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Number 380 November | December 2022

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Green Fischer-Tropsch production
The Dakar ammonia incident
Melamine integration in a fertilizer complex
Decarbonisation of ammonia and methanol

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ISSUE 380
NOVEMBER-DECEMBER 2022

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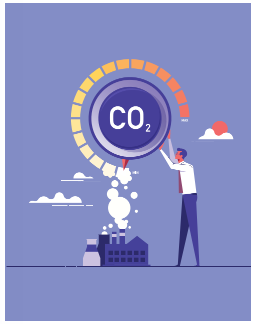

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The politics of ammonia

Fertilizers are always political to some extent, sitting as they do at the intersection of key commodities such as oil and gas on the one hand and food on the other. Markets for major nitrogen derivatives have often been distorted by political decisions to achieve self-sufficiency in fertilizer production, such as in, e.g. China or India. But over the past couple of months ammonia has found itself particularly in the political spotlight, in the context of the ongoing conflict in Ukraine, which continues to shape and indeed re-shape global commodity markets.

At issue is the huge pipeline that runs from Togliatti in southern Russia to the Ukrainian Black Sea coast at Odessa. In happier days, it conveyed up to 2.5 million t/a of ammonia to the export terminal, representing about half of Russia's ammonia exports, and more than 10% of all traded ammonia. Its closure by Ukraine in the early days of the war has removed that ammonia from the market, and Russia has struggled to find other ways to export that ammonia. It has contributed to the current record prices for ammonia of over $1,000/t.

> **"If the fertilizer market is not stabilised, next year the world may run out of food."**

The disruption to exports of food grain from Ukraine, one of the world's largest exporters, has hit food markets hard, especially in the developing world, and fears of famine prompted international pressure to agree a grain export deal via the major port of Odessa. The deal was finally struck on July 22nd with the first ship sailing on August 1st. By the end of October, some 9.3 million tonnes had been shipped. Vessels are stopped in Istanbul and inspected in both directions to make sure that they are not carrying weapons or other warlike supplies. In spite of some hitches following Ukrainian drone attacks on the Russian naval base at Sevastopol, the deal seems to be holding.

The current deal was to last for four months, ending on November 19th, and both sides have been in negotiations for several weeks over its continuance after that date. However, Russia is reportedly pressing for ammonia exports to be included in the new deal, otherwise it will not extend the grain export concession, and they seem to have backing from the United Nations secretary general Antonio Guterres in doing so. On September 23rd, Guterres said: "If the fertilizer market is not stabilised, next year the world may run out of food. It is essential that all countries remove every remaining obstacle to the export of Russian fertilizers. We need to get them to farmers at a reasonable cost and on to fields as soon as possible."

Guterres has personally met with president Putin as well as Turkish president Erdogan, who has acted as an intermediary, to attempt to secure agreement on a resumption of ammonia exports, and there seems to be tentative acceptance in western capitals that Russian ammonia exports should be allowed. Fertilizers (and indeed food) are not part of the sanctions regime on Russia, but withdrawal of access to the SWIFT international banking system has made paying for them more onerous. For that reason, Russia has been insisting that the ammonia deal must also include a relaxation of the SWIFT restrictions. The talks have also bogged down over Ukraine trying to tie them to the release of detainees.

With the November deadline rapidly approaching, it remains to be seen if a deal can be reached. It is in Ukraine's interest for the grain export deal to continue, and Russia's interest for ammonia to be included. Moreover, it is in the interests of farmers and consumers around the world, but particularly in its poorest parts, for both to be allowed. ■

Richard Hands, Editor

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Price Trends

Market Insight courtesy of Argus Media

NITROGEN

Falling gas prices in Europe from the start of September offered some relief to markets that had been badly hit by the record gas price levels seen across the continent as Russian pipeline supplies were progressively shut down or, in the case of the Nordstream 1 line, deliberately sabotaged. Dutch TTF gas prices dropped from over 270 euros/MWh ($80/MMBtu) at the start of September to below €100/MWh ($30/MMBtu) at the end of October – still high by historical standards but their lowest level since July. European gas storage levels were reportedly around 90% at the end of October, with mild weather helping keep demand down.

The fall in gas prices in turn helped ease pressure on European fertilizer producers. Higher prices had already led to dips in demand, with European fertilizer buying down around 20% year on year, though mainly in phosphorus and potash which are less critical for yearly application than nitrogen. At the same time, the relaxation in gas prices has led to capacity restarting. It is estimated that at the start of October only 37% of European fertilizer capacity was operational, but this had risen to 63% by the end of the month.

However, at time of writing this still had yet to filter into ammonia and urea prices. European c.fr ammonia import prices remained at almost $1,200/t at the end of October, with Caribbean f.o.b. rates still above $1,000/t and Middle East offered prices above $900/t. High ammonia prices were causing demand destruction across the board. Deliveries to industrial consumers in northeast Asia were reported to be down 55% year on year for the period 1Q-3Q 2022.

Urea prices, meanwhile, had fallen some way, but remained high, with Middle East f.o.b. prices ranging from $550-600/t and Caribbean prices in a similar range, and these high prices continue to weigh on buying, with Brazilian consumers notably seeming to hold off on purchases.

Another factor weighing on urea markets has been a resumption of exports from China, with an apparent easing of the customs restrictions imposed last year – in practice if not necessarily officially. China exported more than 850,000 tonnes of urea in 3Q 2022, more than double the rates for 1Q and 2Q this year, though still considerably down on 2021's figures, with most of the cargoes destined for India.

As usual, Indian urea buying continues to set the tone for the market. RCF bought 870,000 tonnes of urea in September, and IPL a further 1.5 million tonnes in October for December delivery at delivered prices of around $650/t c.fr, equivalent to an Arab Gulf netback of around $630/t f.o.b. – most of the urea is coming from Middle East producers. ■

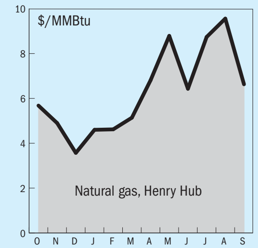
Table 1: **Price indications**

Cash equivalent	mid-Oct	mid-Aug	mid-Jun	mid-Apr
Ammonia ($/t)				
f.o.b. Black Sea	n.m.	n.m.	n.m.	n.m.
f.o.b. Caribbean	1,100-1,200	1,050-1,095	925-950	1,350-1,550
f.o.b. Arab Gulf	890-990	915-1,030	880-970	975-1,150
c.fr N.W. Europe	1,140-1,240	1,165-1,250	1,000-1,085	1,400-1,490
Urea ($/t)				
f.o.b. bulk Black Sea	n.m.	n.m.	n.m.	n.m.
f.o.b. bulk Arab Gulf*	546-631	570-680	535-650	700-850
f.o.b. NOLA barge (metric tonnes)	550-585	465-585	570-595	935-970
f.o.b. bagged China	580-620	475-530	525-625	690-820
DAP ($/t)				
f.o.b. bulk US Gulf	756-808	803-836	822-888	1,001-1,066
UAN (€/tonne)				
f.o.t. ex-tank Rouen, 30%N	683-693	605-609	583	837-859

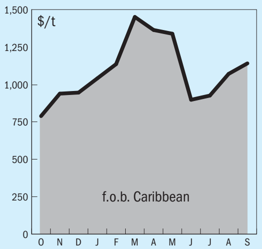
*Notes: n.a. price not available at time of going to press. n.m. no market. * high-end granular.*

END OF MONTH SPOT PRICES

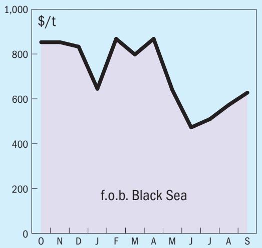
natural gas



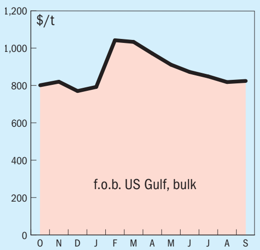
ammonia



urea

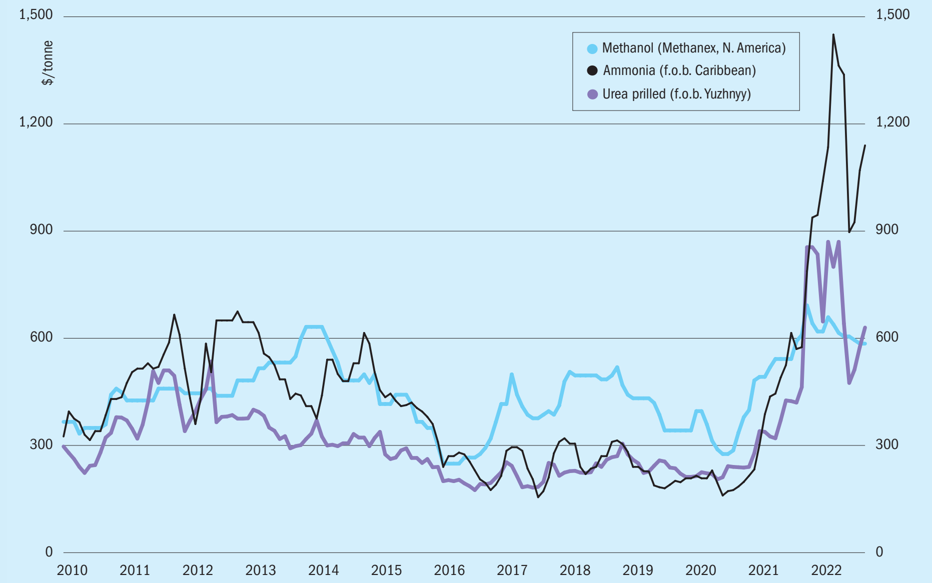


diammonium phosphate



Market Outlook

Historical price trends $/tonne



Source: BCInsight

AMMONIA

- The ammonia market appears to be oversupplied as of the end of October 2022, with a ready availability of spot cargoes. Coupled with increased availability from European producers due to an easing of gas prices, this seemed to indicate bearish market sentiment for the immediate future.
- Buying is also traditionally lower over the winter period and a time of falling ammonia prices, though this year much will hinge upon winter weather across the northern hemisphere and consequent gas demand in Western Europe and North America. A cold snap could see gas prices head back towards their stratospheric mid-year levels and a consequent shutdown in European production.
- A deal for the export of Russia ammonia via Odessa remains under discussion at the UN, but negotiations are difficult. While Russia is still exporting some ammonia, deliveries to major consumers like India and Morocco are down by about 50% year on year.
- At the moment, prices remain relatively stable, but there are some signs of falling prices in most markets.

UREA

- Urea prices have been falling on weak demand. In the US, NOLA prices fell by about $60-70/t in September to around $600-635/t. The US saw little impact on demand from Hurricane Ian but historically low water levels on the Mississippi river after a prolonged period of drought were affecting barge traffic and the ability to move cargoes upriver to consumers.
- Indian c.fr prices fell from around $670/t in September to $650/t c.fr in October, and offer rates at or below $600/t in most major supplying nations. More Indian buying is expected before the end of the year, and it is also believed that Brazil still has to cover some demand and should be back in the market over the coming weeks.
- CF Industries says that it expects prices to rise again going into winter with tight supply and continuing uncertainty in the ammonia market.

METHANOL

- Contract methanol prices have stabilised in most major markets in 3Q 2022. Methanex's reference prices have been a rollover in North America for both September and October at $585/t. European contract prices were stable at €510/t, and Asian contract prices at $410/t. However, high gas prices in Europe in September saw spot methanol rates reach $570/t, with around $^1/_3$ of the continent's methanol capacity shut down, inventories low and rising demand in derivative markets.
- 4Q pricing is seeing stable demand and firmer prices according to Methanex. China in particular is seeing price rises due to low inventories at Chinese ports. Chinese supply from Iran was curtailed due to both planned and unplanned shutdowns in the country.
- In spite of a lull in European gas prices due to mild weather in October, with winter approaching and major Russian pipelines still shut down, the prospects for methanol pricing appear to be higher going into the end of 2022 and start of 2023. ■

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Nitrogen Industry News

DENMARK

Agreement on large-scale electrolysis for ammonia

Topsoe has agreed to supply an initial 500 MW of industrial-scale, solid oxide electrolyser cells (SOEC) to First Ammonia, a US company aiming to produce green ammonia for transportation fuel, power storage and generation, as well as fertilizer, at sites in northern Germany and the southwestern United States. The companies envisage that over the lifetime of the agreement some 5 GW of SOEC electrolysers will be supplied, potentially replacing almost 5 bcm of natural gas and eliminating the emission of 13 million t/a of CO_2 emissions. The facility to manufacture the electrolyser cells will be built in Herning, Denmark, and has recently received a final investment decisions from Topsoe's board.

First Ammonia has been developing sites around the globe for the production of commercial-scale, green ammonia production facilities with first operations planned for 2025. The company says that it will operate all of its plants dynamically to support existing renewable power markets.

Joel Moser, CEO of First Ammonia, said: "We have the utmost confidence in Topsoe and its scientists and engineers... with their cutting edge SOEC electrolysers and industry leading ammonia synthesis, we will develop facilities around the world to produce millions of tons of green ammonia from water and air. Ammonia saved humanity from starvation a century ago as a replacement for depleted sources of fertilizers, in large part due to Topsoe's excellence. Ammonia can save humanity once again as the workhorse of the hydrogen economy, replacing petrochemicals to decarbonise agriculture, transportation and power storage and generation."

Partnership breaks ground on green ammonia project

A Danish partnership comprising Topsoe, Skovgaard Energy, and Vestas has begun construction of a demonstration plant at Ramme near Lemvig in western Jutland that will produce 5,000 t/a of green ammonia based on 50 MW of renewable power from solar and wind, and production of hydrogen via water electrolysis. The project will demonstrate how renewable power can be coupled directly to the ammonia plant while taking fluctuations in power production into account. It is expected to be operational by 2023. The partnership has received 81 million krone (€11 million) in funding from the Danish Energy Technology Development and Demonstration Program (EUDP).

Kim Grøn Knudsen, Chief Strategy and Innovation Officer at Topsoe said: "We are very excited to begin this next chapter going from maturing the project to actually begin construction of this cutting-edge green ammonia plant. The plant will serve as a prime example of how we can replace fossil-based fuels and fertilizer by carbon-neutral alternatives via electrolysis."

UNITED ARAB EMIRATES

Fertiglobe pays $750 million in dividends

Fertiglobe, the strategic partnership between ADNOC and OCI, and the world's largest seaborne exporter of urea and ammonia, says that its general assembly has approved payment of a 1H 2022 cash dividend of $750 million. Ahmed El-Hoshy, Chief Executive Officer of Fertiglobe commented:

"Fertiglobe's very solid first-half performance and approved dividend of $750 million has resulted from powerful earnings momentum, healthy cash conversion and a robust capital structure. The company has achieved strong growth since its landmark IPO on ADX [the Abu Dhabi stock exchange] almost one year ago, and we are delighted to have created significant value for shareholders during that time. As we look ahead to a very promising end to 2022, we will continue to execute on our strategy to create long-term value for all stakeholders."

