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Number 384
July | August 2023

nitrogen+syngas

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Ammonia industry incidents

Ammonium nitrate safety

Low-carbon ammonia production

Future-proofing nitric acid plants

NITROGEN+SYNGAS
ISSUE 384
JULY-AUGUST 2023

BCInsight

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Cover: Ammonium nitrate fertilizer.
Liudmila Chernetska/iStockPhoto.com

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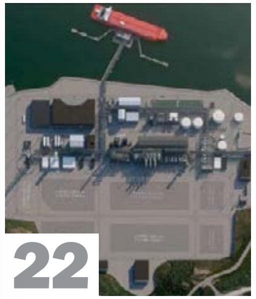

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Large-scale green ammonia development in Norway

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Methanol's continuing rise

> **Investment decisions need to be made now by fleet operators...**

While demand for ammonia remains – for now at least – strongly tied to fertilizer and farming, over the three decades that I've edited this publication, methanol's story has been a very different one, with a succession of major new slices of demand coming every few years from new applications that flare up and then mature or even drop away again. For a while in the 1990s it was MTBE, the oxygenated fuel additive that had a brief flourish in the US before being shut down by leaking fuel tanks leaching into ground water. Then there was dimethyl ether (DME) as a blendstock for LPG, and methanol itself directly blended into gasoline in China to keep up with soaring vehicle fuel demand. More recently, methanol to olefins (MTO) has added almost another 25% of demand over and above existing chemical and fuel uses. But as the world cracks down on coal production and use, China's attempt to use methanol as a way of using domestic coal to replace imported oil seems to have passed its high water mark and begun to recede.

Now the momentum seems to have instead swung behind green methanol as a fuel for maritime applications, and the pace of change is once again as fast as ever. Green methanol production in 2023 is a few hundred thousand tonnes per year, mainly from OCI's BioMCN plant in the Netherlands. However, according to the Methanol Institute there are now around 80 green methanol projects under development, with capacity set to reach a potential 8 million t/a by 2027. This slew of green methanol development is driven by guaranteed demand from shipping companies, who are looking at green methanol as a low carbon alternative to conventional bunker fuels. The International Maritime Organisation has currently set a target of reducing carbon emissions from shipping by 50% by 2050, and many members are pushing for a still greater reduction. Given the operating lifetime of a large vessel, investment decisions need to be made now by fleet operators, and methanol is a solution already to hand. While we have reported on the considerable efforts going into green ammonia as a potential shipping fuel, methanol powered engines are already commercially available, while ammonia engines are still in the development phase. And, as far as fuel availability is concerned, if the demand is there, green methanol capacity can be and is being constructed fairly rapidly.

Methanol producers Methanex and Proman both have their own small fleets of methanol powered tankers, but undoubtedly the biggest boost has come from the strategic decision by shipping giant Maersk to build a fleet of methanol powered container ships. The company now has 25 methanol fuelled vessels on order, many due for commissioning in around 2026-27, at the same time that the new wave of green methanol plants are coming onstream. A large methanol container ship can use 40,000 t/a of methanol fuel. Maersk has entered into strategic partnerships and signed offtake agreements with green methanol producers to try and ensure that fuel is available when the ships are launched. Ferry operator Stena Lines, which began operating a single methanol powered ship in 2015 as an experiment, has now announced that it will convert several more of its ships to methanol use over the next couple of years.

Widespread take-up as a low-carbon shipping fuel has the potential to be even more of a seismic event for the methanol industry than using coal to make olefins was. Maersk calculates that it alone will require 6 million t/a of green methanol by 2030. Adoption by other large shipping firms could push adoption even faster. The International Renewable Energy Agency (IRENA) has suggested in a recent report that green methanol demand could reach 250 million t/a by 2050, more than double the size of the entire current methanol industry.

It's tempting sometimes to play down expectations of a 'next big thing' in methanol. Off the top of my head I can recall just as many false starts as there have been game changers. Does anyone remember methanol as a carbon-based fertilizer? Methanol fuel cells? Methanol as a domestic cooking fuel in the developing world? But there is now serious money and investment going into methanol as a low carbon shipping fuel. This is happening. ■

Richard Hands, Editor

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Price Trends

Market Insight courtesy of Argus Media

NITROGEN

In ammonia markets, spot activity has been limited towards the end of June as the market assesses how the resumption of duties on ammonia imports into the EU will impact suppliers from non-exempt countries, and how falling domestic ammonia prices in China could change the supply/demand balance in east Asia. In the background, volatility in west Europe's natural gas market means northwest European plants continue to face challenging decisions on producing vs importing.

Recent market drivers include an easing in European gas prices. The TTF month-ahead natural gas price has fallen from mid-June's spike, but ammonia output rates at NW European plants may still be curtailed if import prices remain $100/t below regional production costs. There has also been a spot sale from Malaysia – Petronas has sold 3,000-4,000 tonnes of ammonia for prompt delivery to Vietnam at a reported price of $325-335/t f.o.b. The producer's 450,000 t/a Bintulu ammonia plant remains offline as of late June owing to technical issues affecting its start-up. Indian fertilizer producer FACT has issued another tender to buy 7,500 tonnes of ammonia for delivery 11-17th August at Cochin. FACT's 14 June tender was awarded at close to $300/t c.fr.

Finally, there are also signs that China may return to the export market. Falling domestic ammonia prices in China, on the back of new capacity coming online, and lower coal feedstock prices will reduce import demand. China's return to the export market could be imminent.

Urea prices generally rose in the middle of June, along with ammonium nitrate prices, but ammonium sulphate and UAN markets remained weak. Traders sought to buy urea cargoes across the globe, pushing prices up in most regions, with deals for granular urea from the Baltic at $260-280/t f.o.b., from Egypt at $312-335/t f.o.b., from the Middle East at $253-280/t f.o.b., and from China at $308-310/t f.o.b. But import markets were less active and price direction remained mixed. Prilled and granular urea prices fell to between $300-315/t c.fr in southeast Asia, while Brazil trade stalled after offers moved above $290/t c.fr.

Ammonium sulphate markets remain under pressure from ample supply from plants in northwest Europe and China, and price levels fell in every region despite the firm support from urea.

Recent urea market drivers include energy worries – nervousness about the impact of rising energy prices in the northern hemisphere autumn prompted buyers to seek urea prices for August-September loading. There is also seasonal demand – the widespread policy of leaving purchases to the last minute continued to drive trading activity, and particularly supported prices in North Africa and China, in late June. ■

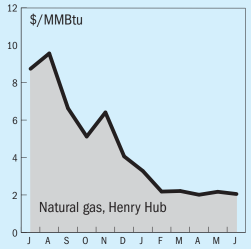
Table 1: **Price indications**

Cash equivalent	mid-Jun	mid-Apr	mid-Feb	mid-Dec
Ammonia ($/t)				
f.o.b. Black Sea	n.m.	n.m.	n.m.	n.m.
f.o.b. Caribbean	270-340	330-400	550-590	975-1,025
f.o.b. Arab Gulf	210-260	250-320	570-600	820-900
c.fr N.W. Europe	355-365	385-410	620-660	975-1,020
Urea ($/t)				
f.o.b. bulk Black Sea	220-285	250-335	320-380	420-530
f.o.b. bulk Arab Gulf*	240-316	300-375	300-355	420-485
f.o.b. NOLA barge (metric tonnes)	294-310	360-385	310-335	495-520
f.o.b. bagged China	270-340	330-370	355-410	440-485
DAP ($/t)				
f.o.b. bulk US Gulf	468-506	627-699	646-678	660-710
UAN (€/tonne)				
f.o.t. ex-tank Rouen, 30%N	253-283	275-310	392-403	575-600

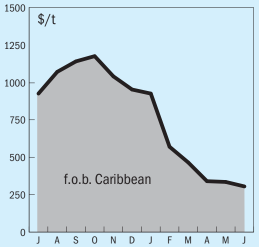
*Notes: n.a. price not available at time of going to press. n.m. no market. * high-end granular.*

END OF MONTH SPOT PRICES

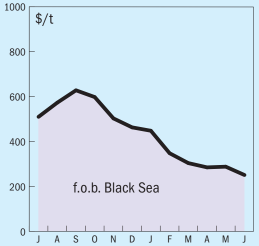
natural gas



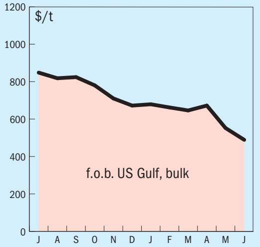
ammonia



urea

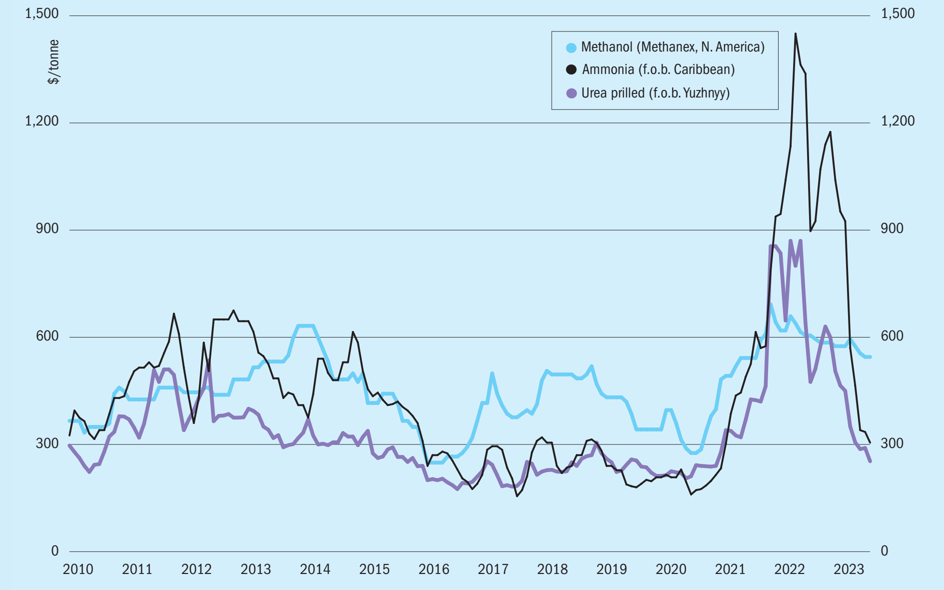


diammonium phosphate



Market Outlook

Historical price trends $/tonne



Source: BCInsight

AMMONIA

- Supply in southeast Asia looks tight for the coming weeks, but further declines in Chinese domestic prices could alter the supply/demand balance in the region in August.
- Prices in Europe look stable for now, but the possibility of further gas price spikes poses a potential upside risk to market prices. For the moment however falling natural gas prices and lower summer demand have allowed ammonia prices to drift downwards. Increased supply from Europe would allow for lower import prices into the continent.
- However, the recent hits on the Togliatti pipeline and lack of prospect of a deal to allow exports of Russian ammonia from the Black Sea also weighs on market sentiment.
- The US ammonia application season closed at the end of May, with traders offloading stock, leading to falling prices in the Mid-West.

UREA

- Farm-level demand is set to reach its weakest point over the next few weeks, and several factories are due to return from planned and unplanned shutdowns, but bouts of short-covering and the risk of rising energy prices could reverse the trend.
- India's June RCF urea tender attracted only 560,000 tonnes out of a target 800,000 tonnes and spot availability out of the Middle East appeared to be limited, pushing prices upwards. Lack of availability from Petronas and Brunei also affected markets east of Suez.
- Cargoes have been seen from China but a large scale return to Chinese exports appears limited at the moment due to export restrictions. However, if China did return to the market it could cool the market still further.
- The reintroduction of European import duties may lift prices there in the short term but gas prices remain the major variable.

METHANOL

- Falling gas prices, especially in Europe, are also having an effect on methanol prices. Methanol prices have fallen by 25% so far this year.
- Ready availability from Iran is also leading to a bearish market for methanol. Iran remains the world's fourth largest producer of methanol and is still able to find export markets, mainly in China, in spite of international sanctions.
- Other factors weighing on the methanol market include falling Chinese coal prices, pulling down the floor price for methanol. The Chinese economy has also been performing more weakly than expected, leading to lower demand expectations. At the same time, MTO margins have also been poor, again affecting merchant demand.
- Spot rates for methanol are considerably lower than contract rates, and this disconnect is expected to pull down prices offered by major producers such as Methanex. ■

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Nitrogen Industry News

EGYPT

EPC contract awarded for new ammonium nitrate plant

Maire SpA subsidiary Tecnimont, together with Orascom Construction SAE, have been awarded a lump sum turn-key engineering procurement and construction contract for new nitric acid and ammonium nitrate plants by the Egyptian Chemical Industries Company ('Kima'). The contract value is approximately $300 million, of which about $220 million relates to Tecnimont activities. Finalisation of the contract is subject to successful execution of the financing package. The scope of work includes mainly engineering, supply of all materials and equipment – to be performed by Tecnimont – as well as construction activities, to be carried out by Orascom Construction.

The plants are expected to be completed in the first half of 2026, and will produce 600 t/d of nitric acid, which will be fully turned into 800 t/d of fertilizer-grade, granulated ammonium nitrate. The plants' output will be sold to local farmers, as well as exported to international markets. The project follows on from Kima's large scale ammonia and urea plants, also built by Tecnimont and Orascom Construction and successfully started up in 2020 in the same industrial complex, located in the Aswan Governorship, Upper Egypt.

Alessandro Bernini, CEO of Maire, commented: "We are really honoured to keep on supporting a prominent player such as Kima in the development of the Egypt's fertilizer value chain. With this award we further consolidate a long-lasting, fruitful relation and strengthen our industrial footprint in North Africa, thanks to our strong capability in executing EPC projects." ■

TURKEY

Johnson Matthey/Uhde to supply IGSAS ammonia plant

Engineering partners thyssenkrupp Uhde and Johnson Matthey have been commissioned by IGSAS – stanbul Gübre Sanayii AŞ, to supply a new ammonia converter cartridge. The cartridge is intended to significantly reduce the pressure in the synthesis loop of the IGSAS ammonia plant while maintaining the nameplate capacity of 1,200 t/d. It will be based on a modular design with removable catalyst beds which enable better accessibility during catalyst filling, and axial-radial flow beds for lower pressure drop, etc. The cartridge, which will be installed in the existing pressure shell, will bring further benefits in terms of safety as no major welding activities are required during installation. The Uhde-designed converter cartridge will use Johnson Matthey's high-performance catalyst *KATALCO*™ 74-1. This combination provides the potential for a further increase in plant capacity in the future, for example with the addition of green ammonia production.

The currently installed cartridge, based on a design by thyssenkrupp Uhde, has reached an extraordinarily long lifetime of 36 years in operation. Usually, replacements are necessary after two catalyst exchange cycles, approximately 20 years. The new equipment is under fabrication, and start-up is scheduled for mid-2024. thyssenkrupp Uhde will perform full supervision services during converter opening, catalyst unloading, cartridge disassembly, converter inspection, cartridge assembly, catalyst filling/activation, startup and performance testing at this time.

Kutay Durna, factory manager at IGSAS, said: "With this upgrade of our plant, we are ready for the future. Key decision points for choosing thyssenkrupp Uhde were the proven reliability of their products combined with reducing the energy consumption in our Kocaeli plant."

UNITED STATES

Contract for new nitrogen complex

KT-Kinetics Technology (KT) has been awarded the early engineering works contract for a new green fertilizer complex in North America by a group of private investors. The complex will include ammonia, urea, and nitric acid production, as well as green urea ammonium nitrate (UAN) as a final product to be distributed in the local fertilizer market. The early works, to be carried out on a reimbursable basis, are aimed at defining the design and the main aspects of the project. Upon successful completion of the early works, and subject to the client's final investment decision, the activities will enter into the EPC phase, which will be carried out by KT in conjunction with another Maire group subsidiaries, Tecnimont, NextChem as technology integrator and Stamicarbon as licensor for the green ammonia technology, and manager of the other process units included in the scope. The complex will be one of the biggest facilities in North America entirely dedicated to the production of green fertilizers. Stamicarbon says that the green ammonia plant will have a capacity of 450 t/d and is expected to start up in 2026.

"Stami Green Ammonia is at the heart of Stamicarbon's innovation program, and we are excited to see this technology implemented in several projects around the world," said Pejman Djavdan, Stamicarbon CEO. "It represents a significant leap forward for the production of green fertilizers based on renewable resources."

EUROPEAN UNION

Ammonia the sticking point for renewable energy target

EU attempts to pass a law committing members to producing 42.5% of their energy from renewable sources by 2030 led to some hard bargaining in mid-June as France pushed for exemptions for hydrogen from nuclear power and legacy gas-based ammonia plants. A group of member states led by France held up approval of the EU renewable energy targets, pushing for more favourable treatment of CO_2-free nuclear energy and an opt-out for ammonia plants that may struggle to switch from gas. France generates around 70% of its electricity from nuclear sources, and has urged the rest of the EU to consider hydrogen generated from electrolysis using nuclear energy as low carbon, even if it is not strictly 'renewable'. Other states pushed back against reopening discussions, which have already taken months to negotiate, and Germany and Spain have been against regarding nuclear energy as a green energy option. Sweden attempted to produce a compromise 'recital' or foreword to the agreement which could state principles without formally reopening negotiations. This says that a "limited number" of ammonia facilities could be given an exemption so long as they could demonstrate that they were transitioning to a phase out of fossil fuel generated hydrogen.

NETHERLANDS

Yara and Cepsa to set up "clean hydrogen corridor"

Yara Clean Ammonia and Cepsa have entered into a strategic partnership to set up the first clean hydrogen maritime corridor between the ports of Algeciras in Spain and Rotterdam for the decarbonisation of European industry and maritime transport. The partnership envisages Yara supplying Cepsa with clean ammonia volumes, which will allow the energy company to get a head start in establishing the clean hydrogen corridor and lead the initiative to serve industrial and maritime customers in Rotterdam and Central Europe.

"Today's agreements are a crucial step towards the long-term viability of the Andalusian Green Hydrogen Valley and the implementation of the first maritime corridor of sustainable fuels that will link the south with the north of Europe. Green hydrogen and its derivatives are the fastest, most viable and competitive solution to accelerate the energy transition in heavy transport and ensure energy independence in Europe. The agreements announced today give our project crucial access to markets, customers and distribution infrastructure: three key elements to unlock the potential of our Hydrogen valley. This is major news for the decarbonization of European shipping and industry and for the planet," said Maarten Wetselaar, CEO of Cepsa.

INDONESIA

Nuclear plant could supply low carbon hydrogen for ammonia

A Danish start-up has entered a $4 billion agreement to build a nuclear-powered ammonia plant in Indonesia. Copenhagen Atomics is leading a four-party group from Denmark that has signed a MoU with two Indonesian state-owned enterprises, to develop an ammonia facility in the city of Bontang. The plant is set to be powered by next-generation nuclear reactors and have a capacity of 1.0 million t/a. Copenhagen Atomics's co-founder, Thomas Jam Pedersen, expects the plant to be able to produce the world's cheapest low-carbon ammonia.

"I believe that with this plant in Indonesia we can get the price of ammonia down to $500 per ton," he says. That compares to $720-1,400/t for wind or solar-generated ammonia in 2020, according to the International Renewable Energy Agency.

SPAIN

Iberdrola to build green ammonia plant

Spanish power company Iberdrola says that it will build the first green ammonia plant in southern Europe, using European funds and an investment estimated at euro 750 million. The company did not specify which country the plant will be in, but it is known to be working with Fertiberia on conversion of some of the latter company's ammonia capacity at Puertollano in Spain to green production.

The announcement is part of a framework agreement signed by the energy company with Trammo, the world's largest maritime trader and distributor of anhydrous ammonia, for the sale and purchase of up to 100,000 tonnes of green ammonia per year from 2026. The facility will be supported by the construction of 500MW of new renewable energy. It will also contribute to the creation of industrial and innovation opportunities in a growing market with a high export component. The plant's green ammonia production will be purchased and sold by Trammo to contribute to the decarbonisation of northern European industry.

UKRAINE

Ammonia pipeline reportedly damaged

The Togliatti-Odessa ammonia pipeline appears to have become damaged during the latest round of fighting in Ukraine. Both Russian and Ukrainian sources identified the place of the breach as Masyutivka in northeastern Ukraine, in Ukrainian-controlled territory but close to the front line, but the Russians blamed a Ukrainian sabotage group, while Ukraine said that the pumping station had been damaged by Russian artillery fire. Resumption of ammonia supplies along the pipeline were part of negotiations concerning the Black Sea grain export deal. Russia had been pushing for resumption of exports via the pipeline and other fertilizer exports as a quid pro quo for allowing the Ukrainians to resume exports of grain from Odessa. The Russian foreign ministry has said repairing the pipeline could take 1-3 months.

In a separate incident, there were also accusations by Ukraine that an ammonia tank at the Crimean Titan plant has been rigged with explosives by Russian defending forces, potentially releasing 200 tonnes of ammonia. The Crimean Titan plant is located in Armyansk, a region on the northernmost tip of Crimea. It is one of the two land-based entryways into the Crimean peninsula from Ukraine.

FINLAND

Hydrogen and ammonia production at Kokkola

H2Cluster Finland, a network of companies and industrial associations, says that one consortium member, Finnish project developer Flexens, is looking to expand the project by developing green hydrogen and ammonia production with a capacity of 350MW of electrolysis. Kokkola, on the west coast of Finland, has existing chemical industry and a deep-water port.

Jim Häggblom, Senior Project Manager at Flexens, said: "The port is one of the two that handle ammonia in Finland, and there are also storage facilities for ammonia right next to the port in the Kokkola Industrial Park." Flexens aims to start production of green ammonia by 2027, with an initial planned capacity of 200,000 t/a. Häggblom continued: "Hydrogen is already being produced in the area, which guarantees an established and safe operating environment. There is also plenty of wind power available and a strong power grid. Besides using hydrogen for ammonia production, we will also be able to sell it to others. There are already potential customers in the area. We also have an opportunity to deliver waste heat from hydrogen production to the district heating network and offer steam from ammonia production to factories nearby."

Häggblom estimated the whole investment to rise to over €700 million which will be provided by investors and supplemented by grants. Flexens' team will be supported by French hydrogen producer Lhyfe, which took a 49% stake in Flexens in March.

SAUDI ARABIA

NEOM Green Hydrogen Company achieves financial closure

NEOM Green Hydrogen Company says that it has now achieved financial closure on the world's largest green hydrogen production facility, with a total investment value of $8.4 billion. The plant is being built at

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Oxagon, in Saudi Arabia's region of NEOM. NGHC has also concluded the engineering, procurement, and construction (EPC) agreement with Air Products as the nominated contractor and system integrator for the entire facility. Air Products has already awarded major contracts to various technology and construction partners.

NEOM Green Hydrogen Company has also secured an exclusive 30-year off-take agreement with Air Products for all the green ammonia produced at the facility, which will unlock the economic potential of renewable energy across the entire value chain. An equal joint venture between ACWA Power, Air Products and NEOM, NGHC's plant will integrate up to 4GW of solar and wind energy to produce up to 600 t/d day of carbon-free hydrogen by the end of 2026, eqivalent to 3,600 t/d of green ammonia.

Nadhmi Al-Nasr, Chairman, NEOM Green Hydrogen Company, and Chief Executive Officer, NEOM said: "This substantial financial backing from the investment community shows the unmatched potential of NGHC's green hydrogen project. With the financial close announced today, we are taking a massive leap towards opening the plant, in line with NEOM's vision to accelerate renewable solutions. At scale, this project is the first-of-its-kind internationally, leading the world in the hydrogen revolution. Harnessing the energy of NEOM's abundant natural resources, NGHC's project will pave the way for the large-scale adoption of green hydrogen, while driving Saudi Vision 2030's sustainable development goals."

Seifi Ghasemi, Chairman, President and Chief Executive Officer, Air Products, added: "Air Products is proud to be shaping the future of energy with first-mover projects like this one, providing clean hydrogen to the world in a sustainable way. Air Products is the exclusive off-taker and will absorb the full production volume of the green hydrogen produced in the form of green ammonia at the NGHC facility to serve global mobility and industrial markets. Producing and exporting green ammonia supports the decarbonisation of these heavy-duty transportation and industrial sectors and will save the world about five million tonnes of carbon dioxide per year. As the primary EPC contractor and system integrator for the facility, we are proud of the significant progress made with engineering and have awarded all major subcontracts for the project. Land preparation is also complete, construction is well underway, and the joint venture team is in place and actively executing to bring green energy to the world by the end of 2026."

