biofuels, electric power, fuel cells, hydrogen, and even a return to wind power, but ammonia and methanol have been among the most prominent, as they are liquid fuels which have a supporting infrastructure already available at many major ports.

Up until now, methanol has appeared to be winning that race, with ammonia lagging on issues like engine design and safety concerns, but there are signs that this may be slowly changing. Norwegian classification society Det Norske Veritas (DNV) maintains a count of orders for new alternative fuelled vessels, and its most recent publication shows interest in ammonia-powered ships picking up. DNV says that there were 23 orders for alternative fuelled vessels in April, of which 12 were methanol powered, seven LNG, and four were ammonia powered. According to DNV, this brings the total orders for the year to date to 93, a 48% increase on that for the first four months of 2023. DNV notes that this also brings ammonia's total for the year up to 9 vessels, showing a growing enthusiasm for ammonia as a fuel.

Methanol however continues to be the most popular alternative fuel overall, with 47 orders in the first four months of 2024, 42% up on last year, and now representing almost exactly half of all orders, outpacing LNG, which was previously popular. There are now 33 methanol fuelled vessels in operation, most of them tankers, particularly the fleet operated by Methanex subsidiary Waterfront Shipping, but there are 248 methanol ships now on order, the majority of them container ships. Danish shipping giant Maersk has been a pioneer in this regard, with 18 very large container ships on order, the first of which, the Ana Maersk, was launched last year and which recently completed a container run from Hamburg, through the Mediterranean and docking in early May at Dubai. This means that by 2027, 270 methanol powered vessels should be in service, representing several million t/a of potential demand. But just as the shipping industry appears to have pivoted from LNG powered vessels to methanol in the past couple of years, it remains possible that similar could happen for ammonia over the next few years. Nine orders this year are only straws in the wind, but could be the start of something bigger. ■

Richard Hands, Editor

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Price Trends

The ammonia market reverted to recent norms at the end of April, with prices more or less unchanged in the east, and several benchmarks west of Suez moving downward in line with May's Tampa settlement. Following a trio of high-priced c.fr spot deals many wondered whether such business would be replicated in Asia, but the hype did not live up to the expectation, with the majority of tonnes continuing to move on a contract basis into the likes of South Korea and Taiwan, China. The $430/t c.fr concluded into China has been attributed to both supply uncertainty and an uptick in domestic demand, though several inland prices declined this week, rendering price direction difficult.

In Southeast Asia, it was much of the same story, with exports continuing to move out of Indonesia at a steady rate, though a degree of tightness could begin to kick in Malaysia, where Petronas will commence a 16-day turnaround at its 450,000 t/year Bintulu facility as of 4th May.

Further west, exports out of the Middle East may suffer further delays after Ma'aden announced that its one-month planned shutdown at its MWSPC II unit would now commence in mid-May, with additional rumours of output woes at Sabic AN, prompted by delays to loadings at Jubail, potentially casting a further shadow over the Eastern hemisphere market. In Turkey, news of a result in Igsas' latest 8,000-10,000 t purchase tender is awaited, amid talk of sanctioned material offered between $390-430/t c.fr.

West of Suez, producers in Algeria continue to push for business in the low-$400s/t f.o.b., though potential buyers remain unwilling to bite for the time being. Import demand into NW Europe remains limited on the spot front, with more stable natural-gas prices continuing to reflect more desirable costs of production by comparison to import cargoes.

In urea markets, with few buyers showing interest, prices are still under pressure. There is little interest in Europe to buy again and producers in Egypt now seem to be faced with looking further afield to place May tonnes. A sale to Turkey was reported to net as low as $280/t f.o.b., but other players in the market think it may achieve $285/t.

Offers from the Middle East were seen at $280-285/t f.o.b., but when SIUCI tested the market for an early-June cargo out of Oman, the best number it could find was understood to have been $275/t. Indonesia continued selling following its 22 April tender and finally placed about 190,000 t at $305.69/t with Australia taking 90,000 t. A prilled tender closes 3 May to test buyer interest.

New Orleans had a quiet end to the month. Rain hampered business and weakness in the global market is not encouraging any unnecessary purchases. First-half May dipped to $295/st and full May saw $280/st f.o.b. NOLA trade. Brazil proved to be volatile and gains seen of late seem to have been swept away with trades as low as $290/t c.fr. Some May cargo may secure a higher price for non-sanctioned material but plentiful supply from Venezuela and Iran saw sales for the month at $290/t c.fr and buyers withdraw from offers of non-sanctioned at $310/t c.fr. ■

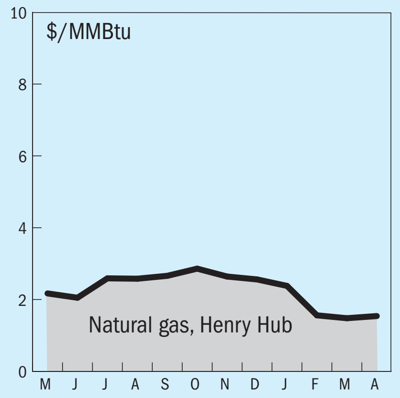
Table 1: **Price indications**

Cash equivalent	**mid-Apr**	**mid-Feb**	**mid-Dec**	**mid-Oct**
Ammonia ($/t)				
f.o.b. Black Sea	n.m	n.m.	n.m.	n.m.
f.o.b. Caribbean	435	395	475-575	525-575
f.o.b. Arab Gulf	270-300	270-350	470	445-550
c.fr N.W. Europe	460-470	470-480	535-545	620-680
Urea ($/t)				
f.o.b. bulk Black Sea	250-260	300-320	273-290	320-390
f.o.b. bulk Arab Gulf*	275-290	345-352	298-302	340-405
f.o.b. NOLA barge (metric tonnes)	285-305	355-360	330-334	370-418
f.o.b. bagged China	300-310	330-335	360-370	365-405
DAP ($/t)				
f.o.b. bulk US Gulf	550-570	550-570	560	550-589
UAN (€/tonne)				
f.o.t. ex-tank Rouen, 30%N	230-240	255-260	309-310	284-315

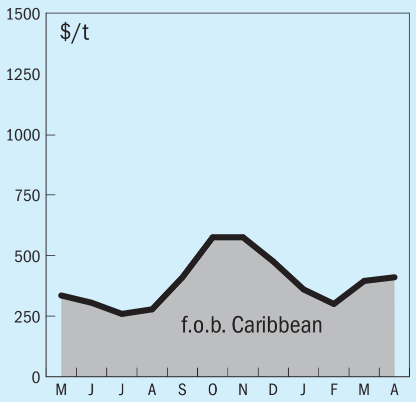
*Notes: n.a. price not available at time of going to press. n.m. no market. * high-end granular.*

END OF MONTH SPOT PRICES

natural gas



ammonia



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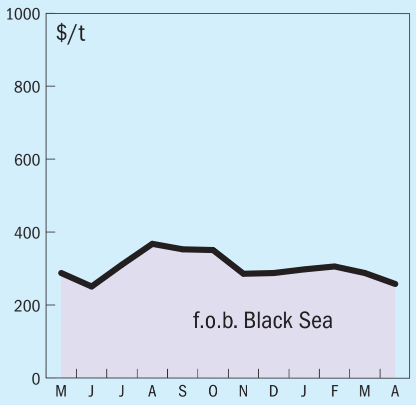
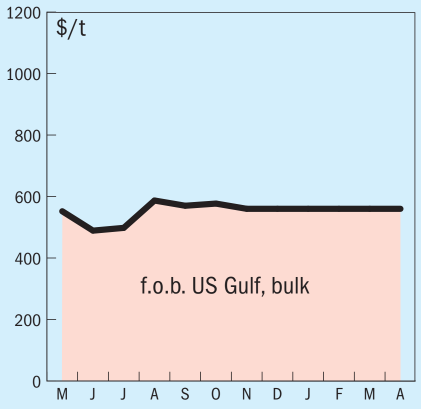


diammonium phosphate



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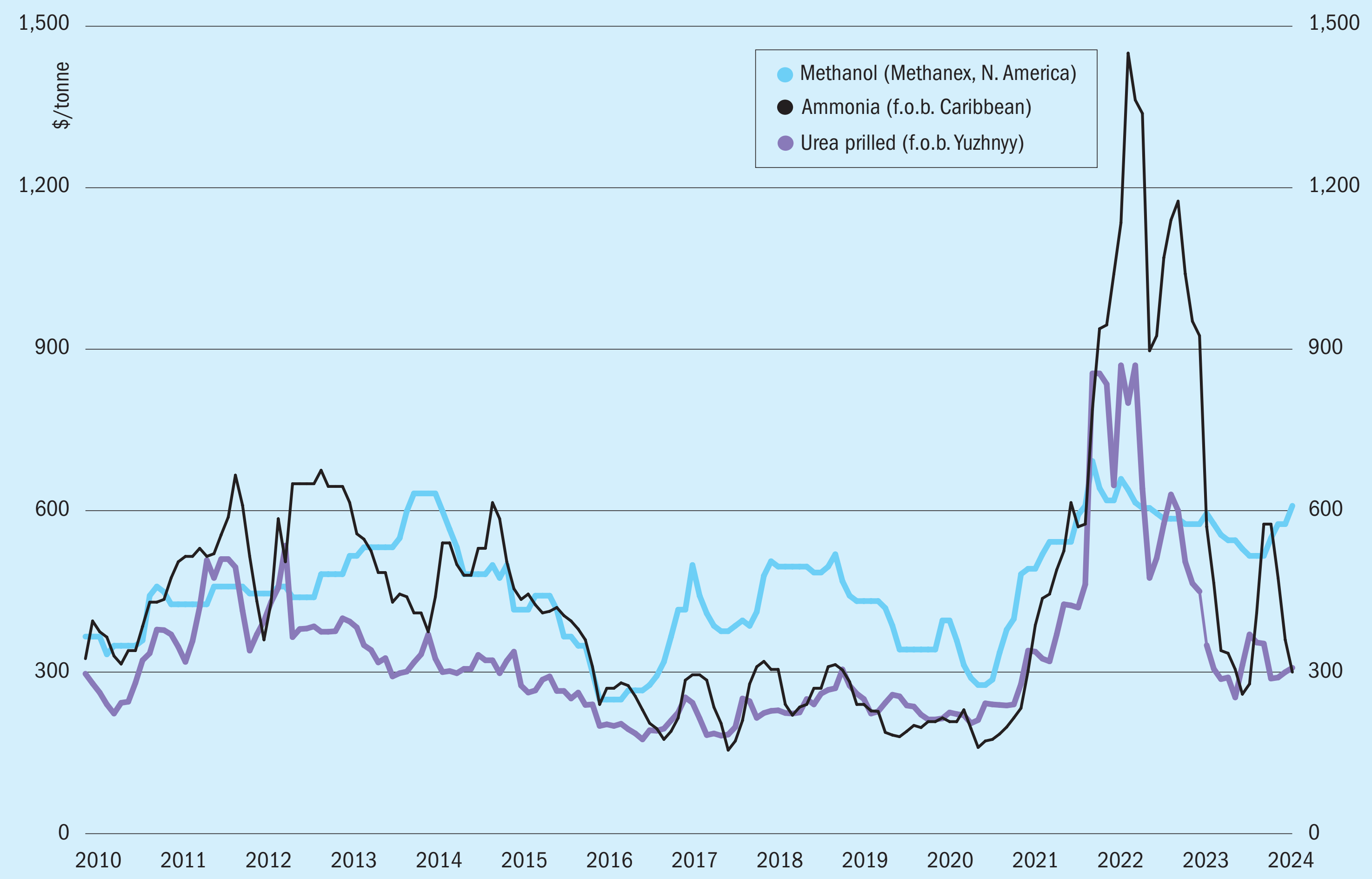
Market Outlook

Historical price trends $/tonne



Source: CRU

AMMONIA

- Prices in the West are unlikely to garner much support moving into the latter stages of Q2. The May Tampa ammonia settlement was settled by Yara and Mosaic at $450/t c.fr, down $25/t on the $475/t c.fr agreed for April. With seasonal domestic demand in the US drawing to a close 2H April, many had anticipated that either a rollover or a slight decline would be agreed.
- Prices in the Far East appear to have registered some support in recent weeks, the prospect of this tailwind lasting beyond June appears unlikely. Petronas says it would be commencing a 16-day maintenance at its 450,000 t/year Bintulu facility as of 4 May.
- In Saudi Arabia, Ma'aden said that the planned curtailment at its 1.1 million t/a Wa'ad Al Shamal Phosphate Company (MWSPC) II unit will begin in mid-May. Netbacks on the group's latest contract shipments remain unchanged at around the $275/t f.o.b. mark, as it continues to receive healthy spot interest from Asia for June deliveries.

UREA

- The market is bearish with little to report on the demand side and length on the supply side of the equation. It is difficult to see which region will step in to soak up June tonnes. India is sitting on 10 million tonnes of inventory and is not expected back into the market any time soon.
- Small granular buyers in Southeast Asia are putting out soft bids at $320-330/t c.fr which seemingly are too low to attract trader interest following a raft of purchases from Indonesia at $305-306/t f.o.b.. Offers in the region have been in the low $330s to $340s/t c.fr.
- There are no fresh updates on China urea export restriction policy. Considering the current firm domestic prices, the export inspection approval time may be delayed to June-July 2024.

METHANOL

- Methanol prices have been rising in North America. Commercial production at the Methanex Geismar 3 plant, which will bring an additional 1.8 million t/a of production, has been delayed due to what the company describes as "complications" with the refractory bricks in the autothermal reformer, possibly until Q4 2024. Continuing strong demand in North America has contributed to the price rises, and the news comes after a series of production outages in the US during Q1.
- Availability was also tight in the Middle East, with supply constrained in Saudi Arabi in March. This had a knock-on effect on major importing regions such as India and China. There have also been plant shutdowns in the Asia-Pacific region, including Malaysia, continuing to tighten availability, and natural gas related production shortages in China and Iran.

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Nitrogen Industry News

UNITED STATES

FEED study for new low-carbon ammonia plant

Topsoe has signed a contract with CF Industries, the world's largest producer of ammonia, for the licensing and engineering supporting a front-end engineering and design (FEED) study of a new low-carbon ammonia plant in Louisiana. CF Industries is evaluating the project in collaboration with leading ammonia marketer Mitsui & Co., Ltd. The project would produce low-carbon ammonia for use as a decarbonised energy source.

Henrik Rasmussen, Managing Director, The Americas, Topsoe, said: "We believe low-carbon ammonia helps unlock the door towards a net zero future. Our technology offers a cost-effective route to producing low carbon ammonia while also enabling carbon capture, at industrial proven scale. CF and Topsoe have a long-standing relationship spanning many decades and we are proud to extend our collaboration with this award." ■

JERA looking for offtake from Exxon plant

JERA says that it has reached a project framework agreement with ExxonMobil to jointly explore low carbon hydrogen and ammonia production project in the United States. ExxonMobil is currently developing what is expected to be the world's largest low-carbon hydrogen production plant at its Baytown Complex east of Houston, Texas, United States. The plant is slated to have an annual production capacity of approximately 900,000 t/a of low-carbon hydrogen and annual production capacity of more than 1.0 million t/a of low-carbon ammonia. The project aims to commence production in 2028. Under the terms of the new agreement, JERA and ExxonMobil will explore JERA's ownership participation in the project and procurement of approximately 500,000 t/a annually of low-carbon ammonia produced by the project for demand in Japan.

"Cooperation among leading companies is essential to establish supply chains for ammonia, hydrogen, and other products that are key to zero-emission thermal power," said Steven Winn, JERA's Senior Managing Executive Officer and Chief Global Strategist. "We believe that working together with ExxonMobil, who is actively promoting investment in carbon capture and storage (CCS) and hydrogen, will contribute to the transition to a global decarbonised society."

BRAZIL

Restart for Araucaria

The board of Petrobras has approved the resumption of operations at the company's Araucária Nitrogenados SA (ANSA) site at Araucaria, Parana state. The plant, which has the capacity to produce 475,000 t/a of ammonia and 720,000 t/a of urea, has been idled 2020. The plant can also produce 450,000 m^3/year of diesel exhaust fluid as a 10% urea solution. Petrobras is moving back into fertilizer production after previously closing down all of its plants, following a strategic review last year, and the first phase is to revamp and restart existing assets. The board directive mandates that ANSA


The Petrobras Araucária Nitrogenados (ANSA) plant, Brazil

PHOTO: PETROBRAS

carry out a detailed survey of the plant, to assess equipment integrity and develop a plan for restarting the unit.

SWEDEN

New duplex tube for acid environments

Alleima has introduces new advanced super-duplex tube tailored for acids. SAF™ 3006 is a high-alloy duplex stainless steel tailored to enhance corrosion resistance in acidic and caustic environments. The new alloy, an upgrade to traditional super-duplex stainless steels, adds to the company's growing duplex portfolio. The main application is heat exchanger tubing exposed to hydrochloric, sulphuric, formic or other acids. Duplex grades, with a 50-50 austenitic-ferritic structure, offer more than twice the strength of standard stainless steels and superior corrosion resistance. The chemical composition involves a high chromium content of 30% and a molybdenum level of 3.2% to maintain good structural stability and balancing of the alloying elements.

"We're thrilled to welcome this new super duplex to our expanding duplex family. It provides that 'missing duplex tool' for customers battling acids in heat exchangers, giving them that extra edge. With the addition of SAF™ 3006, we strengthen our presence in duplex materials tailored for acidic corrosion, where we see strong growth potential. Applications may include caustic evaporators, acid coolers and evaporators," said Eduardo Perea, Market & Product Manager EMEA at Alleima Tube Division.

GERMANY

Heraeus focuses on recycled metals

Heraeus Precious Metals has introduced a new range of products made with 100% recycled precious metals. The recycled material is available under the brand name Circlear and based on a mass balance approach. It comes with a significantly lower carbon footprint, thereby helping customers to meet their sustainability goals. Circlear products are available for seven precious metals including gold, silver, platinum, palladium, rhodium, ruthenium and iridium. A significant portion of Heraeus' precious metal product portfolio can be offered as Circlear, catering to diverse industrial applications, such as chemical products, catalytic gauzes, electrical contacts, and pharmaceutical ingredients.

The Circlear recycled precious metals originate from secondary sources, such as spent chemical or automotive catalysts. Recycled precious metals have the same high quality and purity as material from primary extraction but an up to 98% lower carbon footprint. One kilogram of recycled precious metals saves up to 33 metric tons of CO_2, which equates to the average carbon dioxide emissions of a new EU passenger car traveling more than 300,000 kilometers.

"For decades, circularity has been part of Heraeus Precious Metals' DNA," emphasized André Christl, CEO of Heraeus Precious Metals. "We recognise our customer's growing demand for sustainable solutions. With Circlear, we offer a solution that allows our customers to reduce their Scope 3 carbon footprint and to accurately track their progress towards their sustainability goals."

Mabanaft signs green ammonia supply agreement

German energy company Mabanaft has signed a letter of intent (LoI) with US-based Pattern Energy concerning the supply of green ammonia. The green ammonia would be produced by Pattern Energy at the Port of Argentia, in the Canadian province of Newfoundland and Labrador, starting in 2027. Pattern Energy is looking to build a new facility with an estimated production capacity of 400 t/d of ammonia. As part of the LoI, Mabanaft also plans to evaluate the opportunity to potentially become a co-investor next to Pattern Energy and share ammonia and infrastructure expertise. The green ammonia, produced with wind energy and hydroelectricity, is expected to make an important contribution to supplying industry in northern Germany and beyond with energy from renewable sources. The LoI was signed by representatives of both companies at Mabanaft's headquarters in Hamburg in the presence of the German Federal Minister for Economic Affairs and Climate Action Habeck, the Canadian Minister for Energy and Natural Resources Wilkinson and Hamburg's Senator for Economic Affairs Leonhard.

Catalyst campaign to remove 2 million t/a CO_2e

Clariant has issued an update on its Clariant Climate Campaign, begun in 2021. It offers nitric acid producers who do not use N_2O exhaust gas treatment a free fill of the company's transition metal exchanged EnviCat® N_2O-S catalyst. EnviCat® and other solutions can remove up to 99% of the N_2O formed from ammonia oxidation during nitric acid production. Clariant has more than 20 years' experience in N_2O abatement, with 50 successful installations worldwide, including more than 30 plants with tertiary abatement systems for >99% N_2O removal and 20 with secondary abatement (>95% removal).

Over 66 million tons of nitric acid are produced annually worldwide, mainly for the manufacture of fertilizers. However, around 50% of nitric acid plants run without N_2O reduction, mostly in regions without applicable emission control regulations, leading to emissions equivalent to around 100 million t/a of CO_2 equivalent (CO2e), equivalent to the exhaust emissions of over 21 million passenger cars.

Clariant's campaign will see four successful installations of free N_2O abatement catalysts by the end of 2024, representing 1 million t/a of nitric acid production, and leading to more than 2 million t/a of CO_2e savings, roughly equivalent to taking 500,000 vehicles off the road.

CANADA

Uhde to design fertilizer complex for Saskatchewan

thyssenkrupp Uhde and Genesis Fertilizers have signed a pre-front end engineering and design contract to conceptually develop an integrated fertilizer complex at Belle Plaine, Saskatchewan. The proposed plant will be designed to produce 1,500 t/d of ammonia, 2,600 t/d of urea/UAS granulation, nitric acid and UAN, and will also have the ability to produce Diesel Exhaust Fluid (DEF). thyssenkrupp Uhde will provide engineering solutions for the integration of the product streams of the plant, with a focus on minimising plant emissions. thyssenkrupp Uhde's EnviNOx® technology, for example, will almost completely eliminate nitrogen oxides from nitric acid production. Furthermore, the design of the plant will consider the potential use of renewable-based hydrogen and electricity.

In a press statement, Jason Mann, President and CEO of Genesis Fertilizers said: "Our primary goal is to ensure the supply of fertilizers to the farmers in Western Canada, based on the most advanced technologies available with the lowest possible carbon footprint.

We are pleased to be working with a strong industry partner that offers expertise in all the processes and technologies involved from a single source."

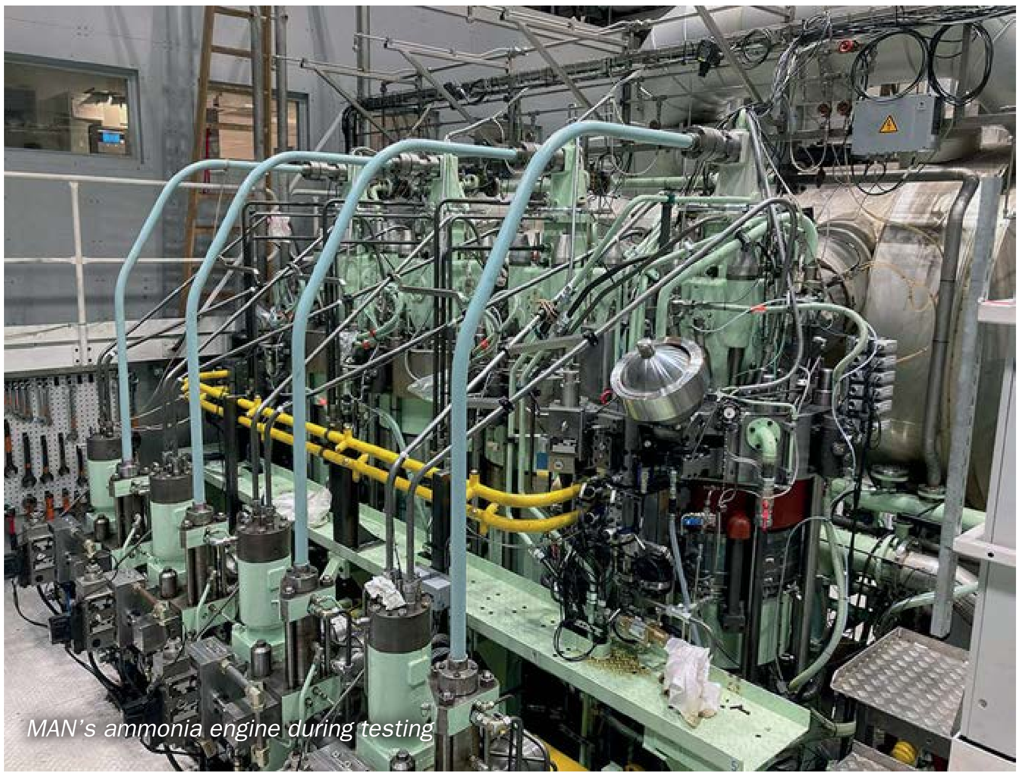
Lucretia Löscher, COO thyssenkrupp Uhde said: "This project is a further proof that the transition of the fertilizer industry towards more sustainability has started. Our expertise in clean fertilizer technologies and their integration is essential to support our customers on their journey to protect the climate."

JAPAN

MAN to supply ammonia engine for bulk freighter

Imabari Shipbuilding will install an MAN B&W 7S60ME-Ammonia engine with selective catalyst reduction (SCR) as part of the construction of a 200,000 dwt class bulk carrier for a joint venture between K Line, NS United and Itochu Corporation. The business represents one of the first projects for MAN Energy Solutions' ammonia-powered engine currently under development in Denmark.

Brian Østergaard Sørensen, Vice President and Head of Research & Development, Two-Stroke at MAN Energy Solutions, said: "This project marks another important milestone in our ammonia-engine development and indeed for the maritime industry in general. It also confirms that we are on the right track in relation to our dual-fuel ammonia concept where we have gained a great understanding of ammonia's unique characteristics as a marine fuel via our two-stroke engine testing, which we started in early June 2023. Equally as important, we are confident of how to handle it safely; it is very satisfying to see our hard work beginning to pay off."



MAN's ammonia engine during testing

PHOTO: MAN

WORLD

Red Sea and Panama crises continue pressuring freight rates

Over the last six months, climate and geopolitical events have disrupted seaborne trade. A record drought in Panama and the unprecedented intensity of attacks on commercial ships by the Houthi rebels in the Red Sea are straining the freight market. Almost 150 ships have been targeted along the latter trade route since the first attack was registered to a non-commercial ship last year.

While vessels in the Panama Canal need to wait for longer to cross it, oil and shipping majors have stopped their vessels from crossing along the Red Sea; and are routing them away from the region. The alternative journey around the Cape of Good Hope in Southern Africa adds around 8.5 days to the journey from East Asia to Europe.

As a result, ship transits through the Panama Canal, Bab el-Mandeb Strait and Suez Canal are falling rapidly, with daily crossings reducing by almost 30%, 65% and 45% from year to date, respectively. With vessel transit along the Panama and Red Sea trade routes amounting to almost 20% of seaborne trade, recent events are already impacting transit volumes and freight costs. The Baltic Dry Index (BDI) has risen more than 30% in March since the Houthi attacks to commercial ships began in November, while the corresponding increase for the Global Container Freight (FBX) has been 143% so far.

As seaborne trade accounts for more than 80% of total global trade, these disruptions have potentially important spillovers to the world economy. In particular, trade in the Red Sea accounts for around 15% of global seaborne trade, and is important for oil and gas, dry bulk and container shipping.

Our central view is that the nature of current disruptions to the seaborne market is short-term, and trade fundamentals will shape the long-term direction of freight rates. World volume trade growth remains weak and has shown signs of stagnation over the last 12 months. As the weather outlook begins to improve in Panama, subdued trade is expected to weigh down on freight rates. For instance, the Panama Canal Authority has recently softened the restrictions on the number of ships that can cross the Canal, starting in January. Although the BDI fell briefly in January back to October levels, it is trending up again as more bulk carriers have been targeted by the Houthi rebels in the Red Sea.