UNITED KINGDOM

IFS launches new online information resource

The International Fertilizer Society has launched FerTechInform, a new online information resource covering technical aspects of fertiliser production. The resource has two complementary parts – an information knowledge base and an interactive forum. The knowledge base contains introductory level information on processes, chemistry, materials and equipment, augmented by links to more detailed or specific resources and related IFS Proceedings. The related forum enables users to interact with each other, supported by a panel of experts who are available to answer questions. Much of the content of the knowledge base has been derived from the IFDC's Fertilizer Manual 'Green Book', with other content provided by the European Fertilizer Blenders Association, Fertilizers Europe and the European Sustainable Phosphorus Platform, among others.

Additive improves nitrogen availability

An innovative trial exploring if a new slurry additive can improve nutrient availability in digestate has shown a 20.3% increase in available nitrogen content and a 29% reduction in dry matter solids after the first year. The *Digest-It* slurry additive from Origin Fertilisers is a live liquid biological bacteria that has been used in digestate for the first time and has been proven to significantly reduce ammonia emissions and increase ammonium nitrogen levels in slurry. The trial took place at a 1.2 MW anaerobic digestion plant in Lincolnshire.

Callum Norman, speciality sales manager at Origin Fertilisers, said: "We are really pleased with the results of the trial. The environmental benefits, such as reduced volatilisation due to the conversion of ammonia into ammonium, and supplying good microbes to the soil, will be a huge benefit to all farms and help contribute towards agriculture reducing its emissions". From a financial perspective, the trial returned a 2:1 cost benefit and only required one application, reducing the labour requirement compared with additives that need ongoing applications.

NETHERLANDS

Partnership backs strategy for zero-emissions ammonia

Leading companies have endorsed a new strategy from the Mission Possible Partnership (MPP) to ramp up production of zero-emissions ammonia, potentially for use as a clean marine fuel. To date, 35 companies have endorsed the plan for action needed in this decade to achieve net-zero emissions by 2050, while contributing significantly to decarbonisation in other sectors of the economy. Signatories to the report include CF Industries, Yara, BASF, and SABIC, and renewable energy providers ACWA Power, Iberdrola, and Ørsted. Support for MPP's strategy spans the ammonia value chain including both current and future buyers of ammonia as a zero-carbon energy carrier, a measure of growing momentum for action in the near-term. The sector generates about one percent of global CO_2 emissions, with demand for ammonia likely to increase by three- to six-fold by mid-century.

Matt Rogers, CEO of MPP said: "This Ammonia Transition Strategy is operationally relevant and industry-backed, not wishful thinking or pie in the sky. We know how to reduce emissions, initially deploying resources and technology available today. The imperative is to act now, in this decade: we're working with industry, supply chains and finance to deliver the clear thinking and asset-by-asset plans to make net zero viable".

Tony Will, CF Industries president and CEO, said: "Achieving net-zero ammonia will not only transform our industry but also help accelerate the world's transition to clean energy. This report is an important milestone, setting forth the opportunities and pathways for the entire industry to reach net zero and highlighting the many important ways that clean ammonia can help decarbonise other industries such as power generation and maritime shipping."

MPP's report maps critical steps for – including emissions data and real-economy milestones – for the sector to achieve net zero emissions by 2050. The strategy forecasts strong demand for both green ammonia (where the hydrogen is produced via electrolysis from renewable electricity and water) and blue ammonia (from hydrogen produced from natural gas with carbon capture) with green ammonia emerging as the dominant material. New applications for green ammonia as an energy carrier – in particular as a marine fuel – could increase demand, as ammonia assumes a larger role in the transition to a green economy. Rapid scaling of near-zero-emissions ammonia production depends on the shipping sector – which is likely to use it as an alternative fuel to heavy fuel oil, and on demand from the power sector – where green ammonia could replace coal in Japan and South Korea.

RUSSIA

Domestic fertilizer purchases up 20% in 2022

According to Russia's Ministry of Agriculture, Russian farmers increased their purchase of mineral fertilizers by 20% year-on-year during the first eight months of 2022, to 4.3 million tonnes nutrient. President of the Russian Fertilizer Producers Association, Andrey Guryev, said: "Nearly 90% of the Ministry mineral fertilizer purchasing plan for 2022, taking into account carryover stocks, has already been fulfilled. The remaining volumes are already under contract and have been included in the production schedule for the rest of the year. All the necessary infrastructure for the transfer and storage of mineral fertilizers to ensure that seasonal field work is carried out throughout the country is in place. The annual supply target will be exceeded."

During the All-Russian Field Day 2022, in the Kaliningrad region on 29 July 2022, Russia's Agriculture Minister, Dmitry Patrushev, said that farmers would purchase 5 million tonnes nutrient this year and that the application rate would be 60 kg nutrient/ha. The Minister also noted that purchases of mineral fertilizers need to be increased to 8 million tonnes nutrient by 2030.

PORTUGAL

NEXTCHEM wins contract for renewable hydrogen and ammonia project

Tecnimont subsidiary NextChem has been awarded a pre-FEED engineering services contract by MadoquaPower2X – a Portuguese/Dutch/Danish consortium led by Madoqua Renewables along with CIP's Energy Transition Fund and Power2X to develop and operate an integrated renewable hydrogen and green ammonia plant at Sines, Portugal. The scope of the agreement covers early studies, technology and process review, modularity and logistics analysis, and the front end loading of engineering required to undertake the permitting and licensing for the project.

MadoquaPower2X will use renewable energy and 500 MW of electrolysis capacity to produce 50,000 t/a of green hydrogen along and up to 500,000 t/a of green ammonia plant in its first phase, avoiding 600,000 t/a of CO_2 emissions. It is the first industrial scale project at the new Sines energy and technological hub.

João Galamba, Portugal's minister for Environment and Energy said: "Climate neutrality by 2050 requires bold decisions on sustainable investments with a focus on energy and climate goals, while allowing economic recovery and MadoquaPower2X in Sines is a good example of this. From ambition we moved to action, and we are pleased to witness this important milestone for MadoquaPower2X and Maire Tecnimont, confirming the right path to meet the goals we have set for energy transition. I congratulate the partners of this project for their commitment and dedication".

ITALY

Eurotecnica wins two more melamine plant contracts

Eurotecnica, the technology arm of the Proman family of companies, has been awarded two contracts for the implementation of large scale high-pressure melamine plants, with capacities of 60,000 t/a and 80,000 t/a respectively. Both plants feature single reactors and use 5th generation proprietary *Euromel®* technology. Together with the previously announced world's largest high pressure melamine plant at 120,000 t/a, the new contracts bring Euromel's total licensed nameplate capacity to more than 1.13 million t/a at 28 facilities worldwide.

SAUDI ARABIA

ACWA Power and KEPCO to explore industrial-scale green hydrogen/ammonia production

Saudi power generator and developer ACWA Power, has signed a memorandum of understanding with the Korea Electric Power Corporation (KEPCO), for a partnership in the development of green hydrogen/ammonia projects in Middle East and decarbonise KEPCO's operations in South Korea. KEPCO company intends to utilise the venture's end products to operate its power plants in South Korea. This is the first agreement of its kind between ACWA Power and KEPCO, though both companies have been joint investors in projects like Rabigh 1 independent power plant in Saudi Arabia for nearly a decade. In order to decarbonise its operations, KEPCO plans to rely increasingly on green ammonia produced from green hydrogen for power generation purposes and is targeting the use of 5-10 million t/a of green ammonia by 2030.

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Paddy Padmanathan, CEO and vice chairman of ACWA Power said: "The world is witnessing the alarming impact of climate change and as pressure rapidly mounts to take immediate, mitigating action, collaborative efforts need to be made to find the right solutions. We are honoured to work with committed, long-term partners like KEPCO to accelerate the exploration of green hydrogen – a solution that can decarbonise entire industries and make a real difference towards reducing global warming."

Lotte Fine Chemical to import 50,000 tonnes of blue ammonia

Korea's Lotte Fine Chemical says that it will import 50,000 tonnes of blue ammonia from Saudi Arabia. Half of the total will come from Aramco subsidiary SABIC, and the remainder from mining company Ma'aden. Ammonia will be shipped to Lotte Fine Chemical's terminal in the southeastern port city of Ulsan by the end of 2022. This is the world's first commercial deal to supply blue ammonia certified by Germany's testing, inspection and certification agency, TUV Rheinland.

MALAYSIA

Malaysia may use ammonia co-firing at coal power plants

Japan's biggest power generator, JERA says that it is collaborating with heavy industry manufacturer IHI Corp to explore ways to expand the use of ammonia as a fuel at coal-fired power plants in Malaysia. The two companies have been working together on co-firing ammonia with coal at a large commercial power plant in Japan to cut carbon dioxide emissions. Under a memorandum of understanding signed by their subsidiaries, JERA Asia and IHI AP, the companies will jointly study ammonia co-firing in thermal power plants in Malaysia to contribute to decarbonisation there, JERA said in a statement. JERA is a joint venture between Tokyo Electric Power and Chubu Electric Power.

UNITED STATES

Nutrien selects thyssenkrupp Uhde for blue ammonia project

Nutrien says that thyssenkrupp Uhde has been selected as technology provider and partner for the world's largest clean ammonia plant, which Nutrien plans to build at its existing Geismar, Louisiana site. The plant will have an expected annual production capacity of 1.2 million t/a and is expected to capture and store more than 90% of its CO_2 emissions to achieve the lowest carbon footprint of any ammonia plant at this scale, with the potential to transition to net-zero emissions with future modifications. The ammonia plant will serve growing demand in agriculture, industrial and emerging energy markets. A final investment decision on the project is expected in 2023, and if approved, full production is anticipated by 2027.

"This partnership marks another important milestone in our commitment to provide solutions to help meet the world's decarbonisation goals through leadership in clean ammonia production," said Trevor Williams, Interim President, Nitrogen and Phosphate at Nutrien. "We are glad to have an experienced partner with both the technology and proven execution competence to join us on this journey as we strive to sustainably feed and fuel the future."

Traditional ammonia plant designs can only achieve carbon capture rates of up to 70% and face significant challenges to reach a net zero design. Nutrien's clean ammonia plant will use autothermal reforming technology to achieve carbon capture rates of at least 90% percent.

ExxonMobil and CF Industries to partner on large-scale CCS project

ExxonMobil and CF Industries have signed an agreement to invest $200 million in a CO_2 dehydration and compression unit at CF Industries' Donaldsonville, Louisiana fertilizer facility. Carbon dioxide captured at Donaldsonville will then be transported using some of Exxon's EnLink Midstream 6,400 km pipeline network, to a geological storage site the company owns in Vermilion Parish, Louisiana, where it will be permanently stored. Up to 2 million t/a of CO_2 emissions could be captured and stored in this way, equivalent to the output of approximately 700,000 gasoline-powered vehicles, according to the project partners. Donaldsonville has a capacity of nearly 8 million t/a of nitrogen products, and CF says that it expects to market up to 1.7 million t/a of blue ammonia as demand for it begins to grow.

"This agreement… ensures that we remain at the forefront of the developing clean energy economy. As we leverage proven carbon capture and sequestration technology, CF Industries will be first-to-market with a significant volume of blue ammonia," said CF Industries' CEO Tony Will. "This will enable us to supply this low-carbon energy source to hard-to-abate industries that increasingly view it as critical to their own decarbonisation goals."

Collaboration on Gulf Coast clean hydrogen/ammonia facility

Air Liquide, Chevron, LyondellBasell and Uniper SE have announced their intent to collaborate on a joint study that will evaluate the development of a hydrogen and ammonia production facility along the US Gulf Coast. The facility could support industrial decarbonisation and mobility applications in the region and expand clean ammonia exports, helping to increase the supply of lower carbon power internationally. If development proceeds, the project could leverage existing advantages along the Gulf Coast, including pipeline infrastructure, to supply lower carbon and renewable hydrogen to local industrial clusters. Likewise, ammonia infrastructure could support exports to both Europe and the Asia Pacific region.

Adam Peters, CEO of Air Liquide North America, said: "Air Liquide is proud to evaluate, with its customers and industry partners, opportunities to further develop and deploy low-carbon and renewable hydrogen, and carbon capture technologies in the region. The Gulf Coast is the ideal location to model hydrogen and carbon capture technologies as immediate pathways to decarbonising hard-to-abate sectors. This project exemplifies Air Liquide's commitment to decarbonizing industrial basins around the world. Prioritising sustainable technologies, like hydrogen and carbon capture, means we can provide energy transition careers for many thousands of American workers while building a more sustainable energy future for all."

KBR wins contract for blue ammonia project

KBR has been awarded a technology contract by Tecnimont for OCI NV's low-carbon blue ammonia project in the United States. Under the terms of the contract, KBR will supply the technology license, basic engineering design, proprietary equipment and catalyst for the 1.1 million t/a blue ammonia plant. Targeting completion by 2025, the project will be designed to transition from blue to green ammonia production as green hydrogen becomes available at larger scale in the future.

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"We are excited to continue to build on our strong relationship with OCI NV and Maire Tecnimont to deliver our market-leading and proven ammonia technology for this energy transition project," said Doug Kelly, KBR President, Technology. "This award is a further testament to KBR's leadership in helping its clients implement effective decarbonisation technologies today on a path to achieving their future ESG objectives."

AUSTRALIA

Lloyd's Register looking at clean ammonia from Pilbara

Lloyd's Register has been selected to undertake key feasibility studies into using clean ammonia to refuel ships at world-scale ports in the Pilbara region of Western Australia. The announcement follows the signing of a collaboration agreement in August between Yara Clean Ammonia and the Pilbara Ports Authority (PPA). Yara Clean Ammonia Vice President Bunkering – Port Relationships & Regulation, Tessa Major said Yara's existing and developing operations in the Pilbara are the perfect catalyst for unlocking new opportunities, and this is strengthened by a shared commitment with PPA to enable decarbonisation in the shipping industry. Lloyd's Register will provide analysis focusing on key factors needed to assess the potential uptake of ammonia refuelling, including the market for clean fuels in shipping; shore side infrastructure requirements; safety considerations; and the regulations required to support ammonia bunkering at Pilbara ports. The execution of the study is expected to take at least 12 months. In September a final investment decision was announced for Project Yuri, which will see a renewable hydrogen plant built adjacent to the Yara Pilbara's existing ammonia plants close to PPA's Dampier port.