INDIA

Deepak Fertilisers to commission ammonia plant

Deepak Fertilisers and Petrochemicals is commissioning its new $530 million ammonia plant at Taloja in Maharashtra. The new 500,000 t/a of capacity will take the total ammonia capacity at the site to 628,700 t/a. KBR and Toyo technology has been licensed for the plant. Gas supply arrangements covering $^2/_3$ of the plant's requirements are already in place, according to Deepak. The expansion will reportedly save the cost of importing ammonia by $75-80/tonne and improve margins for the company. Deepak has been importing ammonia from the Middle East via the JNPT at Mumbai and transporting it to Taloja via 30,000 road tankers trips per year.

CANADA

Ammonia supply chain to Japan

Pembina says that it has signed an agreement with Japanese trading firm Marubeni to establish an end-to-end blue ammonia supply chain that will link Western Canada to Japan and other Asian markets. The memorandum of understanding was signed on May 30th and says that the two companies will jointly develop a production facility on Pembina-owned lands. The facility will produce low carbon hydrogen and ammonia near Fort Saskatchewan, Alberta. The plant is anticipated to produce up to 185,000 t/a of blue hydrogen that will be converted into 1 million t/a of low carbon ammonia. It will use carbon capture technology that will reduce a "significant amount" of CO_2 emissions, Pembina said. The ammonia would be transported via rail to Canada's western coast for shipping to Japan and the wider Asian market.

BOLIVIA

YPFB issues tender for urea project

Bolivia's state oil company YPFB has invited tenders for the front end engineering and design (FEED) of a proposed $1.29 billion ammonia and urea plant. The work will determine the project's technical, financial, economic, legal, social and environmental feasibility, and includes a market study, identifying a location, selecting the best technologies, and drafting technical specifications for the bidding rules to be used in the next stage.

Bolivia currently has a plant, PAU, at Bulo Bulo with the capacity of 1,200 t/d of ammonia and 2,100 t/d of urea. In spite of a troubled development and production history, it reportedly produced 364,000 tonnes of urea in 2022 and is forecast to produce 600,000 t/a in 2023. According to YPFB, PAU has reduced Bolivia's nitrogen fertilizer imports by 99%. The state operator estimates that the new plant's capacity will be double that of the existing one and will aim to supply export markets such as Brazil, Peru, Paraguay and Argentina.

CHINA

First application for UAS granulation process in China

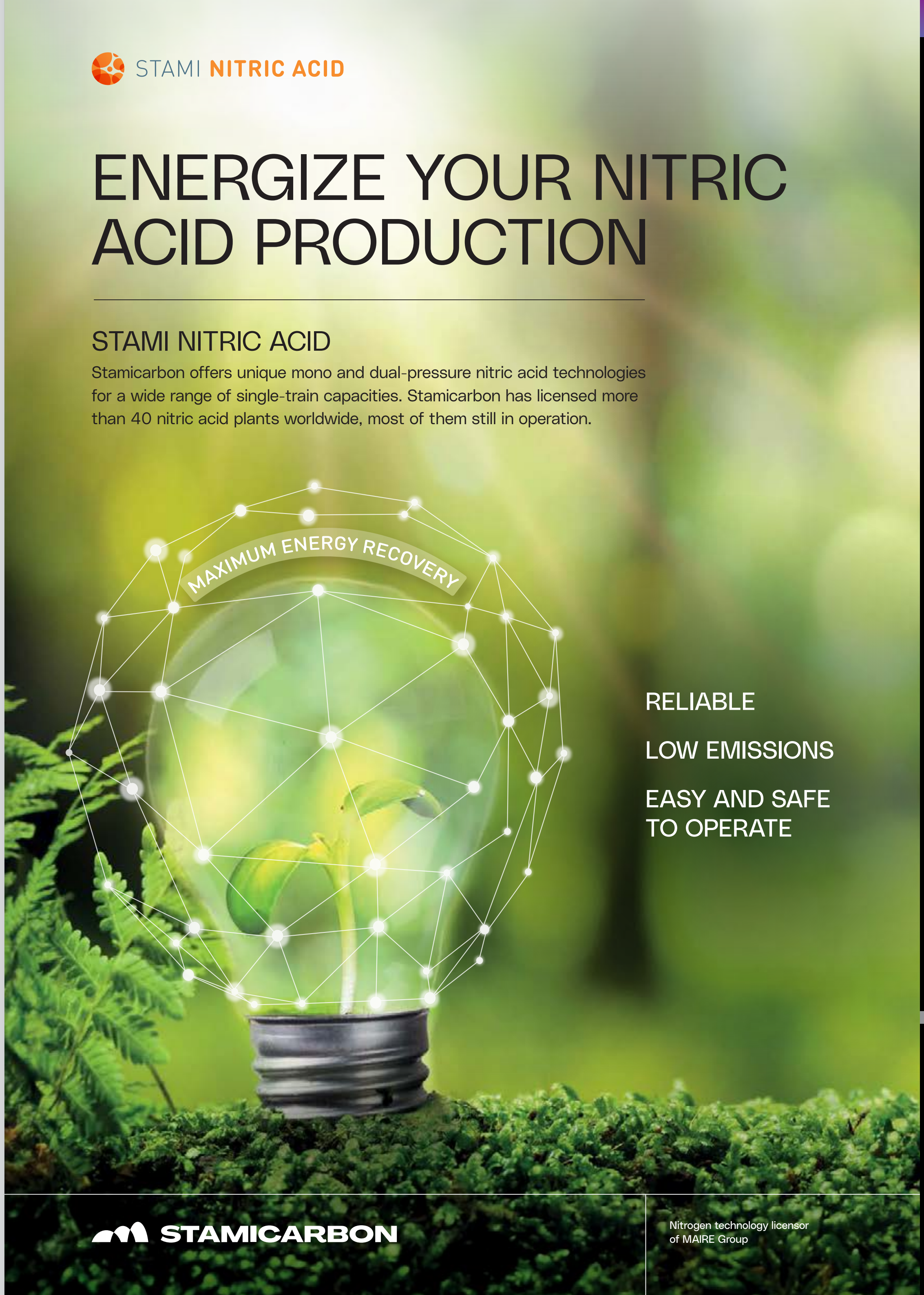
China Tianchen Engineering Corporation has selected Casale's fluid bed urea-ammonium sulphate (UAS) granulation process for the Xinjiang Xinji Energy and Chemicals Co. Ltd.'s Recycling Economy Joint Chemical EPC project. The plant will be located in Tiemenguan city, Xinjiang, China, and will be commissioned by 2025.

Designed to be capable of producing UAS product with a flexible ammonia sulphate content up to 20%, when put into operation the granulation unit will have a production capacity of 1,800 t/d of UAS at maximum ammonia sulphate content. Casale will provides design services and the license for its patented UAS granulation process as well as proprietary equipment to be put into operation in the plant.

BULGARIA

New fertilizer complex for Agropolychim

Casale and Agropolychim have signed an agreement which will ultimately lead the latter to double its nitrogen-based fertilizer production capacity of up to 1.5 million t/a of AN, CAN and UAN. As part of the agreement, Casale will license and engineer a new state-of-the-art dual pressure nitric acid plant that will enhance local green energy production. The plant is planned to be commissioned before the end of 2027. Agropolychim has been operating a dual pressure nitric acid plant based on Casale technology since 1973. ■



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NITROGEN+SYNGAS
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Syngas News

UZBEKISTAN

New MTO plant development

Gas Chemical Complex MTO Central Asia LLC has signed an agreement with Air Products to build a new methanol production facility. Known as Methanol Island, the facility would have a capacity of 1.34 million tons per year, as a part of the Methanol-to-olefin (MTO) gas chemical complex in Uzbekistan. The facility, to be built in the Karakul Free Economic Zone situated in Uzbekistan's Bukhara region, will cover 15 hectares. It is planned to enter operation in 2025 for an expected operational life of 25 years.

The GCC MTO complex will convert natural gas into high value polymer products with a production capacity of over 1.11 million t/a, including 250,000 t/a of polypropylene for the production of artificial fibres, electrical engineering and automotive components; 80,000 t/a of low-density polyethylene for the production of pipes, insulating materials, packaging and food films and mouldings; 100,000 t/a of ethylene vinyl acetate for the production of floor coverings, footwear and sports equipment; 300,000 t/a of polyethylene terephthalate, used for the production of containers, films and synthetic fibres, and 280,000 t/a of high density polyethylene, used for the production of pipes and fittings, barrels, canisters for fuel, freezer containers, safety helmets, furniture fittings.

Local production will help Uzbekistan reach its goal of diversifying the economy, substitute imports and potentially export products to other regions. The methanol facility will ensure the sustainable supply of methanol, hydrogen and other industrial gases such as oxygen and nitrogen, which are essential for the MTO gas chemical complex's production processes.

Masrur Shakirov, General Director of the Gas Chemical Complex MTO, said: "We are delighted to be working with Air Products, the world's leading industrial gases company, as partners in the complex. Air Products has established itself as a reliable supplier of proven solutions that can guarantee us both the high quality and required volume of products we need. Air Products' investments highlight the degree of interest shown by international companies in Uzbekistan's industrial development opportunities." ■

SOUTH KOREA

OCI to fuel first methanol container ship

OCI Global says that it will fuel the first ever green methanol-powered container ship in a new partnership with A.P. Moller-Maersk. OCI will provide ISCC certified biomethanol to power the maiden voyage of Maersk's first dual-fuelled container ship, in what it describes as "a pioneering step towards the decarbonisation of global shipping". The marine sector is responsible for 3% of global greenhouse gas emissions. The vessel leaves South Korea for its maiden voyage this summer, sailing along one of the world's busiest shipping routes to Northern Europe via the Suez Canal, bunkering at several major ports along its journey. OCI is obtaining the approvals and permits required to commercially bunker methanol in several ports on the ship's voyage, including Port of Rotterdam, positioning OCI as the first commercial bunker operator of methanol in these regions.

As the maritime industry navigates increased regulation to accelerate decarbonisation, such as the FuelEU Maritime initiative, OCI anticipates incremental global demand for methanol at 4 million t/a over the next five years, based on current orders from the marine sector, and is taking steps to be a major supplier of that anticipated demand. In February, OCI announced its project with Unibarge to retrofit the first methanol powered bunker barge, to be deployed at the Port of Rotterdam. It has also led the development of green methanol application in vehicle fuels, now placing up to 200,000 t/a equivalent and is growing its suite of low-carbon and green methanol products, including biomethanol, e-methanol, recycled carbon fuel (RCF) methanol, renewable natural gas, ethanol and bio-MTBE. OCI is developing a 1.1 million t/a blue ammonia plant in Texas, scheduled to start production in 2025 and its Egypt Green ammonia facility through Fertiglobe (a strategic partnership between OCI and ADNOC), where the first tons of green ammonia from electrolysis were produced earlier this year.


IMAGE: MAERSK

A computer rending of Maersk's new methanol-powered container ship.

EGYPT

MoU on green methanol plant

Egyptian chemicals firm, the Alexandria National Refining and Petrochemicals Company (ANRPC), has signed a Memorandum of Understanding (MoU) with Norwegian renewables company, Scatec, for the development of a $450 million green methanol production project in collaboration with the Egyptian Bioethanol Company. Announced by Egypt's Ministry of Petroleum and Mineral Resources, the green methanol plant will be located in the port of Damietta and is expected to have an initial production capacity of 40,000 t/a, which could be increased to 200,000 t/a. Egypt's Minister of Petroleum and Mineral Resources, Tarek El-Molla, said that this project is the first of its kind in Egypt and the Middle East and will "contribute to placing Egypt on the global map of nations that produce green fuel for ships."

The project includes the construction of renewable energy stations with capacities of 40 MW for solar power and 120 MW for wind power. The joint development agreement will also involve the development of a 60 MW green hydrogen analyser as well as a seawater desalination plant and a green methanol production and storage station.

GERMANY

IPO for thyssenkrupp nucera

thyssenkrupp AG and thyssenkrupp nucera AG, a provider of technologies for high-efficiency electrolysis plants, have announced an Initial Public Offering (IPO) and listing of thyssenkrupp nucera on the Frankfurt stock exchange. The proceeds are expected to be around €500-600 million and are intended to drive the growth of the alkaline water electrolysis (AWE) technology business of thyssenkrupp nucera. thyssenkrupp AG says that it intends to remain a committed shareholder of thyssenkrupp nucera and will retain a majority stake in the hydrogen technology provider while securing to create a liquid market for the shares of thyssenkrupp nucera following the completion of the IPO.

Werner Ponikwar, CEO of thyssenkrupp nucera said: "With our technology to produce green hydrogen we want to help shape the new era of sustainable energy use. Green hydrogen is a key factor for the decarbonization of the industry and thus the achievement of climate protection targets. Our technology produces green hydrogen on a large scale and supports our customers on their way to climate neutrality."

SWEDEN

Ørsted breaks ground on e-methanol plant

Danish offshore wind developer Ørsted has started the construction of FlagshipONE, Europe's largest e-methanol project. The ground breaking ceremony was held on 24 May in Örnsköldsvik, Sweden, in the presence of political and partner companies representatives. According to Ørsted, this marks the first step in a new green era of shipping, where large-scale methanol production facilities will supply a growing fleet of methanol-powered vessels, which currently counts 110 vessels on order or in operation, up from 80 vessels at the end of 2022.

FlagshipONE is located on the grounds of the biomass-fired combined heat and power plant Hörneborgsverket in Örnsköldsvik, operated by Övik Energi. The methanol from FlagshipONE will be produced using renewable electricity and biogenic carbon dioxide captured from Hörneborgsverket. In addition, the project will use steam, process water, and cooling water from Hörneborgsverket, and excess heat from the e-methanol production process will be delivered back to Övik Energi and integrated into their district heating supply.

Originally developed by Liquid Wind, FlagshipONE was acquired by Ørsted in December 2022 and the final investment decision (FID) was reached. Carbon Clean will supply the carbon capture equipment while the technology package for the facility will come from German company Siemens Energy. The package comprises four proton exchange membrane (PEM) electrolysers with a total capacity of 70 megawatts (MW), as well as the plant-wide electrification and automation systems, including innovative digitalisation solutions (such as the use of digital twins), and the entire power distribution and compressor systems. Expected to become operational in 2025, FlagshipONE will produce around 50,000 tonnes of e-methanol each year.

Commenting on the ground breaking, Anders Nordstrøm, COO of Ørsted P2X, said: "FlagshipONE is a pioneering project that will open a new era for green shipping and for Ørsted. I'm very pleased that we've now started on-site construction together with other green fuel leaders from across the supply chain, and together with representatives from Örnsköldsvik, Västernorrlands Län and Sweden at large. FlagshipONE will be the first project in a new green industry in Sweden, which Ørsted intends to spearhead."

FlagshipONE is the first e-methanol project in the company's green fuel pipeline. It is also developing the 300,000 t/a 'Project Star' in the US Gulf Coast area and the 'Green Fuels for Denmark' project in Copenhagen.

MALAYSIA

Sarawak Methanol project to be onstream next year

The Sarawak Methanol project in Bintulu is expected to be operational by the first quarter of 2024, according to a recent statement by Deputy Minister for International Trade and Investment Datuk Malcolm Mussen Lamoh. In a reply at the State Legislative Assembly, the minister said that the project, under development by Sarawak Petchem Sdn Bhd, reached 90% completion in May. The Sarawak government, through the Sarawak Economic Development Corporation (SEDC) is also developing the Petchem Industrial Park in Tanjung Kidurong, Bintulu, covering around 1,000 acres, and aiming to serve as the main industrial area for the petrochemical industry in Sarawak. The methanol plant will also include a dedicated jetty to allow international tankers or ships to bring methanol to the market. It will have a capacity of 5,000 t/d (1.7 million t/a).

SAUDI ARABIA

NEOM awards contract for world's largest hydrogen plant

Envision Energy says that it has signed a contract to supply 1.67 GW wind turbines with NEOM Green Hydrogen Co for the world's largest utility-scale hydrogen plant powered entirely by renewable energy. The plant is located at Oxagon, in the NEOM development area of Saudi Arabia. Under the contract, Envision's wind turbines will be installed and are expected to be fully operational by 2026.

"This contract represents a significant milestone for both our companies and the industry at large," said Zhang Lei, CEO of Envision Energy. "We are proud to be associated with such an ambitious project that will pave the way for other companies to follow suit in pursuing sustainable initiatives."

"We are extremely excited to collaborate with Envision on this groundbreaking project," said Wolfgang Brand, Vice President of NEOM Green Hydrogen from Air Products. "This milestone demonstrates our shared commitment towards meeting sustainability objectives through project deliveries."

NEOM Green Hydrogen Company aims to produce carbon-free hydrogen using solely renewable energy sources such as wind and solar power to produce up to 600 tonnes per day of carbon-free hydrogen by the end of 2026. ■

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People

Tony Will (right) with Alzbeta Klein, IFA director general.

The International Fertilizer Association (IFA) has announced that Tony Will has been elected as the new Chair of the Association. Will is president and chief executive officer (CEO) of CF Industries, a global manufacturer of hydrogen and nitrogen products for fertilizer, clean energy, emissions abatement and other industrial applications.

"I am honoured to serve as Chair of IFA and help advance this vital organization's mission to promote the efficient and responsible production, distribution and use of plant nutrients," Will said. "Our industry is at the forefront of some of the world's most important challenges, from food security to climate change. I look forward to working with our members and the IFA team to continue our leadership role in addressing these global priorities, collaborating not just within our own industry but with government and other stakeholders as well."

Jeanne Johns, at the time managing director and CEO of Incitec Pivot Ltd., was elected as the new vice chair of the Association.Both Will and Johns serve on the Executive Board of the Association, which also welcomed two further new appointments: Ahmed El Hoshy, CEO of OCI Global and Fertiglobe and Abdulrahman Shamsaddin, CEO of SABIC Agri-Nutrients. Svein Tore Holsether, president and CEO of Yara, remains on the Executive Board as Immediate Past Chair, along with Raviv Zoller, President and CEO, ICL Group and Alzbeta Klein, Director General, IFA. "Helping to feed the world sustainably is at the core of what we do, and IFA is fortunate to have such seasoned executives on our Board," Klein said.

Five new Board Directors were also elected by the membership: Robert Wilt, CEO, Ma'aden; Maen Nsour, President and CEO, Arab Potash; Julian Palliam, president and CEO, Foskor; Yasser Alabassi, President, GPIC; and Wang Bei, General Manager, CNAMPGC Holding Ltd Co. IFA members also re-elected to the Board of Directors David Delaney of Itafos and Suresh Krishnan of Adventz.

However, only four days before the appointments were made, Incitec Pivot Ltd (IPL) announced that Jeanne Johns will be stepping down from her role as the company's managing director and CEO, following investor pressure of the company's performance. IPL said in a statement that Paul Victor, the company's Chief Financial Officer, has been appointed as interim CEO while the board undertakes a comprehensive search process for a permanent CEO. Jeanne will continue to work with the board and Paul Victor until 30th June 2023 to facilitate a smooth transition of her responsibilities. IPL's chief of staff, Liza Somers, has been appointed as interim CFO. Liza has been with IPL for 10 years, holding key leadership positions in the finance team.

IPL chairman Brian Kruger said: "I would like to acknowledge and thank Jeanne for all her efforts and commitment to our company over the past five and a half years. She leaves the company in a very strong financial position and with a solid platform for future growth. Jeanne led the organisation through the very challenging COVID-19 pandemic and has been instrumental in developing our decarbonisation strategy that has received the strong support of our shareholders. Jeanne has also led some significant transactions that will create long-term value for our shareholders, including the urea offtake agreement with Perdaman and the recently announced sale of the Waggaman ammonia manufacturing facility in Lousianna, USA. We wish her all the best in her future endeavours." ■

Calendar 2023/2024

AUGUST

20-24

67th AIChE Safety in Ammonia Plants and Related Facilities Symposium,
MUNICH, Germany
Contact: Ilia Kileen, AIChE
Tel: +1 800 242 4363
Web: www.aiche.org/ammonia

SEPTEMBER

10-15

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

14-15

2nd International Conference, Ukrainian Fertilizer Market, LVIV, Ukraine
Contact: Chem Courier
Email: conf@fert-ua.com
Web: www.fert-ua.com

25-26

World Methanol Conference,
VIENNA, Austria
Contact: David Coates, OPIS
Tel: +1 713 305 0116
Email: dcoates@opisnet.com

OCTOBER

9-11

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

NOVEMBER

27-29

Argus Clean Ammonia Europe Conference,
ANTWERP, Belgium
Contact: Argus Media Group
Tel: +44 (0)20 7780 4340
Email: conferences@argusmedia.com
Web: www.argusmedia.com/en/conferences-events-listing/clean-ammonia-europe

FEBRUARY 2024

5-7

Fertilizer Latino Americano,
MIAMI, Florida, USA
Contact: Argus Media, Ltd
Tel: +44 (0)20 7780 4340
Email: conferences@argusmedia.com

MARCH

4-6

Nitrogen+Syngas Conference 2023,
GOTHENBURG, Sweden
Contact: Michele Bingham, CRU
Tel: +44 (0)20 7903 2159
Email: michele.bingham@crugroup.com

Plant Manager+

Problem No. 68 Chloride stress corrosion cracking risks in urea plants

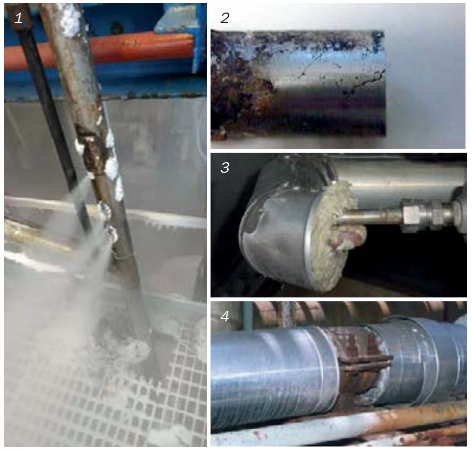
Avoiding chloride contamination is critical in urea plants, not only from the process and utility side but also from the atmospheric side. The applied stainless steels in urea plants are susceptible to detrimental failure modes when chlorides and moisture are present. This UreaKnowHow.com Round Table discussion provides several examples of failures and important prevention measures relating to chloride stress corrosion cracking risks in urea plants. ■

Krzysztof Czachor of Grupa Azoty Zakłady Chemiczne Police in Poland kicks off this round table discussion: I am wondering about a certain issue related to the corrosion of stainless steel in urea plants. Half a year ago, we installed a heating system for pipelines used to empty the synthesis system during maintenance shutdowns. The pipelines are about 40 years old, but since the installation of the heating system made of carbon steel, we have noticed numerous areas of thinning and damage along the route of the heating system installation. What are the possible causes in this situation? Can carbon steel contact with stainless steel cause numerous leaks?

Mark Brouwer of UreaKnowHow.com in the Netherlands replies: It is a common failure mode that when carbon steel tracing is in contact with stainless steel PLUS chlorides are present in the atmosphere (seaside, downwards cooling towers) PLUS moisture is present (bad state of insulation), that chloride stress corrosion cracking can occur in the stainless steel. The reactions are:

$$\mathrm{Fe^{2}+ + 2Cl- \rightarrow FeCl_2}$$

$$\mathrm{FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl}$$



PHOTOS: (1) UREAKNOWHOW.COM ; (2-4) NTT CONSULTANCY

Photos: (1) Leaks in stainless steel HP drain pipelines; (2) SCC in 304 line at location in contact with trace line; (3) Steam tracing without use of spacers; (4) Pipeline support allowing ingress of water.

The lower pH caused by the formation of HCl, helps to accelerate chloride stress corrosion cracking of the stainless steel. Do you see cracks or thinning in the stainless steel?

Prem Baboo, urea expert (retired from NFL and Dangote Fertilizer) from India joins the discussion: Yes, carbon steel contact with stainless steel has caused numerous leaks, also due to galvanic corrosion. Carbon steels contain maximum iron which oxidises when exposed to the environment, creating rust. Acids (HCl and H_2SO_4) at some concentrations are particularly aggressive towards stainless steel. General corrosion can be quite destructive and happens to the entire surface at once during rain and sometimes acid rain.

Krzysztof replies: We have noticed many cracks (like pinholes) after installing tracing six months ago. Prior to that we had no such problems.

Mark provides some examples of pipeline failure: Photos (bottom left) show different examples of pipeline failures.