The situation in the Red Sea remains fluid, but any de-escalation will likely see dry bulk freight rates dropping further and container costs limiting upside movements. However, in a severe downside scenario, we do not rule out renewed pressure on freight rates if the conflict in the Red Sea extends or escalates, leading to higher security risks for shipping majors. An intensification of the Red Sea conflict will result in higher container, dry bulk freight rates and could ultimately lead to higher energy prices.

The global supply chain crisis of 2021-22 saw freight rates soar and queues of ships form offshore major ports. This contributed to the surge in producer prices and consumer price inflation in the US, Europe and other countries. The Global Supply Chain Pressure Index (GSCPI) estimated by the Fed has shown a strong correlation with global PPI inflation over the past few years. Renewed disruptions to supply chains and/or higher energy prices could again cause producer prices to rise which will, in turn, put upward pressure on consumer prices, squeezing consumer real incomes and potentially delaying any

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easing in monetary policy. This threat is probably greatest for Europe, given the importance of the Red Sea route to Westbound container traffic from East Asia. But higher energy prices would affect most countries. However, a return to the inflation rates of 2021-22 is unlikely in all but a worse-case scenario.

IRAN

Urea plant commissioning from May

Hengam Petrochemicals says that its new urea plant at Assaluyeh will begin pre-commissioning in May. The plant's ammonia unit started up at the end of 2023 and, according to Hengam Petrochemicals, has sold eleven vessels worth of liquid ammonia so far. The long-delayed plant has been in development for 17 years.

FRANCE

Yara ordered to remove ammonia from Montoir

The Loire-Atlantique prefecture has given Yara six months to remove all ammonia and ammonium nitrate still remaining at its Montoir-de-Bretagne site. Yara announced that it would be ceasing production at the site, which has the capacity to produce 1,200 t/d of ammonium nitrate, in November 2023, but had intended to turn it into an import terminal. Production stopped in October after a plant outage. However, following a power failure which led to the release of nitrogen-laden water into the Loire on March 29th the local government has ruled that the site must have all chemicals removed from it.

AUSTRALIA

Fertilizer sale may be nearing completion

Although the parties involved have been closed mouthed about the process, there are reports that Incitec Pivot's $1 billion sale of its fertilizer assets to Indonesian fertilizer major Pupuk Kaltim may be nearing a conclusion. Negotiations reportedly began last year after then CEO Jeanne Johns unveiled plans for a demerger of the company's fertilizer assets to allow it to concentrate in its Dyno Nobel mining and industrial explosives business. However, Australia's Foreign Investment Review Board and some opposition politicians in Queensland have expressed concern over the sale to an Indonesian company, given the importance of its fertilisers and diesel exhaust fluid additive business to the Australian food chain and farmers on the East Coast. Other potential bids are understood to be on the table, including from Australian firms Senex Energy and Wesfarmers.

Gibson Island misses project deadlines

Fortescue Metals, which has been developing a major green hydrogen and ammonia project for Gibson Island, Queensland, has missed its revised March deadline for financial closure and a final investment decision on the project. The deadline was previously extended from December 2023 and again from February 2024. The Gibson Island urea plant is owned by Incitec Pivot (although see the story above), and Genex Power is aiming to develop 450 MW of solar electricity generation at the Bulli Creek solar farm. Fortescue then plans to take 337 MW of output from the solar farm to produce hydrogen, which it would then sell to Incitec Pivot for green ammonia and downstream urea production.

Feasibility study on urea from waste

The Australian Fertilizer Corporation (AFC) is reportedly in the process of evaluating the construction of a 1,000 t/d ammonia plant combined with a 500,000 t/a granular urea plant to be based in Gladstone, Queensland. The project would not use conventional natural gas feedstock but gasification of low cost municipal waste streams. Carbon dioxide from the gasification would be used for urea production, with any excess captured and sold commercially nearby.

ARGENTINA

Nutrien to exit Cono Sur

Bloomberg reports that Nutrien is seeking to sell its retail operations in Argentina, Chile and Uruguay in order to focus on Brazil and other global markets. The company said in its annual report that Argentina's currency controls meant it lost money when it transferred currency out of the country because it had to use a more expensive exchange rate. New President Javier Milei has promised to scrap the controls as he seeks to deregulate the economy. Nutrien has a 50% stake in ammonia-urea manufacturer Profertil SA, which it runs as a joint venture with Argentinian state oil company YPF SA. YPF is looking to divest assets to focus on shale drilling.

PHOTO: YARA

Yara's Montoir de Bretagne site, France

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INDIA

Urea imports to end by 2025?

India's Chemicals and Fertilizers Minister Mansukh Mandaviya says that the country will stop importing urea in 2025, following the start-up of several major new urea projects in the country. Four of these are now up and running and a fifth remains under development. He said that Indian urea demand stands at around 35 million t/a, and domestic capacity has risen form 22.5 million t/a in 2014-15 to 31 million t/a. The Talcher urea plant should take that figure to 32.5 million t/a, and it was hoped that new developments in urea technology would make up the remainder of the shortfall. Speaking to domestic press, he said that as well as the new builds, the government is making efforts to promote alternate fertilisers like liquid 'nano' urea and liquid nano di-ammonium phosphate (DAP) to improve soil health. Imports of urea fell to 7.5 million t/a in fertilizer year 2022-23, against 9.1 million t/a the previous year.

Memorandum signed for new ammonia plant

Indian green technology firm Hygenco Green Energies says that it has signed a binding agreement with the Tata Steel Special Economic Zone Industrial Park (GIP), to establish a large-scale green ammonia project in Gopalpur, Odisha State. Hygenco aims to produce 1.1 million t/a of 'green' ammonia from this plant in multiple phases. The company is aiming to commission the first phase of the project by December 2026. This collaboration builds upon the project approval received in February 2024 from the High-Level Clearance Authority of the Chief Minister of Odisha.

Amit Bansal, founder and CEO, Hygenco, said, "Having already demonstrated our mettle in the space of Green Hydrogen by commissioning India's first green hydrogen project earlier this year, we will extend application of our superior technology to this project thereby producing lowest cost green ammonia for our clients. In line with our strategic vision of being a dominant player in this sector worldwide, the produce from this plant, in the initial phase, will be predominantly exported for which advanced discussions with various off-takers are already taking place."

Manikanta Naik, Managing Director, Tata Steel Special Economic Zone Limited, said, "We are very happy to have Hygenco on-board with us at the Industrial Park. This solidifies our Industrial Park as a potential green hydrogen/ammonia hub of the country."

Hygenco has signed several binding long-term offtakes for green hydrogen in India, including a recently commissioned 75 t/a plant for a prominent steel company in Hisar, Haryana. Another for STL (Vendanta Group) at Maharashtra is under construction.

MOROCCO

Collaboration on low carbon ammonia

OCP Group has signed a joint venture agreement with green energy, metals and technology company Fortescue Energy. The 50-50 joint venture aims to supply green hydrogen, ammonia, and fertilizers to Morocco, Europe, and international markets. It includes the potential development of manufacturing facilities and an R&D hub to advance the rapidly growing renewable energy industry in Morocco.

The partners have laid out proposed plans for four cornerstone projects in Morocco, based around large-scale integrated green ammonia and green fertilizer production capacity, including renewables, energy generation, electrolysis, ammonification and fertilizer production; manufacturing of green technology and equipment; a research, development and technology hub, located alongside Mohammed VI Polytechnic University (UM6P) near Marrakech; and collaboration of corporate venture capital funds to drive investment in key technology advancements.

Mostafa Terrab, Chairman and CEO of OCP Group, said: "Our strategic partnership with Fortescue is a testimony to our joint commitment to decarbonisation, driving the development of cutting-edge facilities and delivering competitive renewable energy, products and technology. This is a key step towards fulfilling our vision of simultaneously ensuring global food security and combating climate change.

Dr Andrew Forrest AO, Fortescue Executive Chair and Founder said: "Together, Fortescue and OCP will build a world-leading and globally competitive platform to accompany Morocco's journey into a green energy production, manufacturing, and industrial powerhouse… Morocco will be a major player in the global energy transition given it is home to some of the world's most prospective wind and solar resources, two large coastlines, and is in close proximity to Europe and the Americas."

TURKMENISTAN

Tender for new urea plant

State-run chemical major Turkmenhimiya has announced an international tender for the design and turnkey construction of an integrated ammonia-urea plant. The facility, the capacity of which is still to be determined, will be constructed near the village of Kiyanly in Turkmenistan's western Balkan region. Turkmenhimiya already operates three nitrogen plants in the Central Asian country: Marykarbamid, which has capacity to produce 400,000 t/a ammonia and 640,000 t/a of urea; Tejenkarbamid, which has capacity to produce 350,000 t/a urea; and Garabogazkarbamid, which has capacity to produce 640,000 t/a of ammonia 1.16 million t/a of urea.

NORWAY

KBR to supply ammonia technology

KBR says that it has secured a contract to provide green ammonia technology for Fortescue's Holmaneset green energy project in Norway. KBR will provide the technology license, proprietary engineering design, and front end engineering design (FEED) support engineering services for the Holmaneset green ammonia plant, which will have a capacity of 675 t/d.

The Holmaneset Project is located on the coast of the Nordgulen fjord, 8 km west of Svelgen in western Norway. According to Fortescue, the Holmaneset project will use renewable energy to power an integrated green hydrogen and green ammonia process plant, complete with transmission infrastructure and port facilities, for the transport of green products to the Norwegian and European markets.

"We are excited to work with Fortescue on this project to offer our zero-carbon green ammonia technology," Jay Ibrahim, President for KBR Sustainable Technology Solutions, said. "KBR is a significant contributor in the development of the green energy value chain and decarbonisation of hard-to-abate industries and we look forward to working with Fortescue to advance their ESG objectives". ■

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Syngas News

GERMANY

Start-up for electrically heated steam cracking furnace demonstrator

BASF, SABIC, and Linde have jointly inaugurated the world's first demonstration plant for large-scale electrically heated steam cracking furnaces at BASF's Verbund site in Ludwigshafen, following three years of development, engineering, and construction work. The three companies signed a joint agreement to develop and electrically heated steam cracking furnaces in March 2021.

Steam crackers play a central role in the production of basic chemicals and require a significant amount of energy to break down hydrocarbons into olefins and aromatics. Typically, the reaction is conducted in furnaces at temperatures of about 850°C. Up to now, these temperatures have been reached by using conventional fuels. The demonstration plant aims to show that continuous olefin production is possible using electricity as a heat source. By using electricity from renewable sources, the new technology has the potential to reduce CO_2 emissions of one of the most energy-intensive production processes in the chemical industry by at least 90% compared to technologies commonly used today.

The demonstration plant, which produces olefins, such as ethylene, propylene, and possibly also higher olefins from saturated hydrocarbon feedstock, is fully integrated into the existing steam crackers in Ludwigshafen. The upcoming operation serves the goal of gathering data and experiences about material behaviour and processes under commercial operating conditions for the final development of this innovative technology to industrial market maturity. In two separate demonstration furnaces, two different heating concepts will be tested. While in one furnace, direct heating applies an electric current directly to the cracking coils, in the second furnace, indirect heating uses radiative heat of heating elements placed around the coils. The two electrically heated furnaces together process around 4 tons of hydrocarbon feedstock per hour and consume 6 megawatts of renewable energy.

To support the development of the novel furnace technology, the project was granted €14.8 million by the German Federal Ministry for Economic Affairs and Climate Action under its "Decarbonisation in Industry" funding program. The program is supporting energy-intensive industries in Germany in their efforts to achieve carbon neutrality.

"With the development of electrically operated steam cracking furnaces, we are getting our hands on a key technology that will help to significantly reduce greenhouse gas emissions in the chemical industry. It fills me with pride and joy that we have achieved this success together with our partners SABIC and Linde. The demonstration plant here in Ludwigshafen will provide us with valuable experience on the final step towards the industrial application of this technology", said Dr. Martin Brudermüller, Chairman of the Board of Executive Directors of BASF SE.

Based on the combined knowledge and intellectual property of the three parties collaborating to develop the new technologies, the demonstration unit in Ludwigshafen will be operated by BASF. Linde was responsible for the engineering, procurement, and construction of the plant. Linde will in the future commercialise the developed technologies under the new trademark STARBRIDGE™, enabling the petrochemical industry to decarbonise by replacing conventional fired technologies. ■

CHINA

Methanol engines for Chinese market

MAN Energy Solutions and the China Classification Society (CCS) have signed an agreement over MAN's new L21/31DF-M dual-fuel methanol engines, designed at the company's Danish site in Holeby. It provides for a collaboration between the two companies that will support the new engine in the Chinese market, including all activities associated with its planned type approval test in China in Q4, 2024.

Jiang Botao said: "MAN Energy Solutions, as a globally-renowned ship equipment manufacturer, takes the lead in the technological advancement of marine alternative-fuel engines and has long been one of CCS's most important partners. The introduction of the MAN L21/31 DF-M methanol dual-fuel engine provides shipowners with more choices to achieve their decarbonisation goals. We much appreciate MAN Energy Solutions' contribution and believe that the collaboration between it and CCS in alternative-fuel engines will surely make further contributions to a more sustainable future for the global maritime industry."

ITALY

Collaboration on 'power to X' projects

Maire subsidiary NextChem has agreed to collaborate with Vallourec on the integration of NextChem's proprietary green ammonia technology with Vallourec's Delphy hydrogen storage technology, and its subsequent commercialisation. The two partners will study how to combine the Delphy storage solution in "Power-to-X" and green hydrogen projects where NextChem is involved as technology provider worldwide. Upon completion of the joint feasibility studies, NextChem will act as the exclusive global licensor of the technology package integrating its small-scale green ammonia production technology with Vallourec's hydrogen storage system. The commercialisation of the technology package will be carried out through one of NextChem's subsidiaries.

NextChem has also signed a binding agreement to acquire 100% of GasConTec Gmbh, a German company specialising in technology development and process engineering. GCT owns over 80 patents and significant know-how in the synthesis of low carbon products such as hydrogen, ammonia, methanol, olefins, gasoline and integrated methanol/ammonia processes. In particular, the company's portfolio includes autothermal reforming to produce low carbon hydrogen with very high rates of carbon capture.

The company has also recently finalised the acquisition of 80% of HyDEP S.r.l. and 100% of Dragoni Group S.r.l., through its subsidiary NextChem Tech, both recognised engineering service providers

specialising in the mechanical and electrochemical sectors. Their offer encompasses a broad spectrum of services, ranging from process and mechanical design to validation, prototyping, and certification of water electrolysis, stacks,

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and systems. NextChem will combine its technological know-how with HyDEP and Dragoni Group's competences in electrochemistry to develop and implement its proprietary solutions for green hydrogen production. Moreover, HyDEP's experience in designing and manufacturing small-scale water electrolysis systems will contribute to the development of a hydrogen-based retail network to support the decarbonisation of small-medium enterprises as well as the mobility sector.

NETHERLANDS

Hydrogen import facility for Rotterdam

Global Energy Storage (GES) and Provaris Energy Ltd (Provaris) have entered a collaboration agreement to develop a gaseous hydrogen import facility at the GES terminal in Rotterdam. GES is developing a multi-client, multi-product terminal in Rotterdam, able to import both refrigerated ammonia and compressed hydrogen, with redeliveries into barges, rail, truck and the H_2 grid (HyNetwork) operated by Gasunie.

Under the collaboration, GES and Provaris will complete a comprehensive prefeasibility study to demonstrate the technical and economic viability of berthing and unloading of Provaris' H2Neo compressed hydrogen carriers. Activities will also include the joint marketing of the proposed facility where Provaris will be responsible for the transportation of the hydrogen in the H2Neo carriers and GES responsible for the discharge and injection into the hydrogen grid.

Both parties have a shared belief that the GES terminal in Rotterdam is an ideal site for bulk scale import of green hydrogen given the early connection to the HyNetwork grid for gaseous supply to industrial users in the Port of Rotterdam and key industrials users in Europe. The companies are committed to advancing an energy efficient and timely supply of green hydrogen to industrial users in Europe to support ambitious decarbonization goals.

Peter Vucins, CEO of GES commented: "This collaboration with Provaris showcases the types of partnerships that GES is pursuing to facilitate the Energy Transition through our contribution with storage and logistics solutions, at Rotterdam as well as other existing and future locations. I welcome the opportunity to work closely with Provaris to develop a cost competitive import solution for Rotterdam and European energy customers."

During 2024 GES and Provaris will complete pre-feasibility level studies focused on the jetty facilities to discharge the H2Neo carrier, along with scavenging compression, storage, HyNetwork grid connection, risk and safety, emissions, and other permitting and environmental considerations.

Provaris has advanced the H2Neo hydrogen carrier through an extensive FEED package design approval in December 2022, with a Prototype Tank under construction and testing program underway in Norway to support a final construction approval from Class targeted for mid-2024.

UNITED STATES

Fischer Tropsch production for SAF plant

DG Fuels has chosen Johnson Matthey and bp's co-developed Fischer-Tropsch (F-T) CANS™ technology for its first sustainable aviation fuel (SAF) plant. Located in St James Parish, Louisiana, it will be the largest announced F-T SAF production facility in the world, with a planned capacity of 13,000 bbl/d, providing – after blending to 50% – of producing enough SAF for more than 30,000 transatlantic flights annually. DG Fuels has already secured offtake agreements with Delta Air Lines and Air France-KLM, and has a strategic partnership with Airbus to scale up the use of SAF globally.

The plant is the largest deployment of F-T CANS to date, seven times larger than any previously announced project using this technology. DG Fuels is an emerging leader in renewable hydrogen and biogenic based, synthetic SAF and diesel fuel. The proposed $4 billion DG Fuels plant is planned to produce 600,000 t/a of SAF per year when fully operational. DG Fuels is planning 10 more SAF production plants across the United States. These would be modelled on the Louisiana plant with JM and bp as the partners of choice for these facilities.

The fuel at the Louisiana plant is expected to be produced from waste biomass. DG Fuels is projected to purchase around $120 million of sugar cane waste annually, a third of which is planned to be purchased from St. James Parish farmers. JM and bp's FT CANS technology converts the synthesis gas derived from this biomass to synthetic crude, which is then further processed to produce the synthetic kerosene that is then blended with conventional jet fuel to produce SAF. Current international certification for this SAF requires a blend of up to 50% with fossil kerosene to create "drop-in SAF". Based on a typical widebody aircraft fuel consumption rate travelling the distance from London to New York, the plant's planned SAF production capacity, after blending, is equivalent to the fuel required for over 30,000 transatlantic flights annually, equivalent to more than 3% of annual traffic flying on that route currently. The plant is expected to start production by 2028.

Maurits van Tol, Chief Executive for Catalyst Technologies at Johnson Matthey, said: "The size of this project is truly exciting and would help take the industry closer to wide-scale use of SAF. DG Fuels has ambitious plans and the fact it has secured agreements with major airlines demonstrates there is appetite in the market. Our FT CANS technology enables cost-effective deployment across a wide range of project sizes. We look forward to working with DG Fuels as a long-term partner for SAF production."

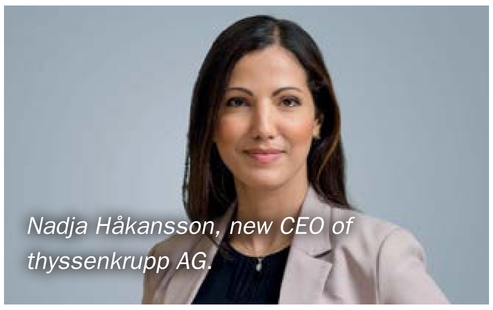
HUNGARY

MOL inaugurates new green hydrogen plant

MOL Group has inaugurated a 10 MW capacity 1,600 t/a green hydrogen plant in Százhalombatta. The €22 million investment will reduce the Danube Refinery's carbon dioxide emissions by 25,000 t/a. The electrolysis unit, created by Plug Power, will gradually replace natural gas-based hydrogen production at the refinery, which currently accounts for one sixth of the MOL Group's total CO_2 emissions. The plant will start producing in the second half of 2024: MOL will use the green hydrogen primarily in its own network for fuel production.

"Using this technology, we are able to achieve the same emissions reduction as if we took roughly 5,500 cars off the road overnight. Today, our new green hydrogen plant is only making MOL's industrial operations greener, but tomorrow it will offer solutions for the whole industry and hydrogen mobility. After Száhalombatta, we will take the technology to the other two fuel production units of the group to make the fuel production process more sustainable at each of MOL Group's refineries," said József Molnár, CEO of MOL Group, at the inauguration ceremony of the new green hydrogen plant.

People



Nadja Håkansson, new CEO of thyssenkrupp AG.

thyssenkrupp AG has announced the appointment of **Nadja Håkansson** as the company's new Chief Executive Officer effective from May 1, 2024. Håkansson, has held various management positions at Siemens and Siemens Energy and has over 18 years of national and international experience in the areas of supply chain management, operations, sales and corporate management. Most recently, as Senior Vice President Region Africa for Siemens Energy, she was responsible for the company's overall portfolio development in the African market. She holds a Master of Science in Industrial Engineering and Management from the Institute of Technology at Linköping University, Sweden.

"We are delighted to welcome Nadja Håkansson to thyssenkrupp Uhde as the new CEO," said Miguel López, CEO of thyssenkrupp AG. "With an extensive background in the energy technology industry, Nadja brings a wealth of experience and leadership to thyssenkrupp Uhde to position the company as an enabler of the industry's transformation towards further CO_2 emissions reduction."

"thyssenkrupp Uhde has significant potential for shaping the green transformation in our industry, and I am honoured to lead this prestigious company as we embark on this exciting journey together," said Nadja Håkansson. "I am looking forward to being part of thyssenkrupp Uhde's engineering competence, to fostering a culture of innovation and to delivering sustainable value to our customers & stakeholders."

Hy2gen has appointed **Astrid Hartwijk** as Chief Operating Officer. Hartwijk has over 25 years of experience with international companies in the energy sector and joins the Hy2gen team as of April 1, 2024.

"I am thrilled to join Hy2gen. I had open and very assuring conversations with the other Board members, Cyril Dufau-Sansot and Bernd Hübner, which gave me the feeling that we can work well together as a team and that I can contribute a lot at Hy2gen. The level of professionalism, what Hy2gen stands for, and the type of investors behind it; everyone is on the same mission to combat climate change by providing renewable fuels“, said Hartwijk of her new role, adding: "It's a fantastic team here at Hy2gen. Working and discovering things together with a diverse group of enthusiastic people, that's what I'm looking forward to the most. My task here will be to move projects from the development stages into reality with speed, focus, and sound business cases. To do that we will need to navigate the still developing regulatory landscapes, markets, and supply chain challenges."

Hartwijk has a degree in chemistry and many years of experience in project management. Her career highlights include positions at Shell as Transformation Director and Business Opportunity Manager for Offshore Facilities, where she has led energy projects from the initiation phase to the start of operations.

Hy2gen's CEO, Cyril Dufau-Sansot, said: "With the appointment of Astrid as COO of Hy2gen AG, we are entering a new era of achievement, where our commitment to shaping the future of sustainable energy will benefit from her experience. She will give a tangible reality to our large-scale project implementation worldwide."

Ameropa has appointed of **Josh Zacharias** to the position of Group CEO, from April 15th. Zacharias was born in Washington DC and is a dual US-Swiss citizen. He graduated from Carleton College with a BA in Mathematics and received an MBA from New York University. He is 44 years old and has held various junior and senior management positions in the USA, Australia, Romania and Switzerland since joining Ameropa in 2009.

Zacharias started in Finance, first as a financial analyst for M&A at the Binningen headquarter, then as Risk Manager and Controller at Ameropa North America, and finally as CFO at Ameropa Australia. In 2013, he moved into the commercial side as Head of Trading at Ameropa Australia and also headed the Browns retail business selling directly to farmers in Australia. In 2018, he returned to Binningen and assumed the role of Group Chief Risk Officer for close to two years. Zacharias is currently CEO of Ameropa's subsidiary Azomures, a nitrogen fertilizer producer in Romania. ■

Calendar 2024

MAY

20-22

IFA Annual Conference, SINGAPORE
Contact: IFA Conference Service, 49 Avenue d'Iena, Paris, F75116, France.
Tel: +33 1 53 93 05 00
Email: ifa@fertilizer.org

JUNE

6-7

NH3 Event, ROTTERDAM, Netherlands
Contact: Stichting NH3 event Europe, Karel Doormanweg 5, 3115 JD Schiedam, The Netherlands
Tel: +31 10 4267275
Email: info@nh3event.com

13-14

34th IMPCA Methanol Mini-Conference, PRAGUE, Czech Republic
Contact: IMPCA, Avenue de Tervueren 270 Tervurenlaan, 1150 Brussels, Belgium
Tel : +32 2 741 86 64
E-mail: info@impca.be

SEPTEMBER

9-12

AIChE Ammonia Safety Symposium, SAN DIEGO, California, USA
Contact: Ilia Kileen, AIChE
Tel: +1 800 242 4363
Web: www.aiche.org/ammonia

29-OCTOBER 4

Ammonium Nitrate/Nitric Acid Conference, MONTREAL, Canada
Contact: Sam Correnti, DynoNobel, Karl Hohenwarter, Borealis.
Email: sam.correnti@am.dynonobel.com, karl.hohenwarter@borealisgroup.com, annaconferencehelp@gmail.com
Web: annawebsite.squarespace.com/

OCTOBER

7-9

Global Syngas Technologies Conference, SAN DIEGO, California, USA
Contact: Global Syngas Technologies Council
PO Box 18456, Sugar Land, TX 77496 USA
Tel: +1 713 703 8196
Email: info@globalsyngas.org

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Plant Manager+

Problem No. 73

Practical guidance on reducing biuret formation in urea

Biuret is a chemical compound with the chemical formula $HN(CONH_2)_2$, also known as carbamylurea. It is a commonly occurring undesirable impurity in urea-based fertilisers, as biuret is toxic to plants. Biuret is formed from urea, according to the following overall reaction:

$$\underset{\text{urea}}{2NH_2CONH_2} \rightarrow \underset{\text{biuret}}{NH_2CONHCONH_2} + \underset{\text{ammonia}}{NH_3}$$

The formation of a relatively high biuret content in urea is a particular problem when urea production plants are running at lower loads. The reasons for this, and potential solutions to it were the topic of a recent discussion on the ureaknowhow.com forum. This article is a summary of that discussion, which involved experienced plant engineers and managers from Saudi Arabia, India, Pakistan, Iran and Venezuela. ■

The discussion was initiated by two queries: The first query was about the relationship between production plant load and biuret content in the final product. The enquirer had one ammonia plant shut down and wanted to utilise all the excess CO_2 from another ammonia plant to maximise urea production. They were worried that product quality would be off spec with respect to biuret if the urea plant was operating at 70% load.

The second query was from someone whose plant had a biuret content in the final product above 0.9 wt-% in one of their units, even when the plant load was 100%. They had tried to reduce this content by using all the recommended procedures (reducing the level of the decomposers holders, reducing the temperature of the high-pressure stripper). They wanted to know if there are any other ways to reduce the biuret content.