Lloyd's Register chief commercial officer Andy McKeran says that the maritime industry has to make some significant investment decisions around alternative fuels in the decade ahead, but maritime value chain stakeholders needed surety on future fuel availability and the existence of landside infrastructure.

"Studies like this one will help give more certainty on the feasibility of the options being considered and will enable the industry to work to address the safety challenges around their safe adoption," Mr McKeran said.

Burrup urea plant expected to get go-ahead this year

Nearby the proposed Dampier development, a $4.2 billion gas-based urea plant is expected to receive a positive final investment decision by the end of 2022, having received a $220 million loan from the Australian government to help cover construction costs. Incitec Pivot's Perdaman urea plant will take gas from Woodside's Scarborough project. The Federal Northern Australia Infrastructure Facility has already lent the Western Australian government $255 million to improve port and water facilities for the project. The project has attracted criticism from Aboriginal and environmental groups because of the proximity of the World Heritage nominated Murujuga rock art, more than one million rock engravings that are up to 40,000 years old, some of which will be relocated for the plant's construction. Fears have also been expressed about the potential for site emissions to damage the rock art.

Green ammonia conversion for Gibson Island

Fortescue Future Industries is moving ahead on plans to partially convert Incitec Pivot Ltd's Gibson Island ammonia facility near Brisbane, Queensland. The project will use large scale electrolysis powered by 500 MW of renewable electricity to convert up to 70,000 t/a of ammonia manufacture to zero carbon production. FFI and Incitec Pivot say planning for the conversion of the ammonia plant is now in its final stages, making a start on front end engineering design while also preparing the groundwork for a final investment decision in 2023. Assuming approvals are granted, first green production could begin in 2025. The federal government's Australian Renewable Energy Agency will provide grant funding of A$13.7 million to defray the A$38 million FEED costs.

Incitec Pivot's Gibson Island plant, Australia.

INDIA

Tecnimont establishes new joint venture

Tecnimont and Metal Craft Constructors Private Ltd (MCCPL) have announced the establishment of Tecni and Metal Private Ltd, a new 51-49 joint venture to focus on efficient construction solutions for the Tecnimont Group's projects in India, combining Tecnimont's experience in planning and construction management retained and MCCPL's long-term experience in providing specialised personnel for different project phases of complex industrial plants, including mechanical and civil engineering and construction, erection and pre-commissioning.

Milind Baride, India EPC Projects Vice President, Maire Tecnimont Group, said: "As we continue to expand Maire Tecnimont Group's industrial footprint in India, it is important that we develop and nurture a robust in-house division focused solely on construction and mechanical works. We stay committed to ensuring the best environmentally performing products and processes, and our new JV Tecni and Metal Private Limited will take us a step closer to becoming the definitive leader in the Indian EPC arena".

MoU on green ammonia project

Jakson Green has signed a memorandum of understanding (MoU) with the government of Rajasthan to invest $2.7 billion in a green hydrogen and ammonia project. The 365,000 t/a project will be developed in phases over the period 2023-2028, along with an integrated hybrid renewable power complex. Jakson Green is an energy transition platform backed by India's Jakson Group. The government of Rajasthan said it would facilitate the project with registrations, approvals and incentives.

Start-up at Barauni urea plant

Hindustan Urvarak & Rasayan Ltd (HURL) began urea production at its new plant at Barauni on October 19th, according to the company. The plant is one of several developed by HURL to boost domestic urea production, and has a capacity of 1.27 million t/a of urea. HURL is a joint venture between Coal India Limited, NTPC, Indian Oil Corporation and the Fertilizer Corporation of India Ltd. It has been mandated by the government to revive urea production at Gorakhpur, Sindri and Barauni with an estimated investment of $3 billion. ■

Syngas News

DENMARK

Maersk orders six more methanol container ships

Maersk has ordered six more 17,000 teu (twenty-foot equivalent unit) container ships capable of running on methanol from Hyundai Heavy Industries (HHI). The order brings Maersk's total order book of dual-fuel vessels capable of running on methanol to 19. Maersk said the new ships will replace existing tonnage in its fleet when they're delivered in 2025. When all 19 vessels on order join the fleet and replace older tonnage, CO_2 savings will be around 2.3 million t/a, according to Maersk. Maersk has committed itself to renewable methanol as a pathway to zero emissions shipping. Its first vessels are due for delivery from Q1 2024. The company has also signed several green methanol fuel supply agreements and joined a partnership to create the first e-methanol plant in Southeast Asia. Maersk is also working with Japanese trading house Mitsui and the American Bureau of Shipping (ABS), to jointly conduct a detailed feasibility study of methanol bunkering logistics in Singapore.

"Green methanol is the best scalable green fuel solution for this decade, and we are excited to see several other shipowners choosing this path. It adds further momentum to the rapid scaling of availability needed to bring down the premium on green methanol and accelerate the evolution of climate neutral shipping," said Palle Laursen, Chief Fleet & Technical Officer at Maersk. ■

Grant for green methanol facility

Danish renewables developer European Energy has received €53 million from the Danish Green Investment Fund (DGIF) for its upcoming green methanol facility in Kassø, claimed to be the largest e-methanol facility in the world to date. The financing will go to the total capital investments in connection with the expansion of the plant.

The future facility will be supplied with renewable energy from the nearby 300 MW Kassø Solar Park developed and built by European Energy. Earlier this year, European Energy ordered a 50 MW electrolyser plant from Siemens Energy. Siemens will design, supply and commission the electrolysis system consisting of three full arrays of its line of proton exchange membrane (PEM) electrolysis products. The end-users of the methanol will be shipping company Maersk and fuel retailer Circle K among others. The start of commercial methanol production is planned for the second half of 2023.

UNITED KINGDOM

FEED for wind-to-hydrogen demonstrator project

Principle Power has been contracted by ERM to advance the front-end engineering design (FEED) for the 10 MW Dolphyn wind-to-hydrogen demonstrator project off the coast of Aberdeen, Scotland. The contract was signed after ERM Dolphyn was awarded £8.62 million of funding from the UK Government, via the Low Carbon Hydrogen Supply 2 Competition.

Dolphyn (Deepwater Offshore Local Production of HYdrogeN) is a concept design to produce large-scale green hydrogen from floating offshore wind. The ERM Dolphyn concept employs a modular design integrating electrolysis and a wind turbine on a moored floating semi-submersible platform based upon proven WindFloat® technology by Principle Power to produce hydrogen from seawater, using wind power as the energy source. ERM and Principle Power have been collaborating on the development of decentralized hydrogen production opportunities since 2019.

JM technology qualified to support Shell green hydrogen production

Shell has qualified Johnson Matthey's (JM) PURAVOC GREEN™ purification catalysts for use in its global hydrogen production projects. JM's catalysts will be used to remove trace oxygen to meet oxygen specifications in the production of high purity, zero carbon hydrogen. Removal of oxygen is critical to make the process safer and more efficient. Deoxygenation is an essential step in the production of green hydrogen and requires a flexible and robust catalyst that can operate under a variety of pressures, relatively low temperatures, and intermittent feed flows.

Green hydrogen has a low carbon footprint compared to alternative fuels and can be used as clean energy and in the production of chemical building blocks such as ammonia and methanol. PURAVOC GREEN catalysts have been carefully designed to be highly efficient within a broad operation envelope and maintain performance over many operation cycles making this a reliable, easy to operate and economic solution.

Jane Toogood, Catalyst Technologies Chief Executive at JM, said "We are committed to catalysing the net zero transition for our customers and addressing the biggest environmental challenges that exist. Finding ways to decarbonise and move towards more sustainable processes is of utmost importance and we are pleased to support Shell's decarbonisation ambition."

ICIS launches renewable hydrogen assessments

ICIS has launched the first hydrogen price assessments to reflect the market value of renewable electricity. This product will support participants with the intelligence needed to develop a liberalised clean hydrogen market and optimise energy transition resources. Covering market-adopted technologies and locations, the assessments have been produced through consultation with energy market participants and are structured to be compliant with European Union and UK government standards for producing renewable hydrogen (Renewable Fuels of Non-Biological Origin). These hydrogen price assessments reflect the business conditions facing renewable hydrogen projects, providing participants with the confidence to make strategic investment plans, conduct bilateral negotiations and navigate volatility.

"ICIS views the provision of pricing for truly renewable hydrogen as a key enabler of the energy transition," Simon Ellis, Head of Hydrogen Analytics at ICIS says. "These assessments are an important step in ICIS's commitment to providing price transparency to the renewable hydrogen market. They are the first true, independent reflection on the cost of producing renewable hydrogen and will give investors the confidence they need to bring capacity online".

GERMANY

Green methane import project

Fortescue Future Industries has signed an agreement with Tree Energy Solutions (TES) to develop the world's largest integrated green hydrogen project to help Europe mitigate its current energy and climate crisis and to bring green molecules to Europe.

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The first phase of this partnership will jointly develop and invest in the supply of 300,000 t/a of green hydrogen with final locations being currently agreed. TES aims to generate green hydrogen using renewable energy, then combine it with captured CO_2 to produce green methane. The methane will then be landed at TES' new import terminal in Wilhelmshaven, Germany, with first deliveries expected to take place in 2026. The project will produce enough green methane to supply 1.5 million households. The partnership are aiming to eventually develop industrial scale green hydrogen production globally with an initial focus on Australia, Europe, Middle East and Africa.

UNITED STATES

Topsoe to supply technology for renewable gasoline plant

Topsoe will deliver technology to HIF Global's planned eFuels facility in Texas. The plant will produce carbon-neutral gasoline sufficient to power over 400,000 vehicles annually. The renewable gasoline will be made by combining green hydrogen made from renewable power and recycled carbon dioxide to produce methanol, which will then be converted to downstream gasoline. Topsoe will deliver basic engineering and a license for methanol synthesis as well as its TIGAS™ gasoline synthesis technology. Later in the project, Topsoe's scope will be extended to supply methanol reactors and catalysts.

Roeland Baan, CEO at Topsoe, said: "We are proud that HIF Global has selected our technology for this truly innovative project which will contribute to decarbonising US transportation. This is our first involvement in a commercial scale Power-to-X facility producing gasoline."

The plant will be built in Matagorda County in Texas, and will produce 200 million gallons per year of carbon-neutral gasoline that can be used in today's cars and gas stations with no modifications required. The power requirement for the plant will be 2 GW, 90% being consumed by electrolysers for the green hydrogen production process. Start of construction is expected by 2023 and first production by 2026.

Converting flared gas into clean hydrogen

H2-Industries says that it has developed a solution to convert environmentally harmful flared gases from oil production to clean hydrogen and solid carbon using pyrolysis. The process is delivered in self-contained 20 or 40-foot ISO containers and can be pre-assembled in a semi-serial manner and shipped for installation to the flaring site. The process provides clean hydrogen bound in liquid organic hydrogen carriers (LOHC). LOHC are organic compounds that can absorb and release hydrogen through chemical reactions.

The only by-product of the process is solid carbon black that can be shipped for export to any place in the world using ISO container tanks. Carbon black is mainly used to strengthen rubber in tyres, but it can also act as a pigment, UV stabiliser, conductive or insulating agent in various rubber, plastic, coating applications, and other everyday use, including hoses, conveyor belts, shoes, and printing. This carbon black can be sold on the world market, where the current prices are between $1,500-2,500/t.

ITALY

Grant awarded for waste to hydrogen plan

Maire Tecnimont subsidiary NextChem has been awarded a €194 million grant for the development of a waste-to-hydrogen plant as part of the EU's IPCEI Hy2Use project. The project will be part of a so-called 'Hydrogen Valley' near Rome, an industrial-scale technological hub for the development of a national supply chain for the production, transport, storage and use of hydrogen in Italy.

The grant will be disbursed during the construction phases of the plant. The next steps concern the start of the project activities and all the necessary permits, in order to ensure the plant start-up in the first half of 2027, in compliance with the funding. In the initial phase a production of 1,500 t/a of hydrogen and 55,000 t/a of ethanol is expected. Production of hydrogen will grow according to demand, up to 20,000 t/a, proportionally reducing the volumes of ethanol. It will use NextChem's proprietary technology, developed by its subsidiary MyRechemical, to convert 200,000 t/a of non-recyclable solid waste as raw material. The European project also includes a contribution of approximately €4 million for additional research and development activities in waste-to-hydrogen technology, leveraging scientific partners such as Enea, Fondazione Bruno Kessler and La Sapienza University of Rome.

Alessandro Bernini, CEO of Maire Tecnimont Group and of NextChem, commented: "We are proud of the goal achieved by Maire Tecnimont Group with NextChem, and of the recognition of the industrial and technological skills of our Country by the European Union to develop a low-carbon and low-cost hydrogen economy. This project, which is unique in the world, represents a milestone in the development of technologies combining circular economy and green chemistry. It enables us to act as pioneers in the decarbonization of hard-to-abate industries, with a model that can be replicated in other countries".

SOUTH AFRICA

Platinum demand for hydrogen production rising rapidly

From next year, platinum group metals (PGM) demand in the hydrogen sector will eclipse 100 000 oz for the first time, according to Metal Focus. PGMs will see year-on-year double-digit growth over the next decade, overtaking more established demand sectors, as the clean energy transition continues.

FINLAND

Methanol plant using cement off-gas

Energy company St1 is planning to build Finland's first methanol plant, which will be located next to the Finnsementti cement factory on the Ihalainen industrial site in Lappeenranta. The plant will use hard-to-abate CO_2 emissions from the factory's limestone raw material, and will have a capacity of approximately 25,000 t/a. If the project advances according to plan, the plant will be operational in 2026. The methanol will be distributed directly through St1's own network for use in maritime transport. St1 said it has studied the production of synthetic methanol with the Lappeenranta University of Technology (LUT). LUT will continue to be heavily involved in developing the project.

"The Nordic market for synthetic fuels will grow considerably in the coming years," said St1's head of energy transition Riitta Silvennoinen. "The timetable of our pilot project would allow Finland access to the first wave of industrial applications and, consequently, the establishment of the synthetic methanol market and solution scaling. The project will also provide the involved parties with important expertise, which will also be used in advancing other Power-to-X projects."

The project has been granted funding of €35.4 million from the Ministry of Economic Affairs and Employment, conditional on receiving approval from the European Commission. ■

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People

Topsoe has made a number of changes to its board. **Kim Saaby Hedegaard** has been appointed as the company's new Executive Vice President, Power-to-X. Hedegaard has served as interim Head of Power-to-X since May 2022. Before that, he held the position as Chief Operations Officer (COO). He joined Topsoe in 1999 and has since held various leadership positions within engineering, technology, and sales. Since 2017, he was responsible for Catalyst Production and Technology globally. He holds a MSc in chemical engineering from the Technical University of Denmark. He is replaced as COO by **Andreas Bruun Jørgensen**.