Imagine if this happened at a stainless steel nozzle of your high pressure urea synthesis equipment! Proper preventative measures need to be taken in the engineering, construction and maintenance phase. For example, during the engineering phase:

- Apply a protective coating on stainless steel in areas where chlorides and moisture are present in the atmosphere.
- Do not insulate if not necessary for reasons of process economics.
- Apply a water-tight finish of insulation jacketing.
- Insulation material should be free from nitrates and chlorides.
- Do not affix chloride-containing stickers to austenitic stainless steels at temperatures exceeding 50°C.
- Pay attention to aspects of construction such as material selection, crevice-free design, weld design, use of cover rings and the use of spacers during the installation of carbon steel steam trace lines.

Additional measures that should be taken for insulated vessels and pipework likely to develop atmospheric corrosion include: application of a protective coating, application of aluminum foil wrap for stainless steel piping and sheltering the equipment items.

For more information, refer to Corrosion and Materials Expert Mr. Giel Notten's Corrosion Engineering Guide: https://fertilizer.academy/product/ntt-corrosion-engineering-guide-feb-2021/ ■

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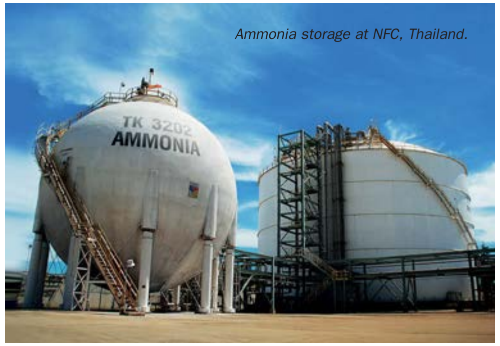
Ammonia storage at NFC, Thailand.

PHOTO: NFC

Ammonia industry accidents

A look at fatal incidents in the ammonia industry over the past two decades.

Ammonia is one of the most widely used chemicals in the world, second only to sulphuric acid in terms of number of tonnes produced per year; 185 million t/a in 2021 according to the International Fertilizer Association (IFA). However, while sulphuric acid is dangerously corrosive, it is a liquid at room temperature and pressure, whereas ammonia must be pressurised and/or refrigerated to liquefy it and make it easier to store and handle. It is also relatively toxic by inhalation. Ammonia vapours disperse quickly when released and forms dense ammonia/air clouds. Although ammonia gas can be safely vented to atmosphere during emergency situations the discharge point must be sufficiently high to prevent downwind plume hitting the ground at high concentrations. As a gas, ammonia irritates and burns the skin, eyes, and respiratory tract. Liquified gas can cause the skin to freeze, as well as permanent damage or blindness to the eyes. Inhalation of ammonia can cause severe irritation of the nose and throat, and life-threatening accumulation of fluid in the lungs (pulmonary oedema). Overall, the main recorded causes of fatalities and injuries during ammonia incidents is either inhalation or burns[1].

Perhaps for this reason, a significant proportion of industrial accidents involving chemicals are related to ammonia releases. Between 2007 and 2017, the US Environmental Protection Agency (EPA) reported that 72% of all chemical accidents in the Mid-west region were ammonia-related. Ammonia is used in a wide variety of industries, from manufacturing (production of plastics, fibres, and other chemicals), agriculture (as a fertilizer), and in the consumer sector as a food additive, cleaning agent, or refrigerant.

Ammonia refrigeration

While 80% of ammonia is used in fertilizer manufacturing, and only 2% in refrigeration systems, the majority of releases and accidents, in fact, occur when ammonia is used as a refrigerant. After the Kigali Amendment to the Montreal Protocol came into effect, many countries have begun exploring new refrigeration alternatives to reduce damage to the ozone layer and mitigate global warming. Due to technical and cost constraints, the use of ammonia as a refrigerant is widespread in industrial refrigeration, especially in large and medium-sized cold storage. This means ammonia is often close to less skilled or trained personnel, and monitoring of corrosion or other mechanical defects may be less thorough than at an ammonia manufacturing facility.

A 2019 survey of ammonia refrigeration incidents over the preceding two decades[1] highlighted the following cases:

On 23rd August 2010, a catastrophic failure of a 12-inch suction pipe on a roof lead to a release of more than 14 tonnes of anhydrous ammonia in Millard Refrigerated Services in Theodore, Alabama. The pressure developed due to hydraulic shock also ruptured the evaporator coil inside the facility. The ammonia cloud travelled 0.25 miles across the river near the plant and affected workers and crew members on ships docked at Millard. One Millard employee lost consciousness and was injured. Nine crew members and 143 offsite contractors reported exposure. The cause was operator error in interrupting a defrost cycle during a restart after a power failure. The evaporator switched directly from defrost mode into refrigeration mode without bleeding hot gas from the evaporator coil, allowing low temperature liquid and hot gas to mix in the same pipe, causing the hot gas void to collapse as it rapidly condensed to liquid. This created pressure shock and ruptured the piping and evaporator coil.

The US Chemical Safety Board, which investigated the Millard incident, commented in its report: "We are seeing too many ammonia releases in our daily incident reviews. Though many are 'small' releases, a high consequence accident that causes multiple injuries to members of the public is a serious one that warrants our examination. Our team will be examining the events that led to the release and ways that the community can be better protected in the future."

On August 31st, 2013, a leak of liquid ammonia at a refrigeration unit of plant in Weng's cold storage Industrial Company in Shanghai killed 15 people and injured 25. Residents up to 15 km downwind in the Zhabei district reported the smell of ammonia. The cause of the accident appeared to be a pipe or valve failure.

On July 7, 2017, a faulty quarter inch valve caused an ammonia leak at Grecian Delight food processing plant in Elk Grove Village which led to an explosion. Ammonia under 150 psi pressure leaked into an 80 x 40-feet room with 20-feet ceiling and a spark led to ignition of the ammonia leading to a blast which ruptured the aluminium facade on the building and hospitalised two workers.

On August 16, 2011, an ammonia leak at the Pilgrim's Pride Plant in Guntersville caused a fire and explosion. The fire was put out within 45 minutes and there were no reported fatalities, but the explosion damaged the plant.

Kamloops incident

Technical Safety BC has recently reported on an accident which occurred on May 26, 2022, when a crew was in the process of cutting up and disassembling two ammonia refrigeration systems at Arctic Glacier Inc. in the Mount Paul Industrial Park in Kamloops, British Columbia. Those present understood that ammonia had been previously removed from both systems. During the removal of a section of the system a valve handle was turned, resulting in a large release of ammonia. The individual who turned the handle was sprayed by the ammonia and moved further into the building. The remaining members of the crew evacuated through a nearby open bay door. The individual who opened the valve was extracted from the building and pronounced dead following the incident. In addition to the fatality, there were multiple ammonia exposures, and a local evacuation.

The investigation found that the failure to remove ammonia from the refrigeration system prior to, or during disassembly was the primary cause of the incident. This was influenced by changes in personnel and their assigned responsibilities and misunderstood communications regarding the work completed. The investigation found that, given the magnitude of the release, a properly functioning ventilation system would not have prevented ammonia concentrations from reaching explosive limits; however, it likely would have lessened the amount of time that the ammonia concentration was combustible and therefore reduced the risk of explosion.

China

Another recent report examines ammonia incidents in the food processing industry in China[2], There were 82 ammonia refrigeration-related accidents in China from 2010 to 2020, resulting in 189 deaths and 1081 injuries (including poisoning). The breakdown of causes was found to be: human error 20.7%; equipment failure 67.1%; material deficiencies 7.3%; external factors 4.9%. Human factors mainly included improper or even illegal operation of facilities. Material factors were defective welding materials, cracked welds, unqualified insulation materials, broken blind bolts, aging flanges, corroded/aging gaskets, and detached pipe caps, with six cases accounting for 7.3% of all accidents. Equipment failures mainly related to ageing compressors and pipes, ruptured tanks and pipes, and loose, rusted, leaking or poorly sealed valves, accounting for 67.1% of total accidents. External causes were mainly due to the presence of open flames, abnormal changes in external temperature, and short-circuiting of wiring, with four cases accounting for 4.9% of all accidents.

Ammonia manufacturing incidents

Ammonia production occurs at high temperatures and pressures. As a result safety is a constant concern and for that reason most operators have comprehensive safety and maintenance regimens which make accidents rare. Potential causes of accidents include catalyst degradation/catalyst tube rupture, runaway reactions, corrosion in reformers, and potential releases from pipes or cracks. Failures can occur in process equipment, machines, control systems that can lead to an accident. Ammonia explosions are rare as the lower explosion limit of ammonia is high (LEL: 16% and HEL: 25%). The auto ignition temperature is 650°C, so ammonia is difficult to ignite. The most common accidents are leaks, with the most important aspect for minimisation of risk being prompt action to shut down the compressor.

Recent ammonia manufacturing incidents have included:

On June 14, 2013, an accident happened at the CF Industries site at Donaldsonville, Louisiana. There was a fire and explosion in one of the four ammonia plants, resulting in one fatality and injuring at least ten people. The fire was brought down in under half an hour and the plant was immediately shut down. Upon investigation it was found that the unit was shut down for maintenance and the workers were pumping nitrogen into a storage vessel. The accident occurred due to overpressure, causing the vessel to rupture.

On December 7, 2015, an accidental ammonia leak caused a fatality and injuries to personnel at Medicine Hat, Alberta. Two contractors were working to weatherproof a large ammonia storage tank and the leak happened when a piece of equipment accidentally struck the tank's valve, releasing ammonia. Both the workers were taken to the hospital but unfortunately one of them died.

On August 16, 2016, an ammonia leak at Petronas chemical facility in Malaysia resulted in two fatalities and three injuries. The leak happened when workers were doing maintenance and were exposed to ammonia from a leaking pipeline. The cause of accident was pipeline failure but the protective equipment could have minimised risk to the workers.

On August 22rd 2016 an ammonia tank collapsed at the Di-Ammonium Phosphate Fertilizer Company Ltd. The 500 tonne tank was half full at the time. A cloud of ammonia affected residents in the vicinity, leading to nearly 200 requiring treatment and 56 hospitalised, though fortunately without fatality due to favourable winds. An investigation found that pressure gauges in the tank and the reserve tank were inoperative at the time, and the condenser, safety valves and pressure vent were also out of order. The tank was also being operated by employees who were not trained for the job.

In 2019, an ammonia tank explosion at a fertilizer facility at Ain Sokhna, Egypt killed 10 workers and critically injured two others, reportedly when the tank failed during a nitrogen purge.

Conclusions

The biggest risk in ammonia operations is leaks from equipment damaged during operations, or subject to improper operation, especially if poor maintenance has led to corrosion and weakening of structures. Though this can become explosive if it encounters an ignition source, the biggest risk is from ammonia inhalation during a release at high pressure. Leaks can be due to valve plugging or valve malfunction; defects in shaft seals, pipe flanges and valve stems; pipe failures due to corrosion, mechanical damage or vibration; and tank material failure. Engineering controls and proper maintenance regimes, proper training, and the provision of proper protective equipment are essential. The US EPA estimates that 95% of ammonia incidents can be avoided through better operator training, improved procedures, and enhanced communication of incidents and near-misses. ■

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Ammonium nitrate and fertilizer safety

Orica's technical grade AN plant, Burrup Peninsula, Western Australia.

PHOTO: ORICA

A new book by leading industry expert **Kish Shah** looks at all aspects of ammonium nitrate production.

In a career spanning more than thirty years at major producers of ammonium nitrate and ammonium nitrate-based products, Kish Shah has come to be regarded as a leading international expert on ammonium nitrate safety. He has represented the fertilizer industry at the relevant UN committees on transport of dangerous goods for many years. Now he has literally written the book on ammonium nitrate (AN), distilling that experience into a 300-page volume: *Ammonium Nitrate and Fertilizer Safety*, with forewords by leading industry figures including Jacob Hansen and Atoine Hoxha of Fertilizers Europe, and Johannes Reivers, a leading light of the AN-NA Conference committee. This is a brief overview of the book and its contents.

History

Ammonium nitrate was first synthesised in 1659 by German chemist Glauber, but its history as an industrial product of course dates from the commercialisation of the Haber-Bosch process after the First World War, leading to commercial production of nitric acid from ammonia, and ammonium nitrate from nitric acid, as a potential cheaper alternative to the coke oven gas derived ammonium sulphate, or nitrates mined from guano deposits on Chilean islands. However, AN's hygroscopic nature meant that it caked badly, to the point of being unusable, and so tended to be used in a mixture with ammonium sulphate to try and ameliorate this somewhat. Even so, cargoes caked in longer storage, and it became common practise to break caked cargoes up using blasting charges from left over war munitions. At least until 11st September 1921, when an AN cargo being blasted at Oppau in Germany detonated, killing more than 500 people.

AN was used for its explosive properties in the inter-war period and during World War II, but a second attempt at its use at a fertilizer happened after the war, by coating the granules in wax to prevent them agglomerating. Again however a major industrial accident, this time at Texas City in 1947 when two vessels carrying AN caught fire and exploded. A similar incident occurred just months later in Brest, France. It was not until the development of the AN prilling process that the compound was able to achieve rapid growth as a fertilizer in the 1960s, replacing ammonium sulphate from caprolactam and other industrial processes. The ammonium nitrate industry and related products (calcium ammonium nitrate, urea ammonium nitrate etc) now amounts to around 50 million t/a of AN.

The 1950s also saw the development of ammonium nitrate/fuel oil (ANFO) as a commercial blasting explosive, using porous AN prills. AN has now become the main material for the commercial explosives industry, accounting for around 90% of solid explosives. The book also covers AN's more minor uses in propellants, as a source for nitrous oxide gas for anaesthesia etc, and in commercial cooling packs.

The third chapter moves on to a brief history of major incidents and their investigation and the consequent evolution of regulation. The US Bureau of Mines, in particular, conducted a great deal of testing and studies into AN properties in response to some industrial accidents. There was also considerable effort put into overcoming the caking properties that had resulted in the Oppau and Texas City accidents. Several additives were proposed for the purpose, with the most popular becoming magnesium oxide or carbonate to achieve the incorporation of magnesium nitrate, which also pushes the AN phase change to a higher temperature.

Major AN accidents in the 1970s at Seveso in Italy and Flixborough in the UK led to a major EU industrial accident directive in 1982, listing AN as technical/explosive grade or fertilizer grade, but the 2001 Toulouse explosion led to the addition of two new categories; fertilizers capable of self-sustaining decomposition; and 'off-spec' material and fertilizers which did not fulfil the detonation test.

Properties

Chapter 4 concerns the physical and chemical properties of AN. One of its unique properties is several different crystal structure phase changes in the solid form. One of these occurs at 32°C, and causes a substantial volume change. In hot conditions, cycling above and below 32°C can lead to the AN breaking up and forming very fine particles. As noted above, the addition of magnesium nitrate can increase this phase change to around 50°C.

AN is highly soluble in water, and absorbs atmospheric moisture at ambient temperatures, depending on humidity. Addition of an internal dessicant such as $MgNO_3$ can reduce moisture ingress to a top layer of 2-3 prills in a heap, but control of the condition of the air or the heap may be needed to be covered with sheeting. AN notionally melts at 169.6°C, but it tends to decompose before it boils. But its low thermal conductivity means that heating or cooling can be limited to a surface layer in bulk. The chapter also gives pH curves and tables of specific heat capacity and enthalpy.

As regards chemical properties, the decomposition reactions are covered. Nitric acid has a catalytic effect on decomposition, as do chloride ions. AN is of course a major oxidising agent. It does not present any major toxicity hazards.

Hazards

Chapter 5-7 covers hazards, beginning with fire. AN is not flammable, but it is an oxidising agent – fires therefore depend upon the presence of other flammable materials. The main risk comes where the AN is mixed with flammable material such as when contaminated with liquid fuel, or when it is in contact with large combustible items such as wooden structural supports and beams. Decomposition, however, presents another hazard with hot AN. As well as normal thermal decomposition, AN can be subject under the right conditions and with sufficient heat input to self-heating, or self-sustaining decomposition ('cigar burning'), and under confinement can even lead to rapidly accelerating decomposition. This latter takes us into the chapter on AN's explosion hazard, both via detonation and deflagration. AN is not classified as an explosive because it requires very energetic initiating impulses. But it can become sensitised by mixing with organic/combustible material, chlorides etc. Kish presents comprehensive models of AN explosive initiation and the results of work carried out by various bodies from the US Bureau of Mines and Queens University Canada to Dutch research organisation TNO under a variety of conditions.

> **"The main risk comes where the AN is mixed with flammable material.**

Compounds

Chapters 8-11 cover mixtures of AN, beginning with urea, and ranging across ammonium sulphate nitrate, calcium ammonium nitrate and compound NPK fertilizers, in each case looking at how their properties such as fire, explosion and other hazards differ from bulk AN.

Safe plant operation

The next section of the books is devoted to production of AN, and particularly safety aspects of manufacture. As AN has both oxidising and corrosive properties, choice of materials for plant construction is important, and the book ranges across steels, concrete, asphalt, wood, process vessels and pipes, conveyor belts, insulation, instruments and control systems. It also describes the main process flowsheets for AN production, including the ICI two stage process, the Uhde AN neutralisation process, the AZF pipe reactor process, and the nitrophosphate or Odda process. Given AN's propensity to absorb moisture and cake, there is a section on granulation and finishing, and also pollution control. The chapter on plant safety covers all of the major hazards than can be encountered in AN plant operation, and gives a checklist of good safety practises.

Storage and handling

Chapters 16-19 cover storage and handling. Different options for storage are detailed, and good principles for the design and maintenance of storage areas, particularly if other materials may be present nearby. Special attention is paid to off-spec and other reject fertilizer materials, and options for handling these safely, as these can be more sensitive to detonation or decomposition, as occurred at Toulouse in 2001. There are also chapters on hot ammonium nitrate solution and design and location of storage tanks, as well as liquid fertilizer such as UAN and its attendant corrosion issues.

After a brief review of AN-based explosives, there are then chapters covering transportation, by road, rail and sea, and security. This section finishes with chapters on consequence analysis of AN incidents and emergency planning and management.

Regulations

The last section of the book details the various tests for measuring oxidising potential, decomposition and reactivity and self-heating tests, and resistance to detonation and deflagration. There is also a comprehensive listing of regulatory instruments covering AN, including the UN harmonised system of classification and labelling of chemicals, and sections on EU and US legislation.

Appendices

The book concludes with a complete listing of the most significant AN accidents from 1920-1950 and all major reported AN accidents from 1950 to the present, by type (fire, explosion, decomposition etc) and with likely causes and key contributing factors. Serious fire or explosion accidents have mainly occurred with solid AN products. The main factors for accidents prior to 1950 were the high detonation sensitivity of some products and the use of unsafe practices to break up caked AN. Since 1950, just four accidents (in Iran 2004, North Korea 2004, China 2015 and Beirut 2020) have accounted for 85% of all 992 fatalities recorded. A high proportion of the explosion accidents involved fires preceding them. The prevention of fires and control or use of the presence of combustible materials where AN is stored or handled remains paramount.

Conclusions

There is a considerable amount of literature on ammonium nitrate hazards and safety, but as far as I am aware there has been no attempt prior to this to draw all of this together into one publication. This book serves as a comprehensive overview of AN manufacture, handling and especially safety and would be a useful primer for anyone working in the industry as well as a reference for those seeking pointers to where more information can be found. It is a hardback with 312 pages, 42 figures, 34 tables and 234 references and can be ordered via www.fertilizerandnitratesafety.com. ■

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Syngas project listing 2023

A round-up of current and proposed projects involving non-nitrogen synthesis gas derivatives, including methanol, hydrogen, synthetic/substitute natural gas (SNG) and gas- and coal-to-liquids (GTL/CTL) plants.

Contractor	Licensor	Company	Location	Product	mt/d	Status	Start-up date
AUSTRALIA							
n.a.	n.a.	Bell Bay Powerfuels	Tasmania	Methanol	600	DE	2027
CANADA							
n.a.	Greyrock Energy	Rocky Mtn Clean Fuels	Carseland, AB	BTL	15	DE	2025
n.a.	Topsoe	Air Products	Edmonton, AB	Hydrogen	1,500	DE	2024
CHILE							
Siemens	JM (DAVY™)	HIF	Punta Arenas	Methanol	350	C	2022
CHINA							
n.a.	Casale	Anhui Tenxin Tech.	Hubei, Mongolia	Methanol	1,500	UC	2023
n.a.	JM (DAVY™)	Ningxia Baofeng	Yinchuan, Ningxia	Methanol	7,200	UC	2024
n.a.	JM (DAVY™)	Jiangsu Sailboat	Lianyungang, Jiangsu	Methanol	300	UC	2023
n.a.	n.a.	Sinopec	Tahe, Xinjiang	Hydrogen	60	UC	2023
n.a.	JM (DAVY™)	Shenhua Baotou	Baotou, Mongolia	Methanol	6,000	DE	2026
n.a.	CRI	Henan Shuncheng	Anyang, Henan	Methanol	330	C	2023
DENMARK							
Technip	Topsoe/Sasol	Arcadia e-Fuels	Vordingborg	Green F-T	240	DE	2026
EGYPT							
n.a.	n.a.	EBIC	Ain Sokhna	Hydrogen	45	UC	2024
n.a.	n.a.	Scatec	Ain Sokhna	Methanol	120	DE	2026
FINLAND							
n.a.	n.a.	Veolia	Äänekoski	Methanol	36	UC	2024
GERMANY							
n.a.	Siemens	Siemens	Wunsiedel	Hydrogen	4	C	2022
INDIA							
EIL	Topsoe	Assam Petchem	Namrup	Methanol	500	C	2023
BHEL	n.a.	Coal India Ltd	Dankuni	Methanol	2,000	FS	2026
INDONESIA							
Samsung	Air Liquide	Petronas	Bintulu, Sarawak	Methanol	5,000	C	2023
n.a.	Topsoe	PT Bukit Asam	Muara Enim	Methanol/DME	6,000	UC	On hold
IRAN							
Namvaran	Topsoe	Badr-e-Shargh Pet Co	Chabahar	Methanol	5,000	UC	2025
PIDEC	Casale	Apadana Methanol	Assaluyeh	Methanol	5,000	UC	2023
n.a.	Casale	Fateh Sanat Kimia	Dayyer	Methanol	5,000	UC	On hold
n.a.	n.a.	IOC	Mathura	Hydrogen	15	BE	2024
ITALY							
n.a.	Tecnimont	Alia Servizi Ambientali	Empoli	Methanol	375	BE	2025
MALAYSIA							
Samsung	Air Liquide	Sarawak Petchem	Sanjung Kidurong	Methanol	5,000	UC	2024
Samsung	n.a.	H2biscus	Sarawak	Methanol	1,400	FS	2027
NETHERLANDS							
n.a.	Casale	Gidara Energy	Amsterdam	Methanol	250	DE	2025
NIGERIA							
n.a.	Air Liquide	Brass Fert & Petchem	Brass Island	Methanol	5,000	DE	2025
RUSSIA							
China Chengda	n.a.	Nakhodka Fertilizer	Nakhodka	Methanol	5,400	UC	2026
n.a.	n.a.	Baltic Gas Chemical	Ust-Luga	Methanol	5,000	DE	On hold
CNCEC	n.a.	GTM One	Khimprom	Methanol	3,000	BE	2025
SAUDI ARABIA							
n.a.	Air Products	Air Products Qudra	Jubail	Hydrogen	415	UC	2023
n.a.	Topsoe	Chemanol	Jubail	Methanol	+300	RE	2023
SINGAPORE							
n.a.	Air Liquide	PTTEP	Singapore	Methanol	150	FS	n.a.
SPAIN							
Tecnicas Reunidas	n.a.	Nascar	Almeria	Methanol	110	FS	2026
SWEDEN							
n.a.	Topsoe	FlagshipONE	Örnsköldsvik	Methanol	150	UC	2025
n.a.	JM (DAVY™)	Perstorp (Project Air)	Stenungsund	Methanol	600	DE	2026
TURKMENISTAN							
Sojitz, KHI	Topsoe	Turkmengaz	Ovadan-Depe	Methanol	n.a.	CA	n.a.
UNITED ARAB EMIRATES							
n.a.	n.a.	Ta'ziz/Proman	Ruwais	Methanol	5,400	P	2025
UNITED KINGDOM							
Linde	JM (DAVY™)	Equinor	Saltend	Hydrogen	380	DE	2027
n.a.	n.a.	Cromarty Clean Fuels	Nigg, Scotland	Methanol	n.a.	FS	n.a.
UNITED STATES							
n.a.	Relocated plant	US Methanol	Charleston, WV	Methanol	480	C	2022
n.a.	JM (DAVY™)	HIF	Matagorda, TX	MTG	1,840	DE	2026
KBR	JM (DAVY™)	Methanex	Geismar, LA	Methanol	5,000	UC	2024
Technip	Topsoe	ExxonMobil	Baytown, TX	Hydrogen	2,700	DE	2028
n.a.	Topsoe	Nacero	Penwell, TX	Methanol/MTJ	5 x 5,000	CA	n.a.
UZBEKISTAN							
Hyundai	Topsoe/Sasol	Oltin Yo'l GTL	Shurtan	GTL	5,000	C	2023
n.a.	Air Products	GCC MTO	Karakul	Methanol/MTO	3,360	DE	2025

KEY

BE: Basic engineering
C: Completed/commissioning
CA: Contract awarded
DE: Design engineering
FS: Feasibility study
n.a.: Information not available
P: Planned/proposed
RE: Revamp
UC: Under construction

Conversion:
1 t/d of hydrogen = 464 Nm³/h
1 t/d of natural gas = 1,400 Nm³/d


PHOTO: METHANEX

Right: Methanex's new Geismar 3 methanol plant in Louisiana, currently under construction.