Biuret formation at reduced loads

In response to these queries, a forum participant suggested that at reduced load biuret can be controlled by the following measures:

- Keep urea solution levels in the holders (separators in the recirculation and evaporation section and the urea solution tank) as low as possible i.e. MP/LP/vacuum section.
- Keep the NH_3/CO_2 ratio slightly on the higher side.
- Maintain the urea stripper temperature ~ 198-200°C for Snamprogetti technology.
- For plants using a prill tower, the urea melt delivery line to the prill tower is normally jacketed with low pressure steam; here the urea melt gets both residence time and temperature. Reduce the jacketing steam in this line during low load operation.
- If dust solution recovery is ongoing, reduce its flow rate.

He went on to say that the maximum allowable limit of biuret in the final product is set 1.0 wt-% at his plant. In normal operating conditions biuret is maintained < 0.9 wt-%, however at low load operation it sometimes exceeds 0.9 wt-%, but remains less than the set limit. If the biuret content exceeds the allowable limit, shipment of product is stopped and the urea is stored in bulk storage, from where it is recovered again in the form of a solution.

At this point, another participant asked if it is possible to add on-spec urea in order to reduce the level of biuret content in the stored off-spec urea.

The reply to this was that off-spec product (whether due to moisture, biuret, prill shape, fines etc.) is diverted to bulk storage (separate from on-spec stored urea). From these off-spec piles of urea, a solution of ~ 70-80 wt-% concentration is prepared to recycle back to the vacuum section.

Handling off-spec urea

A different participant then suggested another solution to handle off spec product: Pour fresh and on-spec urea (directly from the plant) via a tripper over the off-spec product in the bulk storage, until the stored product reaches the acceptable range. When this material is transferred to the bagging system it will then be further mixed more evenly.

A further participant warned against the practice of recycling the off-spec urea by dissolving it in water and passing it again through processing units such as the vacuum and prilling sections, saying that it would not solve quality product problems, as the level of biuret will increase again. In addition, the energy consumption of the steam in the vacuum section will increase.

Other practical steps

There were then several additional suggestions made, by a number of participants in the discussion: In a urea plant biuret formation is caused by two factors: one is residence time and the other is temperature. Therefore:

- Minimise the levels in the urea solution tank, evaporators, rectifier, HP stripper, level tank of rectifier outlet and suction of the melt pump and keep these as low as possible.
- Maintain minimum recommended temperatures in areas with higher than 50 wt-% urea concentration.
- Maintain a higher N/C ratio, if possible.
- Maintain a higher capacity, if possible
- Check the urea melt pump efficiency: if you have lower efficiency you will have a higher temperature difference between the evaporator and the discharge temperature at top of the prill tower.
- Consider having two parallel melt lines to the prill tower. A reduced size line can be used at a low plant load to increase the velocity.
- Consider importing urea solution from other plants (if you have a second production line in the urea plant).
- For a temporary load reduction, the best option is still to store it as off-spec product and then mix it with on-spec product in the appropriate proportion. ■

PHOTO: YARA

New merchant ammonia projects

Although global ammonia supply is set to increase this year, there is a shortage of new merchant capacity after 2024 which may lead to rising prices in the medium term.

The Yara Kara, an ammonia tanker.

Global production of ammonia rebounded in 2023 after a contraction in 2022 caused by the run of extremely high prices following Russia's invasion of Ukraine. Production reached an estimated 192 million t/a in 2023, up from 188 million t/a in 2022. The merchant ammonia market remains a small fraction of this, totalling 14.1 million t/a in 2023, only 7% of production and consumption, and down from 17.1 million t/a in 2022. Much of the fall was due to reduced imports from Europe due to shutdowns of downstream industrial and fertilizer capacity.

Most ammonia is consumed at the point of production, mainly (ca 75%) in captive downstream urea, ammonium nitrate, nitric acid and ammonium phosphate production, as ammonia is more difficult and expensive to transport than most downstream products. Merchant ammonia production therefore skews towards either industrial uses such as caprolactam, acrylonitrile, adipic acid, and isocyanates, or for ammonium phosphate manufacture, which is centred on regions of phosphate mining like Florida, Morocco, Jordan etc. A small amount is imported by urea and ammonium nitrate producers in regions with relatively high domestic gas cost which makes local ammonia production less economic, such as southern Africa.

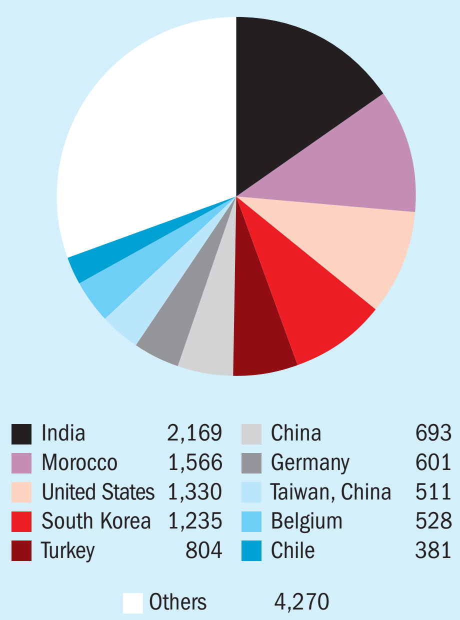
Merchant production is driven by production costs, and is concentrated in low gas cost regions with easy access to ports and overseas shipping. Most of it is in Russia, Trinidad and the Middle East, with the United States also becoming an increasingly important supplier.

Changing patterns of supply and demand

Figures 1 and 2 show the top 10 importers and exports of ammonia in 2023. The largest importers, historically, have been the United States and India, but last year Morocco moved into second place in terms of imports. India is building new ammonia capacity, but this is mostly associated with downstream urea capacity, and the impact on imports for Indian DAP production is expected to be fairly small. Morocco is also increasing its imports for downstream MAP/DAP production. As Figure 2 shows, on the production side, the market is much more concentrated, with the top ten producers responsible for more than 80% of all exports, and the top five responsible for 60 of all exports in 2023.

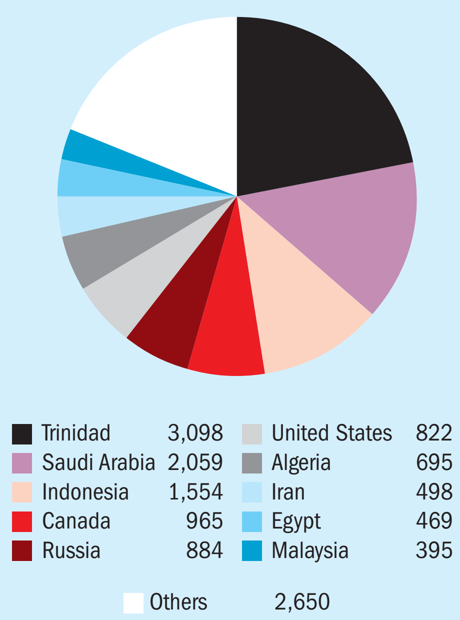
Global ammonia trade is forecast to recover to 17.1 million t/a in 2024, a 2.9 million t/a rebound after the decline last year. This will be driven at least in part by a resumption of Russian exports, with additional demand in Europe, Morocco, and the Far East, stimulated by lower prices and a combination of increasing fertilizer and technical demand.

Fig. 1: **Top 10 importers of ammonia, 2023, thousand tonnes**



Source: CRU

Fig. 2: **Top 10 exporters of ammonia, 2023, thousand tonnes**



Source: CRU

North America

US imports of ammonia have been on a steady downward trend over the past decade as more domestic capacity is built or re-started. This has been a consequence of the shale gas boom which has dramatically reduced US gas feedstock costs. In 2012, at the peak of its import demand, the US bought 7.8 million t/a of ammonia from overseas. Last year this had fallen to 1.3 million t/a, and the US also exported 822,000 t/a, for a net import figure of less than 500,000 tonnes. The start-up of the new 1.3 million t/a Gulf Coast Ammonia plant in Texas City is expected to turn the US into a net exporter, but start-up for this plant has been pushed back from Q1 2024 to most likely Q4 2024 following delays in construction.

Trinidad

Trinidad, conversely, had been facing pressure on its ammonia exports as US demand contracts. Trinidad returned to its position as the largest exporter of ammonia in 2023 due to contractions in Russian exports, but domestic gas supply issues have hit production in recent years, reducing operating rates to below 75%. Trinidad's exports of ammonia were 3.1 million t/a in 2023, but this is down from 5.3 million t/a a few years earlier. However, the gas supply situation has begun easing in 2023, and production from Nutrien and Yara has been improving from 3Q 2023. Trinidad's exports are forecast to reach 4 million t/a in 2024 and remain at that level or even slightly higher over the medium term future.

North Africa

Egypt and North Africa remain major exporters of ammonia, while Morocco is a large next exporter. OCP, the world's largest phosphate company, is continuing to increase its downstream processed phosphate production in Morocco to gain a greater slice of this market. Operating rates at OCP's existing phosphate plants are also improving as the phosphate market rebounds. Overall, Moroccan imports are forecast to rise to 2.3 million t/a in 2024, and continue to rise to 2.8 million t/a by 2028.

Far East

China's ammonia industry has been through a shakeout due to more stringent environmental legislation and a move towards more efficient use of fertilizer and zero growth in fertilizer demand. Overall, China has become a net importer of ammonia (about 690,000 tonnes in 2023), and increasing industrial demand may see this rise to 940,000 t/a this year. There are some capacity increases on the cards which will serve inland areas and probably reduce imports in the medium term.

Elsewhere in the far East, increased technical demand for ammonia in South Korea and Taiwan, China is expected to see imports pick up to 2.1 million t/a in 2024 for the region.

Europe and Russia

Russia's invasion of Ukraine in 2022 has had by far the largest impact on the ammonia market over the past two years. As well as ending grain and oil exports from Odessa, the war also ended ammonia exports, with the closure of the pipeline from Russia. The fall in Russian gas supplies to Europe also led to record gas prices across the continent, leading to a knock-on effect on ammonia markets as European ammonia producers curtailed production. At one point around two thirds of European ammonia production was idled, and ammonia prices surged past \$1,000/t, peaking at over \$1,400/t, even \$1,600/t c.fr NW Europe in April-May 2022, four times their previous average. Since then gas prices have eased and some production has restarted in Europe, bringing ammonia prices back down to more normal levels. Dutch TTF natural gas prices averaged \$37/MMBtu in 2022, but this had fallen back to \$13/MMBtu in 2023, and with increased LNG supply to Europe, a mild winter and reduced consumption rates, this is expected to drop to an average of \$7.90/MMBtu this year, with a longer term average of around \$7.00/MMBtu. This would actually put India back at the top of the ammonia cost curve, whereas Europe has been setting floor prices for the past two years. European ammonia production is expected to recover gradually, from 13.2 million t/a in 2024 to 16.2 million t/a in 2028. Consumption should recover faster, and imports will increase this year and over the medium term.

For Russia, meanwhile there is a new export terminal due to open at Taman either in 2H 2024 or at the start of 2025, with a capacity of 2 million t/a. Russian ammonia exports are expected to increase back up to 1.8 million t/a in 2024, mainly via the Baltic Sea, and longer term there are still expansions planned at Togliatti and Volgafert which could see exports climb to 4.6 million t/a by 2028.

Iran

Iran exported around 498,000 t/a of ammonia in 2023, making it one of the largest exporters in the Gulf, mainly to India. However, it remains constrained by natural gas availability as well as continuing sanctions.

New capacity

New merchant ammonia capacity is relatively limited. Table 1 shows changes in ammonia capacity from 2023-2028. While the Gulf Coast Ammonia plant in the United States will add 1.3 million t/a of merchant ammonia capacity, additional ammonia in Egypt and Russia is balanced to an extent by the closures last year at Gibson Island in Australia and BASF's Ludwigshaven plant. The dates for the Russian plants have been pushed back by sanctions and remain speculative to a degree. Aside from these, the Uzbek and Indonesian plants are fairly firm and have achieved financial closure, with construction due to begin soon. However, there is not a large pipeline of new projects over the next few years, with no new capacity due on-stream in 2025 or 2026.

The ammonia market is at present seeing a degree of overcapacity, with plants restarting in Europe and a great deal of pent-up supply in Russia once export routes are available. But it is likely to tighten over the coming years. New demand from 2024-2028 is forecast to rise by 5.7 million t/a, for phosphate and technical uses as well as some merchant nitrate production in Europe. This will mean that from 2025 the market falls into deficit, with operating rates likely to rise from the present 80% towards 88% by the end of the forecast period and prices rising concomitantly as the market tightens.

Longer term factors

The past two years have seen a supply shock on a scale never before seen in the ammonia industry. But outside of temporary factors which will likely see a reorientation of supply and probably the permanent closure of some capacity in Europe, there are some

Table 1: **Ammonia capacity changes 2023-2028, million t/a***

Plant	Country	Type	Capacity	Net	Date
BASF Ludwigshaven	Germany	Closure	0.44	-0.16	Q1 2023
Gibson Island	Australia	Closure	0.29	-0.09	Q1 2023
NCIC Ain Sukhna	Egypt	Brownfield	0.44	+0.23	Q1 2023
Gulf Coast Ammonia	US	Greenfield	1.26	+1.26	Q3 2024
Acron Novgorod	Russia	Expansion	0.38	+0.16	Q4 2024
EuroChem Kingisepp	Russia	Brownfield	0.91	+0.20	Q1 2027
Ferknesco	Uzbekistan	Greenfield	0.50	+0.16	Q1 2028
Pupuk Pusri III	Indonesia	Brownfield	0.45	-0.07	Q1 2028
Total				**1.69**	

Source: CRU

** Excludes low carbon ammonia projects*

major longer-term factors which will begin to affect the industry later this decade.

One is ammonia's use as a fuel, both for merchant shipping to help decarbonise the shipping industry, and, especially in Japan, as a feedstock to be co-fired in power stations to reduce the carbon impact of the power industry. Demand from the power sector and bunkering for ammonia will see the fuel share of total ammonia demand rising to around 4% in 2030, and possibly to as high as 29% in 2050; Japan alone expects that it will be consuming 3 million t/a of ammonia as fuel for power plants by 2030 and 30 million t/a by 2050.

On the supply side, the generation of ammonia via hydrogen from water electrolysis using renewable energy also has the potential to change the way that the ammonia market works, with some countries with large solar resources potentially becoming major exporters, such as Australia and various Middle Eastern and North African nations. Europe too may be able to use wind to generate ammonia and free itself from the dependence on Russian gas that has caused the current crisis. At the moment these plants are relatively small scale, pilot units, but there are aggressive ambitions in countries such as Norway to completely decarbonise ammonia production within the decade.

CRU expects 10 million t/a of blue and green ammonia capacity to commission from 2024-2028, taking into account greenfield projects which have reached a final investment decision. While 'blue' ammonia with carbon capture and storage, particularly in the US, accounts for most of this, up to 3 million t/a will be green ammonia, and most are expected to be merchant plants which will in theory supply the traded market. The above mentioned demand for ammonia co-firing in Japanese power plants and emerging demand for low carbon ammonia for marine uses are expected to absorb this capacity, but should this demand fall short of expectations there could be additional, albeit higher cost ammonia available to the merchant market. ■

PHOTO: SHUTTERSTOCK

Chinese urea exports

Although it has been a major exporter of urea, increasing Chinese government restrictions have restricted the seasonal window for exports.

A bulk cargo ship at sea.

China is the world's largest producer and consumer of urea. In 2023 it consumed 26.7 million tonnes N of urea (58.7 million t/a product), around one third of all urea consumed worldwide. A focus on self-sufficiency led to over-building of urea capacity during the 1990s and 2000s, leaving China with a large overhang of surplus capacity which it tended to seek export markets for. In 2015, for example, the peak year, China exported 13.7 million tonnes of urea.

However, the Chinese government began measures from 2015 to tackle this, with new more stringent environmental regulations forcing the closure of smaller and less efficient plants, especially those operating on more expensive anthracite coal, and encouraging the construction of new, larger facilities able to take advantage of economies of scale, generally based on cheaper, lower grade bituminous coal. There had also been a number of gas-fed ammonia-urea plants built in the 1990s, but China’s chronic shortage of natural gas for power production means that these plants often suffer from gas supply curtailments, especially during winter. Chinese urea production peaked at 70.8 million t/a in 2015, and thereafter fell quite rapidly, to just 51.9 million t/a in 2018, and only recovering slowly to 62.9 million t/a in 2023 (see Table 1).

At the same time, there were also efforts to cap Chinese fertilizer use and make sure that nutrients were applied more efficiently to fields. Chinese urea consumption fell from 57 million t/a in 2015 to 49 million t/a in 2018, although since then there has been a creeping increase to the present 58.7 million t/a. All of this served to precipitately reduce Chinese urea exports from 13.7 million t/a in 23015 to just 2.4 million t/a in 2018, and while this rebounded to around a 5 million t/a surplus in 2019-2021, the Chinese government imposed export controls in 2021 which it has not relaxed since. Chinese urea exports dropped to 2.8 million t/a in 2022, recovering somewhat to 4.3 million t/a in 2023.

Export restrictions

China has subsidised urea prices to end users to keep prices reasonable for farmers. However, this has often meant that at times of high international urea prices it becomes more profitable for domestic producers to sell their product on the international market. This tended to exacerbate periods of higher domestic pricing, and so in order to keep domestic supply plentiful, China has long maintained restrictions on urea exports. In the 2010s this was achieved by a quota system which restricted exports to certain months of the year when domestic demand was low in order to try and keep domestic production at home at times of high international prices. However, in July 2021, China began asking major urea and ammonium phosphate producers to stop selling abroad. Three urea producers in Shanxi, Hebei and Shandong were asked by the government to suspend applications for China Inspection and Quarantine Certificates. This was followed up in October 2021 by announcement that China would be carrying out

Table 1: **Chinese urea production, consumption and exports, 2015-2024, million t/a**

Year	Production	Consumption	Exports
2015	70.8	57.1	13.7
2016	63.2	53.4	8.9
2017	53.9	49.4	4.7
2018	52.0	49.7	2.4
2019	54.7	49.9	4.9
2020	56.2	50.5	5.5
2021	55.6	50.6	5.3
2022	57.6	54.9	2.8
2023	62.9	58.7	4.3
2024*	66.8	62.6	4.3

Source: CRU **Estimated*

"inspections on import and export chemical fertilizers strictly under the latest regulations," according to a notice from the National Development and Reform Commission (NDRC). The effect was to limit or even suspend exports of some fertilizers, especially phosphates, to ensure domestic supply. The export restrictions have continued into 2022 and 2023 and have had a marked effect on urea exports and international pricing. Restrictions were lifted in March 2023, but reimposed towards the end of the year. A complete pause in export permits from January 2024 has meant that Chinese urea exports effectively ceased, with Q1 exports down to just 25,000 tonnes – a 95% drop year on year - and it has been unclear when they will be relaxed, leading to considerable uncertainty among traders and buyers. Producers/traders were finally allowed to apply for export inspections from 15 March 2024, with an average approval time of 40 working days or effectively 2 months. Applications submitted after 1 May will have an approval time of ten working days. Hence, significant exports are expected to resume only after 15 May 2024. However, the risk around resumption of exports continues to exist as the customs office refused inspections after 15 March.

The uncertainty among buyers has led to some major importers seeking supplies from elsewhere. India, which bought 1.9 million tonnes of Chinese urea in 2023, has been switching away to purchases from Russia, Oman, and Abu Dhabi. Malaysian buyers have likewise been seeking supply from Vietnam and Egypt, and South Korea has likewise been buying from Vietnam instead.

Overall, CRU expects that 2024 exports are forecast to stay at 4.3 million t/a, but the government is likely to raise export barriers if domestic prices become too high (above $360/t).

Domestic demand

Although agriculture demand for urea is expected to increase to 41.2 million t/a in 2024, up from 39.2 million t/a in 2023, due to increased planted area and the application of high-density planting technology, over the, the growth rate for agriculture is likely to continue to be slightly negative due to the promotion of increased fertilizer efficiency. However, the increase in technical demand is likely to largely offset the decline in ag demand. Urea demand for the resin and wood-based panel industry is expected to grow at a CAGR of 4.5% over the period 2023–28, to reach 12 million t/a in 2028, due to the rise in the standard of living. The substitution of ammonia with urea in thermal power plants for selective catalytic reduction of NOx emissions which began in August 2020 is also likely to increase urea demand in this sector from 2.4 million t/a in 2023 to 3.0 million t/a in 2024. Overall demand will nevertheless continue its long slow decline, to 56.1 million t/a in 2028.

Coal prices

Feedstock pricing and availability has been a major issue for Chinese producers. Around 20-25% of Chinese urea capacity uses natural gas as a feedstock, which is virtually unavailable during winter because it is required for power generation. Over the past decade coal prices have been rising, eroding margins, and coal has occasionally not been available at any price. Government targets for Chinese states to reduce CO_2 emissions means that some state governments such as Inner Mongolia and Shanxi are also forcing local urea plants to run at lower rates or not at all.

Nevertheless, increasing use of renewable power and rationalisation in the coal industry is gradually changing the situation. Bituminous coal prices have remained relatively flat at $130-133/t since November 2023, actually reducing the average bituminous-based urea site costs to $202/t, compared to $265/t for September 2022. The thermal coal market was in slight oversupply in 2023, due to strong domestic production, driven by considerations of national energy security and expectations tied to economic recovery. Additionally, there was a record level of seaborne imports following China's decision to lift its ban on Australian coal imports. Port coal stocks achieved record highs through 2023, reaching 26 million tonnes by December 2023, supported by strong coal production, weaker-than-expected economic growth, and stable summer weather. In 2024, market rebalancing is expected as the government balances between the interests of coal mining industry and coal-fired power companies, thereby leading to an average of $124/t.

As a result, domestic urea production is expected to increase by 4 million t/a to reach 66.8 million t/a in 2024 on the back of new capacity additions (net additions of 2.7 million t/a) and improved utilisation rates. Overall, following a steady decline in 2016 –21, net capacity is expected to increase by 5.9 million t/a in 2024 –28, bringing total capacity to 76 million t/a in 2028, the highest since 2018. Most new capacity is based on bituminous coal-based, while closures continue to be predominantly among anthracite-based producers. The share of bituminous-based capacity is expected to rise from 50% in 2023 to 55% in 2028. This implies lower production costs, owing to the lower price for bituminous coal than anthracite.

Urea prices

Price remains the most important factor which could trigger tighter export restrictions.

The government is likely to raise export barriers if domestic prices become too high, especially during or before peak season. The threshold is expected to be above RMB2,300-2,600 ex-works ($320-360/t) for urea. At time of writing, urea prices were assessed at RMB2,100-2,180/t ex-works ($290-301/t) in northern China, with the high end of the range nearing the anticipated threshold. This may be the reason for an apparent about turn on export licenses during April-May. China asked some fertilizer producers to suspend urea exports after domestic prices jumped. Urea futures on the Zhengzhou Commodity Exchange surged almost 50% over a seven-week period from mid-June to the end of July, but have fluctuated since.

CRU expects inland prices will not meet what is deemed a comfortable range by the Chinese government in the coming weeks. This means that, given demand for the spring application season and purchases for summer corn applications, no significant trade volumes are likely to emerge from China before July. The government's focus on ensuring domestic availability is expected to keep the exports range in terms of tonnage between 4.6–4.8 million t/a in 2025-27. Restrictions could be lifted from about 2028, as new capacity comes onstream, prices stabilise at a lower level, and the Chinese government develops confidence in availability and domestic prices are reasonable. ■

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A catalyst for the most demanding HTS applications

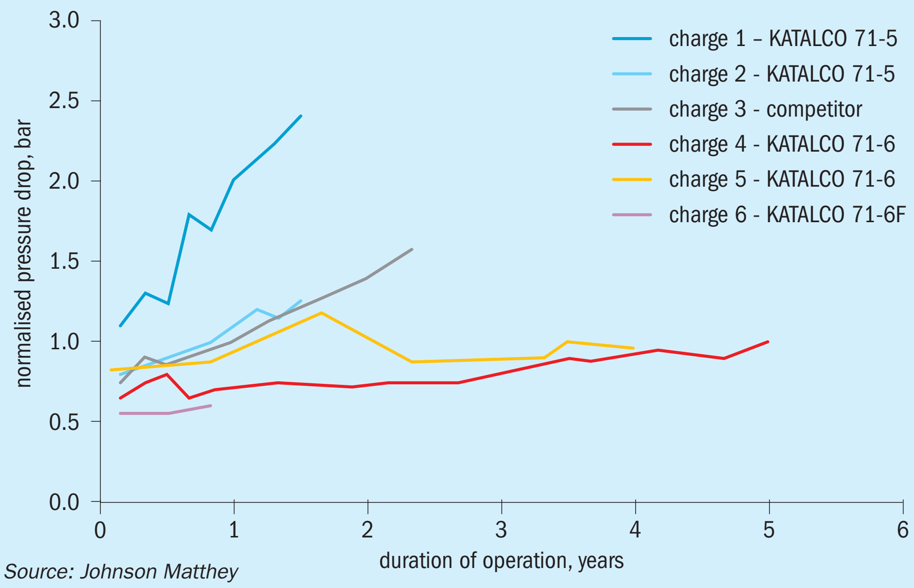
Tim O'Connell and **Emily Viney** of Johnson Matthey introduce KATALCO™ 71-7F, the latest innovation in Johnson Matthey's KATALCO 71 series catalysts for high-temperature shift (HTS) reactions. With its robust innovative 'F' shape providing lower lifetime pressure drop, JM expects KATALCO 71-7F will enable large-scale plants to increase ammonia production in the most demanding HTS applications.

Dedicated ammonia production using natural gas is the dominant route to make ammonia. Currently, most of the ammonia is converted to nitrogen-containing fertilizers. The established manufacturing process to make ammonia from natural gas comprises steam-methane reforming, water-gas shift, methanation, and ammonia synthesis. Steam-methane reforming converts natural gas into CO and H_2 which is sent to the water gas shift (WGS) section. WGS catalyst converts CO into H_2. After the WGS section, methanation removes the remaining CO. This sequence of reactions efficiently and effectively maximises the H_2 generated. In the ammonia synthesis loop, H_2 and N_2 are reacted to produce ammonia. Reliable performance of the shift catalysts therefore maximises the hydrogen feed to the ammonia converter, contributing to ammonia yield from the plant, and therefore to the business success of ammonia manufacturers.

Johnson Matthey has developed KATALCO 71 series catalysts for high-temperature shift (HTS) reactions. Conventional cylinders and F shaped catalysts are available. The 'F' shape innovation provides lower lifetime pressure drop performance. Each of the catalysts in this series, provide a unique mixture of physical and chemical properties.

Improvements in durability of HTS catalysts benefits all manufacturers of hydrogen, and subsequent downstream manufacture of ammonia; however, these performance benefits are exaggerated in the largest plants. Johnson Matthey HTS catalysts have been exposed to the rigours of large ammonia plants with demanding duties, and the KATALCO 71-6 and KATALCO 71-6F catalysts have shown durable, high performance in these plants.

Fig. 1: **Pressure drop advantages owing to durability of KATALCO 71-6 and advanced shape of KATALCO 71-6F in a large-scale ammonia plant**



Source: Johnson Matthey

KATALCO 71-6 possesses superior strength over previous generation KATALCO HTS catalysts. The superior strength of KATALCO 71-6 has indeed shown greater durability in use, whilst delivering a reduction in the volume of catalyst due to its enhanced pore structure and activity.