The company has also appointed **Morten Holm Christiansen** as interim CFO as his predecessor Philip Eickhoff is returning to the healthcare industry. Christiansen previously held the position of CIO and will maintain those responsibilities in parallel with his position as interim CFO. He has had a long career in Maersk and the Novo Nordisk Group as CFO.

Topsoe CEO, Roeland Baan, commented: "We are on a fast track to build a strong commercial position based on our decarbonization solutions, and I have no doubt that Morten with his extensive leadership experience and financial background is the right person to support the organization in delivering on our strategy, while we look for a more permanent solution. Philip [Eickhoff] has done a great job in building a strong foundation and team to help drive our transformation, and I want to thank him for his contribution and dedicated efforts for Topsoe the past two years. I truly wish him all the best in his future endeavours."

Chief Communications & Brand Officer **Kristine Ahrensbach** is also leaving Topsoe. Ahrensbach joined Topsoe in 2014 and was responsible for Marketing the first six years. In her place, **Kasper Westphal Pedersen** is joining Topsoe as Vice President of Communications & Brand and will report to Chief Human Resource Officer, Peter Kirkegaard. Pedersen has a strong track record of working with the sustainability agenda as a Communications executive. For the past seven years, he has worked as Director of Communications & Branding at Rambøll. Prior to that he spent almost ten years as communications agency executive with responsibility for clients within environment, energy and sustainable development, and he has previously worked as Press Secretary to the Danish Minister of Environment.

Tree Energy Solutions (TES) has announced the appointment of **Alexandra Pieton** as Chief Projects Officer and Yves Vercammen as Chief Corporate Officer. The company says that it is building the largest green energy hub in Europe in Wilmeshaven, Germany to convert renewable electricity from solar and wind into green hydrogen and affordable, renewable gas. Pieton brings over 20 years of valuable experience in the global energy industry and has held senior positions in engineering, project execution, operations, and business management in key strategic markets such as the US, U.K., Malaysia, Indonesia and France. **Yves Vercammen** is an energy commodity markets expert with over 25 years of experience in the sector. Since 2018 he has been Transformation Projects Director at energy infrastructure group Fluxys, focusing on the challenges and opportunities related to the energy transition.

The company has also appointed **Cynthia Walker** as CEO of TES Americas and as Chief Strategy Officer of TES Group. She will head the company's newly established office in Houston, Texas.

In these new roles, Cynthia will be responsible for building TES' business in the Americas with an initial emphasis in the US and Canada and for supporting the development of the TES strategic plan and resource allocation. Marco Alverà, CEO of TES Group, said: "I am delighted to welcome Cynthia to our rapidly expanding and multinational team. Cynthia is one of the most well-established energy executives and she holds significant expertise in execution, finance, and development. Her in-depth knowledge of the energy sector and broad skill set will fit in perfectly with TES's game-changing mission to create a net-zero future. Having her on board will further enable us to bolster our growth strategy and our operations particularly in the North American market."

Tountzer Ramadan has becomes head of machine sales for RHEWUM GmbH. He has worked in the sales department at RHEWUM since 2011 and acted as deputy sales manager from 2017 to 2020. He will appoint a deputy at the end of the year.

ClimeCo has appointed **Dan Linsky** as Senior VP, Voluntary Markets, **Emily Damon** as Senior VP, Sustainability, Policy & Advisory, and **Erika Schiller** as Senior VP, Project Development.

Calendar 2022/2023

NOVEMBER

15-17
40th World Methanol Conference, BARCELONA, Spain
Contact: David Coates, Chemical Market Analytics
Email: dcoates@opisnet.com, chemical.events@chemicalmarketanalytics.com
Tel: +1 713 305 0116

29-30
Argus Clean Ammonia Europe Conference, HAMBURG, Germany
Contact: Argus Media Group
Tel: +44 20 7780 4340
Email: conferences@argusmedia.com
Web: www.argusmedia.com/en/conferences-events-listing/clean-ammonia-europe

DECEMBER

7-9
2022 IFS Agronomic Conference, CAMBRIDGE, UK
Contact: International Fertilizer Society, Colchester, CO1 9PR, UK.
Tel: +44 (0)1206 851 819
Email: secretary@fertiliser-society.org

JANUARY 2023

30 – 1 FEBRUARY
Fertilizer Latino Americano, RIO DE JANEIRO, Brazil. Contact: Argus Media Group
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Email: conferences@argusmedia.com

MARCH

6-8
Nitrogen+Syngas Conference 2023, BARCELONA, Spain
Contact: CRU Events
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Fax: +44 (0)20 7903 2172
Email: conferences@crugroup.com

APRIL

17-19
Syngas 2023, BATON ROUGE, Louisiana, USA
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Plant Manager+

Handling leaks in urea plants: part 4

Leaks in the high-pressure synthesis section of a urea plant may lead to catastrophic consequences. UreaKnowHow.com started to collect incidents in an incident database and in 2017 AmmoniaKnowHow.com and UreaKnowHow.com introduced FIORDA, the Fertilizer Industry Operational Risk Database, a global open source risk register for ammonia and urea plants.

Part 1 of this short series of articles on how to handle leaks in urea plants explained why leaks in the high-pressure synthesis section of a urea plant are so critical, part 2 looked at the causes and consequences of leaks, part 3 discussed different measures to prevent carbamate leaks and this final part discusses mitigation measures.

Mitigation measures

Once a carbamate leak occurs most of the time one the only option is to shut down the plant. Ammonium carbamate will dissociate into ammonia and carbon dioxide and thus a carbamate leak forms a health threat due to the presence of ammonia. Key is to act quick and keep the ammonia cloud small.

Install a proper ammonia leak detection system

Installing a proper ammonia leak detection system at critical locations is a good way to detect leaks at an early stage and be able to act quickly. Professionals from the Ammonia Safety & Training Institute (www.ammonia-safety.com) confirm early detection and quick action of an ammonia leak is vital to avoid catastrophes. Critical locations are the high-pressure synthesis section especially at locations which are difficult to reach like for example the top floors. The carbon steel ammonia feed lines and the ammonia and carbamate high pressure pumps are also critical with respect to potential ammonia leaks.

Shut down the plant

In case of a leak, the best option after the leak has been confirmed and located is to shut down the plant. In real situations this is not always an easy choice to make, but when faced with a critical leak as described in part 2, the recommendation is to shut down the plant.

Flush with steam and/or condensate

In case of a small leak, consider flushing away the solids and diluting/absorbing the ammonia from the leak by means of a continuous flush with steam and/or condensate. The leak and integrity of the leaking equipment should be monitored continuously by means of a camera as even flashing ammonium carbamate can corrode carbon steel bolts and nuts as shown in part 1 of this series.

When a flush is applied it is important to be careful that water with ammonia and ammonium carbamate does not drip on high pressure vessels located under the leak. This mixture can cause stress corrosion cracks in the carbon steel pressure bearing wall of these vessels. This risk increases when one uses fine grain carbon steel materials[1].

Do not allow solids to reduce/stop the leak

Do not allow solids to form even if these reduce/stop the leak. One does not know what happens under these solids and ammonium carbamate can still corrode carbon steel parts and even stainless steel parts due to active corrosion as a result of lack of oxygen (see Fig. 1).

Fig. 1: Solids have stopped the leak but created a critical unsafe situation.

Do not install a clamp on ammonium carbamate and ammonia lines. Installing a clamp on a ammonium carbamate line is not allowed for the following reasons:

- One does not know what happens to the materials underneath these solids and ammonium carbamate corrosion will weaken the carbon steel parts and even stainless steel will corrode as a result of lack of oxygen;
- During the installation of the clamp additional, forces will be applied and these extra forces could lead to a rupture due to corrosion that may have occurred due to the leak.
- Installing a clamp on ammonia lines can be very risky and has led to catastrophic events[2].

Clamps when installed should always be considered a temporary solution. Develop a procedure to check its integrity during installation.

References

1. AICHE Ammonia Safety Manual: 1994, Failure of Urea Strippers and Repair Experience, Pota HP, e.o.
2. AICHE Ammonia Safety Manual: 2011, Failure of Urea Strippers and Repair Experience, S G Gedigeri

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Ammonia markets face continuing disruption

The curtailment of ammonia production in Europe and reduction in export supply from Russia has led to an unprecedented year for the merchant ammonia market.

Right: The Togliatti ammonia pipeline, Ukraine.

Ammonia markets have faced severe disruption since the Russian invasion of Ukraine in February. With no resolution to the conflict in sight, markets have had to adjust to a European market where almost two thirds of ammonia production has been shut down and the loss of up to 20% of merchant supply to the market due to sanctions on Russia. The impact has been most severe upon ammonium phosphate producers, but all market participants have been scrambling to keep up.

Demand

Total world ammonia production was 185 million t/a in 2021 according to IFA figures (157.1 million tonnes N), while total volumes shipped across borders were 19.3 million tonnes (15.8 million tonnes N), or just over 10% of the total.

Fertilizer demand represents about two thirds of merchant ammonia consumption, with India, Morocco and Turkey the main recipients, while major industrial importers include South Korea, Taiwan, China and the EU-27 (Figure 1). As noted, fertilizer consumption is mainly for phosphate (mono- and di-ammonium phosphate; MAP/DAP) production, but around 15% of merchant production goes to make urea or other downstream nitrates, in countries such as Mexico or parts of southern Africa.

As can be seen from the fact that the top ten importers take less than half of all merchant ammonia, the market is a fractured one, though some regions such as India, Morocco, northeast Asia and Europe have well developed import hubs.

Production

Ammonia capacity aimed at the merchant market is usually based on low price natural gas in coastal locations for easy access to international shipping. As Figure 2 shows, on the production side, the market is much more concentrated, with the top ten producers responsible for more than 85% of all exports, and the top five responsible for $^2/_3$ of all exports in 2021. It is notable that Ukraine, once one of the largest exporters, has dropped some way out of the top ten, exporting only 100,000 tonnes N of ammonia in 2021, due to a combination of the fighting in the east of the country since 2014, where many of the plants were located, and rising gas prices which have forced the virtual shutdown of the Odessa Port Plant (OPZ). However, a large 2,470 km ammonia pipeline dating back to the Soviet era crosses Ukraine from northeast to southwest, ending at the port of Odessa, and this has traditionally been a major route for Russia merchant ammonia exports, with a capacity of up to 2.5 million t/a of ammonia, and the Black Sea ammonia price has been the traditional benchmark of the ammonia market for many years. The other end of the pipeline is the huge fertilizer complex at TogliattiAzot on the River Volga in Russia's Samara region, which has 3.3 million t/a of ammonia capacity. TogliattiAzot is owned by Uralchem, itself owned by oligarch Dmitry Mazepin. In 2021 Russia exported 66% of its ammonia via the Black Sea and represented 23% of the merchant market.

Market disruptions

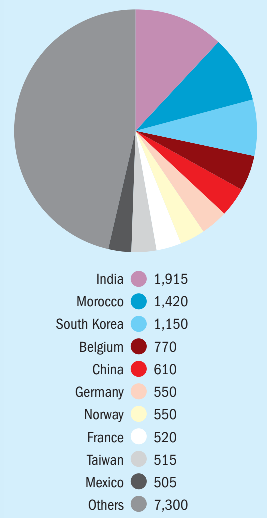
This year has seen unprecedent disruption to the merchant ammonia market, caused mainly by Russia's full-scale invasion of Ukraine in February and the western sanctions that have flowed from it. As well as ending grain and oil exports from Odessa, the war also ended ammonia exports. However, disruption to the ammonia market began some months before the attack as Europe experienced unprecedentedly high natural gas prices. Gas prices for Europe and delivered LNG began rising as early as March 2021 as demand returned post-covid, but saw a series of price spikes from September to December 2021 due to a combination of factors, including rising demand in Asia, unseasonably cold weather, disruptions to pipeline supply from Russia – probably to put pressure on the German government to approve the Nordstream 2 pipeline – and lower than expected generation of electricity from wind due to weather factors. The impact was to force European ammonia producers to lower operating rates or shut down altogether, leading in turn to a surge in additional demand in Europe for ammonia from around the globe, including from the Caribbean, Middle East and as far afield as Southeast Asia.

The attack on Ukraine exacerbated this, shutting off Russian ammonia exports via Odessa, while the concomitant disruption to gas flows into Europe continued to put pressure on European ammonia producers to curtail production. At one point around two thirds of European ammonia production was idled, and ammonia prices surged past \$1,000/t, peaking at over \$1,400/t, even \$1,600/t c.fr NW Europe in April-May, four times their previous average. Since then gas prices have eased and some production has restarted in Europe, bringing ammonia prices back down to levels that are still historically high, but less extreme than those earlier in the year. For the time being, however, Europe continues to set the floor price for ammonia.

The high price of ammonia has affected fertilizer production around the world, and there have been international attempts, brokered by Turkey, to reach a deal over the export of grain and fertilizer, including ammonia, via the port of Odessa, in order to reduce prices and shortages affecting developing countries. This appeared to bear fruit in July when shipments of grain were resumed. By September there were also UN-backed efforts to try and add ammonia to the cargoes that were being exported, with the possibility of restarting the ammonia pipeline. But the tit for tat strikes following Ukraine's attack on the Kerch Bridge in Crimea led to Russia ending the export agreement. At time of writing there were signs that this might be reversed, but the situation remains fluid and unclear.

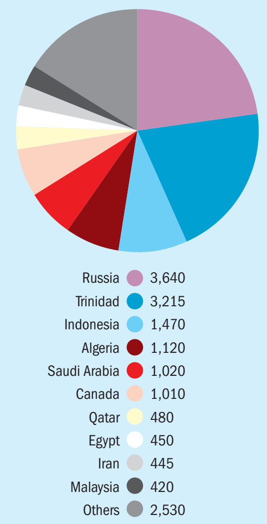
Though Russia's exports via the Black Sea have been curtailed, around $^2/_3$ of Russia ammonia exports go to countries which have not imposed financial sanctions. However, physically arranging shipments and paying for them continues to restrict these exports even at discounted rates to the market price.

Fig. 1: **Top 10 importers of ammonia, 2021, thousand tonnes N**



Source: IFA

Fig. 2: **Top 10 exporters of ammonia, 2021, thousand tonnes N**



Source: IFA

Other changes

Iran is a major producer of ammonia, and has been a major exporter in the past, but the withdrawal of the Trump government from the nuclear deal and reimposition of sanctions has complicated paying for Iranian ammonia and affected levels of exports – most of them (cs 75%) going to India. Iran exported 550,000 tonnes of ammonia last year. There have been attempts this year, led by the Biden administration, to find a new deal over nuclear sanctions, in part to get Iranian oil flowing again as a counterweight to lack of supply from Russia, though this would also presumably affect ammonia exports. However, these have made slow progress, and the recent wave of protests triggered by the death of a female student over the wearing of the hijab is reported to have led to strikes at Iranian petrochemical facilities.