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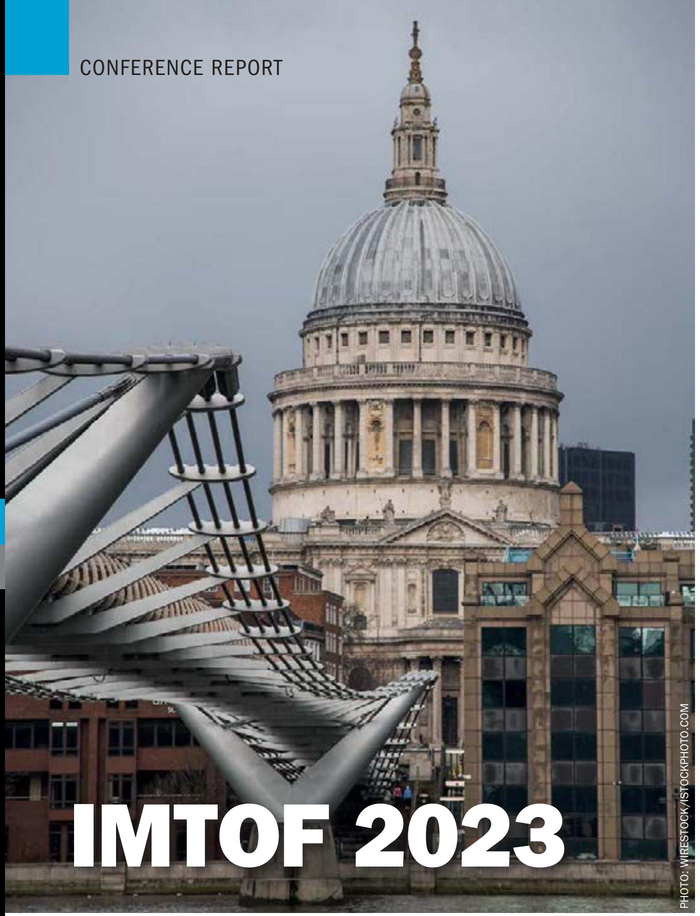


PHOTO: WIRESTOCK/ISTOCKPHOTO.COM

Left: St. Paul's Cathedral, one of the landmarks surrounding IMTOF 2023.

The International Methanol Technology Operators Forum (IMTOF) met at the Leonardo Royal St Paul's hotel in London from June 11th-14th.

As a biannual conference, this was the first time that IMTOF had been able to meet face to face since the covid pandemic, as the 2021 meeting was unable to go ahead. A surprising amount seems to have changed since then, with the pandemic, war, inflation and increasing pressure to decarbonise operations all turning old certainties on their heads.

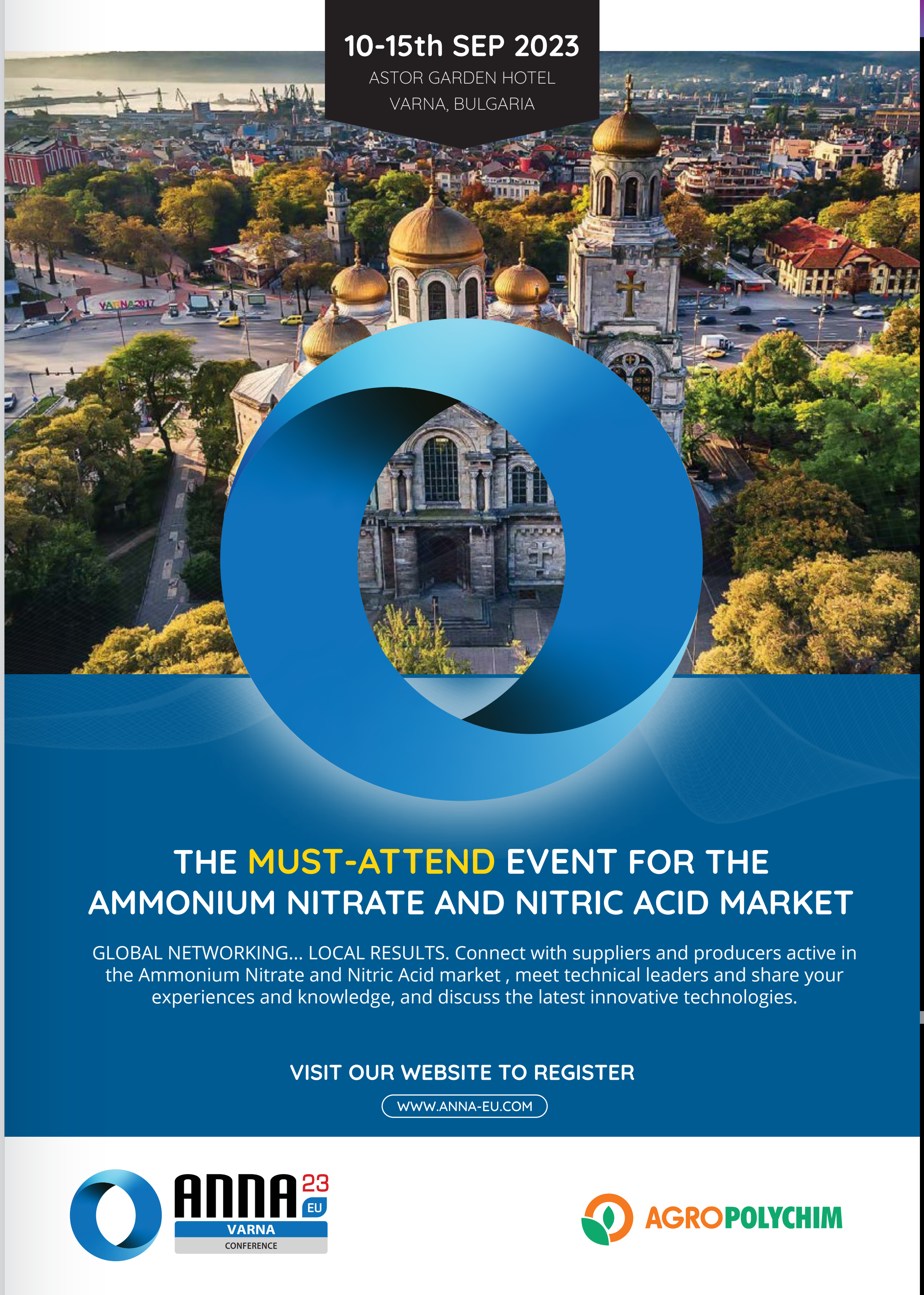
Methanol markets

Mark Berggren of consultants MMSA gave an overview of the methanol market. He noted the way that the world has been turned upside down over the past few years, and noted that, in a sense, the likely closure of coal-based methanol capacity is a major opportunity for improvement in the carbon intensity of methanol production, and prices and margins should support reinvestment. Mark forecast that typical methanol prices of $315-350/t today could be $410-460/t by 2028. Over that period, demand is forecast to grow by 22.7 million t/a, mainly in China. This is more than capacity is likely to increase, so operating rates should improve. However, 2022 was the first year for decades that methanol demand fell, due to a post-pandemic slowdown in China and loss of MTO demand. Europe also saw demand destruction due to the Ukraine war and effects on natural gas pricing. That region is now a 'battleground' for overseas methanol suppliers, and has typically been the first choice for US exporters. Meanwhile, Asia ex-China is the fastest growing region for methanol demand outside China, with biodiesel growth in Indonesia and Indian growth driven by chemical end-uses.

On the supply side, North America is increasingly a net exporter, and offers the best case for new capacity development over the next 4-5 years, including the Methanex Geismar 3 project and another 120,000 t/a at Fairway in 2024. The Middle East remains static as an exporter. New capacity in Iran has been limited by gas availability and high feedstock prices. Overall, 2023 represents something of a low point in industry operating rates, and these will need to increase as demand outstrips supply. New capacity could well be in China unless someone else steps up. As it is, the methanol price floor is set by the coal price, and the price ceiling by the marginal consumers, which are Chinese MTO plants. Coal prices in China are high and this has driven up pricing and led to some demand destruction. MTO capacity integrated with methanol production typically has much better operating rates than those depending on merchant market supply. China is still the main methanol importer, to the tune of around 12 million t/a.

Looking forward, there is the ongoing development of methanol as a marine fuel. However, in well to wheel carbon emission terms, gas-based methanol is still higher than very low sulphur fuel oil (VLSFO) and will need carbon capture or an e-methanol component to compete as a lower carbon fuel source.

Greg Dolan of the Methanol Institute said that the most recent trend in membership of the organisation has been companies involved in methanol shipping and green methanol production. The MI has completed a recent report with IREMA which suggests that the current methanol market of 85 million t/a could achieve 500% growth by 2050. There is still room for gas-based capacity out that far, but new capacity is and will increasingly becoming blue and green. Around 90 renewable methanol projects have already been announced, and while not all will come to fruition, this could represent 8 million t/a by 2027 of fairly firmly predicted capacity. Scale of green plants is increasing from 4-10,000 t/a to 50,100 or even 250,000 t/a, and development is moving from independent developers to major utility



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companies, and there is now interest from oil and gas majors. Much of the anticipated demand will come from the marine sector. Maersk's order of 19 large (16,000 TEU) methanol powered container ships in 2021 was a game changer in that regard, Greg said, representing 600,000 t/a of methanol demand. Maersk has been looking to strategic partnerships with biomethanol producers, and has already secured agreements for 800,000 t/a of supply. If it converted 25% of its fleet to methanol use, that would represent 6 million t/a of low carbon methanol demand by 2030. Methanol powered ships dominate the container fleet order book (around 62%), edging out LNG and fuel oil. Fuel injection systems can be retrofitted to existing engines, and engine development is largely complete. According to DNV, there were 26 methanol powered ships in 2023, but by 2028 this will be 128. ON an energy equivalent basis methanol is already cost competitive with LNG and VLSFO. It is also easily bunkered. On the road, Geely have sold 28,000 M100 cars in China and have introduced a methanol hybrid cars. They expect to supply 50,000 methanol trucks by 2026. China's road vehicles already consume 6.8 million t/a of methanol, as well as another 1.0 million t/a for cooking stoves. In that sense, Greg said, methanol is several years ahead of ammonia, another candidate for low carbon marine fuel, and has far fewer issues with safe handling and toxicity.

There was also an update by Lars Anderson of JM on the formaldehyde market, still one of the key derivatives for methanol. Estimated annual growth rates are still 3.0-3.5% year on year out to 2031, with China continuing to be responsible for half of global demand.

Methanol projects

Paul Bailey of Methanex described work on the Geismar 3 methanol project. Mechanical completion was achieved in early 2023, and electrical works to wire up the various components are now ongoing. There has been a strong focus on safety, with no lost time incidents in over 6.5 million work hours. The plant uses a JM autothermal reforming process. The feed is a hydrogen rich purge gas from Geismar plants 1 and 2, making it a kind of 'cheap combined reformer' setup, and the lowest carbon methanol currently available in North America.

Around 65% of global mega-projects tended to have overruns in either cost or schedule or both, he said. Geismar has had to deal with the covid pandemic, but forethought in the contracting structure allowed more flexibility to pause operations than would have been available with a lump sum turnkey contract. The project restarted in September 2021, and while it is obviously late due to covid, it is still trending to come in on-budget. Key to this has been good relations with contractors.

Michael Macdonald of HIF (Highly Innovative Fuels) gave an update on the various low carbon projects that his company is now working on. The company's original project was in Chile, aiming to monetise wind energy in the Punta Arenas region – a very windy part of Chile, where the turbines have a 75% uptime. But there are also projects in the US now, since the incentives in the Inflation Reduction Act have kickstarted many renewable projects. HIF is also developing facilities in Uruguay and Tasmania.

The Haru Oni demonstration plant in Chile began operation in December 2022 using JM methanol technology. Porsche has been a large investor and the plant converts methanol to gasoline as a drop in replacement fuel for fossil fuel gasoline which is carbon neutral as well as having no sulphur compounds. The MTG process is also more selective than rival methods such as Fischer Tropsch polymerisation. HIF believe that converting renewable hydrogen to gasoline offers the opportunity to decarbonise difficult sectors like aviation. They also aim to move to direct CO_2 capture from air in the longer term, and also have plans to potentially produce jet fuel via MTO followed by oligomerisation, hydrogenation and fractionation.

At Matagorda in Texas, 2GW of nuclear and wind power will be used to generate hydrogen for 4,000 t/d of methanol, which will then be used to produce gasoline. The process can operate flexibly between methanol and gasoline, allowing which stream is prioritised to be dependent on market conditions. The hydrogen block alone covers 30 acres and will be twice the size of the attendant methanol and MTG plants. The project is at the FEED stage, and construction is due to start in 2024 with a $6 billion price tag. Even so, e-gasoline will be delivered to California at prices cost competitive with fossil fuel gasoline, but at an 80% reduction in carbon intensity. The CO_2 source will come from CO_2 recovered from industrial generation in Texas.

Hakan Kihlberg of Perstorp described Project Air, a collaborative project with Uniper to develop a 200,000 t/a green methanol plant in Sweden. Perstorp has committed to reducing Scope 1 and 2 emissions by 46% in 2030 compared to a base year of 2019, but does not see that there is sufficient biomass available at a reasonable price to achieve this using bio-methanol. Hence it has focused on hydrogen electrolysis and e-methanol to feed its future sustainable downstream operations.

Operator experience

GPIC's Mousa Altairei reported on creep damage discovered in the reformer in Bahrain. Some 24 tubes had to be replaced after an inspection and an investigation was launched into why this was. Damage and blockage of the coffin box appeared to have restricted gas flow in the bottom of the reformer, exacerbated by burner degradation and deposit build up leading to fuel gas combustion taking place lower down the reformer.

Kerwyn Mahato and Garrett Ramjattan of PROMAN described a pipe rupture at a large scale methanol facility which caused damage to surrounding equipment and which could have led to injury or fatality if personnel had been in the vicinity. The failure resulted from high mechanical loads on a pipe elbow joint combined with manufacturing defects.

Methanol technology

Daniel Sheldon showcased JM's latest methanol flowsheets, which they call the Flexi Methanol and Precision Methanol processes. Flexi Methanol combines the combined reforming, series loop and radial steam raising converter to produce a flexible but efficient route from natural gas to methanol in a wide range of scenarios. Heat from the converter generates sufficient steam for the new lower steam: carbon ratio and a lower pressure drop, reducing capital cost. Precision Methanol uses autothermal reforming with axial steam raising converters to deliver a simple flowsheet with low equipment count without compromising on efficiency, ideally suited to gas feeds with low inert levels. JM now also offer Switch Methanol, where much of the energy demand can be switched from gas to electricity, potentially significantly lowering carbon intensity of production.

For e-methanol, other routes become available. JM's Connor Langland looked at using tube cooled converters in a green methanol plant. Designing a green methanol plant offers challenges and opportunities compared to a conventional plant. The lack of a reformer obviously lowers the capital cost (while increasing the feed cost), but it means any off-gases cannot be simply fed back into the reformer to destroy impurities. Using CO_2 as a source of carbon also means that the syngas has far less carbon monoxide. CO provides half of the reactor heat in a conventional remover. This lowers the heat reformer duty, but higher water formation means that a higher catalyst volume is required. This has led JM to a converter and loop design tailored for a CO_2 to methanol plant/ The circulation ratio now becomes the most important control parameter for reaction efficiency. A tube-cooled converter has lower power demand compared to an axial steam raising converter at such high flow rates.

Johnathan Mahabir of the University of the West Indies looked at ways of lowering carbon intensity of methanol production using a gas heated reformer. Modelling indicates that using a GHR can lead to 11% higher energy efficiency and 18% resource (feedstock) efficiency compared to ATR or SMR systems.

Iain Roberts of JM looked at ways of decarbonising methanol operations, including using JM's Switch Methanol flowsheet as described above, which can reduce emissions by 80%, as well as the Cleanpace flowsheet using carbon capture and storage to achieve up to 97% reductions in carbon intensity.

Giacomo Rispoli of MyRechemical looked at using gasified municipal waste as a feedstock for methanol production. MyRechemical's flowsheet captures excess CO_2 from methanol production for sequestration or utilisation.

Finally, Philip Lewis of ZEEP presented a slightly pessimistic view of the energy transition, considering the acreage of solar panels required to feed a world scale methanol plant and the increasing difficulty of gaining planning permission for them, and the slow pace of the planning process for carbon capture and storage projects.

Plant monitoring

TUV Rheinland Industrial Services showcased their array of plant monitoring and inspection services, including online nonintrusive inspection and condition monitoring, with reference to work conducted for MOL in Hungary. Reformer tubes, remain the Achilles heel of steam reformers, having to cope with the most strenuous operating conditions. The microstructure of the steel can change over operating lifetime, leaving tubes vulnerable to creep corrosion. Olivia Chung of Quest (formerly Quest Integrity) showed how the two are related and how accurate tube lifetimes can be calculated from metal microstructure measurements.

Catalysts

Unsurprisingly for a company that is a major catalyst manufacturer there was a session on new catalyst developments. JM's Pauline Glen looked at methanol synthesis catalysts, and the way in which the active copper sites were deactivated during operation via sintering. Zinc oxide and alumina are added to reduce this, but analysis of zinc oxide in spent catalysts shows that it too is subject to sintering. JM has now developed a catalyst formulation, KATALCO 51-102 which is doped with a silicon compound that reduces zinc sintering and hence preserves higher activity for longer.

John Brightling, meanwhile, looked at handling of nickel-based catalysts in a methanol plant. Nickel catalysts are used in hydrodesulphurisation pre-treating, as well as in the pre-reformer and reformers, but can lead to the generation of nickel dust, which is a potential respiratory tract carcinogen. This can be mitigated through catalyst structure and composition, better controls on loading and unloading, and better ventilation and atmospheric monitoring, as well as use of the correct personal protective equipment.

Digitisation

Three papers on digital advances closed out the conference on Wednesday. Liam Fleming of JM looked at optimisation of methanol plant operation using the increasing data streams available to plant operators. Jesus Rebordinos of Stamicarbon described operator training simulators and 'digital twin' plants, as well as newer technologies like virtual and augmented reality to improve plant operation. Daniel Sheldon of JM closed with a presentation of the JM-LEVO methanol portal; a new more efficient digital method of performance reporting and communicating with JM service engineers. ■

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Balancing cost and performance

Although the nitric acid industry has an extensive history dating back centuries, nitric acid production continues to be a dynamic process with bespoke system solutions necessary per plant rather than a one size fits all. **Kate Cardonne** of Johnson Matthey discusses strategies to balance the cost and performance in nitric acid production.

When looking at the economic challenges of nitric acid production, it is necessary to create a holistic picture of the factors feeding into the economic value of the catalyst. While one alloy may be favoured due to its extremely high conversion efficiency, it may be uneconomical due to the short lifespan of the catalyst or amount of metal lost over the course of the campaign[1]. These factors coupled with the everchanging platinum group metal (PGM) market conditions are key to determining the best bespoke solution for each plant based on their operating strategy.

When designing a plant, there is an upfront decision to be made regarding the range of operating pressure, which impacts the upfront capital expenditure. This choice is guided by the cost of feedstock and energy where the plant is being built. Medium and low-pressure plants are popular in regions like Europe where feedstock and energy prices are very high, as their design maximises yield and energy efficiency and thus minimises these raw material needs. The higher initial costs are acceptable as the plant's profitability will eventually offset and exceed the starting investment due to a greater production capacity and higher conversion efficiency while keeping operating costs low and requiring fewer changeouts. A high-pressure plant is advantageous in areas where feedstock and energy prices are low like North America because the raw material prices aren't as constraining on design, allowing for a simpler process design with lower associated upfront investment costs. The balance comes with more frequent operational costs; as high-pressure plants have a lower conversion efficiency and thus shorter gauze campaign lengths, there are smaller production totals per campaign and more frequent changeouts. The lower cost barrier to entry warrants an opportunity for high-pressure plants to become profitable quickly[2,3]. Once the decision regarding plant design is set, the resulting parameters influence the gauze catalyst design.

The fundamentals of catalyst design have not changed significantly in over 100 years, considering variables such as fluctuating precious metal prices, meaning that there is a deep understanding available when presented with these constraints to generate favourable design options. In parallel with these external factors, decisions to tailor catalyst design such as extending campaign length, improving efficiency, optimising installed PGM content or reducing N_2O emissions all present as potential solutions to these challenges.

Understanding reaction constraints

The production of nitric acid is intrinsically limited by the reaction kinetics of the ammonia oxidation process with three main products forming upon ammonia reacting with oxygen: nitric oxide (NO), nitrogen (N_2) and nitrous oxide (N_2O). Based on typical plant operating conditions of temperatures ranging from 850–930°C and pressure ranging from atmospheric to approximately 200 psi, selectivity to nitric oxide can be 90-97% (equations 1-3).

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad \Delta H^0 = -907.28\ \text{kJ} \qquad (1)$$

$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O \qquad \Delta H^0 = -1{,}104.9\ \text{kJ} \qquad (2)$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad \Delta H^0 = -1{,}269.0\ \text{kJ} \qquad (3)$$

The goal is to manipulate the operational conditions, as well as the catalyst design, to maximise the selectivity towards NO while minimising the unwanted byproducts. Depending on the reaction conditions, excess ammonia can further react with the nitric oxide and produce additional nitrogen and nitrous oxide, which reduces overall plant efficiency and increases environmental emissions.

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \qquad (4)$$

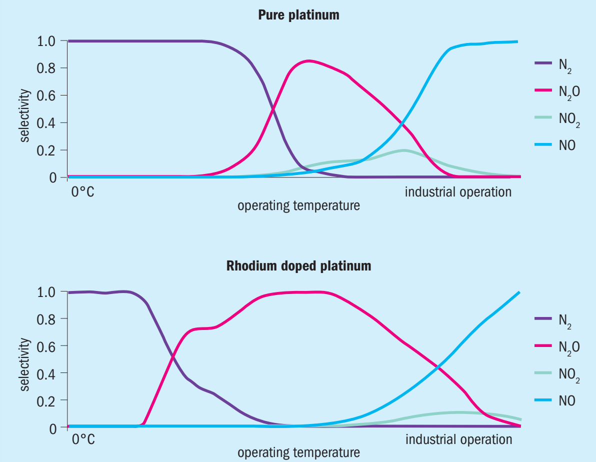
$$2NH_3 + 8NO \rightarrow 5N_2O + 3H_2O \qquad (5)$$

The selectivity weighs greatly on the selected alloy composition, with platinum-rhodium alloys regarded as the industry favoured class. Their combination of low in-situ metal loss and high conversion efficiency in comparison to pure platinum wires over the course of a standard campaign length allows the plant to run at a higher temperature taking advantage of the increase in selectivity to nitric oxide[4,5] (Fig. 1). By further investing in the design of the catalyst pack through wire diameter and gauze layer arrangement, the catalyst design can be tailored to achieve even higher production numbers.