Fig. 1 exemplifies these performance enhancements and the benefits achieved when KATALCO 71-6 and KATALCO 71-6F were installed in a large-scale ammonia plant. KATALCO 71-6 was the fourth charge of HTS catalyst installed in this plant, following significant pressure drop issues experienced with previous HTS installations, which had been KATALCO 71-5 and HTS catalyst supplied by another catalyst manufacturer. KATALCO 71-6 reduced the pressure drop and increased catalyst lifetime, allowing the plant to reduce the frequency of catalyst changes. For the latest charge, KATALCO 71-6F, pressure drop performance is even better, combining durability of KATALCO 71-6 with the advance shape of KATALCO 71-6F. KATALCO 71-6F has provided the most robust catalyst performance since this plant was commissioned.

Johnson Matthey's experience within these demanding plants has driven the development of a new catalyst, KATALCO 71-7F, which extends the physical properties of existing HTS catalysts that Johnson Matthey have observed to be valuable for hydrogen production.

KATALCO 71-7F catalyst testing and performance

Johnson Matthey developed KATALCO 71-6, and subsequently KATALCO 71-6F, to enhance performance within HTS reactors with the sort of demanding duty which thermally ages HTS catalysts. The development of KATALCO 71-6 benefitted from an enhanced pore network which enabled improved transfer of gas through catalyst pellets compared to earlier generations. KATALCO 71-6 also benefitted from an improved intimacy between Fe_3O_4 active sites and Cr and Cu promoters which act to stabilise the Fe_3O_4 active species and the Fe active sites responsible for catalysing the water gas shift reaction. KATALCO 71-7F benefits from a further improvement in intimacy of Cr promoter location, further stabilising Fe_3O_4 active species within the catalyst. KATALCO 71-7F has a similarly robust porous structure to KATALCO 71-6F within catalyst pellets. KATALCO 71-7F maintains the enhanced catalyst shape developed for KATALCO 71-5F and KATALCO 71-6F previously, with improved geometric surface area: volume ratio of the catalyst pellets, which have been shown to have beneficial impact on HTS reactor pressure drop with catalyst ageing.

Johnson Matthey have investigated the strength of HTS catalysts KATALCO 71-5F, KATALCO 71-6F and KATALCO 71-7F and the results are shown in Fig. 2. Strength was measured before and after representative thermal ageing of the three catalysts – what might be considered as 'regular' durability for HTS catalysts. These results show that both KATALCO 71-6F and KATALCO 71-7F maintain catalyst strength after thermal cycling of the catalysts during ageing. KATALCO 71-6F and KATALCO 71-7F are stronger after thermal cycling than KATALCO 71-5F. Whilst KATALCO 71-5F suffers a significant change in strength during ageing, KATALCO 71-5F retains sufficient strength to perform well in numerous commercial settings.

Following the good strength result seen for KATALCO 71-7F compared to KATALCO 71-6F, both catalysts were tested for strength following 'steaming' ageing. This ageing is designed to represent more demanding duty cycles for HTS catalysts, in which the catalysts are exposed to steam during reactor start-up. In Fig. 3, both catalysts show good strength results after 'steaming' ageing. KATALCO 71-7F shows slightly higher strength after 'steaming' ageing than KATALCO 71-6F, also showing slightly higher strength than the test result for thermally aged catalysts.

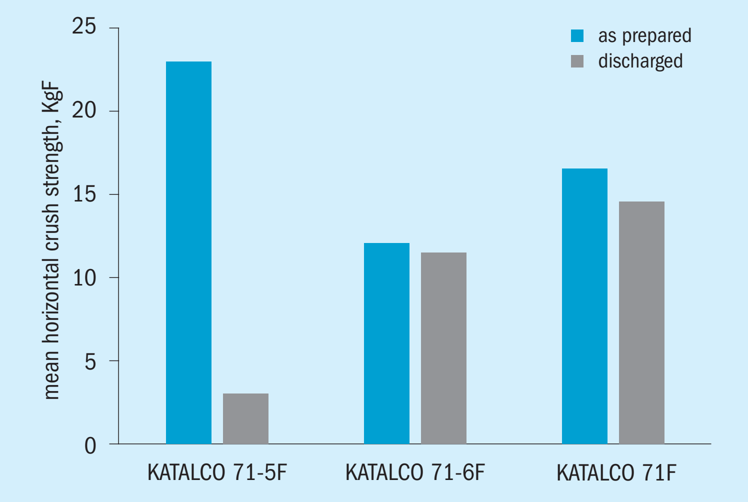
Investigation of long-term durability was assessed using accelerated ageing conditions. KATALCO 71-5F, KATALCO 71-6F and KATALCO 71-7F were tested before and then after each subsequent ageing cycle; the results are shown in Fig. 4. These results show KATALCO 71-7F retains the highest performance following multiple aging cycles. Furthermore, these results show KATALCO 71-7F is an improved catalyst compared to both KATALCO 71-5F and at least equivalent to, if not better than, KATALCO 71-6F. Combining the performance results with the strength results shows KATALCO 71-7F matches and even exceeds the excellent performance of KATALCO 71-6F.

The strength and pressure drop advantages of KATALCO 71-7F, particularly after lifetime ageing, will enable large-scale ammonia plants to incrementally increase ammonia production. Johnson Matthey has developed a model to estimate the potential benefits for ammonia manufacturers. The absolute benefit of lower pressure drop in operation will depend on the cost of natural gas and the ammonia sales price. For a 3,300 t/d plant, with the following assumptions:

- Front end pressure drop: 18.6 bar
- On-stream factor of plant: 90%
- Gas usage: 35 million Btu/tonne of ammonia produced
- Other variable costs: $20/tonne of ammonia produced
- Shutdown time: 7 days per year
- Catalyst life: 4 years

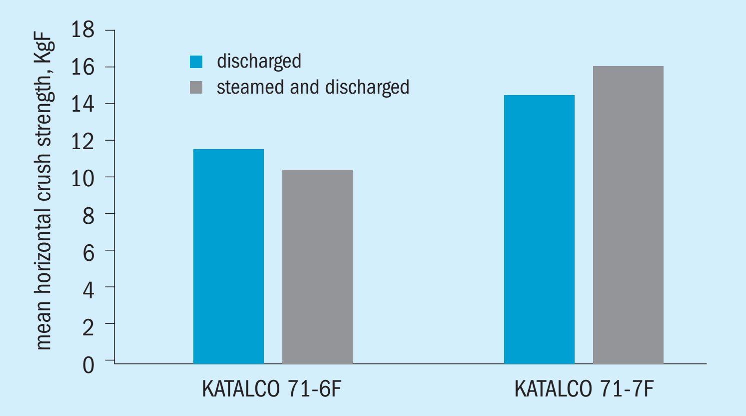
Johnson Matthey calculates a pressure drop benefit of 0.10 bar, resulting in 8.9 t/d extra ammonia production. Table 1 shows the extra sales of ammonia enabled by durable HTS performance from the lower pressure drop within the HTS reactor.

Fig. 2: **Strength comparison for KATALCO HTS catalysts**



Source: Johnson Matthey

Fig. 3: **Strength comparison for KATALCO 71-6F and KATALCO 71-7F after both thermal exposure and steaming exposure**



Source: Johnson Matthey

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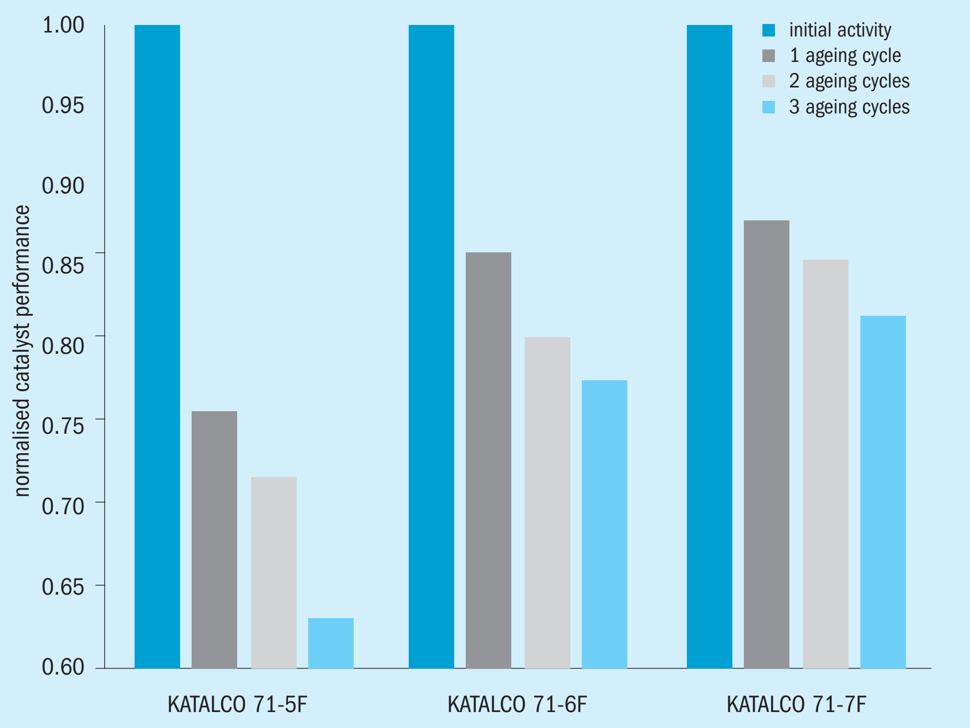
Fig. 4: **Water gas shift catalyst performance for KATALCO HTS after representative thermal ageing**



Source: Johnson Matthey

Table 1: **Extra annual sales of ammonia enabled by durable HTS catalyst performance**

		Gas cost ($/million Btu)	
		2	7
Ammonia price ($/tonne)	300	613k	102k
	600	1,489k	978k

Source: Johnson Matthey

Table 2: **Extra annual sales of ammonia enabled by durable HTS catalyst performance**

Product feature	**KATALCO 71-5F**	**KATALCO 71-6F**	**KATALCO 71-7F**
As prepared strength for catalyst loading (+ for strength)	+++	++	++
Discharged strength at end of life (+ for strength)	+	++	++
Discharged strength after steaming ageing (+ for strength)	-	+	++
Catalyst pressure drop as prepared (+ for 'good performance')	++	++	++
Catalyst pressure drop following 'regular' duty (+ for 'good performance')	+	++	++
Catalyst pressure drop following 'very demanding' duty (+ for 'good performance')	-	++	++

Source: Johnson Matthey

On top of the expected benefit from low-cost gas feed, and higher product sales price, lower pressure drop enabled by strong HTS catalysts with advanced shape design offers significant value to ammonia producers, up to $1.5m extra sales of ammonia annually.

Considering the KATALCO 71-series catalysts, Johnson Matthey predicts that for the most demanding duties, in which the HTS catalyst must be robust to severe and/or frequent deactivating events (such as wetting or thermal stress events), KATALCO 71-7F will offer ammonia manufacturers the most durable performance over the catalyst lifetime. KATALCO 71-6F has previously shown excellent durability and performance in such plants. The results described above are summarised in Table 2. Table 2 shows that for more demanding duties, KATALCO 71-6F and KATALCO 71-7F offer ammonia manufacturers a benefit in strength and pressure drop performance compared to KATALCO 71-5F. Johnson Matthey's test results suggest that the extra strength of KATALCO 71-7F will push the durability of this catalyst beyond the excellent performance delivered by KATALCO 71-6F. For plants with a lower frequency of events which damage the catalyst, or events which have less serious deactivating effect on the catalyst, each of KATALCO 71-5F, KATALCO 71-6F and KATALCO 71-7F may be used successfully by ammonia manufacturers – which is shown in Table 2 on the 'regular' duty line of the table.

Conclusion

Johnson Matthey has developed the KATALCO 71 series 'F' catalyst shape for HTS catalysts which benefits customers through lower lifetime pressure drop, as the nature of the 'F' shape increases voidage in the catalyst bed thereby reducing pressure drop, this offers the potential for increased throughput or efficiency increasing plant profitability.

KATALCO 71-7F has shown an unrivalled combination of strength and performance in testing, outperforming previous generation catalysts under conditions representative of HTS reactors. ■

Reference

O'Connell T. and Viney E.: "*Introducing KATALCO 71-7F the most robust HTS catalyst ever, eliminate pains, benefit from gains*", Nitrogen+Syngas 2024, Gothenburg, Sweden, 4-6 March 2024.

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A new low methanol shift catalyst

Anton Kariagin and **Stefan Gebert** of Clariant discuss the benefits and commercial performance of the new low temperature shift (LTS) catalyst – ShiftMax 217 Plus. A case study demonstrates the benefits of this catalyst, providing ultra-low methanol formation resulting in increased ammonia production and/or energy savings.

Clariant is known for its commitment to innovation, and always puts the interests and needs of its customers as the target for continuous product development. High levels of investment in R&D are maintained every year to enhance existing products and develop new ones.

Ammonia production is one of the most complex processes in the chemical industry and also one of the most studied. There are hundreds of patents and developments in this process, and one might think that there are no more opportunities for further development. In recent years, however, Clariant has launched a new "Plus" catalyst series for ammonia production: ReforMax 210/330 LDP Plus for the primary and secondary reformers, ShiftMax 217 Plus for the low temperature shift and AmoMax 10 Plus for the ammonia synthesis section.

Clariant LTS catalyst

The copper/zinc-based LTS catalyst has a significant impact on the energy efficiency of the plant and consequently on its economics. Therefore, it is extremely important to have a highly active, stable and robust catalyst that ensures long life and high performance and to a certain extent can withstand various upsets during its lifetime, such as sulphur and chloride poisoning, condensation or high temperatures.

In an ammonia plant, a more active LTS catalyst decreases the inert concentration in the ammonia synthesis loop over a longer period of time, reducing purge gas losses and increasing the energy efficiency of ammonia production. As a rule of thumb, 0.1% more CO converted in the LTS means approximately 1% additional ammonia, especially in plants without purge gas recovery units.

Clariant already has one of the best LTS catalysts on the market – ShiftMax 217, which provides excellent crush strength in both the oxide and reduced states for increased robustness, as well as enhanced activity and selectivity for higher conversion at low temperatures and low methanol byproduct formation. Since its introduction in 2010, ShiftMax 217 has been used by more than 60 customers worldwide.

New LTS catalyst ShiftMax 217 Plus

With the recent trend to develop decarbonised ammonia as a transport medium for hydrogen, ammonia producers and licensors tend to harshen the operating conditions of new and existing ammonia plants, making the physical strength and thermal stability of the LTS catalyst more and more important. Additionally, the flow scheme of "blue" ammonia production is often based on a low steam-to-gas ratio concept for higher energy efficiency, resulting in higher methanol by-product formation.

With these existing and future customer needs in mind, Clariant has not stopped with the highly active and robust ShiftMax 217 but has developed ShiftMax 217 Plus, the next-generation LTS catalyst for ultra-low methanol formation and outstanding physical strength while keeping the same high activity of the well-proven ShiftMax 217. By introducing an optimised production process, ShiftMax 217 Plus exhibits a more homogeneous distribution of active metals and promoters within the catalyst matrix, resulting in enhanced catalyst selectivity and, consequently, lower formation of by-products such as methanol.

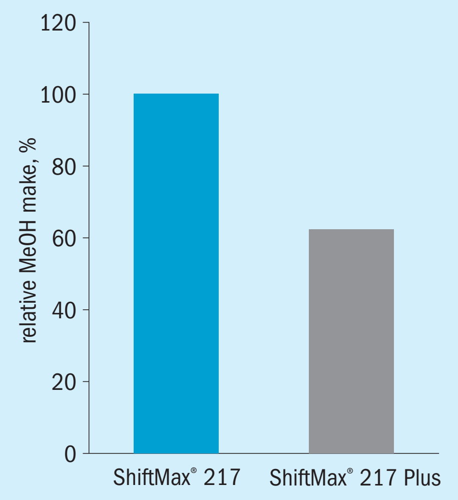
Lower by-product methanol formation

According to the reaction equation, by-product methanol formation consumes hydrogen, leading to hydrogen yield losses and/or lower energy efficiency and technological and environmental challenges such as VOC and COD emissions.

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O + \text{heat}$$

Excessive methanol make will not only contaminate CO_2 and process condensate but will also cause loss of ammonia production. As a rule of thumb, for every one tonne of methanol produced in the LTS reactor, 1.1 tonnes of ammonia are lost. Methanol formation is controlled by gas composition, operating conditions (similar to those required for industrial methanol synthesis), and catalyst type. Therefore, the methanol formation rate can be reduced by increasing the steam-to-gas ratio and/or using low-methanol catalysts.

Fig. 1: **By-product methanol formation**



Source: Clariant

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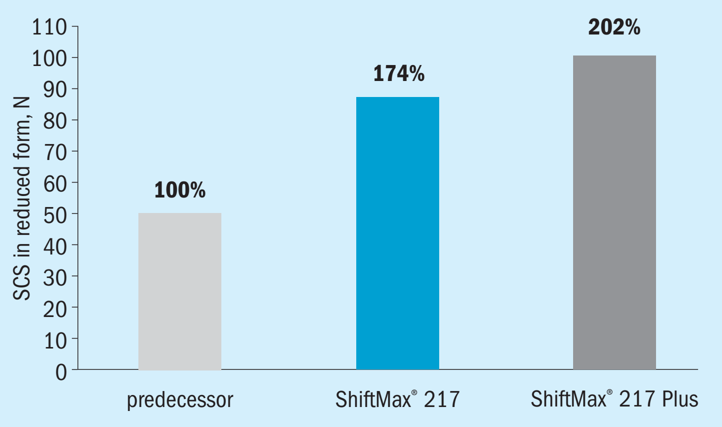
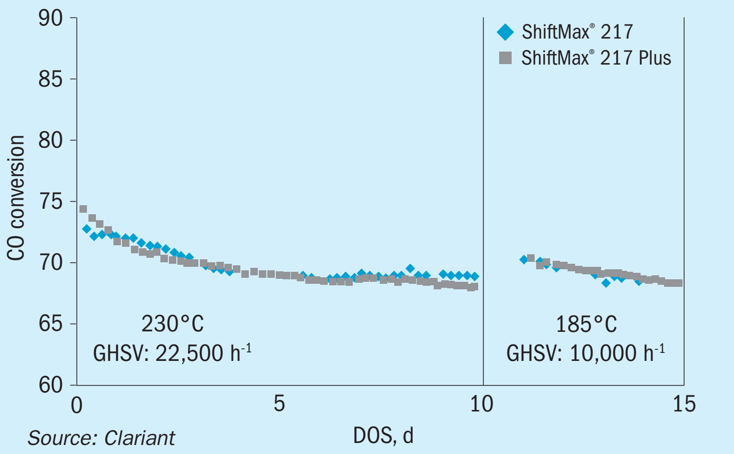
Fig. 2: **Side crush strength after reduction**



Source: Clariant

Fig. 3: **High activity of ShiftMax 217 and ShiftMax 217 Plus**



Source: Clariant

In laboratory tests, ShiftMax 217 Plus demonstrated ultra-low methanol formation without compromising activity. Compared to the commercially proven version ShiftMax 217, the new catalyst provided the same high level of CO conversion but formed 40% less methanol, and provided increased mechanical strength, as shown in Figs 1 to 3.

The ultra-low byproduct methanol formation provides several benefits:

- increased ammonia production and/or energy savings;
- cost savings in the downstream treatment system, e.g., condensate system, solvent regeneration, etc.;
- helps to reduce VOC/COD emissions;
- mitigates capacity limitation due to VOC/COD emissions.

The following case study demonstrates the outstanding reduction of by-product methanol formation that helped the ammonia producer solve its issues with regulatory limits for VOC emissions.

Case study: 50% lower methanol in CO_2 off gas

An ammonia producer in Europe has very strict regulatory limits for VOC emissions, which could result in a high penalty if exceeded.

In 2018, the producer installed the previous generation of Clariant's "low methanol" catalyst ShiftMax 217, which greatly helped to decrease methanol formation and meet the regulatory limits. However, during the start-of-run period, the average methanol formation was still higher than the limits due to the high activity of ShiftMax 217.

It is well known that even with the "low methanol" type of catalyst the highest amount of methanol is formed at the beginning of the run because the activity of the fresh catalyst is high for both reactions during this period of the catalyst life: the targeted shift reaction and the by-product methanol synthesis reaction.

As a result, this ammonia producer still had issues with exceeding the regulatory limits in the start-of-run period after installation of the fresh "low-methanol" catalyst ShiftMax 217.

For the next charge in 2022, Clariant offered the new generation catalyst, ShiftMax 217 Plus, to solve the problem with methanol during the start-of-run period.

At the same time, due to high energy prices, the plant was looking for any opportunity to improve plant economics by increasing ammonia production while decreasing energy consumption, which can be achieved by increasing hydrogen production. Thus, the ability to avoid hydrogen losses by reducing methanol formation was another reason why the ammonia producer selected the ShiftMax 217 Plus catalyst for its LTS reactor.

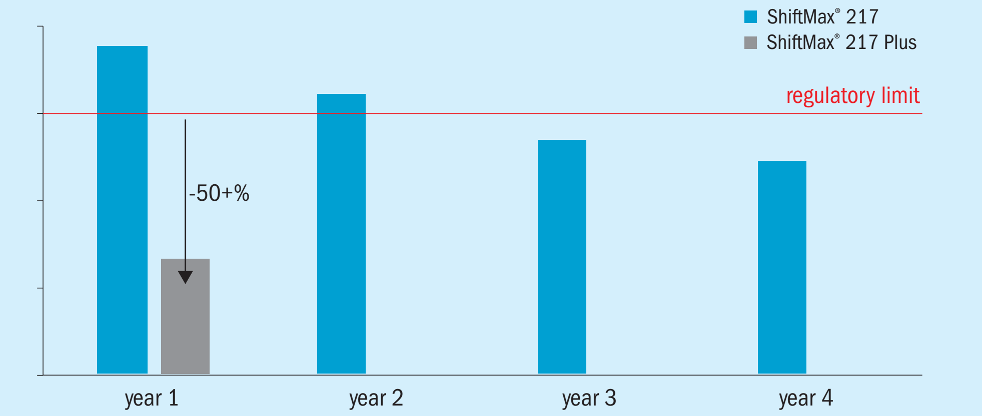
As shown in Fig.4, after the installation of ShiftMax 217 Plus the methanol concentration in the CO_2 knock-out drum during the start-of-run period decreased by more than 50% compared to the same period of the previous ShiftMax 217 catalyst operating under similar conditions. This allowed the plant to easily meet the regulatory limits and to avoid any penalties. Moreover, ShiftMax 217 Plus shows excellent performance at equilibrium at low inlet temperatures below 200°C.

Conclusion

The case story above shows that by understanding the needs of its customers, Clariant was able to launch a new generation of "ultra-low methanol" catalyst ShiftMax 217 Plus, that addresses the following needs:

- energy savings or increased ammonia production, which has a direct impact on the profitability of a plant;
- increased catalyst reliability and longevity;
- improved sustainability to meet new emission regulations for VOC and COD. ■

Fig. 4: **Methanol make of ShiftMax 217 Plus measured in CO_2 off gas**



Source: Clariant

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The future of hydrogen

Low emissions hydrogen is expected to play an increasing role in the syngas-based chemicals industry, but cost and technical challenges remain.

PHOTO: NASA

A liquid hydrogen storage tank at the Kennedy Space Center, Florida.

The need for low-emissions hydrogen and ammonia is expected to accelerate as decarbonisation quickens over the coming decades. Both will play a significant role in decarbonising hard-to-abate sectors including steel, shipping, aviation and fertilizers, and within the wider energy transition generally. Yet uptake across other sectors has a mixed outlook, constrained by the cost and technical challenges of switching to hydrogen or ammonia, and the existence of alternative decarbonisation solutions.

In the face of escalating climate change concerns, the imperative to transition away from fossil fuels to sustainable energy sources has become an unprecedented global challenge. The adverse impacts of greenhouse gas emissions, primarily attributed to the burning of fossil fuels, have propelled the international community to seek alternative solutions that are both ecologically responsible and economically viable. Against this backdrop, low-emissions hydrogen, and its derivative ammonia, have emerged as promising energy carriers with the potential to play a pivotal role in the ongoing energy transition. Analysis conducted by CRU projects low-emissions hydrogen and ammonia demand to reach approximately 160 million t/a and 230 million t/a in 2050, respectively.

Tax credits

The US Inflation Reduction Act (IRA) revised and augmented renewable energy tax credits and introduced new ones for green hydrogen. Where green hydrogen tax credits can be stacked with renewable tax credits – and the full credits obtained – costs of green hydrogen production could be on par with blue or grey hydrogen costs if built before 2032, when the current tax credit regime ends.

There were no specific clean hydrogen tax credits before the IRA. Now, assuming certain wage and apprenticeship requirements are met, new ten-year 45V clean hydrogen production tax credits (PTCs) are available of between \$0.60–3.00/kgH$_2$, depending on emissions. Clean hydrogen facilities must begin construction before 2033 to be eligible for the PTCs. The IRA also introduced new clean hydrogen investment tax credits (ITCs) under IRC (Internal Revenue Code) section 48 of between 6–30%, depending on emissions and again assuming wage and apprenticeship requirements are met. Hydrogen produced with <0.45 kgCO$_2$e/kgH$_2$ can be eligible for 30% ITCs, but this percentage falls as emissions rise towards 4 kgCO$_2$e/kgH$_2$.

As with renewable energy tax credits, clean hydrogen ITCs and PTCs are mutually exclusive. However, renewable energy and hydrogen tax credits can be stacked. Pre-IRA, renewable energy tax credits had a limited impact on green levelised cost of hydrogen (LCoH), while IRA renewable energy tax credits have a bigger effect. CRU estimates that application of IRA renewable energy tax credits will reduce green LCoHs by around \$0.80–1.20/kgH$_2$ over the second half of this decade. This difference would be even larger if IRA clean energy manufacturing tax credits are also included.

Further, to limit emissions from hydrogen production, the US Treasury Department recently proposed rules requiring that renewable electricity used to produce hydrogen is additional to the grid, as well as matched in time and geography for IRC 45V credit eligibility. Temporal matching will be annual at first, then hourly beginning in 2028, with no grandfathering. This may favour more expensive PEM electrolysers which can handle intermittent power better than alkaline electrolysers. The cost difference between using alkaline electrolysers with steady power and high utilisation versus using PEM electrolysers with intermittent power and lower utilisation is generally about \$2.00/kgH$_2$.

Blue and grey hydrogen

Tax credits for carbon capture under IRC 45Q existed before the IRA, but the IRA raised the 12-year IRC 45Q tax credit value and pushed back the credit expiration date. Projects must now begin construction before 2033 rather than the previous 2026 cut-off date. While it is possible to make hydrogen both using steam methane reforming (SMR) and autothermal reforming (ATR), it is estimated that SMR blue hydrogen production is unlikely to meet the IRC 45V and 48 emissions thresholds of 4 kgCO$_2$e/kgH$_2$ in most cases. There is uncertainty over whether ATR blue hydrogen production meets the IRC 45V and 48 emission threshold. If it does, it will likely be limited to a 6% tax credit under IRC 48 or a \$0.6 /kgH$_2$ production tax credit under IRC 45V, as usual assuming that wage and apprenticeship requirements are met. This can be compared to the \$85/tCO$_2$e tax credit (nominal terms) under IRC 45Q.