Meanwhile ammonia sales from Trinidad, the second largest exporter of ammonia, remain curtailed. Trinidad had over the past few years been hit by both rising domestic US production undercutting its exports to North America and gas supply curtailments which have kept the island to below 75% utilisation rates. Trinidadian ammonia exports fell from 5.3 million t/a in 2010 to 4.0 million t/a in 2020, and the figures for 2021 and 1H 2022 have been at similar levels in spite of higher international prices for ammonia. However, higher production is expected to come from an easing of the gas shortage into 2023.

New demand is however likely to come from India, though demand destruction in the DAP market may ease requirements temporarily. Morocco also continues to expand its phosphate production. Chinese exports have also been low as the government continues to prioritise the domestic market, and China has increasingly imported ammonia for its growing caprolactam industry.

On the new capacity side, the 1.3 million t/a Gulf Coast Ammonia plant in the US will reduce US import requirements still further. There is also a new merchant ammonia plant in Oman at Salalah and the new Ma'aden 3 plant in Saudi Arabia will supply ammonia until the DAP line comes on-stream at the site.

At the moment, in the absence of any deal to export Russian ammonia via Odessa, which seems highly unlikely in the current climate, the likelihood is for prices to remain high for the remainder of this year and early 2023 at the very least.

Longer term factors

This year has seen a supply shock on a scale never before seen in the ammonia industry. But outside of temporary factors which will likely see a reorientation of supply and probably the permanent closure of some capacity in Europe, there are some major longer-term factors which will begin to affect the industry later this decade.

One is ammonia's use as a fuel, both for merchant shipping to help decarbonise the shipping industry, and, especially in Japan, as a feedstock to be co-fired in power stations to reduce the carbon impact of the power industry. Japan expects that it will be consuming 3 million t/a of ammonia as fuel for power plants by 2030 and 30 million t/a by 2050.

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

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Green Fischer-Tropsch technology routes

Fischer-Tropsch technology has long offered alternative production routes to synthetic fuels, but has struggled to make a use case outside of some niche applications. Could the greening of the chemical industry offer another way forward for the technology?

Left: The Sierra Biofuels plant, Nevada.

The Fischer-Tropsch polymerisation reaction converts synthesis gas into longer chain hydrocarbons. It was first developed by Franz Fischer and Hans Tropsch at the Kaiser Wilhelm Institute for Coal Research in Mülheim, Germany, in 1925. It effectively allows for the production of synthetic fuels and waxes from any feedstock that can generate syngas. Initially it was seen as a means of converting coal into liquid fuels for countries that were short of oil supplies. The reaction is catalysed by iron or cobalt-based catalysts, though due to the lack of selectivity, a wide variety of side reactions occur allowing for significant variation in end product between feed mixes and catalyst types. Cobalt-based catalysts give a higher yield of middle distillate products and show higher selectivity for paraffinic derivatives at low temperatures; hence, they can be used to produce sustainable aviation fuel (SAF). Iron-based catalysts are suitable for synthesis with low H_2/CO ratio syngas such as derived from low-quality feedstock such as biomass.

During the Second World War, the process was extensively developed by Germany for domestic fuel production, but fell into abeyance after the war when oil became readily available again. It enjoyed a second wind under Sasol in South Africa during the 1970s when South Africa was under sanctions, and gained further momentum when Sasol developed the process to work from a natural gas feed. Gas to liquids (GTL) production did not require the pre-treatment and gasification sections required by coal to liquids (CTL) production, and seemed to offer the possibility of being able to arbitrage cheap natural gas and high oil prices, and led to the building of Sasol's Mossel Bay plant in South Africa in the 1990s and Shell's Middle Distillate Synthesis (SMDS) plant at Bintulu in Malaysia. But natural gas went through a period of being relatively more expensive compared to oil during the 1990s, and so the process did not see another wave of interest until the 2000s, when rising oil prices encouraged another look at alternative feedstocks. This period led to the building of the successful Pearl and Oryx GTL plants in Qatar, but similar projects in Nigeria and Trinidad suffered from long delays and cost overruns.

A major issue for GTL has also been one of opportunity cost – where a large source of natural gas has been available, LNG has often been a more profitable way of monetising it, and therefore the most recent wave of GTL projects has come from central Asian countries that are not able to export gas as GTL and which have occasionally had problems win developing export pipelines. The largest project has been Uzbekistan's 38,000 bbl/d Oltin Yo'l ('Golden Road') GTL plant, though development took more than a decade, and covid delays meant that start-up did not occur until this year. Other routes to synthetic gasoline production are also available, and next door Turkmenistan built what it describes as a 15,500 bbl/d 'GTL' plant using methanol/DME production and downstream methanol to gasoline conversion using Topsoe's TIGAS (Topsoe Improved Gasoline Synthesis) process instead.

Environmental concerns

Perhaps the largest looming issue for CTL and GTL production is the carbon footprint not only of production, but also of the finished product. For this reason, coal-based production is now essentially ruled out in the developed world unless carbon capture and storage is used, and GTL plants could only be considered in the context of stranded or flared natural gas. However, rising costs of oil and gas and falling costs of electrolysis could help tip the balance towards greener production. In this regard, a green Fischer-Tropsch synthetic diesel could offer advantages over molecules such as green ammonia or methanol – both now widely touted as future alternative fuels – in that a complete distribution and sales infrastructure already exists for it.

Municipal waste

One potential green, or perhaps 'pseudo-green' feedstock for green F-T production is municipal solid waste (MSW). The growing lack of landfill space in developed countries is becoming a pressing problem in spite of increased recycling rates. In 2017 China stopped accepting imports of waste from other countries, a particular concern to the US, which exported much unprocessed waste to China, and where landfills and incinerators are running at capacity. This has led to a number of projects to generate power from waste incineration, using the heat generated to drive combined cycle turbines to produce electricity or to heat water or steam for local district heating. However, the wide variety of waste that finds its way into MSW means that there are concerns about emissions, including dioxins and furans, sulphur dioxide and nitrous oxides, heavy metals such as mercury, and so there has been increasing interest in the use of gasification to deal with such waste, allowing for easier clean-up of waste streams, and the generation of power or production of chemicals via syngas.

So far the largest and most successful installation has been Enerkem's waste to fuels plant in Edmonton Alberta. The plant takes 100,000 t/a of Edmonton's MSW under a 25-year supply agreement, amounting to about 30% of the solid waste that the city generates. The plant mainly converts the syngas generated from gasification into 33,000 t/a of methanol and ethanol, though there has been a pilot side plant producing synthetic diesel via Fischer-Tropsch conversion. A similar plant is now under construction at Varennes, Quebec, with completion due in 2023. Enerkem is also pursuing even larger projects in Rotterdam in the Netherlands and Tarragona in Spain, both of which are awaiting a final investment decision.

BP and Davy Process Technology (now Johnson Matthey/JM) jointly developed a Fischer-Tropsch process for GTL production in the 1990s, building a 300 bbl/d demonstrator plant in Alaska in 2002, but were not able to overcome commercial hurdles to its deployment. However, they have improved the process using 'cans' of catalyst in a fixed bed reactor, and via BP-backed US start-up company Fulcrom Bioenergy, they have developed the Sierra Biofuels plant near Reno in Nevada, USA. The plant, which began operations in May 2022, will convert at capacity 175,000 t/a of MSW into 11 million gallons per year (37,000 t/a) of 'sustainable aviation fuel' (SAF). They claim the new process delivers three times the productivity of a conventional multi-tubular fixed bed reactor and halves capital expenditure when compared to traditional FT reactors.

> **"It is finding most traction in the aviation industry, which otherwise believes it will struggle to move to a lower carbon model."**

UK-based Velocys has also developed a Fischer-Tropsch process, first demonstrated at the Envia Energy plant in Oklahoma City, producing 200 bbl/d of synthetic fuel for a few months from MSW before technical issues with the gasifier forced the shutdown of the project. The company is now focusing on SAF projects using the process. The Altalto project at Immingham in northeast Britain will use MSW feedstock to produce up to 1,300 bbl/d of SAF. Planning permission has been granted, and financial closure for the project is currently "targeted for 2024". In the US, it is also developing a project based on woody biomass gasification with carbon capture and storage (CCS). The Bayou Fuels project in Mississippi is aiming to produce 1,600 bbl/d of SAF as well as naphtha.

Biomass

Gasification of biomass waste is another potential source of 'green' Fischer-Tropsch diesel and forms the basis of a number of biomass to liquids (BTL) projects. In addition to the Bayou Fuels plant above, there is another biomass to fuels plant under development using Fischer-Tropsch technology; Red Rock Biofuels, based at Lakeview, Oregon, USA. When at capacity, the plant will produce 1,100 bbl/d of F-T liquids based on forestry and sawmill residues, using a process developed by Frontline BioEnergy and proven at a demonstrator plant in Nevada. However, like many such projects it has had a somewhat tortured path to operation. In spite of the receipt of an estimated $350 million of public funding, the plant is not quite complete, and construction is currently paused while Red Rock is said to be looking for a development partner to help it finish construction.

Gasification of alternative feedstocks has often foundered on the issue of gathering together sufficient material to run a large-scale plant with associated economies of scale. This has particularly bedevilled biomass gasification projects, except those using waste streams from forestry, pulp and paper production, where some of the gathering has already been done, and illustrates one of the advantages of using MSW, where collection at large scales has already been accomplished by the local municipal authority.

Biogas

Biogas is formed from the anaerobic digestion of waste biomass by natural bacteria, either directly recovered from landfill sites, generated from wastewater treatment, or made via deliberate processing of biomass in biodigester reactors. It is mostly methane, carbon dioxide and water, and needs to be dehydrated, with a number of other impurities which also need to be treated during purification. While there are a large number of biogas producing sites, most are small scale, and collecting it for use as a chemical feedstock has not so far been attempted on a commercial scale, though flowsheets for F-T fuel production have been developed. Biogas is usually fed into local natural gas networks instead, earning the producer carbon credits.

Green hydrogen

The explosion of interest in water electrolysis using renewable energy as a way of producing green hydrogen has led to a fourth potential feed for green F-T production,

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Table 1: **Well to wheel carbon emissions of Fisher-Tropsch fuels using different feedstocks**

Feedstock	Process	GHG emissions (g CO_2 eq./MJ)
Crude oil	Conventional refining	80.7-109.3
Methane	GTL/F-T	99.8-105.8
	GTL/F-T + carbon capture	86.2-87.3
	Biogas/F-T	38.0
Green hydrogen	CO_2 hydrogenation/F-T	11.0-28.0
Forestry residues	Gasification/F-T	10.0-13.0
Sugarcane	Gasification/F-T	1.4-9.3
Municipal solid waste	Gasification/F-T	32.9-62.3

Source: Jones et al[1]

in what is sometimes called 'Power to Liquids' (PtL). As with the BTL and waste to fuels alternatives above, it is finding most traction in the aviation industry, which otherwise believes it will struggle to move to a lower carbon model going forward because of the difficulty of using proposed alternative vehicle fuels or battery power in an aircraft.

However, so far demonstrator units based on the technology have been at very small scales. In August 2019, the German government funded the Power-to-X (P2X) project within the Kopernikus initiative and produced kerosene via hydrogen from electrolysis and F-T synthesis, but at only 10 litres/day, though the P2X project plans to scale up capacity to 2,000 litres per day. In Norway, Norsk e-fuel aims to be Europe's first large-scale commercial plant to produce SAF from renewable electricity, water and a combination of atmospheric CO_2 and point sources at Herøya, Norway, with 12.5 million litres per year planned from 2024. The Green Fuels for Denmark consortium is attempting something similar in Denmark with a mix of green hydrogen and methanol alongside SAF. In the UAE, Masdar expects to have a PtL demonstrator plant operational by the end of 2022, and there are other initiatives, mainly in Europe.

As Table 1 shows, green hydrogen potentially offers a low carbon route to SAF, though in fact well to wheel emissions are not much lower than for MSW gasification and can be higher than BTL production. Cost issues also of course bedevil alternative fuel development, though in the current oil and gas price environment, hydrogen electrolysis can look very attractive for regions such as Europe.

A new lease of life?

At present, power to liquids schemes using Fischer-Tropsch conversion are still very much in their infancy, though they have benefited from the huge upsurge in interest in using renewable energy to produce chemicals that has occurred across the board. The application that is looking most favourable is in production of sustainable aviation fuels, where alternatives to kerosene and similar hydrocarbons are much fewer. But for the interim, gasification of municipal waste seems to be leading as a feedstock for its production, and PtL may require more research and development, lowered costs of production and more financial incentives from governments. Norsk e-fuel seems to be the project that is furthest forward towards production at a commercial scale, and it will be interesting to see how it develops over the next few years.

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2022 AIChE Ammonia Safety Symposium

Venkat Pattabathula, a member of the AIChE Ammonia Safety Committee, reports on the American Institute of Chemical Engineers' Safety in Ammonia Plants and Related Facilities Symposium, held at the Hyatt Regency in Chicago, USA, on 11-15 September 2022.

Front: Ahmed Esmael Rahimi (Qatar Fertiliser Company), Seshu Dharmavaram (Air Products), Marc Gilberston (East Dubuque Nitrogen Fertilizer), Venkat Pattabathula (SVP Chemical Plant Services), Mohamad Noueiri (Yara), Dorothy Shaffer (BakerRisk). **Back:** Svend Erik Nielsen (Haldor Topsoe A/S), Taylor Archer (Clariant), Federico Zardi (Casale SA), Umesh Jain (KBR), Harrie Duisters (OCI NV), Klaus Noelker (thyssenkrupp Industrial Solutions AG), Eugene Britton (CF Industries). **Not Pictured:** John Mason (Nutrien), John Brightling (Johnson Matthey), Ashutosh Shukla (FFI).

The 2022 AIChE Ammonia Safety Committee.

The Ammonia Safety Committee is dedicated to improving the safety of plants that manufacture ammonia and related chemicals, such as urea, nitric acid, ammonium nitrate, and methanol. The conference's objective is to improve the safety performance of the ammonia industry. This is achieved by sharing information on incidents, safety practices, and technology improvements in presentations and open discussions.

Attendees who participated in the Symposium included plant managers, production managers, safety managers, process/reliability engineers, and everyone responsible for the safety and performance of ammonia plants or handling facilities. Worldwide experts discuss the latest advances in safe production and use of ammonia, case studies, and lessons learned at these symposiums. From 11-15 September 2022, about 375 engineers from more than 30 countries and 100 companies attended the AIChE's 66th Annual Ammonia Safety Symposium held at the Hyatt Regency in Chicago.