Catalyst design

When considering any changes to a gauze design, a fundamental understanding of the metal utilisation and movement within the pack is essential. The top section of the gauze is the location of primary interaction between the ammonia feed and the catalyst. Based on the reaction selectivity, nitric oxide is favoured by a short reaction path through the gauze pack; therefore, it is ideal for the majority of the ammonia to react within the first few layers of the pack[4]. Excess ammonia deeper in the pack can result in further formation of unwanted byproducts, nitrogen and nitrous oxide. By reacting as much ammonia as possible towards the top of the catalyst pack, there is limited opportunity for byproduct production through direct ammonia oxidation or through the reaction of ammonia with nitric oxide (equations 4 and 5)[5]. These byproducts not only reduce overall plant efficiency, but N_2O has the added impact of potentially breaching emissions legislation, both very costly outcomes.

Fig. 1: **Selectivity trends for ammonia oxidation on pure platinum (top) and rhodium doped platinum (bottom) generated by ab-inito kinetic modelling at 1 bara[3]**



Source: Johnson Matthey

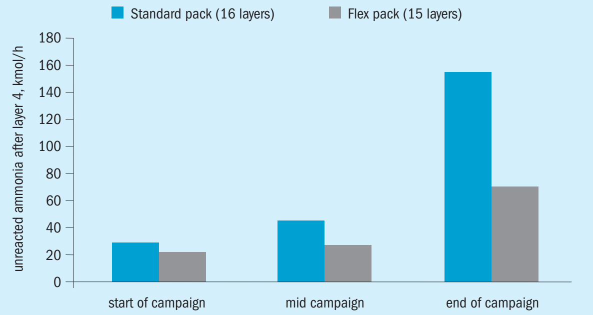
When the gauze is installed, the PGM wire surface restructures and forms cauliflower structures, which greatly increase the catalyst surface available for ammonia oxidation. The additional surface area from the cauliflower formation allows for a high conversion efficiency at the start of the campaign. As these cauliflowers begin to break off, the conversion efficiency decreases and signals the near end of the campaign. The reaction then continues to travel further down the pack, so several catalyst layers are specifically left at the bottom of the pack to react with the ammonia passing through[5]. Because of the overall gauze performance, campaign lengths can be extended where maintenance schedules allow[5,6]. There is an essential balance when designing a catalyst pack between installing too few layers, allowing for ammonia slip, and installing too many layers, resulting in a very heavy pack that increases selectivity towards further NO reduction and byproduct formation (equations 4 and 5).

Based on this knowledge, Johnson Matthey has created a "flex pack" catalyst design in which the top 25-30% of the gauze pack is changed to a thicker wire, but the overall nominal weight is maintained. This thicker wire diameter acts as an increased concentration of PGM at the top of the pack where the bulk of the reaction is occurring, thus increasing the initial number of active catalytic sites[2,5]. This design allows for increased conversion efficiency and/or longer campaign lengths, with some lower layers left in the bottom of the pack to minimise ammonia slip. The thicker wire also aids in the overall goal to design for no ammonia slip through the catalyst during normal operation. In comparison to a standard pack, there is a significant increase in ammonia conversion in the top few layers of the pack (Fig. 2)[4]. Redistributing the catalyst weight in a gauze pack allows excess layers towards the bottom to be removed, yielding the additional economic benefit of either maintaining or reducing the amount of precious metal required, as well as decreasing process related metal losses[5,7].

Campaign lengths

Extending campaign lengths is a goal of many producers due to the associated increase in yield and decrease in production cost. Nitric acid plants tend to land in one of two categories for determining their campaign length: either campaign lengths are predetermined based on a maintenance schedule or plants have no set date for changeout in place. Instead, these plants opt to monitor their conversion efficiency with the goal to run for as long as effectively possible based on their plant-specific threshold[3]. In areas where ammonia feedstock costs are low, the plant can run at a lower efficiency than plants running in areas where feedstock prices are significantly higher. Overall, the industry tends to favour main-

Fig. 2: **Level of unreacted ammonia after the top 4 gauze layers[6]**



Source: Johnson Matthey

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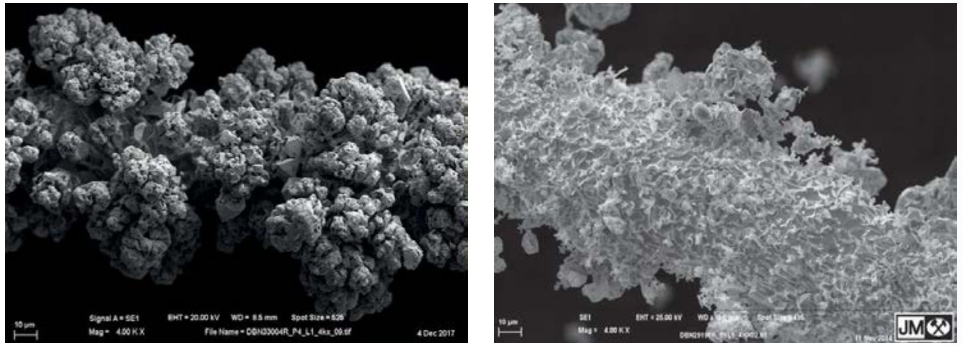


PHOTOS: JOHNSON MATTHEY

Fig. 3: Levels of cauliflowers anticipated in well-run campaign (left) and wire surface showing loss of cauliflower structures after an unexpected plant trip (right)[6]

tenance shutdown campaigns, as they limit any unplanned decrease in process yield or increased metal loss.

Maximum campaign lengths have continued to increase throughout the years with innovations in gauze design, now generally sitting at approximately 90-120 days for high-pressure plants and up to one year for medium-pressure plants before the catalyst needs to be changed out based on performance[5]. The longer a gauze campaign can be extended, the less often the investment of a new gauze needs to be made; therefore, the economic benefit of high-pressure plants transitioning from running four 90-day campaigns per year to three 120-day campaigns is apparent.

Metal losses

Metal losses place a constraint on the campaign length, as plant efficiency notably drops once over 50% of the PGM is lost and consequently warrants a changeout[5]. The addition of rhodium will reduce the overall metal loss from the pack, as these alloys see a reduction in platinum volatility compared to pure platinum (Fig. 1)[5,7]. During a standard gauze campaign, the wire surface restructures to form high surface area growths, referred to as 'cauliflowers', which are beneficial in that they yield high selectivity to NO, but also result in PGM, particularly platinum in oxide form, to be lost to the gas stream. This standard rate of metal loss is only expedited by increases in pressure and nitrogen loading.

Thicker wire

Thicker wire diameters have also been noted to benefit plants that experience a high number of shutdowns or trips throughout their campaign. During a plant trip on a typical gauze with standard wire diameter, the cauliflower structures can be damaged and break off, eliminating the additional surface area that maintains the acceptable conversion efficiency and thus adds to the campaign length (Fig. 3). With the thicker wire, the additional density of PGM on the wire surface allows for the wire to restructure the cauliflowers again after the initial ones are lost, therefore maintaining campaign lengths following shutdowns[6].

N_2O abatement

As previously stated, within the nitric acid production process, there is potential for side reactions to occur based on selectivity in which byproducts form. The one of primary concern for the nitric acid industry is nitrous oxide (N_2O). This greenhouse gas has a global warming potential in the region of 300 times that of carbon dioxide due to its long atmospheric lifetime, posing an environmental threat and also decreasing production yields[8,9]. While government sanctioned emissions limits have been set in certain parts of the world like Europe and Asia, there has been a noticeable trend in an increased sense of corporate responsibility, with companies looking to voluntarily reduce their emissions. Either way, reducing these kinds of emissions is only gaining more traction on the global stage with the heightened awareness of climate change.

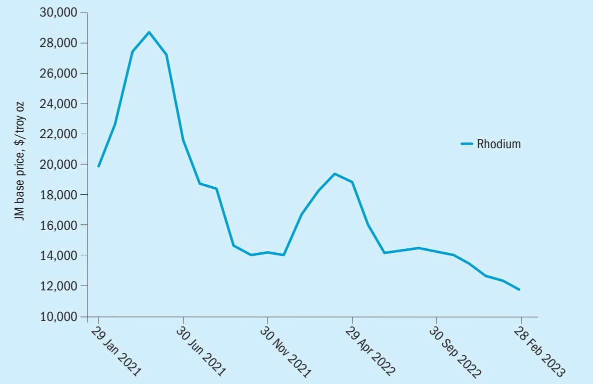
Reducing N_2O within the catalyst pack can be done with either of two main strategies: suppressing N_2O generating side reactions from the start or increasing the amount of N_2O decomposition. Based on catalyst design, the first method has already been addressed as the optimum catalyst design will have heightened selectivity for NO and create as little byproduct as possible. Primary abatement reduces the amount of N_2O formed within the gauze pack during the ammonia oxidation step[8]. Methods of N_2O decomposition are more popular solutions due to their overall effectiveness, lower cost and easier installation process, with the other methods referring to different points in the nitric acid process where the N_2O is destroyed.

Secondary abatement

Secondary abatement utilises a catalyst product to decompose N_2O immediately below the gauze just after it has been formed. While the gauze sits as close to the gas entry point as possible within the basket, the abatement catalyst sits directly below the gauze near the gas exit point; this allows for increased residence time of the gas in the burner and thus increased time for the N_2O decomposition reaction to occur[8]. Any uncertainty surrounding secondary abatement tends to be around the associated pressure drop that comes with replacing the standard supports with catalyst, which can be vetted for its impact on production on an individual plant basis to determine their pressure drop tolerance.

Johnson Matthey markets a Yara catalyst product for secondary abatement, YARA 58-Y1, which consists of pelleted active cobalt aluminate supported on a cerium oxide substrate. Secondary abatement is considered the most cost-effective method of N_2O abatement, as there is typically no major modification of the reactor required. Therefore, the catalyst can be readily placed in the basket with low to no capital expenditure. The installation of this catalyst has shown no effect on ammonia conversion while also potentially providing up to 90% N_2O abatement emission reduction[8]. This significant savings brings the opportunity to obtain GHG emission credits under the Climate Action Reserve programme.

Fig. 4: **Rhodium base price 3-year history**[10]



The Johnson Matthey base prices are the company's quoted offer prices for customers of wholesale quantities of platinum group metals set by trading desks in the USA, Hong Kong and the UK.

Source: Johnson Matthey

Tertiary abatement

Tertiary abatement is considered a reduction process in which the N_2O is removed from the tail gas in a separately installed catalytic reactor located after the absorption column.

Although a tertiary option could yield abatement levels as high as 98%, the cost associated with creating and installing the new vessel is much higher than other abatement options. Tertiary systems typically require plants to increase their stack gas temperatures after the absorption step in order to guarantee appropriate burn off of N_2O emissions and reach expected abatement levels. The degree to which these gases can be reheated could be a limiting factor. While all nitric acid plants should have a tail gas heater, depending on its design, age and size, the necessary reheat temperature for desired abatement may not be achievable[2,8].

Case study: rhodium pricing

Platinum is the key element in nitric acid gauzes due to its ability to withstand operating conditions and remain in its metallic form. Although the platinum-rhodium alloys performed well and satisfied production needs, their overall economic benefit came into question with the surging rhodium prices over the last three years, particularly in the spring of 2021 (Fig. 4). With rhodium prices rising above $25,000 per troy ounce in spring 2021 and peaking just under $29,000 per troy ounce in April 2021, metal pricing greatly impacted the operational spend for precious metal gauze users and will continue to do so[10].

The dynamic PGM market with its changing prices is an economic factor influencing the pack design selected. The changing PGM prices for some nitric acid plants create difficulty when trying to balance contributing factors such as cost and conversion efficiency.

Nitric acid plants have manipulated their designs to maximise either production efficiency or campaign length while minimising the amount of rhodium required in their gauzes, as even a small reduction in the amount of rhodium required can greatly reduce the cost of the total pack and thus reduce the cost of nitric acid production[4]. Two of the key factors impacting the optimisation of catalyst design are burner efficiency and metal loss rate. A range of 0-5% rhodium within the alloy has been identified as the most effective alloy class that balances these variables[2]. Shifting from 5% to 3% rhodium in the alloy allows for cost savings via a reduction in installed PGM value[11]. This option was deemed popular with higher pressure plants (>100 psig) as well as plants running at lower temperatures, which are highly susceptible to rhodium oxide poisoning[5,11].

Conclusion

The key to a high achieving nitric acid plant is balancing performance goals with economic constraints. The optimal gauze design not only considers alloy selections and catalyst distribution throughout the pack, but also the plant's operating strategy and external economic pressures like the PGM market and ammonia cost. ■

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Future-proofing nitric acid plants

Paz Muñoz and **Carmen Perez** of Stamicarbon discuss the strategic selection of future-proof technology for nitric acid plants. To produce nitric acid in a feasible and sustainable way, manufacturers must carefully choose the right technology and consider the capex and opex involved in the production process to ensure long-term profitability.

The continuous increase in the world's population results in rising global food demand. Furthermore, production processes need to be optimised to combat the effects of climate change, with the shift towards more productive agriculture and fossil-free feedstock alternatives.

Major players in the fertilizer industry worldwide are taking steps towards reducing the carbon footprint of fertilizer production. Using renewable energy to produce ammonia paves the way for green fertilizers, including nitric acid, leading to a higher independence from gas production and a more stable market.

Green fertilizer production will become a more prominent theme in the industry, together with maximising the energy recovery of nitric acid plants, and Stamicarbon, nitrogen technology licensor of Maire Group, already plays a role in facilitating this transition. In addition, there is a trend to move towards small-scale production. Producers are striving to decentralise and minimise the need of external resources.

Stami Nitric Acid technology

Stamicarbon's nitric acid technology uses the Ostwald process, where ammonia is converted to nitric acid in two main steps, relying on either mono- or dual-pressure design:

- the oxidation of ammonia (NH_3) to form nitric oxide (NO), which is further oxidised to nitrogen dioxide (NO_2);
- The absorption of the nitrogen dioxide (NO_2) in water (H_2O) to form nitric acid (HNO_3).

One of the key advantages of Stamicarbon's nitric acid technology is its high energy efficiency. The process is designed to minimise heat losses and maximise the recovery of heat from the process streams. This decreases the internal consumption of steam and lowers the operational costs. In addition, Stamicarbon's technology can be combined with co-generation systems to produce electricity.

Stamicarbon's nitric acid technology is also designed with environmental concerns in mind. The technology incorporates measures to minimise emissions of greenhouse gases and other pollutants. The use of modern abatement technology allows for the reduction of nitrogen oxides and nitrous oxide, which can be reduced to almost zero, disposing an environmentally safe tail gas to the atmosphere.

Stamicarbon's expertise in nitric acid technology allows it to provide customised solutions to meet specific customer needs and challenges, ensuring nitric acid production with long-term success and profitability.

In the mono-pressure process (see Fig. 1), oxidation and absorption sections operate at the same pressure level. Different pressure levels are used for the oxidation and absorption sections in the dual-pressure process (see Fig. 2). The oxidation section is operated at pressures between 4 and 6 bar(a), while the absorption section operates between 8 and 12 bar(a), combining the advantages of medium-pressure combustion with the efficiency of high-pressure absorption.

The main characteristic of both processes is a specific heat exchanger network downstream of ammonia oxidation. This configuration has several advantages. On the one hand, the heat exchanging network has specific process conditions selected to prevent corrosion and ensure that no proprietary materials are required for equipment manufacturing. On the other hand, the placement of the third tail gas heater in the ammonia burner vessel, closer to the platinum (Pt) gauzes, enables a tail gas temperature of 480°C to be achieved, which has several advantages:

- the operation of the tertiary abatement system with no addition of a reducing agent (like natural gas) for the nitrous oxide (N_2O) decomposition;
- higher power generation in the expansion turbine, leading to lower steam consumption of the compressor train and higher steam export;
- extra heat recovery step before releasing the tail gas into the atmosphere;
- reduced area required for the heat exchanging section.

Capex and opex analysis

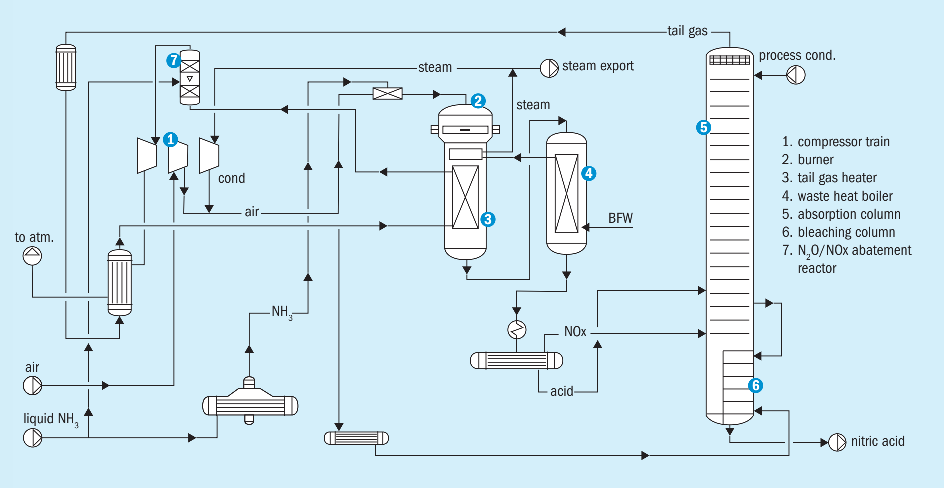
Capital expenditure (capex) and operational expenditure (opex) are important considerations when designing, building, and operating a nitric acid plant. Capex refers to the initial investment or the cost of building a new nitric acid plant or expanding an existing one. This includes the cost of equipment, materials, and labour required to construct the plant. Capex can vary based on the size of the plant, the complexity of the production process, and the location of the facility. Building a large, advanced nitric acid plant can require significant capital investment, while expanding an existing plant may involve less capital expenditure.

Opex refers to the ongoing costs of running the nitric acid plant. This includes the cost of raw materials, energy, maintenance, and labour required for the ongoing production process. Opex costs can vary based on the operational efficiency of the plant, output volume, and regional factors like energy costs and regulations.

Overall, capex and opex are key metrics that must be carefully managed to ensure profitability in the nitric acid industry. Manufacturers can increase their profit margins and remain competitive in the global market by reducing capex and optimising opex.

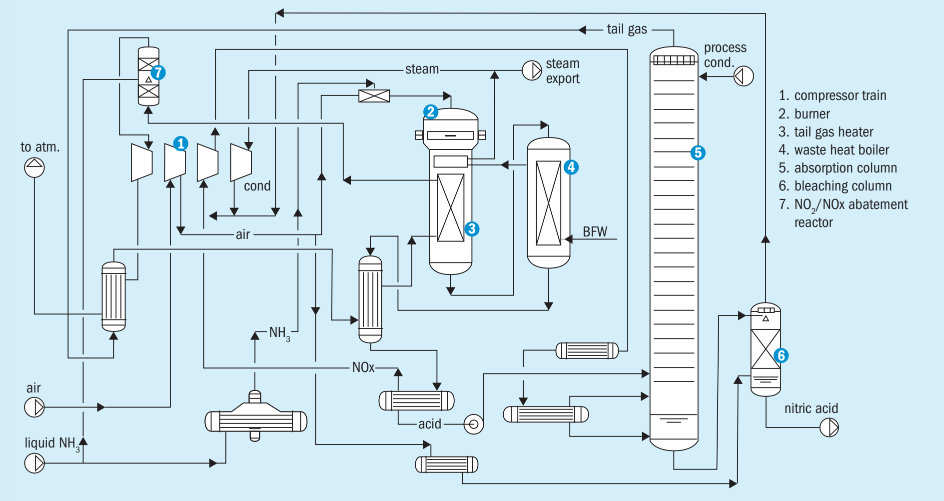
Stamicarbon is able to advise producers on the best technology to select based on specific plant requirements and plant capacity. The choice of nitric acid technology and the careful management of capex

Fig. 1: **Stamicarbon's mono-pressure nitric acid process**



Source: Stamicarbon

Fig. 2: **Stamicarbon's dual-pressure nitric acid process**



Source: Stamicarbon

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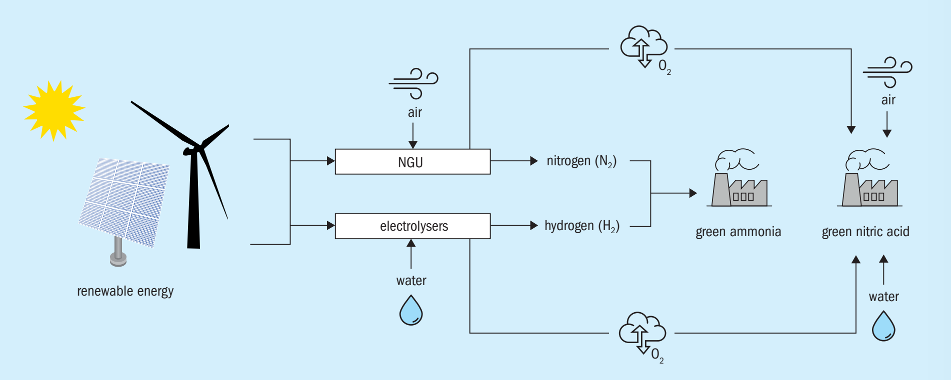
Fig. 3: **Integration of green ammonia and nitric acid technologies**



Source: Stamicarbon

and opex are critical factors in the success and profitability of production. Similarly, when considering opex, Stamicarbon's nitric acid technology offers a range of options to reduce operational expenses, especially by maximising steam export.

The simplicity of the compressor train in a mono-pressure plant and the reduced number of equipment items make the mono-pressure technology more competitive from a capex point of view. However, operating the process at constant pressure compromises the process efficiency. The oxidation of NH_3 to NO on Pt gauzes is more efficient when operating at a lower pressure, while the absorption column is more effective when operating at higher pressure. The use of dual-pressure technology overcomes this challenge since both sections are able to operate at a more optimal pressure, increasing the process efficiency and reducing the total operational costs. However, the compressor train design is more complex, and more items of equipment are required, especially extra heat exchangers, to eliminate the extra compression heat.

Based on these considerations, mono-pressure technology is advised for low plant capacities, while dual-pressure is mostly used for higher plant capacities. It is well known that the threshold for this selection is usually around 400-600 t/d (100% HNO_3). However, producers tend to hesitate on which technology to select when their target production capacity belongs to this range. There is no universal answer to this question since local energy costs and regulations have a strong impact during the plant's lifetime.

Case study

Stamicarbon together with Ballestra S.p.A performed an analysis for a nitric acid plant in Western Asia with a capacity of 450 t/d operating with Stamicarbon's technology. For this capacity, capital and operational expenditures have been studied for both technologies, mono- and dual-pressure, in order to provide a better overview to the customer and help them with their final decision.

The calculations estimated that a dual-pressure plant requires around 25% higher capital expenditure than a mono-pressure plant.

To estimate the operational expenditures of the plants, the following parameters have been considered:

- total NH_3 consumption;
- demin water consumption;
- cooling water consumption;
- demin water consumption;
- steam export HP;
- steam consumption LP;
- electricity consumption;
- precious metal losses.

Other operational expenditures like labour required to operate the plants are considered to be similar for both technologies and not relevant in the comparison. There is an operational cost difference of approx. 1.2m $/year between operating a mono- or a dual-pressure plant. For this specific case, the nitric acid producer could recover the extra cost paid for installing dual-pressure technology in nine years.

Technology integration in a fertilizer complex

Having a whole portfolio of technologies from green ammonia to ammonium nitrate allows Stamicarbon to improve its integration between plants and consequently optimise different technologies to make the full complex more attractive from an economic point of view.

Stamicarbon is integrating Stami Nitric Acid with Stami Green Ammonia in a green fertilizer complex, as already designed for projects in South America and Africa (see Fig. 3).

The innovative process to integrate the production of green ammonia and nitric acid allows the use of pure O_2 in the nitric acid plant (Fig. 4). This reduces the volume of air needed to oxidise ammonia in the first step of nitric acid production. In turn, this can be translated into an increase in steam export and a reduction of the total amount of tail gas released to the atmosphere. As a result, the compressor train and the tail gas treatment section can be downsized and, subsequently, the capex of the plant can be reduced.

This optimised process has several advantages over the conventional method:

- Reduced emissions by recirculating a portion of the tail gas: Even without the change in NOx concentration in the off-gas after treatment, the total amount of pollutants emitted will be lower, reducing the total flow of NOx and N_2O sent to the environment by about 40%.
- Lower catalyst demand due to a lower flow rate through the abatement system: Even at a constant target concentration of NOx and N_2O, the cross-section and reactor height will be downsized, reducing the total volume of the catalyst by up to 40%.
- More positive power balance, therefore steam export increases by more than 30%.
- Less ammonia consumed by the NOx abatement system.
- Conversion increase potential by looping NOx gases back into the reaction (into the burner, bleacher, or both).