IRA 45Q tax credits generally reduce blue LCoH by \$0.15–0.36/kgH$_2$ until they expire in the 2030s. Consequently, blue LCoHs become comparable to grey LCoHs for facilities built in this time period. While this decline is significant, as shown above, the IRA reduces green LCOHs by ~\$3/kgH$_2$ over the period 2024–2032 when renewable and hydrogen tax credits are stacked. However, despite generous IRA credits for green and blue hydrogen, grey hydrogen remains the least costly for most of the period covered.

Outside the US, emissions policies such as the EU Carbon Border Adjustment Mechanism (CBAM) will also affect the value proposition of different types of hydrogen. For markets with the most progressive carbon pricing, such as Europe, importing green or blue hydrogen from the US will be more competitive relative to grey hydrogen due to their lower embedded emissions.

There are other financial incentives that indirectly reduce clean LCoHs, including clean hydrogen manufacturing tax credits and hydrogen hub investments. As indicated earlier, we have not incorporated clean energy manufacturing tax credits into our LCOEs, but these would lower green LCOHs still further.

Green LCoHs will decline below those of blue and grey in the early-2030s, and the lowest cost green hydrogen is expected to be that benefitting from tax credits under IRC 45V. The level of cost reduction will likely prompt faster adoption of green hydrogen and green ammonia – and should help to reduce costs for hard-to-abate sectors.

Sectoral demand

Traditional hydrogen end-uses, including methanol and ammonia production, the latter of which is driven primarily by fertilizer demand, will be major sources of consumption, as decarbonisation drives a switch to less emission-intensive production technologies. Refining will likely undergo a similar transformation, although against a backdrop of declining overall consumption as the share of hydrocarbons in the energy mix declines. Adoption of hydrogen and ammonia in hard-to-abate sectors, such as aviation, shipping and the manufacture of steel, will also generate considerable demand, although many of the technologies needed for their uptake are still in the development phase – with proven commercial viability yet to be demonstrated.

There is less potential for uptake in other sectors, including transport and power generation, where alternative decarbonisation solutions already exist and are proven to be more competitive. Switching to hydrogen or ammonia will incur high infrastructure costs; and the low density of hydrogen has direct implications for equipment used.

Meanwhile, ammonia also poses challenges to its adoption:

- Ammonia is toxic and will cause major harm to humans and the environment if spilled.
- Infrastructure for ammonia trade is highly specialised and would need to be expanded significantly.
- Ammonia 'cracking' to generate hydrogen results in a 15% hydrogen yield loss.
- Ammonia, while carbon-free, is a high-nitrogen fuel that almost certainly will lead to emissions of nitrous oxide (N_2O) which is itself a powerful greenhouse gas. Suitable abatement technologies, alongside sufficient regulation, will therefore be needed to mitigate these emissions.
- Green hydrogen at <\$1.0 /kg will not be achievable as some suggest.

Production costs

Hydrogen production costs are dependent on the technology deployed, the energy source and other local cost factors. Carbon prices are another important consideration for overall competitiveness. Unabated fossil-based hydrogen was (before the global energy crisis at least) the most economically viable option, with costs of <\$2.00/kgH$_2$ according to CRU's Hydrogen Cost Model.

Carbon capture, utilisation and storage (CCUS) adds cost to fossil-based hydrogen production as the CCUS requires additional

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investment and is energy intensive, but the added cost of carbon capture is only about \$0.40–0.50/kgH_2 in an SMR plant. This is because fossil-based hydrogen production processes already incorporate carbon capture, which is a necessary part of the process to produce a pure hydrogen gas stream. Finally, hydrogen produced via electrolysis with low-emission electricity, assuming full costs of electricity are borne, is upwards of \$5–6/kgH_2.

There are a number of forecasts suggesting that the levelised cost of hydrogen (LCoH) will fall below \$2.00/kgH_2 by 2030, and \$1.00/kgH_2 by 2050 – perhaps under optimistic scenarios and in regions with high capacity factors of renewable electricity. However, CRU's own cost assumptions for renewable energy and electrolysers indicates that most countries are still expected to exhibit green hydrogen costs above blue and grey costs by 2050, ranging between \$3–7/kg in real terms – even before the addition of necessary storage and distribution costs. Green ammonia costs also follow the same trajectory, with the cost of green hydrogen forming the largest part of its overall cost structure. Furthermore, as ammonia production requires a constant supply of hydrogen, additional costs associated with overcoming this challenge – if relying on the underlying intermittency of renewable energy – can also be presumed.

The conclusion is that aside from those countries that are expected to have access to low-cost renewable energy, green hydrogen and ammonia costs will still be prohibitively high by 2050, with implementation of subsidy or a carbon price likely needed for the industry to develop.

Offtake agreements the key

While both low-emissions hydrogen and ammonia have emerged as promising energy carriers, with the potential to play a pivotal role in the ongoing energy transition, it is essential to approach the role of hydrogen and ammonia with a realistic lens, acknowledging both their promises and challenges, particularly cost. The pathway to a hydrogen-based economy will require not only technological advancements but also infrastructural investments and systemic changes. In many sectors, this will offset the value that hydrogen or ammonia can deliver, with alternative decarbonisation solutions instead being adopted.

This latter point is reflected most tangibly within the low-emissions project pipeline itself, where just 2% and 4% of hydrogen and ammonia projects have reached a final investment decision, respectively. The missing key for project financing remains the committed offtake, with potential end-users still unconvinced by the lack of policy clarity, high costs and infrastructure requirements of adopting hydrogen or ammonia. There needs to be more focus on potential demand in existing markets such as steel, fertilizer and methanol for faster development and for the industry to move beyond its 'messy middle'.

Learning more

Interested in the future of hydrogen and ammonia? CRU's Low-Emissions Hydrogen and Ammonia Service can validate and test your internal assumptions and support business decisions. ■

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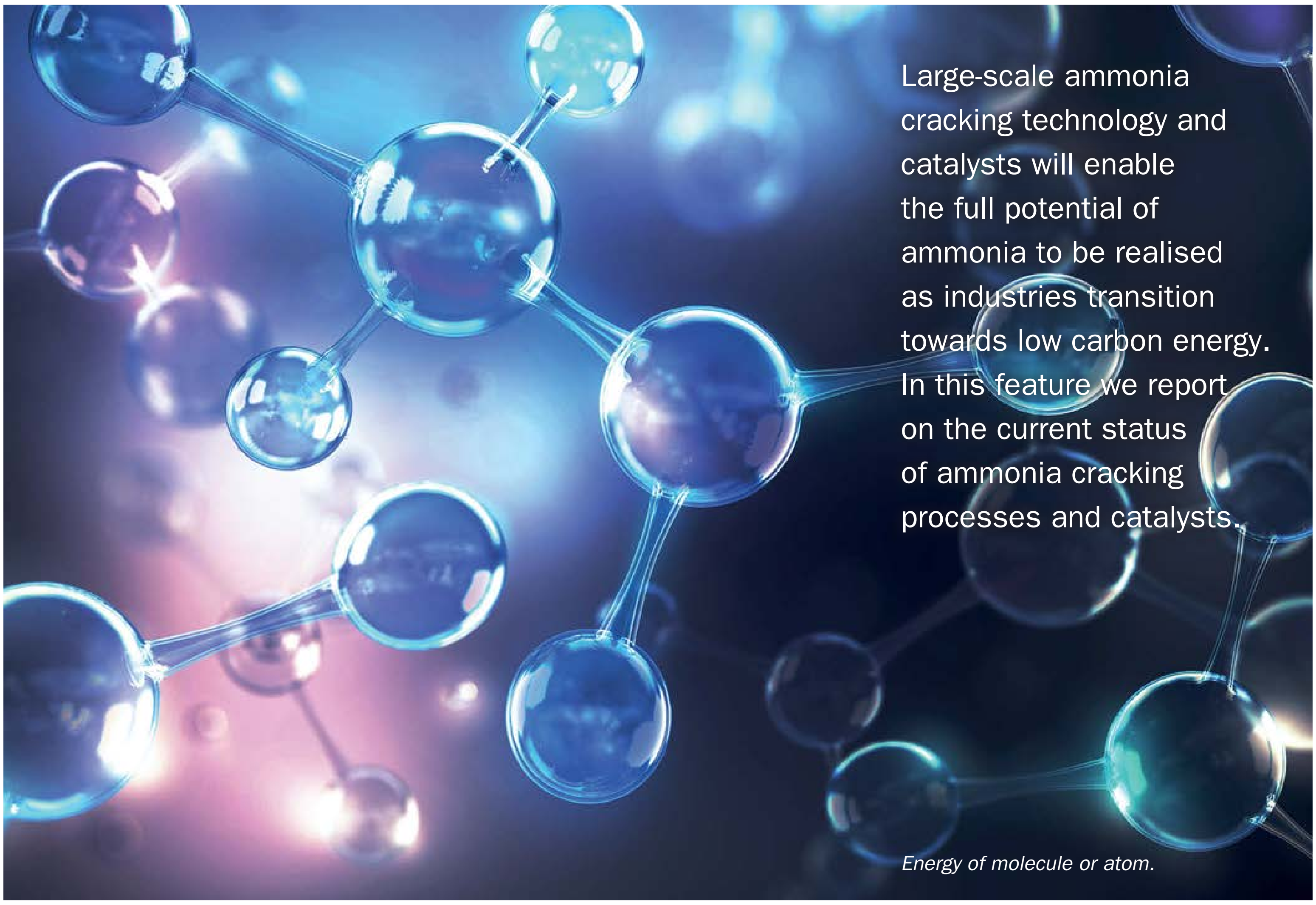
Ammonia in a future hydrogen economy



Large-scale ammonia cracking technology and catalysts will enable the full potential of ammonia to be realised as industries transition towards low carbon energy. In this feature we report on the current status of ammonia cracking processes and catalysts.

Energy of molecule or atom.

PHOTO: ANUSORN NAKDEE / ISTOCKPHOTO.COM

The world is facing an incredible challenge in the race to decarbonisation, imposing a change of landscape in the technologies and fuels used to support sustainable modern-day life in the future. Coal, oil and natural gas have been transported from the parts of the planet which have an abundance of fossil fuels to those which are short of energy for many decades. As the world decarbonises, the challenge will be to transport wind and solar energy from regions where it is in abundance, mainly in the southern hemisphere, to those which are lacking renewable energy, mainly in the northern region of the world.

Both hydrogen and ammonia are predicted to play a major role in this journey to support the decarbonisation of industries and regions around the world.

Hydrogen is known to be a clean and environmentally sustainable energy vector and is taking a leading position as a sustainable fuel of the future. Ammonia can also be used as a fuel in its own right, but many applications require ammonia to be decomposed back to hydrogen prior to use.

One of the current challenges facing hydrogen technologies is its storage and transport. Although hydrogen has a very high energy density on a mass basis (119.7 MJ/kg of lower heating value at 25°C and 1 bar, while gasoline has 44.79 MJ/kg), it has a very low energy density on a volume basis due to its low molecular weight (8.96 GJ/ m^3, compared to gasoline with 31.17 GJ/m^3, both referred to as liquid fuels), which leads to storage difficulties.

The most common method of hydrogen storage nowadays is as a compressed gas at pressures of up to 700 bar at room temperature. Alternative solutions are proposed but they all require a large amount of energy which counterbalances the benefits of the hydrogen molecule as a sustainable energy vector.

In addition, the transport of hydrogen as a liquid requires extremely low temperatures (-252°C), leading to high energy consumption for refrigeration and reheating as well as for new technology and infrastructure. The loss of hydrogen due to evaporation during liquefaction and transport can also be significant.

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Hydrogen tends to diffuse through the material, which is used to contain and transport it, resulting in embrittlement of the storage material.

For these reasons, ammonia is widely regarded as the most economic vector for carbon-free energy storage and transportation of both green and blue hydrogen over long distances. With a volumetric energy density 1.5 times higher than liquid hydrogen, ammonia is considered as a better hydrogen carrier than LOHCs (liquid organic hydrogen carriers) and methanol.

Ammonia has a high hydrogen content (17.8% by weight and a volumetric density of 121 kg H_2/m^3 at 10 bar) and is carbon-free. It has an energy density in volume of 13.6 GJ/m^3, a value that falls between hydrogen and gasoline. If the ammonia used in the process is produced through renewable resources, the entire hydrogen production process has a very low carbon footprint. Ammonia liquefies at low pressure, 8.6 bar at 20°C, so its transport and storage are relatively easy. With regard to safety issues, ammonia has a narrow combustion range, compared to that of hydrogen, and a concentration as low as 5 ppm can be detected easily by smell.

Ammonia can be stored and transported using existing infrastructure. Green or blue ammonia could be produced in countries rich in energy resources, such as abundant renewable energy or low-cost feedstock, e.g., South Africa, Australia, the Middle East etc., and transported with tankers overseas to target energy import countries, e.g., Europe, Japan, Korea etc. Finally, ammonia can be cracked into hydrogen and nitrogen in a centralised large scale cracking plant at or near the harbour or in decentralised cracking stations located inland. However, ammonia cracking is an energy intensive process, particularly when operating at elevated pressures for direct utilisation of pressurised hydrogen.

Both the technology and the catalysts for cracking ammonia have been around for decades, but apart from in the niche heavy water production process, until recently, the market for cracking ammonia has been focused on the small-scale delivery of hydrogen or nitrogen as utilities, in areas where the gases were hard and uneconomical to transport, and efficiency was not a key criterion.

The existing commercialised ammonia cracking units are fully electricity driven, have a very small capacity and operate at equilibrium-favoured conditions (low pressure, very high temperature). Both the technology and the catalysts used in these units serve the installed purpose, but they are not suitable for what the industry is looking for in terms of efficient, low-carbon hydrogen production to support the energy transition market.

The commercial success of clean hydrogen production through ammonia cracking hinges on technology and catalyst development, delivering world scale plants with high efficiency, high reliability and high environmental standards and performance.

Ammonia cracking technology and catalysts

Ammonia cracking technology

The market for large-scale ammonia dissociation for low-carbon hydrogen is new, however the technology elements to dissociate ammonia at scale are established and proven in operation, bearing great resemblance to steam methane reforming plants that are currently used to make most of the world's hydrogen. Ammonia cracking has similar chemical, heat transfer, heat management and engineering challenges. However, in order to serve large-scale hydrogen ammonia cracking technology will need to satisfy new requirements as shown in Table 1.

Ammonia cracking catalysts

The catalyst to drive the ammonia cracking reaction is a field of intense study. The performance of the catalyst is critical to the economic success of the facility. Underperformance can lead to reduced hydrogen yield and/or increased environmental (NOx) emissions, which will impact the profitability of the facility.

Catalyst activity, stability, mechanical robustness, guaranteed life, availability of supply and manufacturing capacity are all important factors for commercial success.

Hydrogen release via ammonia cracking is an endothermic reaction favoured at high temperatures close to 1,000°C.

$$2NH_3 \rightarrow N_2 + 3H_2 \quad (\Delta H = 46.22\ kJ/mol)$$

In the presence of a catalyst the process temperature can be significantly lowered, reducing the overall energy consumption of the process. Depending on the operating conditions, base or precious group metals can be considered. Nickel (Ni) and ruthenium (Ru) are known to be efficient catalysts and are commercially available.

The general agreement is that ruthenium is the most active metal for low temperature applications (around 500°C), but its scarcity and high cost make its large-scale application less attractive. Although nickel is less active than ruthenium, it is interesting due to it relatively low cost, but is only active at high temperatures (600 to 800°C), which also brings with it challenges. Due to the high process temperatures, it requires an effective integration of process heat to minimise losses. At high temperatures and pressure, ammonia causes nitriding of steel pipes on one end of the reactor, and hydrogen may cause high temperature hydrogen attack (HTHA) on the other, requiring smart choices of construction materials and process parameters to minimise these effects.

In the following sections we report on the latest developments and cutting-edge solutions in ammonia cracking technology and catalysts as presented at the Nitrogen+Syngas 2024 Conference, in Gothenburg, Sweden. ■

Table 1: **Comparison of past and future ammonia cracking technology requirements**

	Past technology	Future technology
Capacity	Small scale	Large scale
Energy input	Electricity	Self sufficient (some electricity import as utility)
Operating pressure	Near atmospheric	Higher (e.g., >20 bar)
Operating temperature	High (850-900°C)	Lower (<700°C)
Energy efficiency	Low	Highest
Technology readiness	Ready	High

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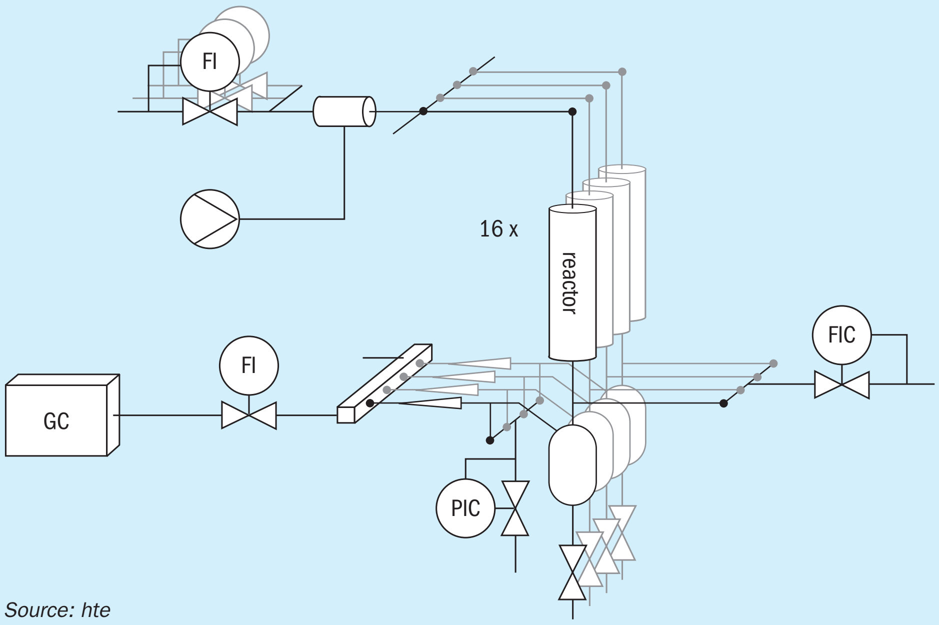
hte GmbH

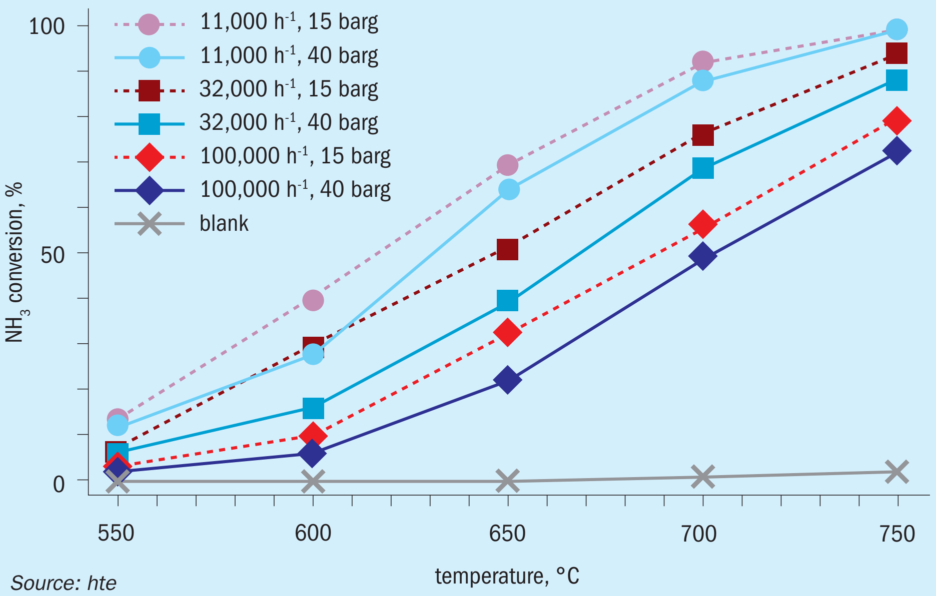
Accelerated assessment of new ammonia cracking catalysts

Fig. 1: **Simplified scheme of hte's high throughput testing setup**



Source: hte

Fig. 2: **NH_3 cracking over an Fe-based catalyst using hte's advanced high throughput technology (95% NH_3, 5,000 ppm H_2O, Ar as balance and internal standard, 550 to 750°C, 15 and 40 barg, 11,000 to 100,000 h^{-1}).**



Source: hte

hte – the high throughput experimentation company - actively accelerates and enhances R&D in the field of catalysis as a service provider to its customers, enabling cost-effective innovations and reduced time to market for new products. Typical R&D projects address screening of newly developed or optimised materials, process optimisation, accelerated aging tests, generation of data sets for kinetic modelling, commercial catalyst benchmarking, quality control of different catalyst batches, or (co-)feed studies.

The high throughput approach accelerates catalyst assessment, while offering parallelised testing at a broad range of process parameters. hte's unique reactor technology enables catalyst testing for NH_3 cracking under industrially relevant conditions, including high temperatures (up to 750°C) combined with elevated pressures (up to 50 barg) as well as reliable dosing of trace water, addressing the research gap of current NH_3 cracking R&D.

Further research to advance the commercialisation of NH_3 cracking within customer projects requires focusing on catalyst stability under different process conditions, which can be supported by hte's accelerated aging test protocols as well as parallel difference testing.

A versatile 16 fold parallel fixed bed reactor setup similar to a test unit validated and utilised for a recent reverse water-gas shift study was modified for processing NH_3. After upgrading the high throughput setup for NH_3 processing, the suitability of the unit for this chemistry was demonstrated during validation experiments using an in-house prepared Fe-based catalyst. The high throughput testing equipment (Fig. 1) included mass flow controllers for individual dosing of H_2, N_2, and Ar, and high-precision syringe pumps for liquid dosing of NH_3 and H_2O. The feed mixture was distributed equally among the 16 parallel reactors. Catalyst performance testing was conducted using a particle size fraction of the catalyst diluted in inert material to minimise temperature gradients. The reactor effluent gas was analysed using an in-house configured multi-detector online gas chromatograph (GC). Fully automated unit operation and monitoring was realised using hte's process control software (hteControl). Data evaluation was performed using the myhte software solution, specifically developed for handling large amounts of data produced by high throughput setups.

Experiments were designed to investigate the influence of temperature, pressure, and GHSV on the conversion of NH_3 using an Fe-based catalyst via loading of different volumes of the catalyst and performing temperature ramps from 550-750°C at 15 and 40 barg (Fig. 2). The results showed that NH_3 conversion increased with temperature, reaching >97% at 750°C and 11,000 h^{-1}. Increasing GHSV and reactor pressure resulted in reduced NH_3 conversion, which is in line with thermodynamics. The apparent activation energy at low conversion levels was calculated as 140-160 kJ/mol and is comparable with literature values. The blank reactors showed only minimal conversion of <1% up to 700°C and 2% at 750°C, verifying the suitability and inert behaviour of the reactor concept for potential generation of kinetic data sets. Variation of the feed rate by a factor of two and increasing the pressure to 50 barg further expands the parameter field explored during the study, demonstrating the flexibility of the unit.

Additional experiments alongside the temperature screening were conducted to assess the stability and performance of the catalyst. One reactor was maintained at a constant temperature of 650°C to test the performance stability. A run-in behaviour of the catalyst was observed during the start-up, emphasising the need for a stabilisation phase when testing catalysts for NH_3 cracking under high temperature and pressure conditions. The initial activity of 80% NH_3 conversion decreased to around 65% during steady state operation at 40 barg.

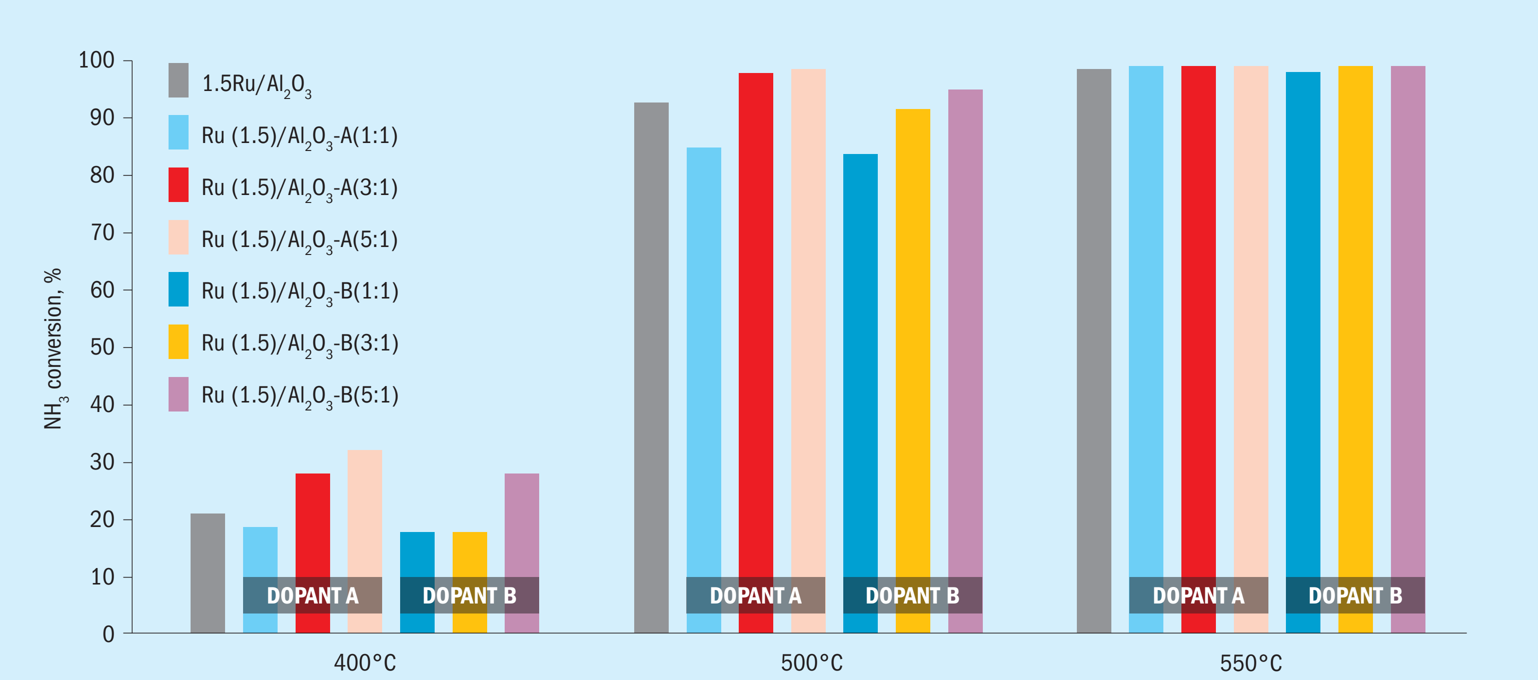
As the fitness of the technology and equipment was proven, the high throughput unit was used in subsequent customer projects. One exemplary project involved benchmarking of four different commercial catalysts while screening a wide range of parameters. GHSV was screened in parallel by loading the same catalyst to different volumes. Individual reactor heaters allowed fast screening of temperatures and, furthermore, NH_3 feed concentration was varied by flexible dosing of the individual feed components. A lead material was identified, achieving equilibrium NH_3 conversion already at 650°C under industrially relevant conditions, demonstrating state-of-the-art properties. ■

Reference: Mutz B., Baumgarten R., Fritsch C. (hte): "*Accelerating process optimization and catalyst ranking in high-pressure NH_3 cracking enabled by advanced high throughput technology*", presented at Nitrogen+Syngas 2024, Gothenburg, Sweden, 4-6 March 2024.