Ammonia as an energy carrier

This year's keynote speech, Technical, Social and Safety Aspects of Ammonia as a Carbon Free Energy Carrier" was presented by Tobias Birwe of thyssenkrupp Industrial Solutions (tkIS). Tobias said that of the 180 million t/a of ammonia produced every year, around 80% is used for fertilizer production, and around 20 million t/a is globally traded. But new uses are coming, particularly ammonia as an energy/hydrogen carrier. Social and commercial drivers include the objective announced by EU and G8 leaders to reduce greenhouse gas (GHG) emissions by 80% below 1990 levels by 2050. Over the coming decade, non-hydropower renewables capacity is expected to grow by just over 1,400 GW, totalling 2,770 GW, and the cost of solar and wind power has seen an 80% decrease over the past decade. Recent subsidy-free offshore wind bids in Europe close to or below $20/MWh have been seen. Since 2010, the cost of electrolysis has fallen by 60%, from between $10-15/kg of hydrogen to as low as $4-6/kg today. President of the European Commission, Ursula von der Leyen, has warned China and other large fossil fuel producers to find a way to price carbon at home or risk being hit by the EU with a planned CO2 tax on imports. The World Bank expects carbon pricing to be at least in the range of $40-80/tCO_2e$ by 2020 and $50-100/tCO_2e$ by 2030 to deliver on the Paris Agreement targets.

Ammonia is an ideal hydrogen and energy carrier. Hydrogen liquefies only at extremely low temperatures: -253°C, and this consumes up 40% of the energy bound in the hydrogen. Ammonia liquefies at around -33°C and has a higher energy density than hydrogen (by volume): 33% more energy. Renewable ammonia will either come from

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blue (carbon capture and storage coupled with conventional reforming technologies) or green sources, the latter using the electrolysis of water via renewable energy. However, greenhouse gas (GHG) accounting will be crucial, measuring the carbon emissions that contribute to a company's or entity's carbon footprint, including both direct and indirect carbon emissions.

On the energy side, ammonia can be co-fired in fossil power stations, though it faces challenges in burning slower than other fuels and being more difficult to ignite, as well as generating NOx. Tests have been conducted, in particular in Japan, mixing ammonia with coal in power plants, This requires only minor changes to existing power plants. In coal-importing countries, power stations are also often located at sea, ideal also for ammonia import. Plants have some experience with ammonia handling due to its use in the SCR unit for NOx removal.

Looking to the future, it will be possible to develop gas turbines for ammonia or ammonia/natural gas mixtures. This requires a larger combustion chamber and can be a difficult match if the variation of mixing rates is foreseen. In existing gas turbine power stations changes of fuel also changes the heat recovery balance. But a demonstrator 100% ammonia gas turbine was tested in 2016 in Japan. Mitsubishi Power is now developing a 40-MW class ammonia turbine derived from its H-25 series for industrial use and power generation, and is targeting commercialisation "in or around" 2025.

Fuel cells for hydrogen are commercially available but expensive and requires the intermediate step of cracking traded NH_3 to H_2 and N_2. Residual NH_3 has to be removed to generate 99.97% H_2. Ammonia fuel cells could solve this problem.

Finally, ammonia has been suggested for internal combustion engines for ships. Ongoing developments include co-firing with methane, light oil, etc with NOx removal by ammonia SCR. Developers include MAN Energy Solutions and Wärtsila, supported by European Union funds. They are targeting a commercially available engine by 2024; later also retrofit packages for existing engines. A breakthrough in the marine sector is expected to lead to progress in the development of ammonia-fueled propulsion engines for other purposes such as cars.

As a hydrogen carrier, ammonia must be 'cracked' to decompose at elevated temperature with a catalyst. It can replace fossil energy or feedstock sources if ammonia is not an option. However, there are inherent inefficiencies in converting hydrogen into and then back from ammonia. ■

SAFETY INCIDENTS

The key safety-related papers were:

Catastrophic failure of primary reformer due to mixed feed crossover piping rupture

Catastrophic failure of an ammonia plant primary reformer occurred due to a mixed feed cross-over piping longitudinal weld seam failure. This weld seam failure was the direct cause of an initial loss of primary containment that induced a reverse flow condition, resulting in the complete failure of other major components throughout the reformer. This paper presented the sequence of events and associated root causes that failed the mixed feed cross-over piping. Learnings were shared as the potential exists for other operators to have a similar type of failure.

Failure of the primary reformer mixed feed cross-over piping was the direct cause of the first loss of primary containment. This induced a reverse flow condition which exposed the reformer components to temperatures above their design limits to the point of failure. The mixed feed cross-over piping failure mechanism was determined to be hot/solidification cracking during fabrication due to incorrect weld geometry. This, in addition to the piping, creep expected for this piping system, resulting in a significant reduction in the expected life of the piping, which resulted in premature failure.

The following actions were recommended following this incident:

- Implement additional NDE requirements for new pipe procurement to improve inspection confidence.
- Perform NDE on existing plant piping operating within the creep region to ensure serviceability.
- Conduct an engineering review of the reforming section to determine the need to enhance the safeguards in this plant section, including mitigation against reverse flow.
- Conduct a review of all piping in elevated temperature and pressure services to identify the use of similar material in similar services and evaluate on a case-by-case basis.

Primary reformer air-steam coil alloy 800HT tube failure

This paper discussed the inspection and failure analysis findings and the effects of creep and high-temperature degradation on the alloy 800HT air-steam coil tubes in a primary reformer convection section. The recommendations, including planned replacement opportunities, were discussed. This paper included the benefits of proactive process monitoring, which indicated a leak in the air-steam coil before the turnaround. It further highlighted the importance of conducting destructive testing within turnaround scope in aging facilities to determine the root causes of failures.

The integrity of convection coil tubes is vital to the continued operations of primary reformers. It is very important to schedule and conduct inspections of these tubes during turnarounds to ascertain their integrity. Alloy 800HT has proven to be an excellent material for this service; however, this material is susceptible to creep and high-temperature degradation over a prolonged period. Aging facilities should plan for replacements based on inspection and metallographic examination results.

Ammonia release during ammonia import activity

On July 21, 2018, an incident occurred at an ammonia import facility that resulted in the accidental release of ammonia vapour. A thorough investigation identified the causes of the incident, which resulted in the quick connect/disconnect coupler disconnecting from the ship manifold flange, releasing approximately 1,000 kg of ammonia. Thankfully no one was injured, but the incident provided key learnings for the industry on safeguarding against similar future incidents.

A combination of factors led to the failure of different safeguards in the ammonia import process, resulting in the accidental release of ammonia vapour.

This incident has highlighted the importance of the following items: refresher training; procedural checks throughout the job cycle; preventative maintenance is designed in conjunction with the OEM, and project design reviews utilising human factors analysis.

Key lessons learned included:

- Hazards relating to all aspects of the unloading process must be identified, controlled and understood by all personnel involved.
- Maintenance strategies must incorporate all manufacturers' specifications.
- All procedures created for the use of specific plant equipment must be completed by competent personnel with in-depth knowledge of the equipment and in conjunction with the manufacturer's operating manual and specifications.
- All personnel involved in high-risk activities must be regularly verified as competent to perform those tasks.
- Critical equipment involved in high-risk tasks should have hard controls installed to prevent assumptions or mistakes and to prevent the system from progressing in an uncontrolled state.

Methanator temperature runaway results in a fire

In the 1990s and early 2000s, at least two known methanator runaways in North America resulted in equipment overheating and loss of containment. The particular incident addressed in this paper is one of those two. It occurred during the start-up of a hydrogen plant while reducing a fresh charge of methanator catalyst. Piping in the methanator circuit overheated, resulting in a large fire. Although this incident occurred almost three decades ago, it underscores the importance of having and following well-written procedures, safety instrumented systems, layers of protection, and risk awareness.

It is extremely important to maintain and follow written procedures covering potential safety scenarios to ensure appropriate safety systems and safeguards are functioning correctly. It is important to have clear written procedures which cover unusual situations and recognize safety risks. The procedures at the time of this event did not include the causes and effects of high liquid levels in the V-308 product hydrogen knockout pot or high-pressure drop in the C-303 absorber. There was also no discussion of the catalyst reduction requirements in the start-up procedure written for standard plant start-ups. The operating procedures were revised to include clear guidance for these situations.

It is also important to follow written procedures. In this case, the NMP solvent was not checked for water content to verify that it was low. More importantly, the methanator was not bypassed when the outlet temperature rose above 850°F (454°C).

This incident also emphasised that safety instrumented systems are needed to safeguard against high-risk scenarios. To protect against methanator runaways, hydrogen plants are now equipped with highly instrumented trip systems that quickly bypass the methanator on high bed temperatures using a voting system. Previous technical papers presented at this Symposium have discussed methanator trip systems in detail.

Finally, safeguards that are in place need to be checked to ensure they are functioning properly. In this case, the CO_2 analyser incorrectly displayed false low CO_2 concentrations. Layers of protection are important. In this case, the second layer of protection would have been to manually sample and analyse the gas to verify it contained less than 2% CO_2 before feeding it to the methanator.

The Dakar ammonia accident

This incident is detailed in a separate paper in this issue. ■

Next year's Symposium will be in Munich, Germany, 20-24 August.

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The Dakar ammonia accident

Seshu Dharmavaram of Air Products and **Venkat Pattabhathula** of SVP Chemical Plant Services describe the Dakar ammonia accident, which occurred in Senegal on March 24th, 1992. It is claimed to be the worst industrial ammonia accident ever, leaving 129 dead and 1,150 injured.

Understanding and managing the hazards of pressurised anhydrous ammonia is extremely important to prevent significant accidents. Many incidents have occurred in the industry in producing, transporting, and using anhydrous ammonia. The Dakar accident is the worst ammonia accident in terms of fatalities and this article describes the incident and an analysis of the consequences observed. It is important to review the details of the accident to derive lessons that all stakeholders can utilise.

The Dakar accident

The accident happened at a peanut oil processing facility operated by Sonacos SA, where ammonia was used to detoxify the product. Anhydrous ammonia was stored in a portable tank commissioned in 1983 and repaired in 1991, before the incident. The weld repairs made were on cracks detected on the tank's surface. Frequent overfilling of the tank (which was "authorized" to hold 17.7 tonnes) was one of the primary causes noted in the reports. An overpressure inside the tank led to its catastrophic failure. The debris from the explosion of the tank truck also pierced process equipment (e.g. hoses) containing liquid ammonia under pressure. The release of 22 tonnes of liquid ammonia was reported. A two-phase flow of ammonia fluid (vapor plus liquid as fine aerosol) formed a dense vapor cloud and spread over a significant distance resulting in injuries and fatalities. The dense plume settled over the oil mill, nearby offices, and adjacent restaurants where people were present at lunchtime. Forty-one people died immediately, and many others were transported to the nearest trauma center. Ultimately (after a month), the total numbers were determined to be one hundred twenty-nine fatalities and 1,150 injuries.

Most of the injuries and fatalities resulted from inhalation of ammonia at high enough concentrations to cause respiratory lesions, edema in the lungs, and skin/eyes irritation. Near the release location, many of the fatalities resulted from direct skin exposure and cold burns and inhalation of high concentrations. Fortunately, because of the Ramadan holidays, the schools nearby were closed, and restaurants were less crowded. Otherwise, the number of fatalities and injuries could have been much higher.

Process operation

Peanuts and peanut oil were among the top commodities exported from Senegal in the 1990s. To extract peanut oil from peanuts, anhydrous ammonia was used to detoxify the product at a peanut oil mill in Dakar which Sonacos SA owned. Anhydrous ammonia was brought to the mill by a road truck from a fertilizer company nearby that stored large quantities of cold liquid ammonia in spheres. The tank was then placed at the mill for use as a storage vessel since no other storage tanks were present at the mill.

The details of the ammonia tank that exploded were as follows:

- Diameter: 2.2 m
- Thickness: 11 mm
- Volume: 33.5 m^3
- Construction material: Annealed hardened steel
- Construction year: 1983
- Last maintenance year: 1991

The tank was built by a French company in 1983 and certified as compliant with regulations. From 1983 to 1991, the tank truck was frequently overfilled beyond the authorised 17.7-tonne filling limit. The overfilling led to overpressure and crack formation that was detected in 1991. The crack was welded but not annealed. After the repairs were done, the truck continued to be overfilled on the day before the accident. The tank was filled with 22,180 kg of liquid ammonia under pressure and was placed at the mill.

Around 1:30 to 2:00 PM (during a shift change), on March 24, 1992, the tank suddenly burst open along the middle with the two portions propelled in different directions. The collision from the tank contacting the buildings caused significant damage and debris (Figs. 1-3). The chassis and axle from the truck were found up to 200 meters away beyond the facility boundary. Anhydrous ammonia from the tank was re-leased almost instantaneously, and heavy, dense clouds spread well beyond the facility into the industrial and residential neighborhoods. The debris caused the failure of a hose connected to the process vessel, with the discharge continuing for at least half an hour.

Fig. 1: Front of the tank.

Fig. 2: Front of the tank.

Fig. 3: The rear of the tank.

Weather

During the time of the accident, the temperature was 26°C, with a wind speed of 4 ms-1 from the north. These weather conditions were used for the consequence analysis discussed below.

Medical treatment

On April 2, 1992, US Ambassador Katherine Shirley declared a disaster and requested the purchase of emergency respiratory and cardiac monitoring equipment. Pulse oximeters and ECG cardioscopes with accessories were procured and immediately dispatched to Senegal. The equipment was donated to the intensive care unit at Dakar's Trauma Center, where victims seriously injured by accident were being treated. Nine days after the equipment was received, USAID/Senegal representatives met with the Trauma Center staff and were told by the physician in charge that the equipment had made a difference between life and death. Of the more than 400 patients admitted to the Center, only 31 remained under treatment. In mid-April. the total death count from the accident was 129 people.

The patients treated for minor skin lesions developed pulmonary edema (fluid build-up in the lungs) in the trauma center. Most of the people killed near the tank explosion and release were in semi-confined locations (mill, restaurants, damaged buildings, and in the streets nearby). Among the injured were emergency responders that were ill-prepared to deal with an event of this magnitude.

A detailed chronological study based on an autopsy of people that died revealed that the victims were between 3 months and 74 years old. The cause of death was identified as the aftereffects of pneumopathy (pulmonary infection, bronchiectasis, and pulmonary fibrosis). The intensity of lesions and mortality was pro-portional to the quantity of inhaled ammonia per m^3 of air.