These advantages of integrating the oxygen stream into the standard technology (mono- or dual-pressure) can be translated into a reduction of capex and opex.

Regarding opex, it is important to consider the increase in steam export and the reduction of N_2O emissions, since the N_2O can be translated into CO_2 equivalents, converted into savings of operational cost.

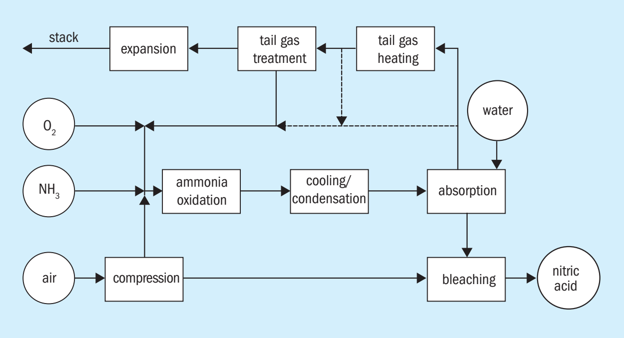
Based on the local prices and considering only the increase in steam export, the cost reduction is higher than 5 $/t of nitric acid, compared to the conventional mono-pressure concept. This is equivalent to more than one million USD per year of savings for a plant of 450 t/d.

Besides, carbon taxes and/or even carbon capture benefits are being implemented in an increasing number of locations around the globe. If this reduction is considered and the N_2O sent to the atmosphere is converted into CO_2 equivalents, by implementing the integrated concept with oxygen addition, the cost reduction might be higher than 1% of the total operational costs when considering a capacity of 450 t/d. It is important to be aware that this tax is being applied in more and more locations and it is continuously being increased over the years, which implies a more significant reduction of operational costs in the upcoming future.

The following advantages refer to capital costs of the oxygen integration concept over the conventional mono-pressure technology. These advantages are not quantified in terms of capex savings.

- Regarding the absorption column there would be a reduction in height due to the higher oxygen content in the stream, while maintaining the diameter as in the conventional concept.
- The air compressor needed requires about 50% less power than in the standard concept.
- The tail gas expander could be smaller since the flow of tail gas that is sent to the stack is reduced by more than 40%.
- The size of the tertiary abatement reactor is reduced in the oxygen integration concept since there is less tail gas to be treated, which involves a reduction of the catalyst volume for the N_2O and NOx removal beds of about 40%.

Fig. 4: **Oxygen integration in nitric acid technology**



Source: Stamicarbon

> **Capex and opex are key metrics that must be carefully managed to ensure profitability in the nitric acid industry.**

Alongside this reduction of capital costs, there is an additional component that needs to be added to the capital costs of the oxygen integration concept in the case of mono-pressure technology: a small compressor to overcome the pressure drop in the tail gas to be recirculated is needed.

By implementing the O_2 integration concept, not only is it possible to provide a use for the O_2, usually considered a side product and vented to the atmosphere, it also provides a significant reduction in capital cost compared to a standard mono-pressure technology, while reducing the operational costs as well.

Most of the integrations of green ammonia and nitric acid are done in order to produce green nitrates or UAN as a final product. Several synergies can also be found in the waste streams of some processes, such as urea or AN production, that might be used as feed streams in other plants. Integration is also important in the utilities network to match the balances of steam and cooling water.

The road ahead – digitalisation

The biggest challenges to optimising the operation of a plant are maximising the capacity, bringing it to its best point of steady production and at the same time reducing the plant downtime aiming to improve margins. Besides these challenges, the world is committed to building a greener, better world in the upcoming years. Digital tools provide solutions to increase plant efficiency and reduce total operational costs by allowing users to control and optimise their processes and systems through well-trained and well-informed personnel. This will enable the producers to reduce waste, save energy and produce fertilizers in a safe, cost-effective, profitable and sustainable way.

Stamicarbon is now offering the Operator Training Simulator and the Process Monitor as part of grass root projects and for existing plants. While the Training Simulator focuses on well-trained operators and engineers, the Stami Digital Process Monitor provides operators, engineers, and management with real-time insight into their plant performance. These solutions are available for all the products in Stamicarbon's portfolio, including the nitric acid technology. ■

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A new adsorptive CO_2 removal process

Linde has developed a new adsorptive carbon dioxide removal process, called HISORP® CC, including but not limited to blue ammonia production. Based on a combination of mature technologies the process overcomes the drawbacks of traditional CO_2 removal techniques and provides a carbon capture rate of greater than 99%. **Thomas Ried** discusses the pros and cons of different process configurations for CO_2 removal and the benefits of the new technology.

To slow down or even limit global warming requires a significant reduction in greenhouse gas emissions within the next decades. Global ammonia production contributes to approx. 2% of the total carbon dioxide emissions worldwide, so this industry has a significant potential to reduce global greenhouse gas emissions. The highest carbon dioxide reduction is achieved by producing green ammonia with 100% renewable power. However, green ammonia still faces challenges, e.g., cost and availability of green power. An alternative solution for the short and medium term, transitional phase is blue ammonia, which is still produced from fossil feedstock, but with significantly reduced carbon dioxide emissions. These emissions are avoided by capturing and sequestration or utilisation of the generated carbon dioxide.

CO_2 removal processes

Carbon dioxide can be removed by applying absorption, adsorption, condensation, or membrane processes. Each of the different carbon dioxide removal techniques has its advantages and disadvantages.

Absorption: The most popular absorption processes are amine-based washing or Rectisol units. Absorption processes can remove carbon dioxide selectively, which results in a high carbon dioxide concentration. One of the major drawbacks of these processes is the thermal energy requirement for regeneration of the washing agent. In large industrial plants, steam is usually used for the regeneration. Steam is typically produced by firing fossil fuels, which will cause additional carbon dioxide emissions. Moreover, the purified gas and also the carbon dioxide is either saturated with water or methanol and carbon dioxide is recovered at low pressure. Consequently, carbon dioxide needs to be dried and compressed or liquefied for transportation.

Adsorption: Carbon dioxide removal by adsorption can be done by pressure swing adsorption (PSA) or temperature swing adsorption (TSA). For bulk removal and in particular if the feed is provided at higher pressure (larger than 7 bar), PSA units are superior. The big advantage of adsorption processes is that no consumption, handling, and disposal of chemicals is required. Additionally for PSA units, no thermal energy is needed, adsorption units are very flexible and simple to operate. Moreover, they can easily be skid-mounted and prefabricated. This minimises construction costs and reduces the uncertainties of a stick-built unit at the construction side. The major drawback is the lower achievable carbon dioxide purity. As the adsorption is less selective than absorption, the carbon dioxide will always be contaminated with other components like hydrogen, water, carbon monoxide, nitrogen, or methane. Similar to the absorption processes, the carbon dioxide is recovered at low pressure.

Condensation: As carbon dioxide removal by condensation is operated at temperatures below 0°C, the gas needs to be dried upstream. Otherwise freezing of water and hence blocking of valves, piping and heat exchanger passages may occur.

Additionally, cooling and condensing the gas requires significant refrigeration capacity, which requires large machines. Advantageous is the high achievable carbon dioxide purity.

Membrane: A membrane separates components with a thin, semipermeable barrier on the basis of different permeate velocities. Some components, e.g., hydrogen, pass through the membrane quickly, while others, like hydrocarbons, require more time. Membranes are cost-efficient units, which need no regeneration; however, additional machinery might be required as they demand a certain pressure ratio of feed to permeate. Similar to a PSA, the carbon dioxide cannot be recovered with high purity.

To overcome the drawbacks of these processes, different carbon dioxide removal/purification techniques have to be combined to produce carbon dioxide with the requested purity.

HISORP® CC

Linde has developed an adsorptive carbon dioxide removal process, called HISORP® CC. It is a highly flexible, hybrid solution combining mature, proven Linde inhouse technologies, consisting of pressure swing adsorption (PSA) for carbon dioxide enrichment, gas dehydration, for example by temperature swing adsorption (TSA), gas compression by multistage turbo compressors and a cryogenic purification unit.

Following the Linde Ammonia Concept (LAC™), ammonia is produced from pure hydrogen and nitrogen. To decarbonise the hydrogen production, the carbon dioxide removal can either be placed in the syngas, after the carbon monoxide shift converter, in the hydrogen PSA tail gas, or in the flue gas.

If HISORP® CC is placed in the syngas, the lowest specific energy demand per tonne of removed carbon dioxide can be achieved. The highest carbon capture rates (>99%) can be realised by carbon dioxide removal from the hydrogen PSA tail gas or from the flue gas and provide the optimum solutions to retrofit existing plants.

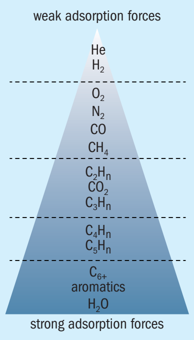
FUNDAMENTALS OF ADSORPTION

Adsorption is the attachment of a molecule from the gas or liquid phase to a solid surface (the adsorbent). During adsorption, energy will be released in form of heat. The energy is called adsorption enthalpy and serves as an indication for the adsorption forces. Fig. 1 shows a ranking of adsorption forces for different components for technically applied adsorbents. It illustrates that adsorption can be applied for the purification of hydrogen since hydrogen is hardly adsorbed.

Moreover, it shows that carbon dioxide has medium adsorption forces and so it can easily be separated from hydrogen, oxygen, nitrogen, carbon monoxide and methane. Water has even higher adsorption forces than carbon dioxide, that is why carbon dioxide and water can only be separated together from hydrogen, nitrogen, etc. in one stage.

As adsorption is a batch process, at least two adsorbers are required to establish a quasi-continuous process. One adsorber is in the adsorption mode, while the other adsorber is in the regeneration mode. The method of regeneration provides the most popular basis to classify adsorption processes. Pressure swing and temperature swing adsorption units are widely applied. ■

Fig. 1: **Adsorption forces of different components**



Source: Linde

Depending on the product requirements, the carbon dioxide can be delivered in liquid state or be compressed above supercritical pressure. Decarbonisation of the nitrogen generation as well as the ammonia synthesis can be performed by switching from conventional power supply to renewable power.

LAC with SMR and HISORP® CC

In a conventional hydrogen production plant based on steam methane reforming (SMR), there are several potential locations for carbon dioxide removal.

Fig. 2 indicates three different locations for carbon dioxide removal.

Option 1: Carbon dioxide can be removed from the syngas downstream of the carbon monoxide shift converter. To enhance hydrogen production, the equilibrium of the water-gas shift reaction should be shifted towards hydrogen as much as possible. Therefore, a two-stage shift with high and low temperature, or an isothermal shift is proposed. Depending on the feedstock and the process conditions, the carbon dioxide content at this location varies between approx. 15 and 25 mol-%. Even if the total carbon dioxide amount is removed from the shifted syngas, the carbon footprint of the total hydrogen production can only be reduced by 60-75%. The rest of the carbon dioxide is still emitted via the flue gas from the burners. The carbon dioxide content in the flue gas can be further reduced by using carbon free fuels, e.g., hydrogen. As the syngas is at elevated pressure, the specific energy demand per tonne of removed carbon dioxide is lowest of all three options. The HISORP® CC unit will be designed with minimal pressure drop, e.g., 500 mbar and without hydrogen loss.

Option 2: In the second option, HISORP® CC is applied in the hydrogen PSA tail gas. The carbon dioxide content in the tail gas varies between 38 to 60 mol-%. The large range is due to the influence of the feedstock, the process conditions, and the PSA recovery rate. The carbon capture rate is similar to option 1. However, the overall carbon capture rate can be increased far above 90%, even as high as 99%, if the carbon dioxide depleted tail gas is recycled to the reformer as feed and if the fossil fuel of the burner is substituted by e.g., hydrogen or carbon dioxide depleted syngas. As a result, the flue gas is almost free of carbon dioxide. The total recycle is possible as methane and carbon monoxide are converted to hydrogen and no removal for trace impurities like nitrogen is required. The nitrogen can leave the hydrogen production via the purified hydrogen. The recycle will increase the size of the syngas production plant.

Option 2 has a slightly higher specific energy demand to remove the carbon dioxide compared to option 1. However, much higher carbon capture rates can be achieved with the tail gas recycle. Alternatively, the carbon dioxide depleted tail gas can be routed to a second hydrogen PSA to recover additional hydrogen. As a result, either the feed consumption can be reduced, or the overall hydrogen production can be increased. If the ammonia loop and also the ASU have some spare capacity, even the ammonia production can be enhanced. Option 2 represents a good solution for the retrofit of existing hydrogen plants as only minor changes like adjusting the burners for carbon dioxide depleted tail gas, are required. The specific energy demand of the second option is slightly higher than for the first option, as the hydrogen PSA tail gas has low pressure and thus compression is required.

Option 3: The third option is the removal of carbon dioxide form the flue gas which has a carbon dioxide content of 15 to 22 mol-%.

As the flue gas is emitted at atmospheric pressure, gas compression is required. Due to large flue gas streams and the low pressure, the compression is very energy intensive. As a consequence, this option requires the highest specific energy demand per tonne of removed carbon dioxide. To optimise the opex, the pressurised and carbon dioxide depleted flue gas can be sent to an expansion turbine. With the additional machinery at least a portion of the electrical energy can be regained. The carbon dioxide enrichment within the HISORP® CC process can be done either by pressure swing or by vacuum swing adsorption. The vacuum enhances the desorption and thus increases the recovery rate and the capacity of the PSA.

The big advantage of post carbon capture is the high carbon capture rate >99% and that no modification of an existing plant is required. Thus, making it the optimum retrofit solution. As almost all

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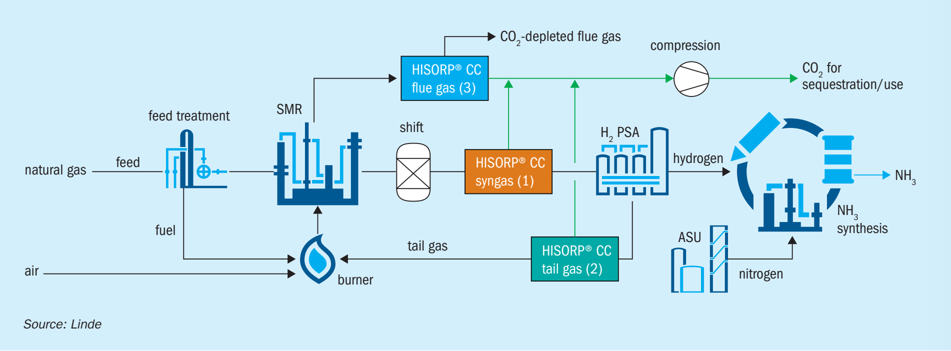
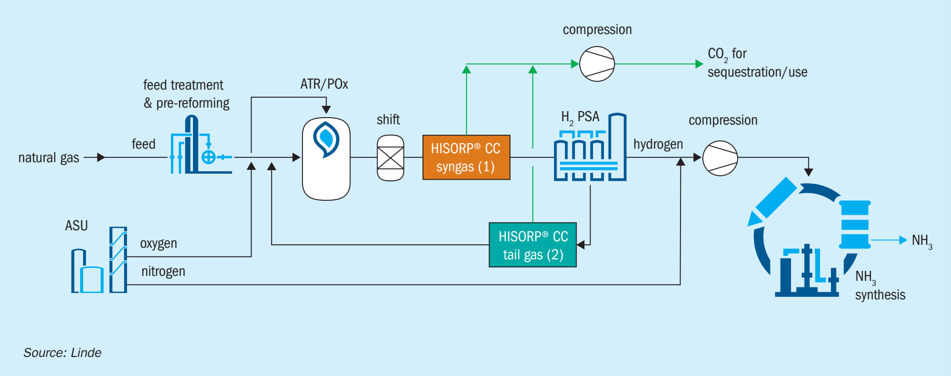
Fig. 2: **Block flow diagram of the LAC™ with SMR and carbon dioxide removal by HISORP® CC**



Source: Linde

Fig. 3: **Block flow diagram of the LAC™ with ATR or POx and carbon dioxide removal by HISORP® CC**



Source: Linde

carbon atoms from the feed and fuel end up in the flue gas as carbon dioxide, the achievable carbon capture rate is maximum for this option. Unlike absorption processes, HISORP® CC has no sensitivity to oxygen, which is a strong benefit for the flue gas application compared to alternative processes. HISORP® CC can also be implemented in other industries to recover carbon dioxide from the flue gas, e.g., from cement, lime, or steel plants.

With all three options the carbon dioxide at the outlet of HISORP® CC is dry and at a pressure of approx. 7 bar(a), unlike absorptions processes, which is sent a real benefit when the carbon dioxide has to be compressed to supercritical pressure for transportation and sequestration. For the compression an integrally geared turbo compressor can be applied. As the carbon dioxide is dry, no knock-out drums after the interstage coolers are required. Moreover, the material selection for this compressor is less challenging than for the compression of wet carbon dioxide.

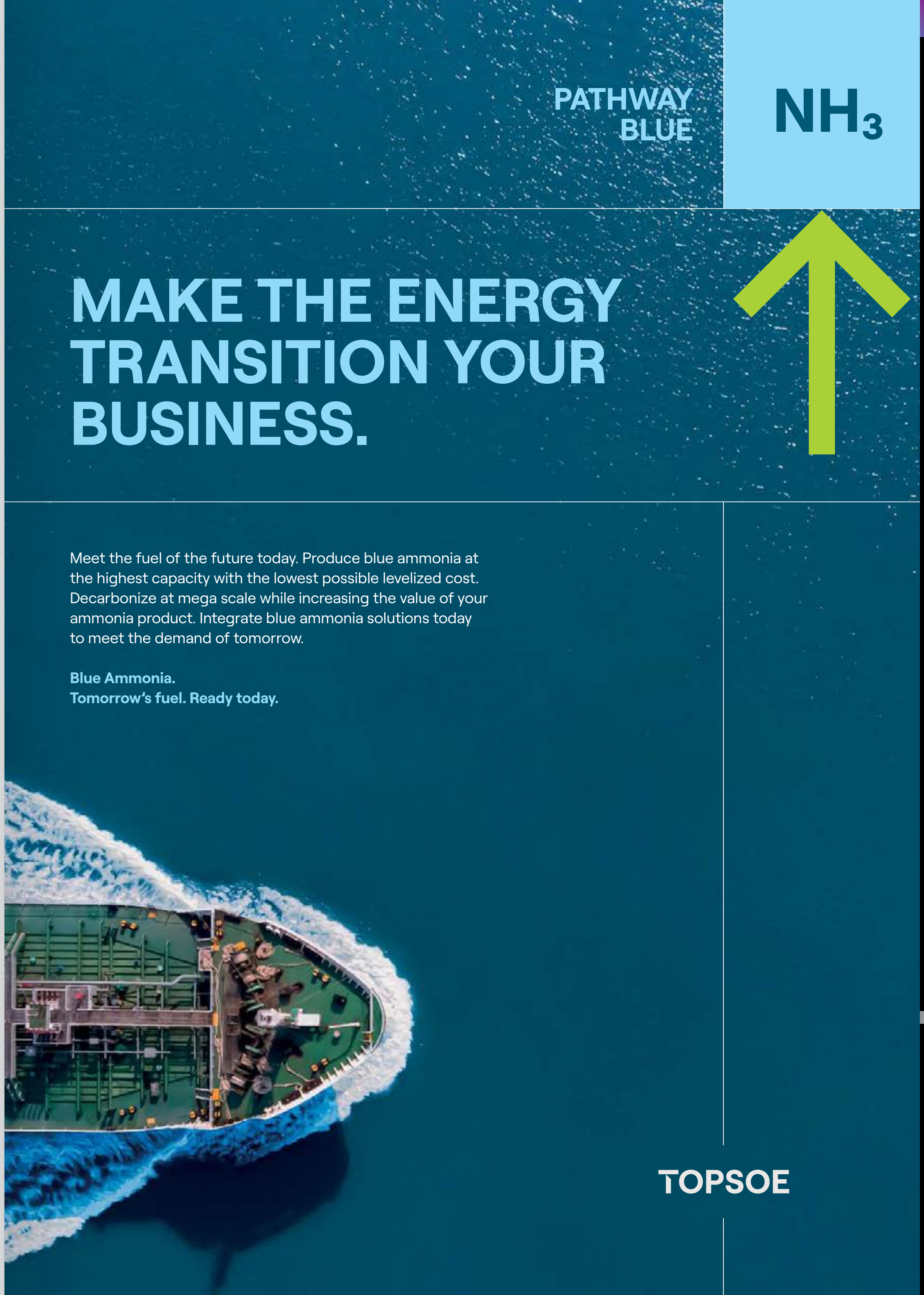
LAC with ATR or POx and HISORP® CC

HISORP® CC can also be applied in the LAC™, where the hydrogen is produced by ATR or POx as an alternative to SMR. Oxygen will be required and can be provided by the ASU.

Fig. 3 shows an overview of options where HISORP® CC can be applied in the LAC™ for these cases. The flue gas option is not shown here, as for the ATR or the POx concept only a minor amount of flue gas is generated in a fired heater, which is not shown in Fig. 3 for simplification. This additional fired heater is required, for example, for feed heating, for steam production or steam superheating. In principle, HISORP® CC can be applied in the flue gas of the fired heater, if fossil fuel is applied. Options 1 and 2 are similar to the SMR alternative. Compared to the SMR options, the specific energy demand is slightly lower, as the carbon dioxide content is typically higher due to the reduced methane slip of the ATR or POx.

For option 2, HISORP® CC in the hydrogen PSA tail gas, a total recycle of the tail gas is not possible. Otherwise, argon will accumulate within the loop. Argon enters the system via the oxygen and cannot leave the hydrogen production via the purified hydrogen as argon is disadvantageous in the ammonia synthesis loop.

Figs 2 and 3 show the production of ammonia from natural gas, but the procedure can also be applied to other feedstocks like naphtha, coal, or biomass. ■



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Ammonia production at scale with the lowest carbon intensity

Hydrocarbon-based production of ammonia carries an unavoidable carbon footprint. But one of the best methods for mitigating that footprint is already here: ultra-low carbon-intensity ammonia production, also known as "blue" ammonia. With blue ammonia production, a typical ammonia plant can sequester or repurpose game-changing volumes of carbon dioxide that would otherwise end up in the atmosphere. To help foster an optimal understanding of the benefits, **Ameet Kakoti** and **Per Juul Dahl** of Topsoe A/S provide an overview of the technologies that can help any ammonia operation achieve and maintain sustainable operations – sooner rather than later.

The world depends on ammonia for a variety of reasons and lately it has been gaining traction for use as an energy carrier and/or source. High-volume production of ammonia necessitates the use of fossil sources, the environmental impact of which will need to be controlled and reduced as the energy transition progresses.

The production of ammonia releases CO_2 during two key processes:

- syngas preparation, which delivers a CO_2 stream that is pure enough for immediate sequestration or use;
- flue gas emission from steam reformers and fired heaters, which often delivers a CO_2 stream of insufficient purity, thereby necessitating additional separation costs.

Reducing the financial impact of carbon-footprint management entails reducing flue gas emissions and capturing as much of the remainder CO_2 as possible in the syngas preparation stage for removal. Rather than viewing this as a business obstacle, Topsoe encourages producers to embrace an opportunity to implement process solutions that can transform business for the better.

Establishing a low-carbon ammonia standard

Conventional ammonia production, which is based on steam-methane reformer (SMR) technology, emits around 0.48 kg of CO_2 per kg of ammonia in the flue gas stream. Topsoe's SynCOR™ technology can reduce that volume to approximately 0.31 kg CO_2 per kg of ammonia.

An international standard for blue production doesn't exist yet; such production is typically classified as resulting in less than 0.2 kg of CO_2 per kg of ammonia, which can be met by Topsoe's ultra-low carbon-intensity process – SynCOR Ammonia™, which can reduce emissions by more than 99%. Such market-leading efficiency is facilitated by process layouts that integrate systems capable of removing maximised volumes of pure CO_2 from syngas, as well as the use of high-performance flue gas-capture units.

CO_2 capture percentage standards are driven by the expectation that these emissions will be taxed more heavily in the coming years, and that captured CO_2 will generate income from its sale and repurposing. As such, the higher the standard maintained, the greater the overall profitability of the operation.