HERAEUS

Ruthenium catalysts for conversion of ammonia into hydrogen

Fig. 1: **Ammonia conversion depending on dopants**



Source: Heraeus

Ruthenium is a rare and precious metal and is typically a minor component in ores containing platinum group metals (PGMs). The majority of the available ruthenium is obtained as a byproduct in platinum mining, e.g., in Russia, South Africa and Zimbabwe. Such countries have large reserves of PGMs, including ruthenium, and hence represent the main sources worldwide. Heraeus, as a precious metal and global technology group company, has established supply chains and partnerships with various suppliers and is able to ensure a continuous and reliable supply of ruthenium and other precious metals for its products and services. In addition, Heraeus provides refining and a recycling service for PGM processing to meet the demands of customers and clients to reuse valuable natural resources.

Metal recycling offers several benefits:

- Conserves valuable natural resources and less virgin ore needs to be mined.
- Energy savings contribute to reduction of greenhouse gas (GHG) emissions. Recycling of metals avoids significant energy consumption compared to extracting and refining metals from virgin ore.
- Economic impact: the recycling industry provides a source of secondary raw

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materials, reducing the dependence on imports and promoting local economy.

- Environmental benefits are the reduction of soil erosion, deforestation, and habitat destruction. In addition, water and air pollution associated with mining is avoided.

Heraeus benefits from several decades of experience in recycling services in the field of PGMs and has established a business loop from collecting precious metal waste, to regaining raw metal via recycling, to producing precious metal contained products like catalysts. The regained precious metals are named as secondary or green metals. Heraeus uses green metals, which have a CO_2 footprint of less than 98.5% compared to the primary metals, to produce new batch catalysts.

Heraeus ruthenium-based catalysts for ammonia cracking show high catalyst activities at relatively low process temperatures of 400 to 600°C (NH_3 conversion reaches close to 100% up to 550°C), compared to commercial Ni-based catalysts with process temperatures of 600 to 800°C (NH_3 conversion reaches close to 100% up to 750°C). In addition, Heraeus has improved catalytic activity by systematic studies of, e.g., catalyst support, metal precursors, loading, and dopants. The optimised Ru nanoparticles have a diameter of 6 nm. In studies, two dopants resulted in an improved activity and an increase of 10% in ammonia conversion was observed at 400°C (Fig. 1). This increase in activity of the Ru-based catalysts could be explained by the improved electron donation from the dopants to the support material, which enables charge balancing of the intermediary steps of ammonia cracking.

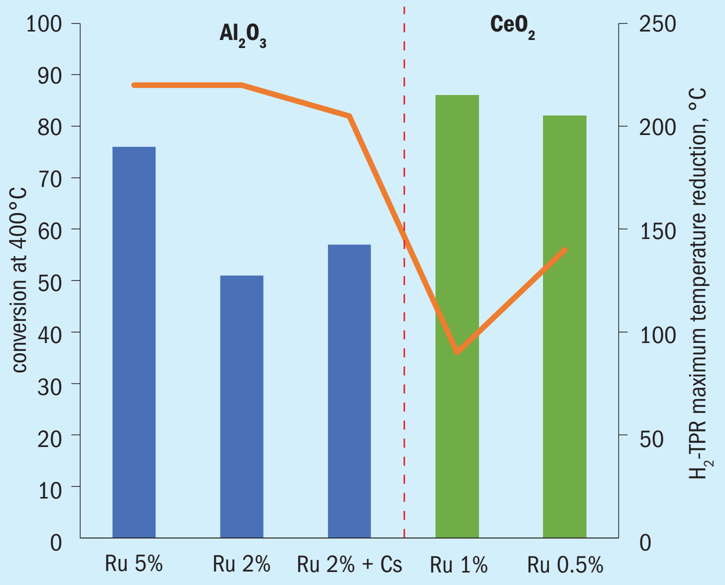
Heraeus Ru-based catalysts can be supplied in different shapes, e.g., small spheres, medium and large tablets, to fit the application in adiabatic or tube reactors. Customers benefit from the high activity of the catalyst at low process temperatures leading to energy efficiency and reduced total cost of ownership. ■

Reference: Chang K.-C. (Heraus Precious Metals): "*Precious metal catalyst: The key to hydrogen economy – ruthenium catalysts enable the efficient conversion of ammonia into hydrogen*", presented at Nitrogen+Syngas 2024, Gothenburg, Sweden, 4-6 March 2024.

ENERCAT AND LYNAS

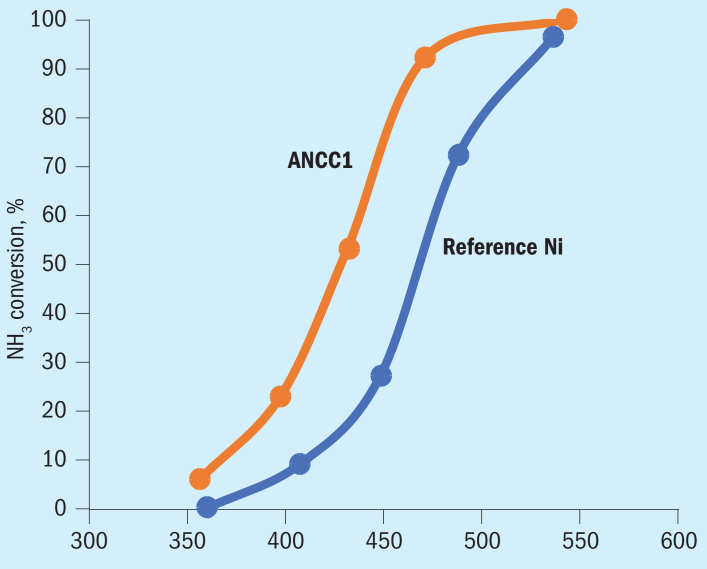
Advanced ammonia cracking catalysts

Fig. 1: **NH_3 conversion measured at 400°C vs H_2-TPR max. temp. reduction – for respectively Ru-Al_2O_3 based catalysts (blue bars) and Ru-CeO_2 based catalysts (green bars).**



Source: Enercat/Lynas

Fig. 2: **NH_3 conversion (%) vs outlet cat. temp. (°C); $[NH_3]$ inlet = 10% - SV = 10000h^{-1} – Atm.P; reference Ni supported on alumina model coated catalyst (blue) vs base metal supported on rare earths oxides (ANCC1) (orange)**



Source: Enercat/Lynas

EnerCat, an expert in catalytic formulations and advanced materials solutions, has developed advanced ammonia cracking catalysts which show the best trade-off between NH_3 conversion at low temperature (i.e. below 450°C) and a massive reduction of costly Ru particles. It is evidenced that the combination of Ru oxides and rare earth based oxides (such as ceria, CeO_2) with a proprietary process leads to a much higher dispersion of the Ru aggregates and much faster reducibility properties as measured by H_2-TPR (hydrogen temperature programmed reduction – a technique used for catalyst characterisation). The new advanced catalysts with ultra low loading of Ru show high activity below 500°C and extremely stable performance in a large temperature window. Fig. 1 shows the relation between the temperature at which the Ru oxide crystallites are reduced and the NH_3 conversion rate at 400°C for two types of support (alumina vs ceria). These results dismiss the widely held view that the higher the Ru loading, the higher the activity.

Further examination and laboratory trials are needed to better understand the catalytic mechanism and the 'true' nature of the active sites. EnerCat and its partner Lynas have already launched some fundamental deep characterisation studies with academics which should lead to additional technical communications soon.

Ru-free catalysts have also been investigated. Fig. 2 shows the NH_3 conversion performance of two Ru-free transition metal catalysts. The reference Ni-based catalyst (REF Ni) shows a rather 'moderate' activity up to 500°C, in line with the prior art. At 500°C, conversion reaches 80% and over 90% at 550°C. In contrast the innovative transition metal and ceria-based catalyst (ANCC1) achieves 98% conversion from 500°C, offering better performance between 400 and 500°C.

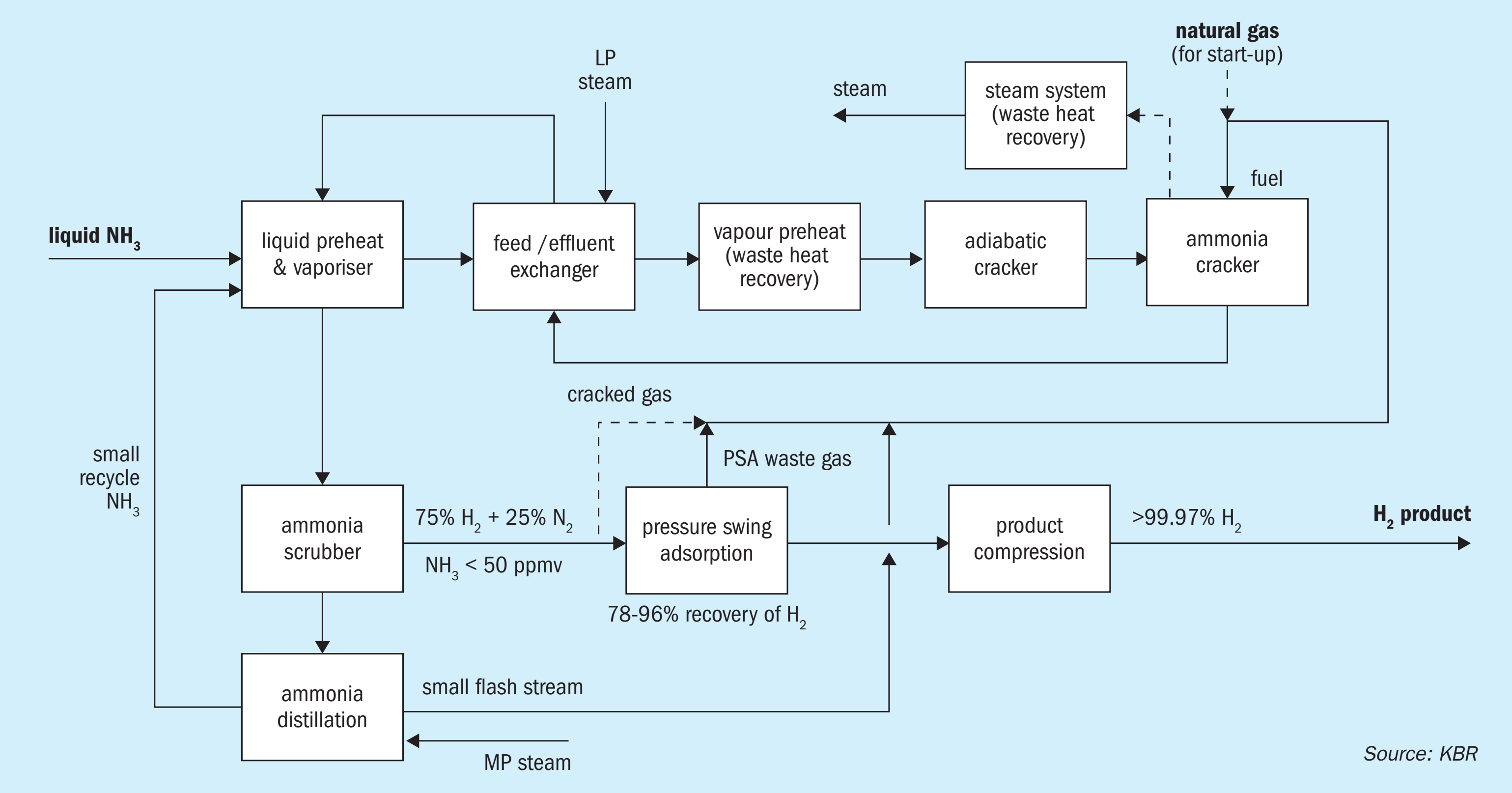
These results confirm the value of combining rare earth oxides and transition metals to initiate the NH_3 decomposition at lower temperatures. Nevertheless, these results show it is difficult, in the absence of noble metals such as Ru, to achieve higher performance levels (>80%) from 400 or 450°C, which remains a priority target for many applications. ■

Reference: Lahougue A., Le Moël G., Rohart E. (EnerCat) and Ding J. and Benaissa H. (Lynas): "*Advanced NH_3 cracking catalysts with outstanding low temperature activity and durability*", presented at Nitrogen+Syngas 2024, Gothenburg, Sweden, 4-6 March 2024.

KBR AND CLARIANT

Ammonia cracking catalysts for KBR's H2ACT℠ process

Fig. 1: **H2ACT℠ block flow diagram**



Source: KBR

KBR's approach to commercialising ammonia cracking technology is to develop a flow scheme based on robust risk mitigation strategies, focusing on inherently safe design principles and partnering with world-leading catalyst suppliers such as Clariant to guarantee commercial success.

A block flow diagram for a typical KBR H2ACT℠ ammonia cracking plant, including all process unit operations for delivery of high pressure, high purity hydrogen is shown in Fig. 1.

Liquid ammonia from OSBL storage is pumped to the required system pressure. The liquid ammonia feedstock is preheated and vaporised via heat integration within the process. Liquid ammonia vaporisation is also partially provided by excess LP steam available from the small steam system of the ammonia cracking plant.

Vaporised ammonia is preheated via heat integration in the process and subsequently by recovering heat from the convection section of the fuel fired ammonia cracker, before being directed to the reactor system for dissociation.

The reactor system consists of an adiabatic dissociation reactor (pre-cracker) in series with an isothermal, fuel-fired cracker (ammonia cracking furnace or ammonia cracker). The cracking reaction is performed under presence of catalyst in both reactors – with catalyst formulation optimized for each reactor characteristics and application.

All ammonia dissociation (for both reactors) is driven by heat from the fuel-fired ammonia cracker. The ammonia cracking furnace design is based on the well-proven KBR down-fired primary reformer design with hundreds of references in ammonia production, from small to large scale capacity and decades of experience and knowhow.

The heat source for the ammonia cracking furnace is fuel from the process, consisting of tail gas from the hydrogen purification section, supplemented by cracked gas (H_2/N_2) (or optionally supplemented by natural gas).

The ammonia cracking furnace is designed to attain maximum thermal efficiency by utilising process waste gases as part of the fuel, as well as by recovering heat in the convection section from the flue gases for feed vaporization, preheat and dissociation.

The furnace convection section is furnished with a selective catalytic reduction (SCR) system as standard, able to meet the most stringent environmental emission requirements.

Cracked product purification is based on well-proven and often-used processes:

- Ammonia recovery by a simple water-based ammonia absorption/distillation unit, designed and in operation in a multitude of KBR ammonia plants worldwide. After this unit, the hydrogen purity is 75 mol-% dry.
- Nitrogen removal using standard pressure swing adsorption (PSA), a proven, reliable and cost-effective technology used in a variety of industries.

Including these units, the hydrogen product can be delivered at any purity >99.97 mol-%. Hydrogen purity requirement can vary significantly depending on the hydrogen product off-taker. For a centralised large-scale cracking unit, any proportion of the product can be sent to an additional purification unit (PSA) for further nitrogen removal, for example, to produce very high purity hydrogen for mobility applications.

Typical hydrogen delivery pressure of around 30 barg is achievable without additional hydrogen compression. For higher delivery pressure, a hydrogen compressor is included in the flow scheme.

Scale and performance

H2ACT℠ can deliver hydrogen at mega scale and any purity depending on the industrial application. The performance of the H2ACT℠ ammonia cracking plant is consistently maintained across the entire capacity range, from small to mega-scale production, and across the operating envelope of the plant.

Clariant catalysts for ammonia cracking

Clariant has developed and offers highly innovative catalysts for ammonia cracking. Clariant has over 40 years of experience in manufacturing ammonia cracking catalysts for the small-scale cracking units in the market today. Coupled with Clariant's long history in providing nickel-based catalysts for steam methane reforming, Clariant is ideally positioned to offer catalysts for the ammonia cracking market with high technology readiness, established manufacturing and high performance.

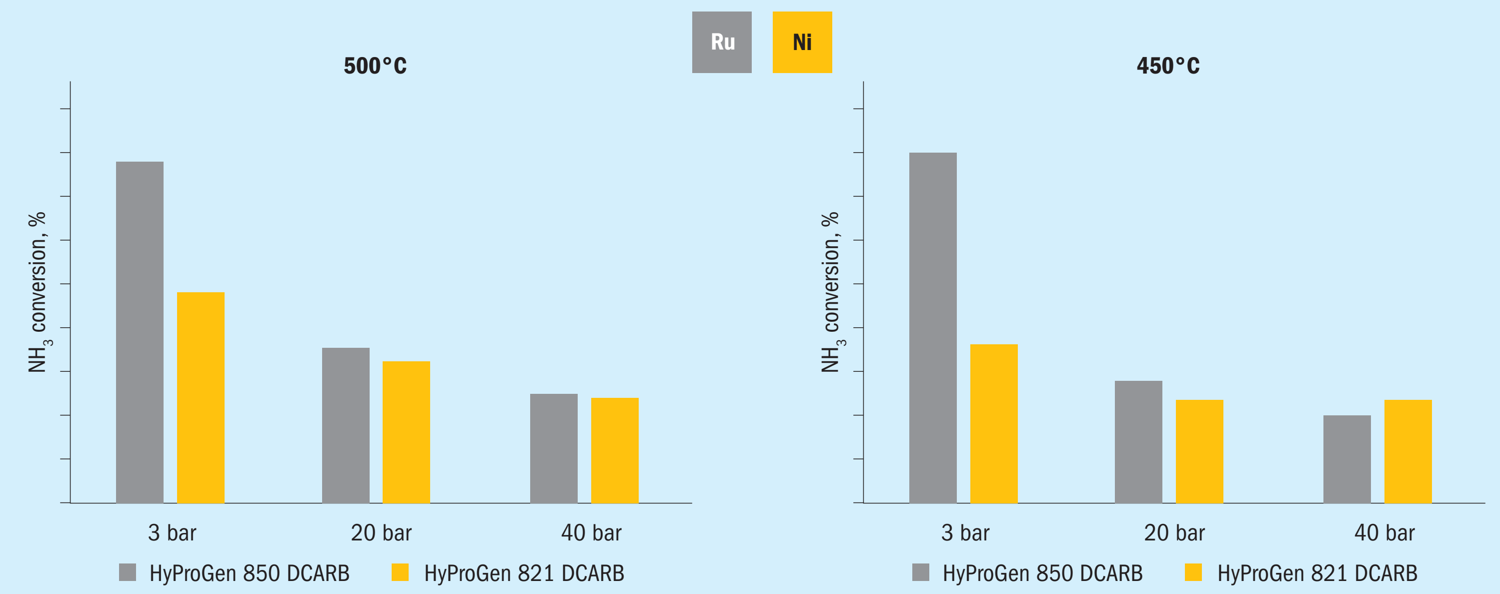
Clariant's ammonia cracking catalyst portfolio comprises the following:

- HyProGen® 830 DCARB: A nickel-based catalyst designed for high temperature applications (up to 750 °C). Due to its mechanical robustness, it can be used in reformer-type fired tubular reactors.
- HyProGen® 820 / 821 DCARB: A nickel-based catalyst designed for moderate-temperature applications (420 to 650°C) in adiabatic reactors. Combines superior activity with high thermal resistance against deactivation.
- HyProGen® 850 DCARB: A highly active ruthenium-based catalyst designed for low temperature applications (400 to 600°C). Suitable for smaller and more compact plant designs.

Clariant catalyst testing for H2ACT℠

Clariant is running an ongoing R&D program in order to ensure that the catalysts show excellent activity and stability under the conditions of H2ACT℠. Hence, all tests are performed at relevant conditions in alignment with KBR, e.g., pressures up to 40 bar and realistic feed composition with 2,000 to 5,000 ppm water.

Fig. 2: **Activity comparison between nickel and ruthenium catalysts based on different pressures.**



Source: Clariant

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H2ACT^{SM} comprises two reactors, a pre-cracker and the fired tubular main cracker (ammonia cracking furnace). Two completely different types of catalysts must be applied to address the needs and requirements of each reactor.

Pre-cracker (adiabatic reactor)

In the pre-cracker of H2ACT^{SM}, highly active bulk nickel catalysts can be applied as mechanical stability requirements are lower for this type of reactor. A two-layer concept is applied with a top layer of HyProGen 820 DCARB, which has high thermal stability, and a bottom layer of the highly active HyProGen 821 DCARB, which offers an efficient alternative to ruthenium-based catalysts.

While ruthenium-based catalysts are typically sensitive to water, especially at high pressure and temperature, Clariant's nickel pre-cracking catalysts are very robust in the presence of water.

Ruthenium-based catalysts have two additional drawbacks compared to nickel-based catalysts: Firstly, they suffer from rapid deactivation at moderate to high temperatures. Secondly, the activity of ruthenium declines strongly with pressure: Fig. 2 shows that the activity of Ni-based HyProGen 821 DCARB is close to the 2 wt-% Ru benchmark at 40 bar.

In order to study the robustness of the catalysts against thermal deactivation under H2ACT^{SM} conditions, several rapid ageing tests were performed. Typically, such tests are performed at temperatures roughly 50 to 100 °C higher than the operating conditions in order to observe the catalytic activity over time and evaluate the expected lifetime and performance. In most catalytic processes two stages of deactivation can be detected: a fast initial deactivation followed by a relative stabilisation of the performance. In order to determine if the catalytic activity reaches a stable state, the test must be sufficiently long. Therefore, up to eight aging cycles were performed. In the case of HyProGen 820, DCARB aging was performed at 750°C, hence around 100°C higher than the maximum expected operating temperatures. Stable performance was achieved after five ageing cycles. Analogous tests were performed with HyProGen 821 DCARB at lower temperatures.

Fired tubular reactor (ammonia cracking furnace)

In the fired multi-tubular-reactor of H2ACT^{SM}, the main conversion will occur at temperatures up to 700°C. For this type of application, the catalyst needs to show good activity and more importantly, excellent mechanical stability as well as a low pressure drop. Clariant has been producing such catalysts since the 1950s for use in steam reforming applications at temperatures over 800°C and pressures exceeding 40 bar.

HyProGen 830 DCARB combines high activity with good thermal stability. Furthermore, this catalyst has already been proven in commercial fired multi-tubular reactors, showing tremendous mechanical stability.

In order also to prove the long-term stability of HyProGen 830 DCARB, additional rapid ageing tests were performed which showed the initial deactivation was quite small, and a highly stable performance was achieved after just four ageing cycles, showcasing the excellent thermal stability of HyProGen 830 DCARB.

To prove the catalyst performance under H2ACT conditions in the main cracker, a modified feed composition was used which mimics the real inlet composition of the main cracker: HyProGen 830 DCARB achieves nearly 99% NH_3 conversion at 675°C, approaching the thermodynamic equilibrium at both start of run and after eight subsequent ageing cycles (at 750°C).

In summary, combining Clariant's catalyst expertise with KBR's technology and equipment capabilities offers an effective and low-risk solution for ammonia dissociation into hydrogen, and mitigates risks for commercial ammonia cracking projects, completing the sustainable ammonia to hydrogen value chain. ■

Reference: Krinninger C., Stylianou E.: "*State-of-the-art ammonia cracking catalysts for KBR H2ACTSM process*", presented at Nitrogen+Syngas 2024, Gothenburg, Sweden, 4-6 March 2024.

JGC GROUP

Technology development and demonstration of ammonia cracking

JGC, Kubota, and Taiyo Nippon Sanso are jointly carrying out an R&D project on large-scale ammonia cracking technology for low-carbon hydrogen production by a tubular ammonia cracking furnace as part of NEDO's development of technologies for building a competitive hydrogen supply chain.

JGC's scope is to supervise the project, design and develop the entire ammonia cracking process and furnace, plan the demonstration, and estimate the costs, targeting a large-scale, highly efficient and zero-emission ammonia cracking system in the order of 100,000 t H_2/year capacity for a commercial plant in around 2030. Kubota's scope is to research and develop ammonia cracking tubes, while Taiyo Nippon Sanso will research and develop hydrogen gas purification systems (PSA). In addition, JGC is outsourcing research to Idemitsu Kosan to support with examination of the demonstration site and planning of the demonstration phase.

The product hydrogen specification will determine the optimum ammonia cracking conditions and key design parameters such as cracking temperature and pressure and hydrogen purification inlet and outlet conditions.

The cracking temperature and pressure, in particular, will have a huge influence on the ammonia conversion rate and therefore residual ammonia, which may have an impact on the hydrogen recovery rate of the hydrogen purification unit.

If a higher temperature is selected, the conversion rate will be higher, but it will require higher fuel consumption and higher grade of cracking tube material or thicker cracking tube. If a lower pressure is selected, the conversion rate will be

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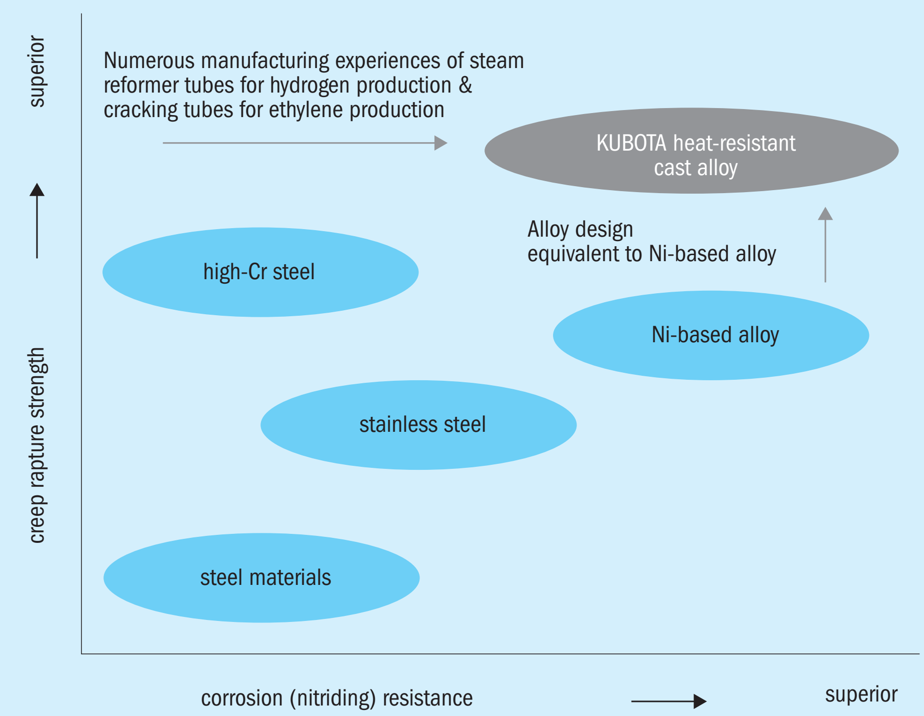
Fig. 1: **Key characteristics and direction of tube metal development**



Source: JGC Holdings Corporation

higher, but it will require more power consumption to compress product hydrogen to meet the users' requirement.

To speed up time to commercialisation, existing technologies will be utilised as much as possible. However, there are some areas of research and development required for commercialisation.

One important area of investigation is the issue of nitride corrosion in cracking tubes and process piping, which needs to be carefully addressed, since it will have huge impact on the reliability and lifetime of the system. In addition, tube materials with high creep rupture strength are required, suitable for high-temperature and high-pressure environments over a long lifetime. Kubota is analysing resistance to nitriding for an existing tube line-up. In addition, Kubota is developing materials dedicated to ammonia cracking tubes (see Fig. 1).