Primary cause: overfilling

A systematic root cause analysis of the Dakar accident can yield multiple causal factors (related to design, operation, hazards management, etc.) resulting in the incident. However, there is one primary cause (overfilling) that is obvious and has resulted in and continues to cause numerous incidents throughout the world.

Understanding the hazards of overfilling and determining the 'filling ratio' for a variety of containers (cylinders, tanks, etc.) to avoid incidents like this Dakar accident has

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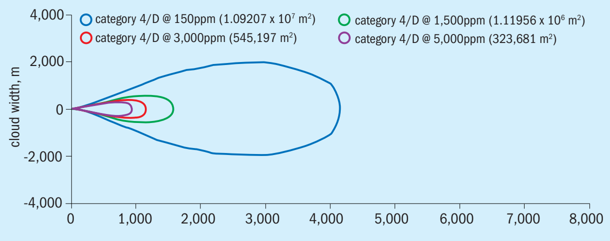
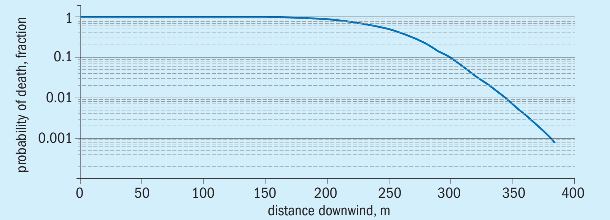
Fig. 4: **Maximum footprint for the instantaneous release of 22 tonnes**



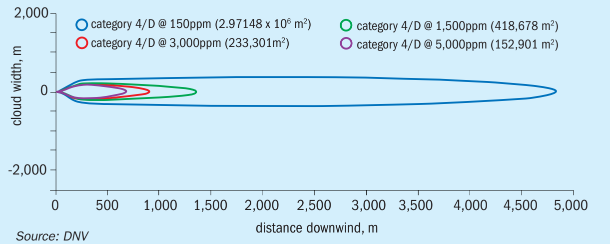
Source: DNV

Fig. 5: **Probability of fatality vs distance for the instantaneous release of 22 tonnes**



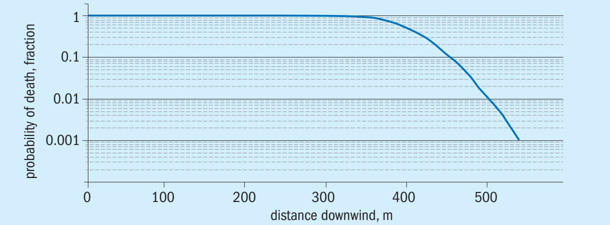
Source: DNV

Fig. 6: **Maximum footprint for the continuous release from a 3-inch hose**



Source: DNV

Fig. 7: **Probability of fatality vs distance for the continuous release from a 3-inch hose**



Source: DNV

been widely recognised. Overfilling of high pressure compressed gases can result in overpressure and loss of containment.

The filling ratio is defined as: "the ratio of the mass of gas to the mass of water at 15°C that would fill completely fitted ready for use". For high-pressure liquified gases (like anhydrous ammonia), the filling ratio is determined such that the settled pressure at 65°C does not exceed the test pressure of the pressure receptacles. The minimum test pressure typically re-quired is 1 MPa (10 bar). If relevant data are not available for high-pressure liquified gases, the maximum filling ratio is determined as follows:

FR = 8.5 x 10-4 x dg x Ph

where

dg = gas density (at 15°C, 1 bar) (in kg/m³)

Ph = minimum test pressure (in bar)

For a tank (or any other receptacle) containing anhydrous ammonia under pressure, it is best to ensure that the filling ratio does not exceed 0.53. The tank in the Dakar accident was overfilled to almost the full volumetric capacity of the vessel (33.5 m³) before the day of the accident.

Consequence analysis

An analysis of the consequences of the ammonia releases during the incident on March 24, 1992, can be done using the release and weather data that is available. The Emergency Response Planning Guideline (ERPG) concentrations published by the American Industrial Hygienists Association can be used to determine the acute toxicity effects. The ERPG-2 and ERPG-3 concentrations for ammonia are 150 ppm and 1,500 ppm, respectively. ERPG-2 is a concentration above which irreversible injuries can occur. Very serious injuries and potential fatalities can occur based on exposure time at concentrations above ERPG-3.

The probability of fatality can be determined using Specified Level of Toxicity (SLOT) and Significant Likelihood of Death (SLOD), and Dangerous Toxic Load (DTL) data published by the UK Health and Safety Executive. On March 24, 1992, around 22 tonnes were instantaneously released when the tank exploded. In addition, loss of containment from a hose connected to the process tank continued for a significant period of time.

The DNV PHAST model was used to model the release and dispersion of the heavy gas cloud from the two scenarios (instantaneous release: 22 tonnes; and continuous release: hose failure). The maximum footprint generated by the instantaneous release of 22 tonnes is shown in Figure 4. The injury concentrations (ERPG-2) extend to more than 4 km and with a width of about 4 km. The distance to ERPG-3 is about 1.5 km, the zone within which there might have been serious injuries and fatalities. The cloud would have been visible only up to a 900 m. Figure 5 shows an estimate of distances for the higher probability of fatalities. Up to a distance to almost 200 m, the probability of fatality is 100%, and then it drops to 0.1% by 500 m, primarily because the exposure time is shorter for an instantaneous release.

The maximum footprint generated by the continuous release from a 3-inch hole (e.g., hose failure) is shown in Figure 6. The plume is narrower (less than 1 km), but the injury concentrations (ERPG-2) extend to almost 5 km. The distance to ERPG-3 is less than 1.5 km, again the zone where there might have been serious injuries and fatalities. The visible range would have also been around 900 m. Figure 10 shows an estimate of distances to a high probability of fatalities. Up to a distance of almost 400 m, the probability of fatality is 100%.

Based on the proximity of the population near the paper mill that has been reported, it is therefore not surprising that 1,150 people were injured, and there were 129 fatalities. Because of a religious holiday (Ramadan), the population off-site, especially in nearby schools and restaurants, was a lot lower. If this incident had occurred on any other day, the injuries and fatalities would have been higher.

Table 1: **Potential lessons from Dakar accident**

Lesson category	Potential causal factors
Technical	• Poor understanding of hazards of anhydrous ammonia under pressure • Improper design and utilisation of equipment and protection systems; inadequate design basis documentation • Inadequate or no hazard reviews, consequences, and risk analysis
Operations	• Lack of training and competency development • Poor emergency response planning and procedures • Improper testing and inspection of equipment and control systems • Failure to understand the gravity of an abnormal situation and potential consequences
Leadership	• Lack of safety concerns at senior leadership levels • No policies, procedures, or guidance documents related to process safety • Lack of risk assessment and management practices • Failure to be open/receptive, bad safety culture • No sense of vulnerability and failure to equip plants with required re-sources
Government regulations/ Industry standards	• Lack of process safety regulations and standards • Absence of toxic substance management policies and procedures • Poor emergency management and lack of coordination of community response • Ad-hoc siting of hazardous industrial operations • Lack of controlling land use and poor zoning of land use • Poor implementation of safety audits and recommendations

Lessons learned

A detailed analysis of the causal factors can only be done using evidence (preserved/protected) and related data from the day of the accident. After a period of 30 years, it is almost impossible to reconstruct all the details based on limited data that is currently available in public literature. However, some general lesson categories (related to technology, operations, management, etc.) and generic causes can still be extracted. Table 1 below provides a summary of lesson categories and high-level causes, that can be broadly leveraged to prevent such incidents from happening.

In addition to the primary cause (i.e. overfilling) noted above, there were many failures in the following categories: technical; operations; facility/corporate leadership; government oversight; and industrial standards/governance. These are all important for safe operation of ammonia facilities in all global locations.

An industrial standards organisation for ammonia (such as exist for other chemicals like chlorine – Chlorine Institute, Eurochlor) might improve process safety performance in all jurisdictions, particularly in developing countries. The production and use of anhydrous ammonia is expected to increase dramatically across the world in the next few years.

In Senegal, anhydrous ammonia will continue to be used in large quantities since it is needed to detoxify agricultural commodities (i.e. nut oils) to eliminate aflatoxins. The demand is high and likely to increase over time. Ammonia is currently seen as a "formidable and indispensable killer" resulting from the Dakar accident in Senegal. Lessons from Dakar and other incidents can be effectively used and leveraged to improve the perception of ammonia and promote its safe handling everywhere.

Summary

The Bhopal accident was the worst industrial accident, but the Dakar accident on March 24, 1992, is the worst ammonia industrial accident ever. It was also the worst industrial accident in Senegal. High pressure in a portable tank resulted in the crack spreading and splitting the tank into two parts and a loss of containment of 22 tonnes of ammonia. The debris also damaged process equipment and resulted in an extended release from a hose failure.

An analysis of the consequences of the ammonia release scenarios demonstrates that the estimated distances for potential fatalities (1 km) and injuries (4 to 5 km) is very significant, with 129 fatalities and 1,150 injuries that occurred on March 24, 1992.

It has been well argued and proven that accidents like those that occurred at Bhopal and Dakar in developing countries (India and Senegal), can occur in developed countries, too, even with more robust regulations and industry standards. But it is essential to continue developing and implementing standards for safe designs, operations, and governance and thus improve process safety performance at anhydrous ammonia storage and handling facilities. ■

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33

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Łukasiewicz New Chemical Syntheses Institute

Grupa Azoty

Novel catalyst for H_2 production in a low temperature range

Catalysts are of crucial importance in a number of chemical processes and hence, their quality has a direct impact on the efficiency and operating costs of chemical plants. This refers especially to ammonia production, since this process is energy-consuming.

The performance of water-gas shift section (WGS: $CO+H_2O \rightleftharpoons CO_2+H_2$) is one of the crucial factors determining techno-economic operation of NH_3 plant as up to 20% of H_2 for NH_3 production is obtained via reduction of steam with CO over heterogeneous catalysts. Due to the fact that WGS reaction is exothermic, CO conversion and equivalent H_2 production are favored at lower temperature. Moreover, that leads to the lower H_2 loss at methanation stage and decreased inert content in NH_3 synthesis loop. It implies the key role of low-temperature WGS (LTS) catalyst.

The catalyst applied to run this reaction is one of the highest total cost and moreover, it has strong impact on the total efficiency of industrial-scale NH_3 production. A typical LTS catalyst is based on the $Cu/ZnO/Al_2O_3$ formula. The comparative study of LTS commercial catalysts shows small differences in composition and macro-properties. Each catalyst contains 3 main components: CuO (20-60 wt.%), ZnO (15-60 wt.%), Al_2O_3 (10-40 wt.%) and all of these catalysts are offered in the form of cylindrical pellets. LTS reaction runs on Cu metallic and Cu/ZnO interface. It is desirable to obtain Cu^0 in high dispersion during catalyst precursor preparation and activation, and to form the catalytic material into porous pellet with high accessibility of active phase (low diffusion limitations).

Apart from LTS reaction, methanol synthesis runs on CuZnAl catalyst which brings numerous detrimental consequences. Therefore, catalysts with better selectivity (methanol synthesis is significantly limited) are offered. Such products are doped with Cs and/or K compounds. These additions also improve catalysts' self-protection against poisons.

Users' expectations regarding LTS catalysts correspond to technological requirements aim to decrease energy consumption per product's mass unit. Therefore, design of LTS products is focused on efficient catalysts operated at decreased steam/gas ratio with high activity at the lowest possible temperature corresponding with the dew point (even <180°C).

A join R&D works carried out by Łukasiewicz – INS and Grupa Azoty S.A. (POIR.04.01.04-00-0002/19) are focused on a new catalyst for LTS process with the main goal to design a catalyst of favorable form and outstanding parameters (crush strength, bulk density, improved activity and thermal stability) and series of other properties which enable thermodynamically beneficial long-term performance in a low-temperature range. The innovation of novel LTS catalyst design is based on two pillars:

Fig. 1: Surface properties and activity comparison

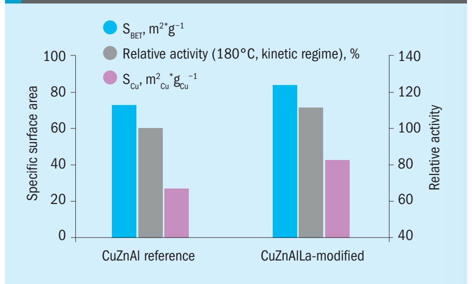
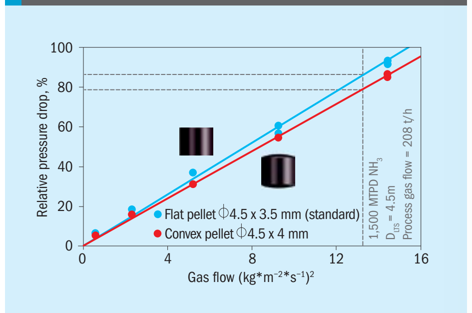


Fig. 2: The pressure drop along fixed-bed related with the LTS catalyst pellet geometry



1) Sophisticated modification of the catalyst's precursor formula as well as its synthesis and thermal treatment conditions. The results of investigations shows that the modification of the CuZnAl catalyst with La compound directly corresponds to the advantageous impact on its surface and pore structure resulting enhanced activity and thermal stability.
2) Modified catalyst's pellet form leading to the reduced pressure drop through the converter.

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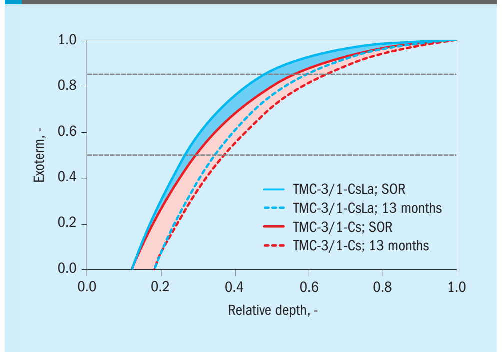
Increased specific surface area and active Cu metal surface area of novel CuZnAlLa catalyst (comparing to the reference one) corresponds with higher activity at the temperature as low as 180°C (Fig. 1).

The change of catalyst body geometry from flat pellet into convex one leads to substantial Δp decrease – ca. 6% for typical axial LTS converter (Fig. 2).

The trial charge of the new La-modified TMC-3/1-Cs (TMC-3/1-CsLa) catalyst has been in operation for over a year in NH_3 plant. Operational data shows sharp exotherm profile, high activity and lower rate of the exotherm movement along the length of the catalyst bed comparing to the charge operated during the previous campaign (Fig. 3).