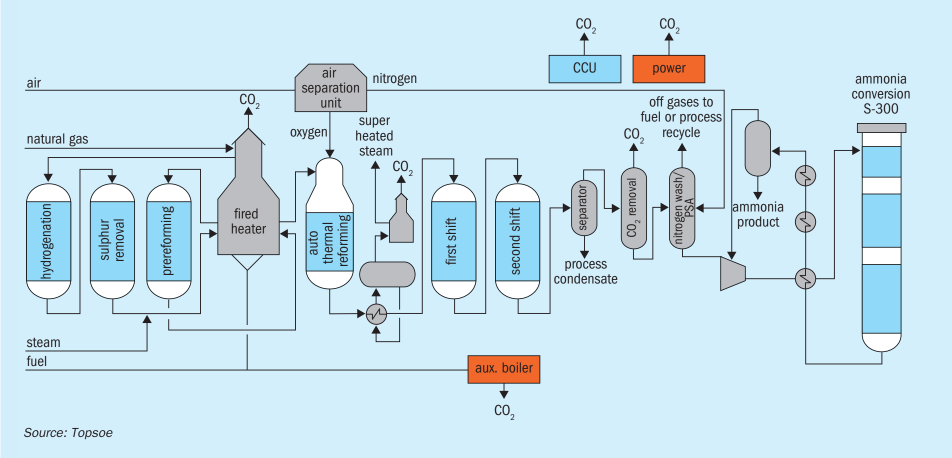
The Topsoe ammonia process can be configured in a variety of ways governing energy import and export. Some process schemes produce their own power, while others may need power import. As such, when comparing different process schemes, it's important to include the CO_2 emission value of any imports and exclude the emission value of any exports. This provides the most accurate comparison of process designs and ensures that the right selection is made.

Preparing for the future

Hydrocarbon feeds aren't going away anytime soon, so in order to produce blue ammonia, what needs to change is how those feeds are processed. Carbon emissions from ammonia production fall into two categories, indirect or direct emissions. Indirect emissions are related to power import and emissions from the auxiliary boiler, and direct emissions are driven by the heat required for the reforming process and the removal of carbon from the feedstock to prepare synthesis gas for ammonia production.

Indirect emissions need to be addressed and it is a process which is expected to be central to the gas and power producers to minimise emissions at source (Scope 2 and Scope 3). With time, more and more renewable power coming onstream, Scope 2 emissions will trend favourably toward minimal to no emissions. The same applies for carbon emissions from leakages as that is a major emission source and high on the agenda to be cut. This is already done in practice in gas piped in Norway with lowest emissions.

Fig. 1: **SynCOR Ammonia™ process layout**



Source: Topsoe

In the syngas conversion process, carbon released from pre-combustion capture is sufficiently pure for further repurposing. Carbon is also released during the reforming step, which requires significant heat. The heat is typically provided by burning hydrocarbon fuels, resulting in flue gas emissions containing large quantities of CO_2. There are two ways to reduce these flue gas emissions:

- integration of flue gas capture systems, which capture more than 90% of the emissions; such systems have been available for decades and are often utilised in revamps of existing plants;
- increasing syngas-generation capacity, resulting in greater CO_2 volume and excess hydrogen; the hydrogen can be used as fuel during the reforming process.

While the former method can help position older setups for profitable business in the sustainable era, the latter is ideal for new ammonia plants, as it proves advantageous when pursuing decarbonisation goals. Producing usable hydrogen is, in most cases, far more cost-efficient than removing and purifying the carbon from the flue gas stream.

Reforming technologies

The optimisation of the decarbonisation is then directed towards the required heat input for the reforming section, as it is one of the largest point sources of CO_2, besides the captured CO_2 from the synthesis gas.

Almost all ammonia plants in operation, use steam reforming as part of the synthesis gas generation. More than 20 years ago, i.e., before decarbonisation took off, Topsoe introduced the SynCOR concept for large-scale synthesis gas generation. The SynCOR concept is a synthesis gas generation technology using autothermal reforming, operating with a steam to carbon ratio, typically at 0.6. The technology has today achieved more than 300 operating years of large to very large scale industrial reliable operation.

A typical SynCOR Ammonia plant is shown in Fig. 1. Synthesis-gas generation corresponding to 10,000 t/d ammonia can be produced in one SynCOR reactor which makes it fundamentally different from all other available reforming solutions. The major difference is the operation with a low steam-to-carbon ratio of 0.6, which is about 4-5 times less steam than required for tubular steam reforming. This reduces the amount of heat input for the reforming section drastically, and thereby the fuel requirement directly leading to a lower CO_2 emission.

Therefore, the use of SynCOR is beneficial in cases where there is a desire to decarbonise, since it requires either a smaller flue gas capture unit or has less need for excess hydrogen for fuel. This is a major advantage compared to steam reformer-based solutions. And with SynCOR Ammonia, carbon intensity is much lower when compared to a traditional steam methane reformer. SynCOR Ammonia starts with a carbon capture rate of about 87% compared to an SMR plant with a carbon capture rate of about 75% directly from the process gas, pre-combustion process, which is inherently present in an ammonia process.

Case comparison

Regardless of the technology selected, the blue ammonia production process is already well defined and reliably proven, so what matters is the parameters driving production: carbon intensity (CI), carbon recovery (CR), and the levelised cost of ammonia (LCOA). These parameters will impact the facility's energy balance, as shown in Fig. 2.

CI and CR are currently regarded as the most effective means of measuring the success of blue production in terms of CO_2 reduction, and a plant's CR goals will impact overall capex and opex. With that in mind, a SynCOR Ammonia plant can start with a lower capture rate before revamping increasing to a higher rate as needed.

Topsoe has the widest portfolio of reforming technologies available in the

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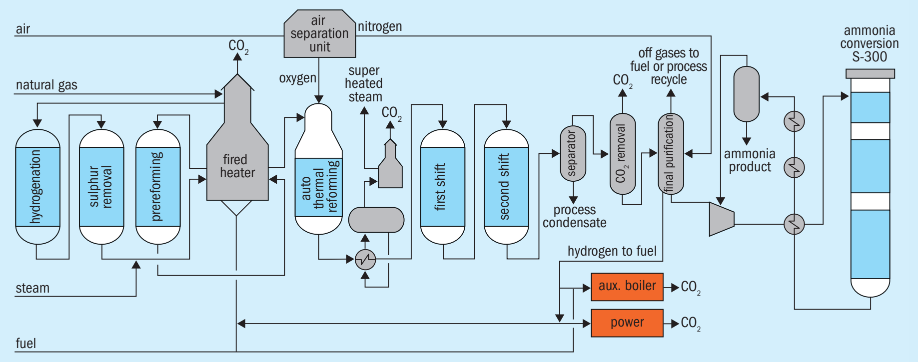
Fig. 2: **Schematic diagram of SynCOR Blue NH_3 process for 90%+ carbon recovery**



Source: Topsoe

Table 1: **Case comparison**

	Case C1	Case C2	Case C3
Carbon recovery, %	87	90	99
Excess H_2 production for fuel, %	0	4.3	15.3
LCOA	100	100.9	106.6
Opex, %	100	101.9	107.4
Capex, %	100	102.9	109.2

Source: Topsoe

market, so if large- or mega-scale output is the goal, SynCOR is the ideal choice on account of its low capex and opex, owing to its single-reactor layout and optimised steam-to-carbon ratio. All of this allow a SynCOR-equipped facility to benefit from economy of scale.

The reduction of CI through pre-combustion capture, which utilises a CO_2 removal process inherent to the process itself, is a simpler matter than flue gas capture (post combustion capture), so many blue processes begin there. This is instrumental in SynCOR's ability to minimise CI, for example.

To provide a fair comparison, Topsoe has compiled three cases involving SynCOR plants at a capacity of 4,000 t/d.

Case 1 (Base case): A newly built unit with a shift section and pre-combustion carbon capture, as is common in traditional ammonia plants. The captured CO_2 is compressed to 162 barg before being liquefied for transport or storage, while the syngas is purified in a cryogenic nitrogen wash unit, resulting in inert, free makeup gas to the ammonia synthesis loop.

Case 2 (Minimal hydrogen firing): This case is similar to the base case, but a portion of the syngas/hydrogen-rich gas serves as fuel, increasing carbon recovery to 90%. As a result of hydrogen firing, additional syngas is produced.

Case 3 (Hydrogen-rich gas as main fuel): Here, the fuel setup enables an even higher carbon recovery rate of 99%. The major difference from the second case lies in the minimisation of natural-gas volume, supplemented in turn by hydrogen-rich gas. Under normal conditions, methane containing off gases from the purification unit would be recycled to the reforming stage, but with hydrogen firing, additional syngas is instead produced – a net win in terms of operational efficiency and energy savings. Topsoe has a patent pending for this technology.

Table 1 illustrates opex and capex for each of the four cases, in conjunction with the assumptions listed in Tables 2 and 3.

Based on the data obtained, it can be concluded that:

- Case C1 provides for the lowest opex and capex.
- Case C2 demonstrates attractive capex as a result of burning a limited amount of excess hydrogen as a fuel replacement, with a 90% capture rate and lower LCOA.
- Case C3 shows that a certain increase in both capex and opex can be expected as carbon-capture rates progress toward 99%.

Table 2: **Assumed utility prices**

Utility	Price, €
Natural gas, €/MMBTU	4
Power, €/MWh	100
DMW, €/m³	1
Steam, €/t	13.5
CO_2 credit for emission avoided, €/t	25
PSA off gas export credit, €/MMBTU	4

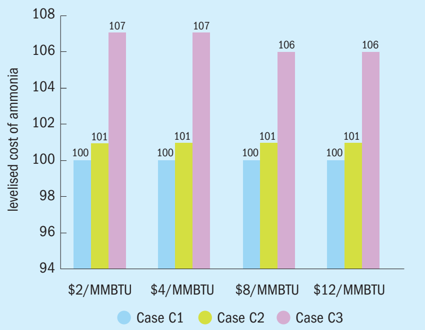
Source: Topsoe

Table 3: **Operational parameters**

Parameter	Value
CO_2 emission due to power import, g/kWh	255
Operations and maintenance cost, €/year	4% of TIC
Discount factor, %	12
Yearly hours of operation, hours	8,500
Plant lifetime for LCOA evaluation, years	20

Source: Topsoe

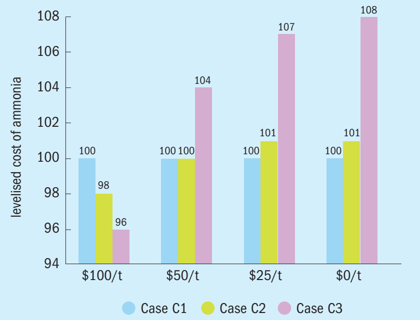
Fig. 3: **Levelised cost of ammonia (LCOA) with varying natural gas (NG) price**



Note: LCOA normalised to Case C1 (base case)

Source: Topsoe

Fig. 4: **Levelised cost of ammonia (LCOA) with varying CO_2 credit**



Note: LCOA normalised to Case C1 (base case)

Source: Topsoe

All of this helps us understand that technology selection ultimately hinges on the need to achieve certain targets in as cost-effective a manner as possible. LCOA is certainly important, as it influences the plant's layout according to utility costs, CO_2 taxes and credits, and opex/capex. The case study makes it clear that, as expected, reducing emissions will cost a bit more, but it also shows that selection of the correct technology, in accordance with boundary conditions, can also impact results.

Thus, the key takeaway is that when it comes to blue production, there's no one-size-fits-all solution, which is a good thing. Adjustable concepts can be optimised more readily and effectively.

Fig. 3 exhibits that case C3 has the highest LCOA because of excess hydrogen production and increased capex, while Case C1 exhibits the lowest LCOA – and these conditions remain valid across a broad spectrum of natural-gas prices, implying that the levelised cost of ammonia production is not very sensitive to NG prices over different CI.

What changes things is carbon credit, which makes layout selection much more crucial, as shown in Fig. 4.

Here, it becomes clear that credit variation has an impact on LCOA; without credit, Case C3 delivers the highest LCOA, while C1 delivers the lowest, but when CO_2 taxes are higher, C3 suddenly becomes much more attractive.

As with the energy transition policies announced globally, carbon credits and carbon pricing mechanisms/carbon emission penalties are imminent and thereby higher carbon capture rate/ lower carbon intensity will secure a long-term sustainable ammonia production for the investors.

Conclusion

As a major component of the sustainable energy transition, blue ammonia will need to be produced at never-before-seen capacities. This will challenge traditional, tubular reformer-based solutions, both in terms of opex and capex but also in terms of emission management, which will necessitate additional expenditure. The cost effectiveness of Topsoe's SynCOR Ammonia process stands out when compared to other available reforming technologies.

Instead of following the traditional steam methane reforming process scheme, nowadays several well-proven, mature options are available and much more suited for high-efficiency blue production. As SynCOR plants already begin with the lowest CI, it will be relatively easier to transition to blue ammonia production at large scale when compared to traditional reforming technologies. Depending on operational criteria and future availability of renewable power, SynCOR can deliver the lowest LCOA in addition to the lowest CI, all at economy of scale, while future proofing ammonia businesses with the means to integrate zero-carbon power for the lowest possible emissions. ■

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Barents Blue Ammonia project

Horisont Energi has the aspiration to develop the most carbon and energy efficient blue ammonia plant in the world, an environmentally friendly plant with a focus on sustainable solutions. This article describes the main features of the Barents Blue Ammonia project, such as 99% carbon capture rate target, a high degree of modularisation, winterisation, infrastructure for ammonia and CO_2 management and the provision for future expansion.

Bjørgulf Haukelidsæter Eidesen (Horisont Energi) and Andrea Zambianco and Massimiliano Sala (Saipem S.p.A.)

Barents Blue Ammonia project

Horisont Energi, an independent Norwegian energy company, is developing a large-scale blue ammonia complex in Finnmark, Norway, (Fig. 1), exploiting the favourable combination of feedstock gas availability, cold climate conditions which allows higher process efficiency, and proximity to offshore CO_2 storage.

In 2021 Saipem started work on the concept study for the Barents Blue Ammonia project and was subsequently awarded the extension of the engineering services, currently ongoing, to optimise the overall complex by integrating the process, utilities and offsites.

The plant

Topsoe's SynCOR Ammonia™ process, which is based on autothermal reforming (ATR), was the technology selected for the Barents Blue Ammonia project.

ATR is emerging as a promising application for the new generation of large-scale ammonia plants and is well referenced in other syngas applications, e.g., methanol and gas-to-liquids. The first large-scale ammonia project based on SynCOR Ammonia™ is currently under execution by Saipem.

For blue ammonia there is an inherent advantage in the use of ATR; most of the natural gas is used as feedstock and the CO_2 generated in the reforming section can therefore be easily captured in the conventional CO_2 removal unit, while only a small

IMAGES: SAIPEM

Fig. 1: Plant location of Barents Blue ammonia project, Finmark, Norway.

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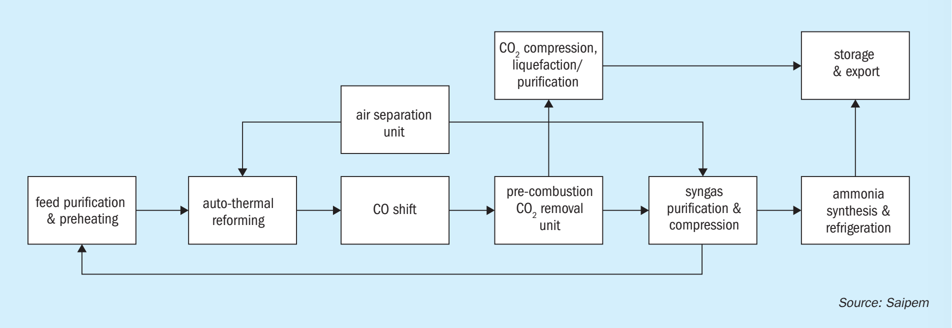
Fig. 2: **Ammonia plant scheme**



Source: Saipem

portion is used directly as fuel, eventually resulting in reduced CO_2 emissions to the atmosphere. As a consequence, the CO_2 capture rate achievable without modifications to the process scheme (i.e., simply conditioning and storing the captured CO_2) is higher for the ATR than for the steam methane reformer (SMR) which is typically in the range of 80-88%. Taking into consideration the capture rate, an ATR-based plant is inherently a blue ammonia plant and does not require post-combustion CO_2 capture from the flue gas. To further improve the capture rate, among various alternatives, it is convenient to use off-gas from the syngas purification along with purified syngas recycled as fuel in the fired heater, without excessive oversize of the front end, as depicted in Fig. 2.

The integration of the utilities with the ammonia plant, and in particular the optimisation of the steam and power network, is a key element in the design of the overall complex.

Extensive use of electrical over direct steam turbine drivers increases the overall efficiency of the complex. The plant electrical power requirements are mainly satisfied by internal power generation by means of steam turbine generator (STG) with limited renewable electricity from the grid.

A thorough value engineering exercise has been carried out to identify all possible opportunities to increase efficiency in normal operation: for instance, excess syngas generated in the ammonia front-end section for fuel is expanded to generate 3-4 MW electric power.

Optimisation of the efficiency has been evaluated in conjunction with other key design parameters such as reliability and operability; therefore, the plant is designed to operate without some of the energy recovery features.

In addition, the low steam-to-carbon ratio enables large-scale capacity; in fact, all the units in the plant have equipment that falls within the referenced size of operating plants or generally requiring minimum scale up.

Barents Blue Ammonia is a fully automated plant with integrated energy management; another advantage of ATR is that it is possible to maximise automation with inherently efficient and safe operation. It significantly reduces the risk of human error resulting in less lost time accidents, increasing plant availability and reducing the environmental impact of flaring caused by erroneous upset situations.

In addition to the CO_2 emission, the plant is designed to minimise the overall impact to the environment with the main focus on noise, effluents and emissions (e.g. mitigation measures implemented after a dedicated noise study, DeNox system implemented, etc.).

Carbon capture rate: 99% target

Barents Blue Ammonia project will capture and permanently store approximately 2 million t/a of CO_2 per ammonia train, which corresponds to the CO_2 emissions generated from more than 400,000 cars.

The CO_2 is captured from the synthesis gas using standard capture technology already included in conventional plants.

The CO_2 emission from the fired heater upstream of the ATR is minimised thanks to the hydrogen-rich gas from the front end. The increase of the front-end size has been evaluated to be more economical and efficient than the implementation of a post combustion CO_2 capture unit in the fired heater exhaust.

The selection of the most adequate process scheme is driven by both plant operating conditions and/or the use of the available utilities at site. The 99% target includes the contribution of all the other sections of the complex: utilities and offsites.

The steam generated by process heat recovery is used to drive the major compressors and to generate electric power by means of STG. With the minimum supplementary steam generated by the auxiliary boiler, which is using hydrogen-rich gas as fuel during normal operation, it is possible to close the steam and power balance, avoiding additional CO_2 emission in the utilities section.

The design has also been tailored to reduce CO_2 emissions during commissioning and start-up; dedicated studies have been carried out to identify a suitable design and features to also minimise CO_2 emission during transient scenarios (e.g., minimising the flaring and the use of natural gas as fuel in the auxiliary boiler).

The capture rate is not the only parameter to measure the environmental sustainability of a blue ammonia project: another important parameter is the carbon intensity which takes into account not only the emissions generated in the process but also the emissions associated to the imported electricity. Maximisation of the efficiency reduces the natural gas consumption and the relevant contribution to the carbon intensity, while the availability of renewable energy from grid is essential to maintain a low overall index. According to the study performed by Saipem, Barents Blue Ammonia carbon intensity (tCO_2eq/t product) for scope 1 and 2 is 0.0169 while the benchmark for a modern grey ammonia plant in Europe is 1.694.

Winterisation

The cold climate in the region represents a challenge but also an opportunity for the project to improve the plant's efficiency. For example, the utilities scheme uses cold sea water (8°C) as a direct cooling media for the STG condensers and a cooling water loop (13°C) provides robust plant cooling with high thermal efficiency.

The building is heated by hot water, while process winterisation is provided by electrical tracing. Where possible, waste heat from the plant is used to improve efficiency and further reduce CO_2 emissions. For example, the heat pump circuit has been integrated with process streams for winterisation purposes.

High degree of modularisation

Modularisation offers several advantages in terms of safety and costs for a location where the mobilisation of huge construction manpower is not possible and/or access at site is difficult or not possible for a prolonged period such as in Finnmark.

A deep analysis of the optimum size of the modules considering logistic constraints, cost and time-effectiveness and availability of yards has been performed to optimise the strategy. As result of the investigations, the overall complex has been modularised to a large extent (>90% on total equipment count). The process sub-units fit within single big modules to minimise the hook-ups and pre-commissioning works at site.

This project has the advantage of having a location with direct access to the sea, which allows the offloading of large modules, with more than 5,000 t per module and maximum dimension of approximately 100 x 30 x 36 m (L x W x H) per module.

Infrastructure for ammonia and CO_2 management

The ammonia is stored in a rock cavern physically located under the site thus enhancing safety, reducing the thermal dispersion and minimising the associated boil off refrigeration energy consumption. This provides a very efficient solution from the energy point of view. The capacity is 120,000 m³.

Permanent offshore CO_2 storage, which can be reached by pipeline or by ship has been considered. In the latter case, an intermediate CO_2 storage would be required. Depending on the CO_2 purity target, a purification and chilling section might have been required affecting the overall energy plant consumption. Transportation by pipeline has less strict requirements and is the base case for storing CO_2 in the Polaris reservoir.

Provision for future expansion

Since the early stages of the project, possible future expansions have been duly considered. Proper design allows safe and efficient expansion even when the first train is already in operation. The optimised choice for the common utilities and offsites minimises the overall cost over the project life.

Modularisation offers significant advantages for future expansion with the possibility to replicate modules for the additional train and utility modules already designed.

Site preparation, sea water intake, raw water tank, fire tank, main electrical substation, main control room, ammonia storage, the jetty and its loading system have all been designed taking into consideration the expected overall expansion. ■

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Hydrogen production with >99% CO_2 recovery

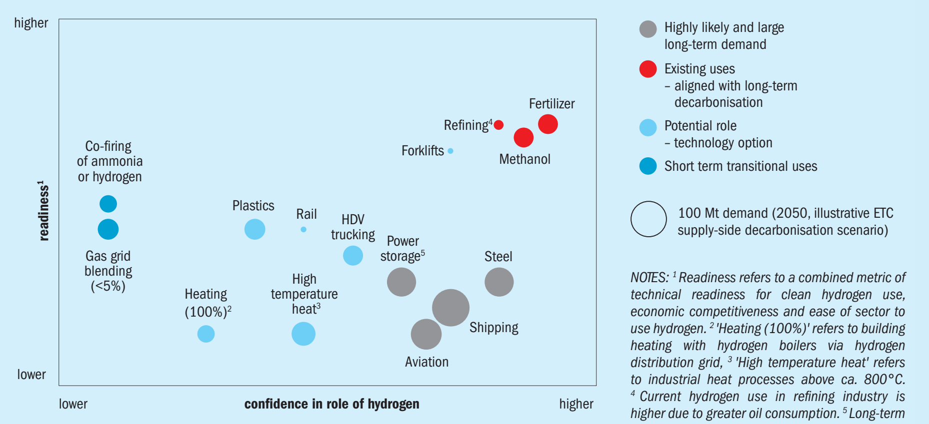
The world’s transition toward the use of hydrogen and ammonia as clean energy and fuel sources will depend upon production technologies that are affordable, scalable, and meet net zero carbon targets. 8 Rivers recently introduced $^8RH_2$, a groundbreaking solution that offers world-leading efficiency in hydrogen production and captures over 99% of CO_2 emissions. **Maulik Shelat** of 8 Rivers provides an overview of the technology with a comparison to other low-carbon hydrogen production technologies.

Hydrogen and ammonia are widely expected to play key roles in the global energy transition. McKinsey & Company forecasts that the ability of clean hydrogen and ammonia to reduce emissions from hard-to-abate sectors would enable it to eliminate 80 Gt of cumulative CO_2 emissions by 2050, accounting for 20% of annual emissions abatement in the year of 2050 (Hydrogen Council 2022). As shown in Fig. 1, the most anticipated applications for clean hydrogen include heavy-duty transportation (e.g., long-haul trucking, maritime shipping, and aviation), provision of high-grade and intensity industrial heat, power generation and storage, and industrial feedstocks for materials like steel and cement. Clean ammonia, on the other hand, will be used in fertilizer production, and is expected to play a large role in transporting clean hydrogen. Because of its higher boiling point, it can be transported in liquid form more cost-efficiently than hydrogen and then be converted back to hydrogen (a process called “cracking”) upon arrival at its destination. The transportation of ammonia by ship offers a practical decarbonisation solution for countries that face geographical limitations in scaling up renewable power generation or clean hydrogen production, such as Japan, where LNG import terminal conversion into ammonia import facilities are in evaluation (Atchison 2023).