A second area of focus is hydrogen purification by PSA to remove nitrogen, residual ammonia and water in order to meet the product hydrogen specification. The influence of residual ammonia on hydrogen recovery rate needs to be addressed, since it may have an impact on the overall energy efficiency.

Project status and demonstration plan

The ammonia cracking demonstration site will be at Idemitsu Kosan's former refinery site in Yamaguchi Pref., Japan. The FEED for the demonstration plant will be carried out in 2024, with the aim to propose the demonstration project to NEDO in 2025. ■

Reference: Kai M.: "*Technology development and demonstration of an integrated control system for green ammonia and chemical production and ammonia cracking*", presented at Nitrogen+Syngas 2024, Gothenburg, Sweden, 4-6 March 2024.

JOHNSON MATTHEY

Johnson Matthey's world scale ammonia cracking process

Johnson Matthey (JM) has developed an ammonia cracking process which is suitable for deployment for large scale hydrogen (or cracked gas) production. It has been developed using JM's core competencies of catalyst design, process design and chemical plant scale up to de-risk the technology.

The key unit operations are the ammonia cracker which decomposes ammonia to hydrogen and nitrogen, and the separation system which purifies the hydrogen product. The ammonia cracking reactor is similar in principle to a steam-methane reformer (SMR), and JM has applied significant experience from its market leading position in designing SMR's for the methanol industry. Sensible and reaction heat is supplied to the process via combustion of a fuel. Heat is recovered at the exit of the cracker and exit of the flue duct through heat integration within the process; this is a common approach within SMR based processes which has been adapted to the lower temperature conditions associated with the ammonia cracking flowsheet. Abatement technologies are installed within the flue duct to minimise emissions such as NOx and N_2O.

In a departure from established technologies, JM's ammonia cracker is fuelled by a blend of ammonia, hydrogen, and nitrogen. This removes the requirement for an external fuel or energy source, with the fuel derived from the pressure swing adsorption (PSA) tail gas and a portion of the ammonia fed to plant. JM has tested the combustion characteristics of these novel fuel blends, gaining insight into the flame characteristics and emissions associated with the departure from combusting natural gas. To purify the hydrogen stream, a combination of ammonia scrubbing, and pressure swing adsorption have been selected, with both technologies proven at scale in similar industrial applications.

JM ammonia cracker

JM offers a top-fired ammonia cracker which has been developed from JM's world leading design for large scale SMRs. Key changes include catalyst and reaction chemistry, fuel composition, environmental controls, and metallurgy. Heat recovery from the flue duct has been configured to accommodate efficiency, controllability, operability, and capital cost considerations.

Catalyst selection

The cracker uses JM's established range of KATALCO 27 series of ammonia cracking catalysts, which have been offered commercially for over 50 years.

KATALCO 27-200MQ is a nickel-based, high activity, ammonia cracking catalyst. The QUADRALOBE shape enhances radial heat transfer across the tube, and the shape of the pellet reduces pressure drop growth with time on-line.

Within a multi-tubular reactor, such as an ammonia cracker, the burners provide radiant and convective heat to the tubes. The endothermic nature of the ammonia cracking reaction leads to a radial temperature gradient across the catalyst filled tubes. The catalyst pellets help mix the bulk gas, promote heat transfer and minimise the aforementioned radial heat gradient within the tube. 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. 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.

Concerns have been expressed by the industry that the relatively small amounts of moisture contained within merchant ammonia can deactivate certain types of ammonia cracking catalyst. JM has conducted testing to confirm that this is not the case with KATALCO 27 series.

JM is also investing in extensive characterisation of the ammonia cracking reaction both for product development and to better understand aspects such as reaction kinetics, product activation and chemical inhibition. The driver for this work is that whilst existing small-scale applications can tolerate a degree of under or over performance, relatively small changes in performance will be critical to the economics of world scale ammonia cracking plants and it is essential that sufficient knowhow exists to allow such plants to be optimised at the design stage.

Ammonia combustion

Ammonia has been proposed as a fuel for many years. Although having a reputation for being difficult to burn and for generating high concentrations of nitrogen oxides there are some obvious advantages for deploying it as a fuel in an ammonia cracking process.

The use of ammonia as a fuel leads to synergistic benefits in that the process is more tolerant to ammonia slip from the cracker and there is no necessity for a high efficiency PSA unit. This is because, ammonia slip from the cracker and PSA off gas can be used as fuel for the ammonia cracker. The ammonia fuel saved can then be used as feedstock. Emission levels <0.1kg $CO_{2\text{-e}}/kgH_2$ can be achieved.

JM has commissioned full scale burner tests to verify the practicality of using ammonia as a fuel and to confirm emission levels. These have been carried out under a wide range of conditions including start-up, shutdown, and normal operation.

The results have been used to validate JM's design tools for use in designing ammonia crackers.

Ammonium nitrate and ammonium nitrite

Ammonium nitrate, and ammonium nitrite, can form when both ammonia and NOx are present at relatively low temperatures. Under the right circumstances, both can be explosive and there are many publicised examples in the nitric acid industry.

Although there should be little prospect of forming such substances during normal operation JM has mapped out a safe operating window which considers failure conditions and forms the basis of its ammonia cracker design. JM has also filed patent applications on the topic.

Metallurgy

JM has selected metallurgies that have been demonstrated in relevant service and has also used computational materials engineering to further its understanding of alloy degradation under ammonia cracking service. In addition, JM is conducting materials test work to further validate and enhance its understanding of the performance of alloys in ammonia cracking service. Patent applications have also been filed relating to techniques which can be used to reduce the severity of nitriding.

Emission control

JM is a leader in emissions control technology and is ideally placed to optimise the development and placement of emission control products within an ammonia cracking flowsheet. The pollutants of concern are acid forming oxides of nitrogen, ammonia and nitrous oxide and JM has solutions to meet regulatory requirements.

- **Acid forming oxides of nitrogen (NOx):** As might be expected, the presence of ammonia in a fuel tends to promote the formation of NOx. In JM's ammonia cracking process, the resulting NOx concentration remains within JM's range of experience and abatement solutions are available to achieve any known regulatory standard.
- **Ammonia (NH_3):** JM has offered ammonia abatement products for many years and JM's abatement solution design meets known regulatory standards.
- **Nitrous oxide (N_2O):** JM has offered N_2O abatement products for many years. Test work has been carried out to extend the operating window of an existing product to allow optimised N_2O abatement within an ammonia cracking flowsheet.

Cyclic operation

Cyclic operation poses a challenge in terms of both mechanical integrity and catalyst longevity. JM's ammonia cracking process has been designed to accommodate the fluctuations in plant load that will be required in a renewables powered economy.

Ammonia removal

JM chooses to remove ammonia upstream of the PSA unit. This has the advantage of allowing the PSA unit to be designed and optimised to remove less strongly adsorbed substances such as nitrogen. The ammonia that is recovered is used as fuel in the ammonia cracker, the net result being that overall performance of the plant is only weakly dependent on the performance of the ammonia cracker.

Pressure swing adsorption

Separation of hydrogen from the cracked gas stream is critical to achieve the required purity of the product stream.

PSA is a well-established separation technology that is proven at scale required for this flowsheet and can achieve hydrogen recovery rates of 90% or above. PSA units are used in existing hydrogen production plants and can achieve the required hydrogen purity level for this application.

The tail gas from the PSA unit contains nitrogen, unrecovered hydrogen and residual ammonia and is used as a fuel source for the ammonia cracker. PSA is selected over other types of gas separation processes due to the high capacity of unit required and high purity of hydrogen product (>99.96 mol-% can be achieved).

Reference: Pach J. Johnson Matthey):“*World scale ammonia cracking*”, presented at Nitrogen+Syngas 2024, Gothenburg, Sweden, 4-6 March 2024.

TECHNIP ENERGIES

Low energy intensity ammonia cracking

Technip Energies (T.EN), with a 60 year track record in technology development, innovation and EPC project delivery is poised to supply highly-competitive solutions to any hydrogen producer, on both low-carbon and carbon-free platforms. T.EN, a leader in the acceleration of the energy transition, is introducing its patented and scalable high-efficiency ammonia cracking solution.

The selection of proven catalyst is a cornerstone of the T.EN cracking process and ensures robust performance of the process. The catalyst selection for this application is a well-proven commercial catalyst platform designed for high-temperature applications. It combines excellent activity with very high thermal stability over a wide operating range.

The T.EN technology utilises a high-grade heat recovery, or “recuperative” concept. The highest value heat contained in the cracked gas is directly recovered and diverted back towards the reaction zone sustaining the cracking reaction. The design of the recuperative catalyst tube achieves simultaneously higher throughput and higher heat recovery in the integrated process compared to a conventional pellet-packed tubular reactor layout.

Downstream of the ammonia cracking process, the cracked gas comprises mainly a hydrogen/nitrogen mixture, plus a small amount of unconverted ammonia. The mixture is cooled and purified to reach the desired product specifications. The product purification unit can be customised based on client/off-taker needs to achieve a hydrogen purity of 99.9% or more.

Zero carbon footprint is achieved via combustion of carbon-free fuel, i.e. ammonia, hydrogen/nitrogen fuel mixture and/or pure hydrogen.

Key performance indicators

Technip Energies’ high-efficiency ammonia cracking process minimises heat loss, maximises exergy, and minimises external energy supply, thus maximising the energy efficiency of the process. Table 1 summarises the key performance indicators for the process.

Hydrogen purity may vary between 75 to 99.9+% depending on end-user application requirements.

Key benefits

Ammonia cracking is an endothermic process, meaning it requires energy input to sustain the reaction. Unlike the steam-methane reforming process, ammonia cracking does not mandate steam generation. In conventional hydrogen production, steam is required as feed to the process. Steam is needed to sustain feedstock conversion, to manage carbon formation, and to sustain the water-gas shift reaction. Thus, for hydrogen production, the valorisation of available energy in the form of incremental steam production may make economic sense, as it helps to achieve both high overall thermal efficiency and low specific conversion energy.

Steam is not required to sustain the ammonia cracking reaction or process, and therefore diversion of feed and fuel energy towards raising (export) steam correlates to additional systems and equipment, process complexity, and introduces a second energetic product. Therefore, the incentive is high to absolutely minimise the portion of energy invested to produce hydrogen, and economics are generally enhanced by maximising conversion of ammonia to product hydrogen. By optimising process heat integration, including T.EN’s recuperative technology features, steam production and systems are completely eliminated, while the thermal efficiency is maximised. On the contrary, where steam co-production is advantageous, these features are simply added back, being analogous to conventional hydrogen production unit features.

Table 1: **Key plant performance indicators**

Parameter	Value
H_2 purity, %	up to 99.9+
Delivery pressure, barg	according to client requirements
Delivery temperature, °C	according to client requirements
Carbon intensity (direct), kg CO_2 / kg H_2	0
Plant efficiency, % (LHV feed / LHV product)	92
Product yield, % (H_2 contained in product / H_2 contained in feed)	81

Source: Technip Energies

Described another way, Technip Energies’ high-efficiency ammonia cracking process offers the opportunity to utilise high-grade heat to make hydrogen, not byproducts, and to unlock incremental cracking efficiency.

Process heat integration is maximised by exploiting “pinch” principles. Avoiding a steam generation system in the process eliminates “flat spots” which inevitably lead to large temperature approaches, and exergy loss. Downgrade of valuable high-temperature heat to steam generation is avoided (i.e. a very large 750°C vs. 250°C temperature approach). Furthermore, process integration leads to reduced fuel-firing demand, a smaller main reactor, and minimum conversion energy. Simultaneously maximising efficiency, maximising yield and minimising fuel demand combine to ultimately pay out as lower cost of production.

1 47 2 48 3 49 4 50 5 51 6 52 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46

Experience

Having already successfully cracked ammonia at various scales for hydrogen production in refinery and utility settings, Technip Energies is accelerating the roll-out of ammonia cracking solutions. Combining decades of expertise in high-temperature process systems and equipment – particularly around hydrogen production, steam-methane reformers, steam cracking, ammonia plants and high-temperature processes in general – T.EN has a proven track record to deliver hydrogen from ammonia sources:

- Ammonia cracking for start-up of world scale hydrogen plants
- Ammonia cracking for supplying hydrogen to de-oxo units
- Recuperative reactor solutions, suitable for ammonia cracking (TPR and EARTH®)
- Steam methane reforming (SMR) with > 275 plants worldwide
- Customised catalyst co-development for EARTH®
- Ultra-low NOx burners (LSV® and TSWB®)
- Delivery of fully modularised plants ■

Reference: Liouta M. (T.EN) "*Low energy intensity ammonia cracking*", presented at Nitrogen+Syngas 2024, Gothenburg, Sweden, 4-6 March 2024.

THYSSENKRUPP UHDE

Optimisation of the ammonia decomposition process

thyssenkrupp Uhde offers all steps of the process chain for ammonia decomposition or cracking to hydrogen (green or blue hydrogen – ammonia synthesis – ammonia decomposition to hydrogen) and has investigated various technical options for the ammonia decomposition process. Different process configurations have been assessed for their effect on energy efficiency and CO_2 intensity, which, among others, also depend on the selection of the process heat source. This also impacts the decision between centralised and localised hydrogen production.

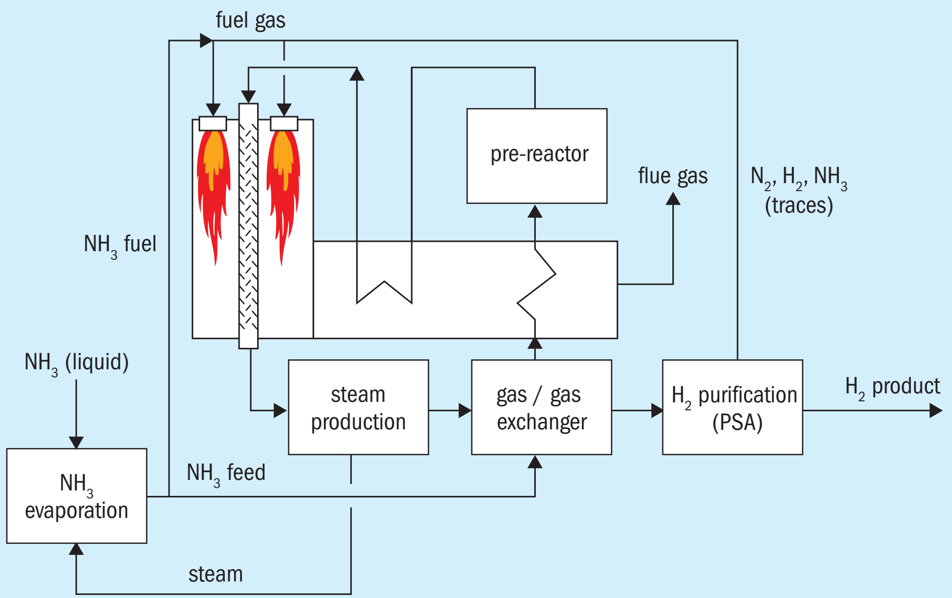
Three process configurations were investigated in more detail and are discussed here, distinguished by the type of energy supply:

- Case 1: Self-sustaining process: The required energy is provided by the combustion of a part of the feed and/or product stream.
- Case 2: Process with external fuel source. The required energy is provided by combustion of a fuel supplied from outside.
- Case 3: Process with electrical heating. The required energy is provided by electric heaters.

Fig. 1 shows a simplified flowsheet for Case 1. A pre-reactor has been added to enhance the efficiency. The other cases are derived from Case 1:

- Case 2: No use of NH_3 for firing, replaced by natural gas firing instead.
- Case 3: Adiabatic reactors with intermediate electrical heating, fired heater for utilisation of PSA off-gas, no use of NH_3 for firing.

Fig. 1: **Simplified flowsheet for the cracking process, Case 1.**



Source: thyssenkrupp Uhde

Table 1: **Battery limit conditions for all process configurations**

Ammonia feed	–33°C, 3.0 MPa a (–27°F, 435 psi a)
H_2 product (purity 99.97% H_2)	42°C, 1.6 MPa a (108°F, 232 psi a)
NG fuel (assumed as 100% CH_4)	25°C, 0.11 MPa a (77°F, 16 psi a)
Scope of evaluation	Process with feed, fuel, electricity; plus electricity for cooling water supply

Source: thyssenkrupp Uhde

All processes are designed in such a way that they do not export any off-gas or steam. Waste heat is utilised by the process as far as reasonably possible. The battery limit conditions are set as per Table 1.

Efficiency comparison

Table 2 shows a qualitative comparison of the processes.

A quantitative analysis is provided in

Table 2: **Pros and cons of different process configurations (options can also be combined)**

	Case 1	Case 2	Case 3
Description	Process with internal fuel source (self-sustaining process)	Process with external fuel source	Process with electrical heating
Advantage	No direct CO_2 emission	High yield by full conversion of feedstock to H_2	High yield by full conversion of feedstock to H_2 Less energy loss by flue gas
Disadvantage	Lower yield by consumption of feedstock as energy Energy loss by flue gas	CO_2 emission depending on selected fuel Energy loss by flue gas	CO_2 emission depending on selected power source Expensive energy source

Source: thyssenkrupp Uhde

Table 3: **Comparison of energy efficiencies**

	Case 1	**Case 2**	**Case 3**
Feed NH_3, kg/h	25,000	25,000	25,000
Product H_2, kg/h	3,470	3,771	3,777
Stoichiometric efficiency, %	78.00	84.76	84.91
Relative yield, %	89.52	97.28	97.45
Feed + fuel, MW	128.9	140.1 (3)	128.9
Electric power, MW	0.9	1.0	11.2
Energy efficiency, % (1),(2)	88.70/87.79	88.70/87.79	89.44/79.85
Energy demand, MJ/kg H_2(2)	136.07	136.07	149.61

(1) no efficiency factor for electricity; (2) 40% efficiency factor for electricity; (3) incl. 11.2 MW natural gas fuel

Source: thyssenkrupp Uhde

Table 4: **Comparison of CO_2 emission factors of different cracking processes for green and blue ammonia, using different electricity sources for the cracking process**

	Case 1	**Case 2**	**Case 3**
CO_2 emission using green ammonia			
Electric power to NH_3 decomposition: wind, kg CO_2/kg H_2	0.812	1.332	0.776
Electric power to NH_3 decomposition: grid mix, kg CO_2/kg H_2	0.937	1.458	2.228
CO_2 emission, using blue ammonia			
Electric power to NH_3 decompostion: wind, kg CO_2/kg H_2	1.464	1.933	1.376
Electric power to NH_3 decompostion: grid mix, kg CO_2/kg H_2	1.590	2.058	2.828

Source: thyssenkrupp Uhde

Table 3. In all cases, the theoretical total H_2 content of the input is 2,198 kmol/h.

The efficiency of the basic process has been improved by adding an adiabatic pre-reactor. This also helps to solve some design challenges. The efficiency increase mainly originates from lower overall firing duty and less heat loss with the flue gas. The pre-reactor design is therefore also adopted in Case 2.

The stoichiometric efficiency from Case 1 can be increased if less feed/product is used for heating by replacing it with another fuel or electricity. This is done in Cases 2 and 3. The theoretical maximum plant yield is therefore determined by the hydrogen yield of the pressure swing adsorption unit. However, this does not necessarily increase the energy efficiency.

For a process consuming fuel and electric power, electric power input is handled by considering a specific conversion efficiency when the combustion of a fuel produces electric power.

All of the above processes consume a small amount of electricity for pump and compressor power. In Cases 1 and 2, the electric power supply is only 0.7% of the total energy of the process. In Case 3 however, a significant amount (8%) of the energy comes as electric power, and its proper valuation has a significant impact on the efficiency figure. For Table 3, 40% conversion efficiency has been used.

For comparison, H_2 production by steam methane reforming has an energy consumption of approx. 140 MJ/kg, expressed by the natural gas LHV.

All processes generate an off-gas stream containing unconverted ammonia. In Cases 1 and 2 this is sent to the cracker firing. Since this is an attractive solution, this is also done in Case 3, i.e. this process includes firing, and only part of the energy is supplied by electric power. The high electricity consumption of Case 3 per ton of H_2 produced (Table 3) is about 9% of that of the production of the same amount of H_2 by water electrolysis.

CO_2 greenhouse gas emission

CO_2 greenhouse gas (GHG) emissions for the whole process chain of ammonia production and cracking has been compared by assuming different production pathways (green and blue) for the ammonia fed to the cracking processes (Cases 1, 2, 3), whereby each cracking process can be differentiated again by the CO_2 load of the electric power used (e.g., renewables only vs. average grid).

To achieve a low CO_2 footprint, the ammonia has to be either green or blue. Specific CO_2 emissions for ammonia production are:

- **Green ammonia:** Ammonia from hydrogen via water electrolysis and nitrogen via air separation, both driven by renewable power. No GHG emission by the ammonia process and electricity generation, but GHG emission associated with the installation of the facility, e.g., in a wind farm: 0.112 kg CO_2/kg NH_3.

- **Blue ammonia:** Ammonia from steam reforming of natural gas, CO_2 emissions reduced by CO_2 capture and sequestration: 0.2 kg CO_2/kg NH_3. Expressed as hydrogen, this would mean 1.1 kg CO_2/kg H_2, which would satisfy the conditions of being below 2.0 defined by the US Infrastructure Bill 2021 for "clean hydrogen". There is no unique definition and CO_2 emission standard because several degrees of CO_2 capture are possible.

For comparison, a convectional ammonia plant based on steam reforming of natural gas has a CO_2 emission of about 1.7 kg CO_2/kg NH_3.

Since the purpose of using ammonia as a hydrogen carrier is based on the idea that ammonia is produced in a place where renewable power is abundantly available at a low cost, and it is transported to a place where such renewable power is expensive (like Europe), it is a realistic assumption that renewable power is available in a limited amount and at a high cost only at the cracker location.

Table 4 compares the resulting specific emission factors for the full process chains (basis: CO_2 equivalent of electric power for wind and grid mix (Germany 2018) = 0.0112 and 0.5 kg CO_2/kWh respectively).

For Case 2, a comparison with Case 1 shows that heating by natural gas increases the CO_2 emission by about 0.5 kg CO_2/kg H_2.

For Case 3, a comparison with Case 1 shows that electric heating has a small net CO_2 saving if cracking power is from renewable sources. There is a significant increase if it is taken as a grid mix.

Process variants

The flowsheet from Fig. 1 can be modified to match certain special applications, for example:

- **Steam export:** If the ammonia cracking plant is co-located with a steam consuming facility, the firing of the furnace can be increased in order to make more waste heat available for steam generation and superheating.
- **Use of hydrogen/nitrogen mixture:** In certain applications where hydrogen shall be used as a fuel, it might not be required to separate the nitrogen. In this case, the "hydrogen purification" step can be omitted and the gas from the cracker outlet can be used.
- **Integration into a gas turbine process:** An application of hydrogen use might be its combustion in a stationary gas turbine, e.g., for power generation. If the gas turbine is part of a cogeneration process (production of steam from hot turbine exhaust gases and consumption in a steam turbine), the waste heat from the cracker can be integrated into this process by using it for additional steam generation and/or superheating.

Centralised vs. local H_2 production

Centralised and localised hydrogen production both have their pros and cons as regards safety, economic feasibility and CO_2 avoidance. The safety of both options strongly depends on the selections made for inland transport and storage of ammonia and hydrogen, while process economics, highest energy efficiency and avoidance of CO_2 emissions favour ammonia cracking in large, centralised units. ■

Reference: Elischewski J., Kleyensteiber A., Noelker K. (thyssenkrupp Uhde) "*Optimization of the ammonia decomposition process*", presented at Nitrogen+Syngas 2024, Gothenburg, Sweden, 4-6 March 2024.

CASALE SA

Novel ammonia cracking technology for the global energy transition

Leader in technological innovation, Casale aims to play an active role in the energy transition continuously enriching its portfolio with new advanced sustainable solutions including its latest next generation ammonia cracking technology.

Developed in cooperation with market-leading catalyst manufacturers, the process is based on Casale's long and successful experience in material selection for processes operated in environments rich in ammonia and hydrogen at high pressure and temperature, minimising the technology risk.

Covered by two patents, the new Casale ammonia cracking technology was first launched in 2021 and has continued to be improved and optimised over time to cover all specific client needs in terms of performance and cost.

Different process configurations for a wide range of single train plant capacities have been studied and developed from the completely self-sustaining scheme to the low-carbon scheme.

During the Nitrogen + Syngas 2024 Conference, Casale took the opportunity to formally launch the trade name of its ammonia cracking technology, MACH2, which stands for Mega Ammonia Cracking for H_2 production.

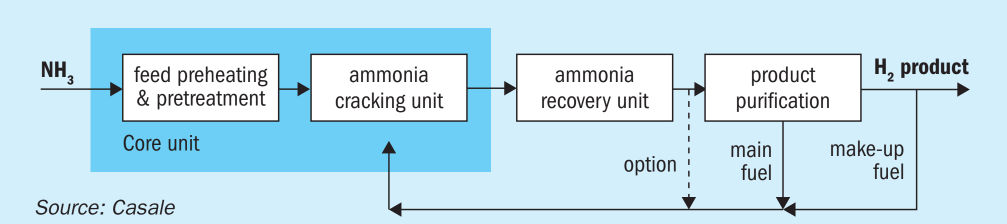
Casale ammonia cracking technology offers the highest single train plant capacity on the market, covering a wide range of hydrogen plant capacities, ranging from 5 t/d to 1,300 t/d of pure hydrogen (up to Grade 5 hydrogen purity).

Fig. 1 shows a simplified block flow diagrams of Casale's self-sustaining scheme.

The process scheme consists of four main sections: feed preheating and pretreatment, ammonia cracking, ammonia recovery and product purification. In the preheating and pretreatment section, liquid ammonia is vaporised and preheated up to the temperature required for the reaction. The preheated ammonia then reaches the core unit, the ammonia cracking section, where the ammonia decomposition takes place. The resulting cracked gas is finally sent to the hydrogen purification section, consisting of well-known and proven technologies commonly used in different industrial processes:

- Ammonia recovery unit based on H_2O/NH_3 absorption and distillation technologies where unconverted ammonia is recovered and recycled to reduce consumption.

Fig. 1: **Ammonia cracking technology – simplified self-sustaining scheme**



Source: Casale

Table 1: **Components modeled in simulation**

KPI	Self-sustaining case	Low-carbon case (5)
H_2 plant capacity, t/d H_2	from 5 up to 1,300+	from 5 up to 1,300+
NH_3 specific consumption, t NH_3 / t H_2	up to 7.2	up to 6.4
H_2 production efficiency (η_{H_2}), mol-%(1)	up to 78 (3,4)	up to 87 (3,4)
Energy efficiency (η_E), %(2)	up to 89	up to 90(5)
H_2 product pressure	as required (40 max w/o H_2 compressor)	
Steam export, t_{steam} / t H_2	0	
H_2 purity, %	up to grade 5 (99.999% H_2)	
CO_2 emission, kg CO_2 / kg H_2	0	up to 0.3 (3,5)
Max NOx emissions, ppmv	according to local regulation or even lower	
Turndown, %	40	

Notes:

1. H_2 production molar efficiency calculated according to:

$$\eta_{H2} = \frac{Q_{H_2\,PRODUCT}}{1.5 * Q_{NH_3\,FEED}}$$

2. Energy efficiency calculated according to:
Power conversion factor 50% (1,720 kcal/h).

$$\eta_E = \frac{Q_{H_2\,PRODUCT} * LHV_{H_2}}{Q_{NH_3\,FEED} * LHV_{NH_3} + Q_{FUEL} * LHV_{FUEL} + E_{EL} * \kappa_{el}}$$

3. PSA performances are affected by the H_2 purity required.

4. Referred to a single PSA configuration. Greater than 85% achievable with external fuel source and/or with double PSA configuration.

5. 100% CH_4 assumed as external fuel source.

Source: Casale

- Hydrogen PSA unit where the H_2 is recovered and purified up to the required level.

The process scheme can be customised and optimised according to customer needs (capex vs opex).

Casale ammonia cracking reactor

Casale has developed different ammonia cracking reactor design concepts and configurations depending on the size of the hydrogen production plant.

Its ammonia cracking unit is mainly composed of a combination of adiabatic cracker reactors and an ammonia cracking furnace. The ammonia cracker design duplicates concepts from proven reaction furnace designs, like the steam methane reformer, wherever practical, coupled with Casale unique revamping expertise on all existing SMR types and configurations and know-how on material behaviour when exposed to an ammonia and hydrogen environment (creep, hydrogen attack, nitriding). This places Casale in the unmatched position to be able to always select the best engineering solution for every component of the ammonia cracker furnace to ensure the highest reliability.

Technology readiness level (TRL)

All unit operations in the ammonia cracking scheme reach the highest technology readiness level (TRL 9) except for the ammonia cracking catalyst (TRL 7) as its technology is only mature for small-scale systems. Large-scale applications are still being validated and tested by major catalyst manufacturers for further optimisation and improvements.

As the testing and validation proceeds, proving its operation in dedicated demo units, the catalyst TRL level is inevitably destined to rise, reaching the maximum level when the first large-scale plant is built.

Scalability of the Casale ammonia cracking plant is mainly limited by the performance of current catalysts available on the market rather than the catalytic furnace unit size.

Casale ammonia cracking KPIs

The main key performance indicators (KPIs) for the two main Casale process schemes valid for the entire single train plant capacity range are provided in Table 1.

The self-sustaining (CO_2 free) scheme is dedicated to large capacity in which a small quantity of hydrogen product is used as make-up fuel.

The low-carbon alternative considers both the case of complete heat balance with external fuel and the case in which a fixed amount of the cracked gas at the PSA inlet is burned with a minimum external fuel gas contribution for control purpose. Pure methane has been considered for the performance evaluation.

The contribution of cracked gas leads to a higher ammonia feed consumption, as part of the feed is used as fuel, while minimising CO_2 emissions. Conversely, the complete use of external NG fuel as make-up allows the ammonia feed consumption to be decreased, but results in a higher CO_2 emission.

Key performance indicators are affected by specific project requirements in terms of hydrogen purity, carbon intensity, product delivery pressure, utilities system, capex vs opex optimisation, etc.

Thanks to its background and experience, Casale can provide a simple, flexible and customised technology which can be tailored to specific plant needs with a well proven solution that is immediately available.

Improving and optimising catalyst performance for large-scale ammonia cracking units is fundamental for further process improvements and Casale is highly engaged in continuously evaluating the most promising and new-generation catalysts to implement in its own technology to continue to provide the best technological solutions for a better future. ■

Reference: Pipino A. and Panza S.: "*Novel ammonia cracking technology: The response to the global energy transition challenge*", presented at Nitrogen+Syngas 2024, Gothenburg, Sweden, 4-6 March 2024.

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46
47 48 49 50 51 52

Ammonia combustion for large furnaces

Ammonia has been recognised as an advantageous hydrogen and energy carrier. This article focuses on the use of ammonia as fuel in steam reformers and ammonia crackers in order to reduce or completely eliminate direct CO_2 emissions. Ammonia combustion knowledge is especially important for ammonia crackers with respect to the recycling of unconverted ammonia. Air Liquide is constructing an industrial scale pilot plant in Antwerp, planned to be operational in 2024, that will be used to demonstrate ammonia cracking and combustion in a process furnace with a multiple burner configuration.

Bhupesh Dhungel, Kenneth Kaiser, Guillaume Lodier, Michael Lutz, Remi Tsiava, Dieter Ulber, Lorenzo Vicari and Bryce Williams.

Ammonia (NH_3) is the second largest volume commodity chemical. Global production of ammonia is approximately 185 million t/a (2020) of which 20 million t/a are traded globally thanks to relatively simple transport requirements and more than 200 maritime ammonia terminals. The global ammonia market is expected to double in size by 2050 with an increasing portion being produced in a non-conventional manner. Produced by either renewable power (e.g. hydrogen produced from the electrolysis of water) or by hydrogen from fossil fuels with carbon capture and storage, ammonia offers two alternative pathways to supply decarbonised hydrogen or energy. In either case, this non-conventional ammonia will play a key role in connecting regions rich in low carbon or renewable energy to those in demand of it. Ammonia as an energy carrier is thus expected to be a key enabler towards a decarbonised world.

As part of its ADVANCE strategy to further decarbonise its plants, Air Liquide's ammonia cracking technology development is a critical step to unlock access to additional low carbon and renewable hydrogen derived from imported ammonia. Air Liquide licenses, builds, owns and operates traditional hydrocarbon-based steam methane reformers, autothermal reformers, partial oxidation reactors, and is currently implementing its own carbon capture technologies, i.e. Cryocap™, Recticap™ and amine wash solutions, both on the process and flue gas side in order to reduce CO_2 emissions of its plants. Combustion knowledge is essential for these technologies, especially with increasing use of hydrogen, biogas and ammonia as new fuels.

Air Liquide will start up an industrial scale pilot plant for ammonia cracking and combustion in Antwerp in 2024 to gain valuable combustion knowledge.

Applications of ammonia combustion

As an energy carrier, once shipped to high energy demand countries, ammonia can be used directly as a fuel in existing and new plants according to the following equation:

$$2NH_3 + 1.5\ O_2 \rightarrow N_2 + 3H_2O + 635\ kJ$$

It is already under development for use in power production in gas turbines[1], but also as a co-fuel for coal fired power plants[2]. Similarly, engine manufacturers consider ammonia as one of the fuel options for maritime decarbonisation. Outside of several notable demonstrations, large-scale use as fuel has never been applied in reformers (e.g. fired heaters, hydrogen production reformers, ethylene crackers) and other energy-intensive industries such as glass, cement and steel.

Ammonia cracking

In hydrogen production units via ammonia cracking, ammonia is split into hydrogen and nitrogen, the hydrogen is separated at high purity and the remaining components, nitrogen, non-separated hydrogen and unconverted ammonia are recycled as an off-gas fuel to the process. This off gas mainly consists of nitrogen and has a rather low calorific value which makes it challenging to combust. Direct use of ammonia vapour as a trim fuel – to close the heat demand for the endothermic cracking reaction – is the ultimate goal.

Indeed, either cracked gas (N_2/H_2 mixture) from the process or product are technical solutions with the highest technology readiness level (TRL). However, ammonia combustion is especially beneficial for ammonia crackers with respect to the recycling of unconverted ammonia. The unconverted ammonia can be tolerated in the process and subsequently recycled to the fuel. Furthermore, using product hydrogen as trim fuel is less economical, since all the hydrogen production equipment would be oversized with consequently higher capex.

Depending on the required hydrogen purity at the battery limit and the overall process integration, the required fuel flow to balance the heat demand will change and the fuel mixture of ammonia trim fuel and process off gas will be different in composition and combustion properties.

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46
47 48 49 50 51 52

Steam methane reforming

In SMR plants, direct application of referenced carbon capture units on the process side combined with the use of ammonia as trim fuel for the firing side are crucial for reaching minimum CO_2 emissions. In particular, hydrocarbon fuel substitution by ammonia in reformers for the production of carbon monoxide can significantly reduce the carbon footprint of the product. Moreover, since cold ammonia will be available at the plant, further heat integration and energy reductions are possible, depending on customer needs.

Challenges in ammonia combustion

Ammonia is an interesting carbon-free fuel, but its implementation in industrial systems raises technical challenges.

Firstly, the low flammability of this reactive species reflects on the fundamental properties of combustion when it is used as a fuel or co-fuel. 1D unstretched premixed flame simulations were launched to quantify the impact of the ammonia contribution to the total fuel power, NH_3 duty, on the laminar flame speed, which quantifies the speed of consumption of the fresh gas by the flame front. The higher it is, the stronger the flame anchoring is. Various co-fuel compositions were considered: BF1 and BF2 correspond to classical SMR fuel compositions (containing a mixture of CH_4, CO_2 and H_2), and GF1 and GF2 correspond to pure hydrogen and hydrogen/nitrogen fuel mixtures. The results are plotted in Fig. 1. Ammonia co-fuelling clearly results in decreased laminar flame speed levels, whatever the co-fuel composition.

Extinction strain rate in 1D counterflow flames is another important fundamental combustion property. It quantifies the flame resistance to turbulent straining. The higher it is, the stronger the flame is. Here again, it can be readily seen that ammonia tends to weaken the flame. From an industrial perspective, lower flame speed and extinction strain rate translate into technical challenges in flame stabilisation requiring know-how development and burner technologies to be adapted.

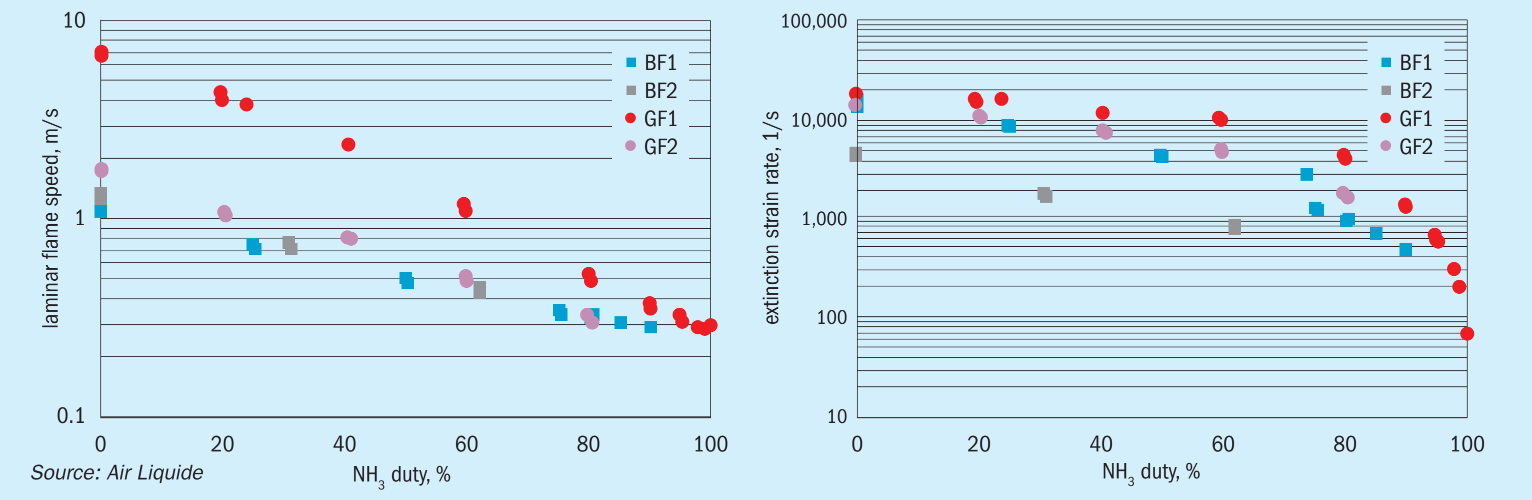
Finally, the main concern about ammonia combustion is related to the higher formation of NOx compared to a standard SMR. Global NOx emission regulations are becoming increasingly stringent, especially in those countries where ammonia cracking will be operated. Dedicated flue gas NOx abatement systems, such as selective catalytic reduction (SCR), are needed in order to remain below statutory limits. For existing units, the switch to ammonia as trim fuel could challenge the available plot space of the deNOx unit.

In order to design new and retrofit existing furnaces for ammonia fuel, Air Liquide invested in ammonia combustion capabilities at its in-house facilities and performed hundreds of test points at

Fig. 2: **Air Liquide's new ammonia combustion platform in Delaware**

Source: Air Liquide

Fig. 1: **Impact of ammonia co-fuelling on fundamental properties of combustion, from 1D simulations. Laminar flame speed vs ammonia duty in overall burner duty (left). Extinction strain rate vs ammonia duty in overall burner duty (right). Various co-fuel compositions are represented: co-fuel with carbonated species (blue and grey) and H_2 and mixture of H_2/N_2 fuels (red and pink).**



Source: Air Liquide

different conditions, coupled with improved combustion models, leading to optimised combustion conditions. Air Liquide has covered the whole range of furnace operation requirements, from start-up to normal operation, in order to guarantee safe and reliable operation. This includes using an efficient combustion and small deNOx system to satisfy all emissions limits in terms of NOx, particularly N_2O, and also NH_3 slip to the atmosphere.

Experimental test bench

Air Liquide recently upgraded its combustion test platform at Innovation Campus Delaware (ICD) to enable ammonia firing (Fig. 2). The test facility is capable of firing rates up to 6 MW for oxyfuel combustion and up to 2.5 MW for air firing. The enclosure itself (Fig. 3) is 8 feet (2.4 m) in diameter and 22 feet (6.7 m) in length. At the front face of the enclosure, a large opening is provided for mounting different test burners. Several viewports, probe access ports, camera ports and thermocouple ports are available to enable required measurements.

To simulate burner tests with different fuel blends, natural gas, hydrogen, carbon dioxide and nitrogen are available at the combustion test platform. H_2, CO_2 and N_2 are supplied from bulk tanks at the facility. For the supply of ammonia, a bulk tank (Fig. 4) of 1,000 gallon (1,980 kg) capacity was recently installed by Airgas, an Air Liquide company in the United States.

To enable vaporisation of anhydrous ammonia, the tank system consists of a vaporiser (175 kW capacity) allowing continuous gaseous ammonia flow up to 2 MW firing rate. Several ammonia sensors, which are tied to the control system, are installed around the tank, inside the control room and on the combustion platform to ensure the system will shut down safely if ammonia leakage is detected.

Flow control skids complying with the NFPA standard for ammonia and hydrogen were added to enable safe firing of the fuel blends (Fig. 4). The test facility also has NFPA-compliant natural gas and oxygen flow control systems. Ammonia and hydrogen flow control skids have high and low flow branches to enable accurate control at both low and high flow rates.

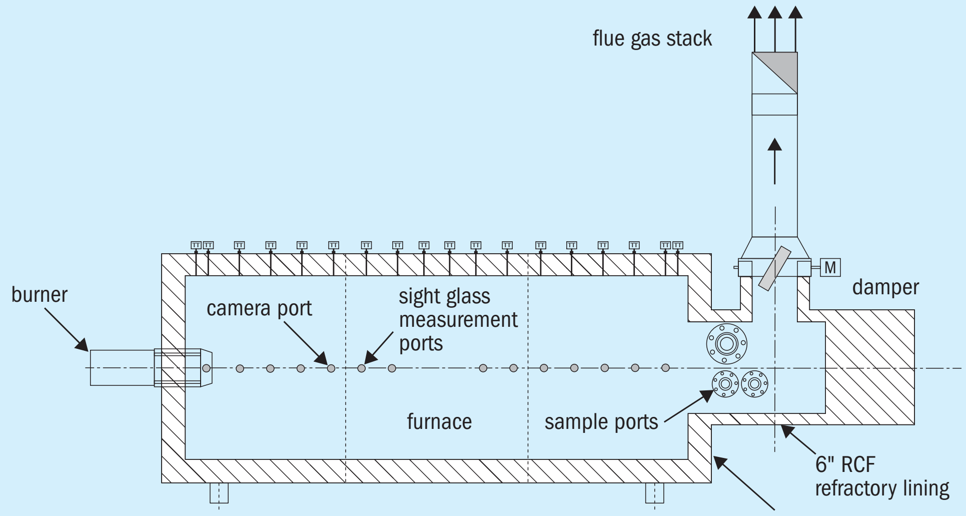
Either air or oxygen can be used for combustion tests depending on the test requirement. Air can be preheated up to 450°C, to enable testing at realistic process conditions.

Parameters that can be measured are:

- flow rates, temperature and pressure of all the gases used for the test;
- burner back pressure vs. firing rates;
- furnace wall temperature profile, obtained via crown thermocouples;
- heat flux profile obtained via the water cooling system;
- flame imaging and IR images for flame dimensions;
- furnace exit gas concentrations (NO, N_2O, NO_2, NH_3, CO, CO_2, O_2) via continuous emission monitoring analysers, NH_3 analyser and FTIR;
- fast acting pressure transmitter to evaluate flame stability;
- burner block temperature.

Tests have been carried out with various full scale, commercial burners (fuel-staged, air-staged and new technologies for ammonia firing) between 1 to 2 MW burner duty with the aim of determining flame stability, emissions and heat transfer characteristics for the whole operating envelope to be used in plants.

Fig. 3: **Schematic view of combustion test furnace at ICD**



Source: Air Liquide

Fig. 4: **Ammonia tank at ICD being filled by Airgas personnel (left). Flow control skids for NH_3 and H_2 (right).**

Source: Air Liquide

Experimental test results

Ammonia combustion tests have been performed in Air Liquide's new ammonia combustion platform and several theoretical assumptions were validated but also unexpected results were obtained. The detailed test results and analytical data can be used for the design of steam reformer revamps and ammonia cracking plants.

Ammonia combustion has been proven in the experimental campaign both for fuel-staged and air-staged burners. A wealth of measurement data has been generated and practical knowledge, for example on flame scanner adaptation, has been gathered.

Flame stability varies significantly with combustion parameters, especially the fuel composition and ammonia duty contribution, but also temperature. The large parameter variations in the test program reveal a stable and safe operating window, and new combustion safeguards have been developed for the industrial furnace.

Small amounts of ammonia in the fuel mixture are almost one to one converted into NOx emission and lead to significantly higher NOx in ammonia combustion compared to hydrocarbon combustion. However, the NOx emissions do not scale in proportion to the ammonia content in the fuel. Functional relationships have been established between process-specific burner design, operating parameters and emissions. The NOx level of the optimised combustion solution is such that stringent emission limits can be achieved with a special deNOx system.

Higher NOx emissions during ammonia combustion can be understood according to the fuel-NOx kinetic pathway. The NOx emission level varies with process parameter changes in a different manner than hydrocarbon combustion. For example, the air to fuel ratio has a more pronounced influence, whereas the influence of the combustion air preheat and flame temperature is less important.

The formation of N_2O can be avoided by the appropriate selection of combustion parameters for the process-specific burner design and furnace.

Modelling tools

Modelling is a complementary and important approach to shed light on ammonia combustion and support the design of industrial units where it is implemented for energy production purposes.

Ammonia is used as fuel for endothermic reactions, so being able to predict the heat transfer processes is crucial to design reliable and efficient fireboxes. Recognising this strategic challenge, two simulation tools have been developed internally at Air Liquide at the Innovation Campus Paris (ICP): 3-dimensional (3D) computational fluid dynamics (CFD) software and 1-dimensional (1D) software. Previously successfully used to support SMR firebox competitive design, these simulation tools have been adapted to handle ammonia combustion and cracking reactions.

On the one hand, the CFD tool is dedicated to optimising the firebox layout, see left picture in Fig. 6. It includes two coupled physical solvers. Firstly, a 3D CFD solver is in charge of describing the physical processes involved in the combustion chamber. An effective burner model is implemented, making it possible to handle firebox simulations involving hundreds of burners at a reasonable computational

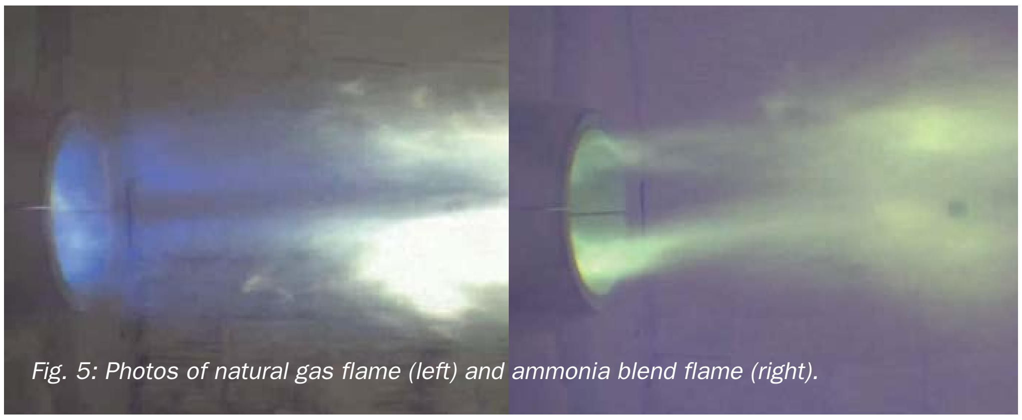
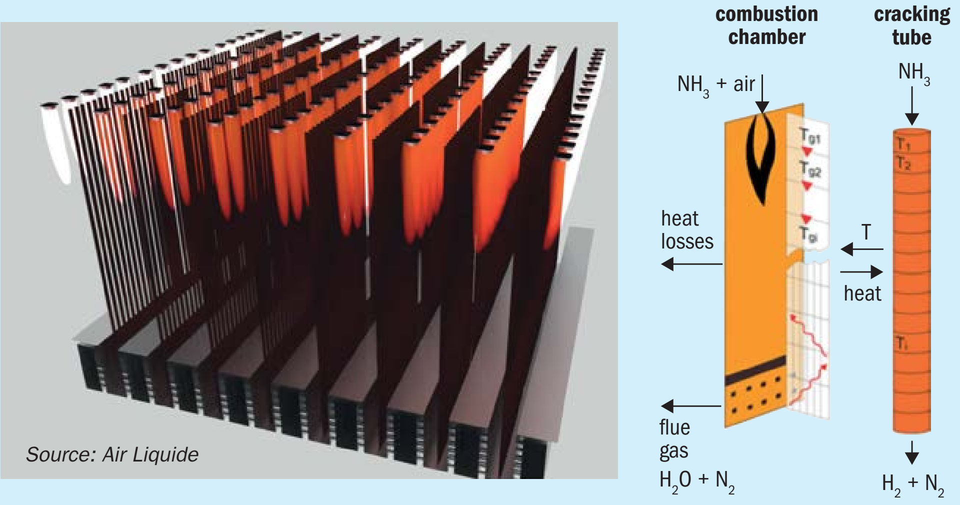


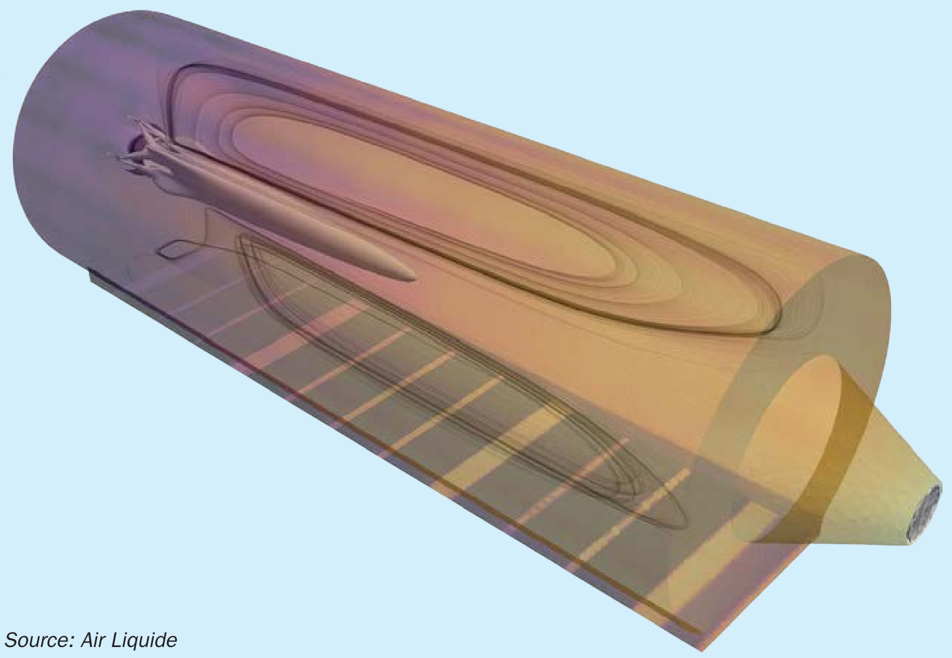
Fig. 5: Photos of natural gas flame (left) and ammonia blend flame (right).

Fig. 6: **Air Liquide firebox simulation tools dedicated to the design of ammonia crackers. The CFD tool to evaluate the 3-dimensional distribution of heat within the firebox (left). The 1D tool for fast screening of innovative technological solutions (right).**



Source: Air Liquide

Fig. 7: **Advanced CFD simulation of a burner in the OCTP combustion chamber. The walls are coloured by the temperature levels. The flame is identified by the velocity isocontour 40 m/s. Flow streamlines are provided to identify the toroidal recirculation zone developing in the whole combustion chamber**



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time. This model is validated by comparison with advanced CFD simulations of detailed burners, see Fig. 7, also used to gain a deeper understanding of ammonia combustion, as a complement to the experimental tests. Similar to hydrogen combustion, the ratio of the two main radiating species, carbon dioxide and steam, change and thus the radiative properties of the flue gas are different in ammonia combustion compared to hydrocarbon combustion. Radiation and turbulent patterns resulting from the flame interaction are described and their impact on heat flux profiles for each individual tube is reflected. Secondly, the 1D tube model describes the heat transfer process from the tube skin to the catalyst bed as well as the heterogeneous catalytic reactions. Data gathered from catalyst test benches are used for kinetic model validation. This computationally demanding software has been launched on the Air Liquide supercomputer at ICP.

On the other hand, the 1D software tool is designed for fast evaluation of innovative solutions, see right picture in Fig. 6. It includes the same tube model as the CFD tool and a computationally effective combustion chamber model. It can be launched on a laptop and is fully adapted to fast sensitivity analysis and benchmarking.

Radiation is the dominant mode of heat transfer within a firebox and its accurate modelling has required special care in Air Liquide internal software. The physical model accuracy is ensured through a calibration procedure making the most of the valuable data obtained in test benches such as the combustion platform previously described for the industrial scale pilot plant for ammonia cracking and combustion in Antwerp.

Conclusions and next steps

Ammonia combustion is an important technology brick for various applications. Air Liquide's combustion platform offers the opportunity to perform extensive tests on existing and new burner designs and fuel mixtures (relevant for combustion of NH_3, natural gas, H_2, N_2, off gases or syngas mixtures from biomass gasification). Simulation of such results with sound physical models adds understanding and enables confidence in the design process.

As already announced, the final step in the development of ammonia combustion in large furnaces and especially in ammonia crackers will be realised in an industrial scale furnace with several cracking tubes and burners. The industrial scale pilot plant at Antwerp will not only allow demonstration of the cracking technology, it will also provide the final validation step of ammonia combustion in a process furnace with a multiple burner configuration. The plant is under construction and is planned to be operational in 2024.

The pilot plant at Antwerp and the numerous test results will be exploited to further improve the accuracy of the model predictions for a wide range of operating conditions, in the combustion chamber as well as in the cracking tubes. ■

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