A question of scale and speed

The IEA estimates that hydrogen use will need to increase from 94 Mt in 2021 to 200 Mt in 2030 to be on track for net zero emissions by 2050, 100 Mt of which will need to come from low-emission production (International Energy Agency 2022). To meet this increase in demand for clean hydrogen, production technology deployment will be dependent on carbon intensity (CI), technical readiness, and infrastructure scalability. Two leading technology contenders are hydrogen formed via renewable energy, such as electrolysis, and hydrogen formed via natural gas reformation with post-combustion carbon capture. Unfortunately, the first cannot currently scale at the speed, price point, and volume needed to meet forecasted demand and, while the second offers scalability, it only captures ~90-95% of carbon.

Fig. 1: **Potential uses of hydrogen in low carbon economy**



NOTES: [1] Readiness refers to a combined metric of technical readiness for clean hydrogen use, economic competitiveness and ease of sector to use hydrogen. [2] 'Heating (100%)' refers to building heating with hydrogen boilers via hydrogen distribution grid, [3] 'High temperature heat' refers to industrial heat processes above ca. 800°C. [4] Current hydrogen use in refining industry is higher due to greater oil consumption. [5] Long-term energy storage for the power system.

Source: Energy Transitions Commission 2021

Recently, however, 8 Rivers announced the commercialisation of its second generation $^8RH_2$ technology – a new process that provides the scalability and deployment speed of established blue hydrogen processes plus greater than 99% carbon capture.

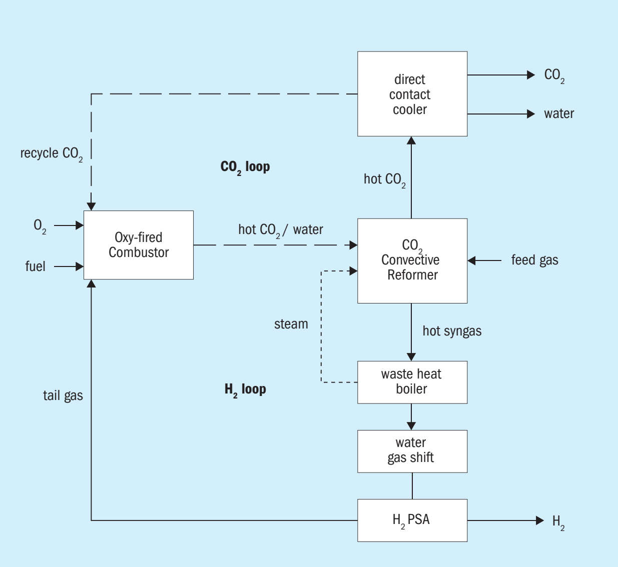
Limitations on existing hydrogen production technologies

Two conventional large-scale hydrogen production methods are steam methane reforming (SMR) and autothermal reforming (ATR). Both are suitable for combination with carbon capture and sequestration (CCS), but both struggle to break the 95% carbon capture threshold put forth by think tanks such as the Rocky Mountain Institute (RMI) as the minimum for viable long-term investment (Weiss, et al. 2022). SMR currently tops out at 90% capture, and ATR at around 95%.

In both SMR and ATR, hydrogen is formed from natural gas (or methane) through chemical reactions in the presence of a catalyst. SMR reacts methane with steam, with heat delivered by an external combustion process. Thus, two gaseous flow streams exiting the reformer are isolated – dilute combustion flue gas and pressurized syngas (H_2, CO, CO_2, H_2O, and unreacted CH_4) from which H_2 is later separated. Alternatively, ATR has only one flow stream and no external heat source, as the methane is partially oxidised with oxygen in the presence of steam to drive the reaction. The single flow stream exiting the ATR reformer is high-pressure syngas.

For both of these processes, recovering CO_2 requires back-end carbon capture. Conventional technologies use absorption and stripping, often with amine-based systems, which requires significant equipment and energy demand – driving up capex and opex. Amine liquids absorb CO_2 from the gases that pass through the column. The amine with absorbed CO_2 is then sent to a stripper column where it is lowered in pressure and heated to liberate and capture the CO_2. Due to the low concentrations from two main sources of CO_2 generation in these conventional processes, back-end CO_2 separation processes are energy-intensive and lack the means to efficiently capture 100% of CO_2. Therefore, some of the CO_2 is released to the atmosphere along with the nitrogen, oxygen, and other gases rather than captured for sequestration. The high pressure of the ATR process enables a higher recovery of up to 95% of CO_2 whereas the low-pressure flue gas stream of the SMR process reduces overall SMR capture efficiency to 90%.

Fig. 2: **8 Rivers’ $^8RH_2$ Gen 2 process flow**



Source: 8 Rivers

8 Rivers’ $^8RH_2$ process

In contrast to SMR and ATR, the $^8RH_2$ process attains greater than 99% CO_2 capture at lower capital and operating costs than its peers by employing 8 Rivers’ new CO_2 Convective Reformer (CCR) technology. While the $^8RH_2$ reformation process leverages much of the same equipment and process flow of established SMR processes, the CCR enables a pure stream of high pressure and temperature CO_2 to deliver the heat to the reformation reaction. The result is two separate flow streams of flue gas and syngas, similar to SMR, but at high pressures, similar to ATR. However, unlike either of the existing processes, $^8RH_2$’s use of CO_2 as the working fluid enables inherent capture of pipeline-ready CO_2 without post-combustion carbon capture – saving cost and energy consumption while increasing capture. Furthermore, the CCR is a prefabricated, compact tube-in-tube (bayonet) design with catalyst filled in an annular space and the product stream exiting from a central tube. This enables the hydrogen production process to operate more efficiently by exchanging heat between the product gas stream and the reforming gas stream. Additionally, as the CCR tubes are not exposed to direct flame, they can be packed in a much tighter configuration. This design allows the CCR to have a smaller footprint and to be prefabricated for faster and cheaper installation.

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$^8RH_2$ process description

To start, $^8RH_2$ reforms the hydrocarbon feed – which is natural gas combined with steam – in a device called the CO_2 Convective Reformer, or CCR. A traditional convective reformer, its bayonet design contains tubes filled with catalyst that enable the conversion of natural gas and steam into syngas (H_2, CO, unconverted CH_4, and some CO_2 leftover from the chemical reaction). The heat of reaction is provided by a high temperature and pressure CO_2 stream produced by combusting hydrocarbon fuel (natural gas + process tail gas) in presence of pure oxygen using recycled CO_2 as a diluent (as opposed to nitrogen in the case of air fired combustion).

The generated syngas from the CCR goes to the waste heat boiler, where it is quenched to around 650°F (342°C). Once cooled, the syngas goes through the water gas shift process, where the CO combines with more steam to produce additional hydrogen and CO_2. After another cool down, the mixture goes through the hydrogen pressure swing adsorption (PSA) process, which separates the hydrogen from everything else, including the CO_2. The residual tail gas has the CO_2 generated on the process side, plus any unconverted methane and CO.

Once separated from the hydrogen, the tail gas is cycled to the Oxy-fired Combustor – a device that burns the tail gas with pure oxygen, additional methane fuel, and recycled CO_2 as a dilutant. This combustion produces two components: hot CO_2 and steam which pass through the CCR. At the same time, process feed gas (CH_4 and steam) travels through the CCR via separate tubes filled with catalyst. Thus, the hot CO_2 from the Oxy-fired Combustor remains physically isolated but delivers the heat necessary to reform the process gas into syngas.

Exiting the CCR, the now cooler but still high-pressure CO_2 from the Oxy-fired Combustor, is further cooled in a direct contact cooler and then sent for sequestration while a portion is recycled to the oxy-combustor. Meanwhile, the pure hydrogen is extracted and the remaining tail gas is sent to the oxy-combustor. The result is a process that looks similar to SMR, and uses existing equipment, but that inherently delivers hydrogen and pipeline quality CO_2.

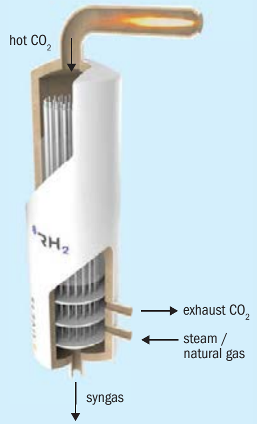
Ultra-low carbon hydrogen

Investment and commercialisation of ultra-low-carbon hydrogen and ammonia at significant volumes and at rapid speeds is needed now to bridge the decarbonisation gap as other technologies continue their development pathways. The focus of 8 Rivers is on speed, feasibility, and cost-effectiveness, all while keeping emissions reduction at the forefront of efforts.

> **… a groundbreaking solution that offers world-leading efficiency in hydrogen production and captures over 99% of CO_2 emissions.**

The $^8RH_2$ process inherently captures CO_2 for sequestration without a back-end CO_2 separation process. This unique aspect enables $^8RH_2$ Gen 2 to produce low cost, ultra-low CI hydrogen. Levelised cost of hydrogen produced via $^8RH_2$ Gen 2 technology is expected to be 5-10% lower than traditional hydrogen production technologies while capturing nearly all of the CO_2. It is the most economical, efficient, and effective method compared to its low-carbon, natural-gas-powered hydrogen peers, and when combined with responsibly sourced natural gas, its lifetime emissions intensity can be as low as hydrogen production via renewables, depending on the method's technology, on-site power generation, and other setup details. $^8RH_2$ Gen 2 technology is available for commercialisation today to enable deployment of affordable and large-scale hydrogen and ammonia to meet the world's increasing demand for clean fuels, energy and other industrial uses. ■

Fig. 3: **8 Rivers' CO_2 Convective Reformer**



Source: 8 Rivers

Key take-aways

- Clean hydrogen and ammonia are critical to the net-zero transition but renewable energy powered methods likely cannot scale quickly enough and existing SMR/ATR reformation with CCS misses capturing 5-10% or more of CO_2 emissions.
- 8 Rivers' new $^8RH_2$ Gen 2 technology leverages existing equipment and infrastructure in a novel process to inherently capture pipeline quality CO_2 without requiring back-end carbon capture.
- $^8RH_2$ delivers greater than 99% carbon capture at lower costs than competing technologies.

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Catalysts to tackle the challenges of ammonia cracking

Highly efficient ammonia synthesis and subsequent cracking to hydrogen are key processes in the transition to the green hydrogen economy. Catalysts play an important role in the ammonia cracking process. Clariant offers both nickel and precious metal catalysts for this application and research on robust catalysts that allow lower temperatures for increased energy efficiency is ongoing.

Demand for clean energy is driving interest in green hydrogen (H_2) worldwide, with further impetus coming from the need for energy independence. While hydrogen is a proven and clean-burning fuel, it also involves several logistical challenges, especially in the case of green hydrogen. Produced using renewable energy sources, green hydrogen requires long-range transport from the Global South, where solar power is in abundance and growing, to northern geographies (Fig. 1). Conversion to ammonia (NH_3) for storage and transportation, then reconversion to hydrogen at the point of use, offers the safest and most cost-effective solution.

Central Europe and the Asia Pacific region, particularly Japan and Korea, have huge potential as markets for hydrogen due to their high energy consumption and resource constraints. Blue hydrogen, produced by non-renewable energy sources, is seen critical by certain governmental bodies and an increasingly aware public. Nevertheless, it can be an important stepping stone on the path to low greenhouse gas (GHG) emissions, as the CO_2 emissions resulting from its production can be reduced by up to more than 99% through the use of a suitable carbon capture and sequestration (CCS) technology.

Considering Germany's position as Europe's economic and industrial powerhouse, it is no surprise that representatives of the Berlin government have recently discussed green hydrogen on state visits to Africa and South Asia as well as to southern European countries. These regions are predestined to produce renewable-based hydrogen at low cost.

The long haul to the green hydrogen economy

This brings us back to the question of logistics. Currently, hydrogen is transported and stored mainly in the form of liquid compressed hydrogen. This has the disadvantage of needing to be stored either under high pressure (350-700 bar) or at extremely low temperatures (-253°C). This specialised handling raises costs. Another possible technology, known as liquid organic hydrogen carriers (LOHC), is a non-toxic solution that can be applied within the existing fuel network. Clariant is involved in this hydrogen transportation technology, supplying its EleMax® catalysts to the LOHC technology provider Hydrogenious.

However, where long-range transport is required, by far the most efficient and cost-effective solution to date is conversion to ammonia, thanks to its stability and very high energy density (Fig. 2). Ammonia can then be shipped to markets using the existing global ammonia infrastructure and is classified as non-flammable in transit.

Ammonia is the second-most widely produced commodity chemical in the world (after sulphuric acid), with a production volume of 183 million tonnes in 2020. As around 18-20 million t/a is already shipped internationally, its worldwide distribution system, which mainly serves the fertilizer and chemicals industries, is safe and well-established. (Reference: Irena Innovation Outlook Renewable Ammonia 2022).

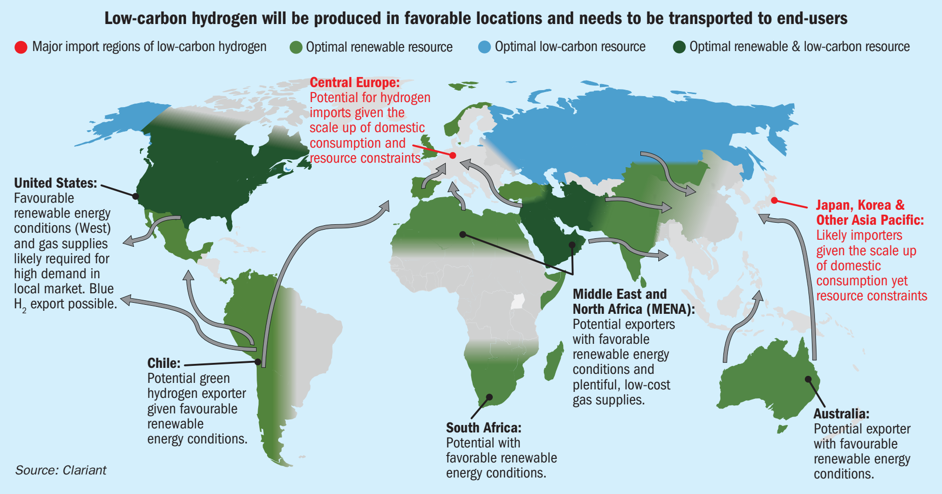
The subsequent cracking process to reconvert ammonia to hydrogen can then take place in centralised large-scale plants located near ports or in smaller decentralised facilities e.g., in urban areas.

Centralised and decentralised ammonia cracking each have certain advantages, depending on the intended point of use. For large-scale processing of more than, e.g., 1,000 t/d of ammonia to feed hydrogen into the energy grid, major industrial plants are clearly favourable. These can be built to employ proven nickel catalysts to meet the needs of industrial consumers like municipalities or steel, cement and chemical companies. Decentralised facilities, in contrast, are suitable for small-scale processing of several hundred kilos of ammonia per hour using ruthenium catalysts, resulting in high-purity hydrogen e.g., for fuel cell applications. Ideal locations are near filling stations supplying hydrogen for vehicles.

Ammonia cracking: already proven on a small scale

Ammonia cracking, or dissociation, is an endothermic reaction requiring 46 kJ per mole of ammonia. The thermodynamic

Fig. 1: **World map of low-carbon hydrogen production and import/export**



Central Europe: Potential for hydrogen imports given the scale up of domestic consumption and resource constraints

United States: Favourable renewable energy conditions (West) and gas supplies likely required for high demand in local market. Blue H_2 export possible.

Chile: Potential green hydrogen exporter given favourable renewable energy conditions.

South Africa: Potential with favorable renewable energy conditions.

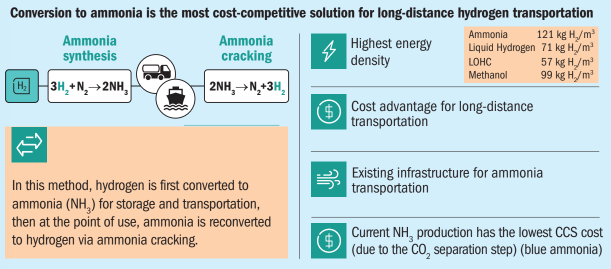
Middle East and North Africa (MENA): Potential exporters with favorable renewable energy conditions and plentiful, low-cost gas supplies.

Japan, Korea & Other Asia Pacific: Likely importers given the scale up of domestic consumption yet resource constraints

Australia: Potential exporter with favourable renewable energy conditions.

Source: Clariant

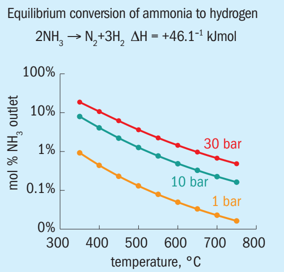
Fig. 2: **Ammonia cracking chemistry and ammonia advantages for long-distance transportation**



In this method, hydrogen is first converted to ammonia (NH_3) for storage and transportation, then at the point of use, ammonia is reconverted to hydrogen via ammonia cracking.

Source: Clariant

Fig. 3: **Ammonia cracking reaction and thermodynamics**



Source: Clariant

Table 1: **Operating conditions of a small-scale ammonia cracker**

	Cracker type 1	**Cracker type 2**
Application	Steel industry	Pharma, food, chemicals...
H_2 capacity, Nm³/h	10-300	750
NH_3 capacity, t/d	0.2-5	2 x 2 (two units)
Configuration	Electrical furnace and PSA	Vaporiser and electrical furnace
Catalyst	Nickel	Nickel
Operating temperature, °C	800-900	850-1,000
Product purity	>98%	75% H_2, 25% N_2, 0.05% NH_3
References	>5	>25
Typical catalyst lifetime	>5 years	>5 years

Source: Clariant

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equilibrium favours high temperatures and low pressures (see Fig. 3).

Depending on the temperatures used in the reaction, catalysts based on either precious metal or nickel are applied. Typical flow sheets comprise the following process steps: ammonia vaporisation, cracking, heat recovery and hydrogen separation/purification.

Small ammonia crackers have already been in operation for more than 50 years, especially in India, where they are used in different industries on a small scale. These small crackers with a capacity of around 10-750 Nm³/h H_2 typically run at low pressures and high temperatures. They are not optimised for energy-efficient operation (see Table 1).

The new generation of centralised crackers to meet industrial and municipal needs must run with a higher level of efficiency to deliver cost-effective green hydrogen. For this reason, these are not directly comparable to the small-scale crackers in India.

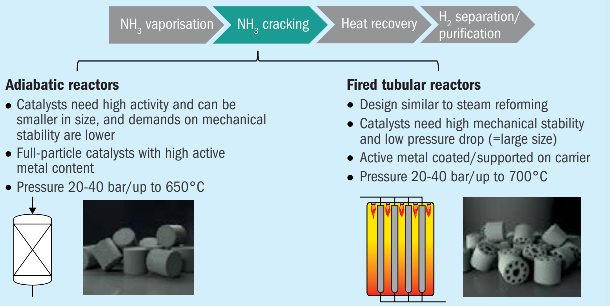
In most cases, ammonia cracking plants will have two types of reactors, as shown in Fig. 4.

Adiabatic reactors

In the pre-cracker reactor (adiabatic), partial conversion of the ammonia occurs in order to reduce the heat duty required in the downstream fired tubular reactor. Inlet temperatures of the pre-cracker are up to 650°C, while outlet temperatures are around 400°C. Pressures of up to 50 bar are applied, depending on the needed application for the hydrogen. In terms of catalyst type, nickel-based catalysts like HyProGen 820 DCARB show excellent stability against sintering as well as high activity (Fig. 5). This catalyst has been stress tested under harsh conditions: 600°C, high GHSV of 15,000 h^{-1}, and it maintained stable activity with a high and stable conversion.

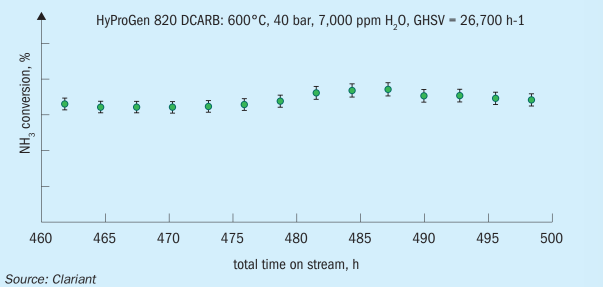
Another nickel-based catalyst, HyProGen® 821 DCARB, is even more active and therefore offers an energy-efficient alternative to ruthenium-based catalysts in adiabatic reactors. In testing (Fig. 6), it has exhibited more robustness against water than its ruthenium counterparts. Ruthenium catalysts have two main downsides, which hamper their application in large-scale crackers: Their activity decreases strongly with pressure, and they tend to suffer from deactivation at moderate to high temperatures.

Fig. 4: **NH_3 cracking process scheme and reactor types**



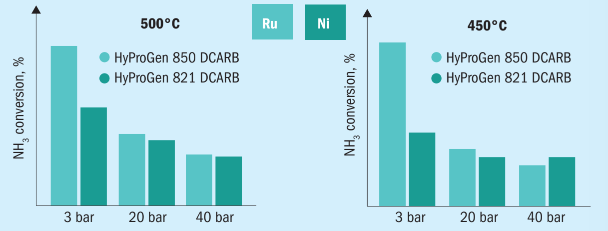
Source: Clariant

Fig. 5: **Rapid aging test shows high stability of HyProGen 820 DCARB**



Source: Clariant

Fig. 6: **Comparison of HyProGen 821 DCARB and ruthenium catalyst benchmark**



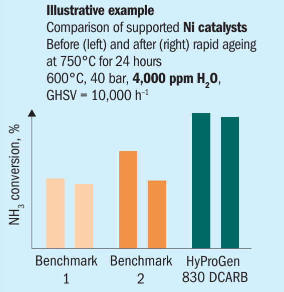
Source: Clariant

Fired tubular reactors

In the fired multi-tubular reactors, comparable to a steam reformer, the main conversions 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, which operate in steam reforming applications at temperatures over 800°C and pressures exceeding 40 bars.

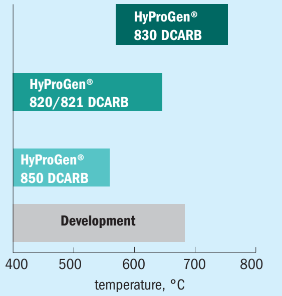
Fig. 7 illustrates the high-pressure performance of three different nickel catalysts. Benchmark 1 shows high thermal stability but low activity, while benchmark 2 shows high activity but low thermal stability. Only HyProGen 830 DCARB combines high activity with good thermal stability. This catalyst has already been proven in commercial fired multi-tubular reactors, where it shows tremendous mechanical stability.

Fig. 7: **Activity & stability comparison HyProGen 830 DCARB versus two nickel catalyst benchmarks**



Source: Clariant

Fig. 8: **Temperature range of Clariant's ammonia cracking catalysts**



Source: Clariant

The future of catalysts: Nickel vs. precious metal

Clariant's catalyst portfolio covers a wide range of solutions, which is continuously expanding. These include: HyProGen® 830 DCARB, a nickel-based catalyst designed for high-temperature applications, which – thanks to its mechanical robustness – is suitable for reformer-type fired tubular reactors; HyProGen® 820 DCARB and 821 DCARB nickel-based catalysts designed for moderate-temperature applications in adiabatic reactors, which combine superior activity with high thermal resistance against deactivation; HyProGen® 850 DCARB, a highly active ruthenium-based catalyst designed for low-temperature applications. Research on robust catalysts that allow lower temperatures for increased energy efficiency is ongoing (Fig. 8).

Ultimately, Clariant researchers foresee the greatest potential in nickel-based catalysts in both adiabatic and fired tubular reactors. One consideration is that ruthenium is one of the rarest metals on the planet, while nickel ore is mined on several continents in abundance. In addition, nickel is readily recyclable, contributing to the circular economy.

Ongoing research indicates that nickel-based catalysts can offer versatility in adiabatic and fired tubular systems of various sizes. ■

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