Fig. 3: The exotherm shift along the catalyst bed



Analysis of TMC-3/1-CsLa operational data proves a very good performance and quality of the new catalyst. Thanks to this, better technological parameters (high degree of CO conversion, low deactivation rate) were obtained as compared to catalysts previously exploited in the same plant. The expected high-performance life-time of the new TMC-3/1-CsLa trial charge is very long.

Properties of novel TMC-3/1 catalysts

- High and stable activity due to optimized catalyst formula – Cu dispersed in specific oxide matrix,
- Alkali promoted catalyst with high selectivity,
- Good poison retention at the inlet section of the bed, self-guarding properties,
- Convex pellet form available,
- High crush strength of fresh as well as catalyst pellets after reduction.

Benefits of novel TMC-3/1 catalysts

- Possible to carry out the LTS process under more thermodynamically favorable conditions with very low ATE, enabling the increase of CO conversion and larger H_2 production,
- Suppressed H_2 loss for by-product formation,
- High crush strength and durability of catalyst pellets after reduction leading to the increased tolerance to the unexpected upsets (multiple immediate shutdown and restart, wetting, flooding etc.),
- Low pressure drop due to the improved geometry of pellets,
- Low rate of the exotherm shift along the bed,
- Safe and long service life without catalyst replacement.

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Melamine integration in a fertilizer complex

The latest improvements to melamine process technology now make it even easier to integrate a melamine plant with an ammonia and urea fertilizer complex. **Guido Canti** of Eurotecnica and **Marc Wieschalla** of thyssenkrupp Uhde discuss the benefits of plant integration.

The use of mineral fertilizer is an essential component of sustainable agriculture. Mineral fertilizers are applied in order to balance the gap between the nutrients required for optimal crop development and the nutrients supplied by the soil and available organic sources. One of the most widely used mineral fertilizers is urea, obtained from carbon dioxide and ammonia. Both reactants are brought together under high pressure where they form carbamate as an intermediate product and subsequently urea and water in the second step. Finally, urea is concentrated and solidified either by prilling or granulation.

Ammonia plants are typically designed to produce market grade ammonia, having at the same time a side stream of carbon dioxide. This latter stream is sometimes vented to the atmosphere or, more often, used as a feedstock for urea production. The amount of ammonia and carbon dioxide provided by an ammonia plant is not usually balanced for the stoichiometric production of urea. In most cases, ammonia is present in excess.

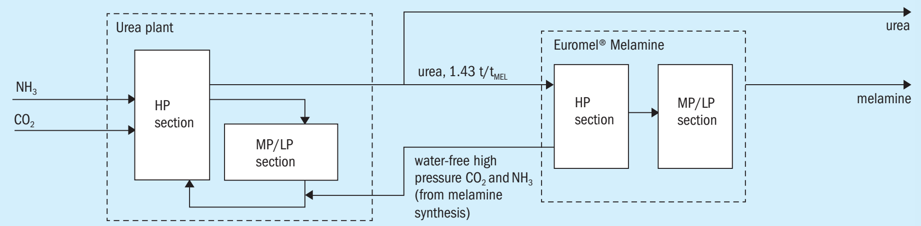
Additional sources of carbon dioxide are present in most ammonia/urea plants, namely, the reformer flue gases and boiler flue gases. Using the excess ammonia together with the additional carbon dioxide source allows the urea plant capacity to be increased by 10 to 15%. This capacity increase can be executed by modifying the synthesis loop either by adapting the existing equipment or adding a section, depending on the technology of the plant and its size or age. Should a urea capacity increase be required, concepts like debottlenecking without licensor involvement, "more in - more out" or the MP add-on based on Stamicarbon technology are suitable to comply with end-user desires. Capacity increases above 10% to even 100% can be achieved. However, in this case the ammonia plant requires revamping as well in order to provide higher amounts of ammonia. If the higher demand of steam needs to be mitigated, older Stamicarbon plants can be equipped with an MP flash using the low energy technology of Stamicarbon which reduces the steam consumption of the urea melt process. In the event that a different licensor technology is applied in the existing urea melt plant, different concepts are available that can be used to reduce energy consumption.

As the demand for urea grows by 2-3% per year and thus at a slower pace than the capacity increase achievable from plant debottlenecking, it can be useful to consider the production of alternative products to solidified urea fertilizer, such as Ad Blue® (diesel exhaust pollution control) or melamine. While the modifications to an existing urea melt plant are relatively simple the same upgrade on the finishing section (either prilling or granulation) can prove difficult: a prilling tower cannot be modified and a granulation section is rather limited in terms of acceptable flowrates. However, granulation plants are usually designed with additional margin for recovery after washing e.g. up to 10%. With a capacity increase of the urea melt plant the recovery capability reduces.

Melamine, a direct derivative of urea melt, can be considered for debottlenecking, ensuring the complete utilisation of any excess ammonia/carbon dioxide and producing a valuable compound.

To produce melamine, urea molecules are joined under pressure in an endothermic non-catalytic reaction that generates melamine, ammonia and carbon dioxide. These off-gases are sent back to the urea plant to be recovered as fresh urea. Fig. 1 shows a simplified block diagram of the two plants.

Fig. 1: **Typical Euromel® plant integration scheme**



Source: ICIS ILOR (melamine), Indexmundi (urea)

A second feed stream of ammonia ensures the complete transformation of urea to melamine and guarantees that no by-products are formed. All ammonia is fully recovered in the urea plant, with no modification of the ammonia balance of the complex.

Leading melamine licensor Eurotecnica SpA has recently marketed its fifth generation (G5) technology which improves the process by minimising the energy consumption and ensuring its long-standing no solid, no liquid effluent policy, thus ensuring, as per previous generations, a total zero-pollution plant.

One of the main features of this technology is its ability to simplify the integration of the melamine plant with its urea counterpart by means of a single liquid carbamate tie-in.

An existing urea plant can be safely and smoothly modified for the connection to a melamine plant; at the same time an increase in capacity can be achieved by using, for example, the existing excess ammonia.

This results in several positive effects on the urea plant such as:

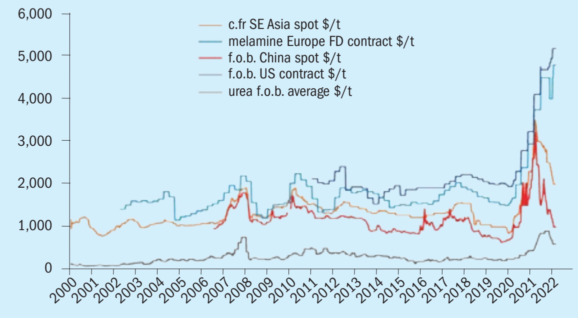
- higher ammonia plant utilisation;
- no need to revamp the prilling or granulation section;
- guarantees on urea quality unaffected;
- no loss of ammonia and carbon dioxide, they are fully recovered in the urea plant;
- easy integration with the existing facilities;
- no changes to the water balance (scrubbing water for the melamine plant is taken from the waste-water system of the urea plant).

The same advantages can be obtained for a new urea plant under design or an existing facility to be revamped.

For both new and existing urea plants the modifications required to link the melamine and urea plant can be easily implemented and are briefly described in Table 1.

As the carbon dioxide captured in melamine production is stored in this compound for the long term, melamine production can also be regarded as a means to mitigate climate change. Melamine production, in itself, has a negative carbon footprint and its economic exploitation benefits the complex end-user without any impact on the environment in terms of greenhouse gases release.

Fig. 2: **Price trends for melamine and urea**



Source: ICIS ILOR (melamine), Indexmundi (urea)

Melamine is also a high value product. This is reflected in the price, which was between $2,600 to $3,000 per tonne in 2021. Urea has been traded around $220/t for a long time and has reached peaks of $1,200/t in the recent past (see Fig. 2).

Because both urea and melamine tend to crystallise easily, an EP/C contractor, experienced in urea technologies, can transfer its knowledge to the melamine process, contributing to a well-working melamine plant. thyssenkrupp Industrial Solutions AG's Business Unit Uhde (Uhde) has more than 60 years of experience building and revamping various urea melt and granulation plants and consequently is one of the most suitable EP/C contractors also when it comes to melamine plant erection. During its long-term involvement in urea, Uhde has developed its own solutions and advanced technologies within licensor designs. For example, Uhde has developed an emission-free vent stack within the urea melt plant, the application of self-regulating pumps, which cannot cavitate and are used for the melt delivery from the melt plant to the granulator, and melt flushing in the evaporation unit of the melt plant in order to dissolve any biuret deposits efficiently. All three examples contribute to reduced emissions and a higher availability of the plant. In addition, Uhde can provide information on the flushing of process lines and advice on tracing and insulation, which can be applied to boost plant performance, increase plant availability, reduce emissions, ensure plant safety or simply provide trouble-free operation of the plant. Uhde know-how can make a difference when it comes to plant safety, reliability and efficiency.

Combining this know-how with the latest generation of melamine technology provided by Eurotecnica SpA can help to protect the environment while providing a fast payback time for the end user ■

Table 1: **Measures to link a urea melt plant with a melamine plant**

Description	Revamp measures	Preparation of new plant for later connection of melamine plant
Export of urea solution 70-75% from urea solution tank. A dedicated evaporation to concentrate up to 99.7% will be provided in the melamine plant.	Installation of a T-piece downstream of the pump. Modification of the pump to handle higher flow.	Installation of a spool piece downstream of the pump which can be exchanged with a T-piece later.
Import of carbamate condensate directly to the HP synthesis loop.	Installation of a tie-in on urea HP synthesis loop.	Installation of a tie-in with blind upstream urea HP synthesis loop.

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The merits of methanol and ammonia co-production

Casale has developed a range of methanol-ammonia coproduction processes to match different requirements according to product capacity.

To derive the maximum benefit from economies of scale and to achieve the lowest production cost, it may be desirable to build a single-train plant that is designed for the integrated coproduction of ammonia and methanol.

For this purpose, Casale has developed the new Methanol-Ammonia-Casale-Coproduction (MAC²) processes. Having a single integrated plant to produce ammonia and methanol compared to two standalone ammonia and methanol plants offers big advantages as discussed below.

MAC²8000™ process

MAC²8000™ technology for the coproduction of ammonia and methanol is based on a common front-end section with a conventional steam-reforming unit followed by an auto-thermal reforming unit fed with oxygen and equipped with a Casale patented burner (see Fig. 1).

The produced syngas is then divided between the ammonia unit and the methanol unit.

The ammonia unit, for both warm and cold ammonia production, is based on Casale plate-cooled axial-radial MTS, third party technology for CO_2 removal, syngas drying and the liquid nitrogen wash unit, and a Casale patented 3-bed ammonia synthesis converter with two internal interchangers.

The methanol unit is a high efficiency synthesis section installed with a Casale IMC plate-cooled axial-radial reactor. Final purification of the product is performed in a distillation section based on a three-column design.

The necessary oxygen and nitrogen are provided by a dedicated air separation unit.

A PSA unit is provided to recover hydrogen from the methanol synthesis loop purge which is then sent to the ammonia plant (syngas compressor suction).

The coproduction process is characterised by full flexibility to adjust the production of each product almost independently from the other.

The coproduction process is suitable for single line plants with an overall capacity of up to 8,000 t/d (ammonia + methanol) with a full range of splits between methanol and ammonia production.

Key benefits

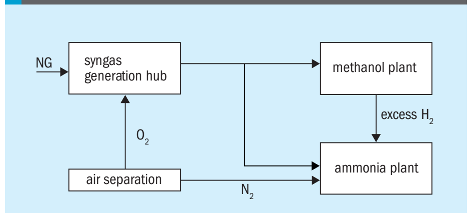
MAC²8000™ offers major capital cost benefits for the producer. Compared to independent new methanol and ammonia units, sized for the same capacities, the coproduction design strategy allows the installation of a single syngas generation section and the sharing of utilities and the operating and production facilities. Furthermore, the exploitation of hydrogen from the methanol plant leads to a proportional reduction of the ammonia plant front-end equipment size. Optionally, since carbon dioxide is balanced with ammonia, ammonia can be totally converted to urea, thereby maximising urea production.

Key technologies

Key technologies of the MAC²8000™ process include:

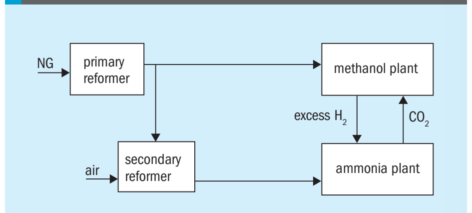
- Casale reactors: pre-reformer, medium temperature shift, IMC methanol converter and ammonia converter;
- high-efficiency auto-thermal reformer;
- ammonia loop waste heat boiler.

Fig. 1: MAC²8000™ process



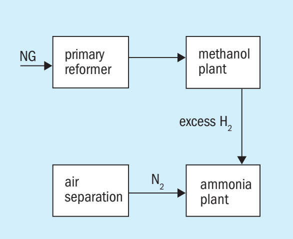
Source: Casale

Fig. 2: MAC²4000™ process



Source: Casale

Fig. 3: MAC²4000M™ process



Source: Casale

MAC²4000™ process

MAC²4000™ technology for the coproduction of ammonia and methanol is based on a common front-end section with a conventional steam-reforming unit followed by a secondary reforming unit, for the ammonia train only, fed with air and equipped with a Casale patented burner (see Fig. 2).

The syngas, produced by the primary reformer, is divided between the ammonia unit and the methanol unit.

The ammonia unit, for both warm and cold ammonia production, is based on Casale axial-radial HTS and LTS, third party technology for CO_2 removal and the methanation section, and a Casale patented 3-bed ammonia synthesis converter with two internal interchangers.

The methanol unit is a high efficiency synthesis section installed with a Casale plate-cooled IMC reactor. Final purification of the product is performed in a distillation section based on a two- or three-column design depending on the methanol plant capacity and energy efficiency targets.

A PSA unit is provided to recover hydrogen from the methanol synthesis loop purge which is then sent to the ammonia plant (syngas compressor suction).

Carbon dioxide from the CO_2 removal stripper can be routed to the methanol synloop to increase the methanol plant capacity.

The coproduction process is characterised by full flexibility to adjust the production of each product almost independently from the other.

The coproduction process is suitable for single line plants with an overall capacity of up to 4,000 t/d (ammonia + methanol) with a full range of splits between methanol and ammonia production.

MAC²4000™ is also applicable, as a general concept, for the revamping of existing plants.

In particular, for an ammonia plant revamping project for ammonia and methanol coproduction, the final optimal ratio between methanol production and ammonia production is up to 1 to 3. For example, a 1,600 t/d ammonia plant could provide 400 t/d of methanol and 1,200 t/d of ammonia. The MAC²4000™ process is reversible and therefore the plant production ratio can be selected based on the main market indicators (methanol production can also be stopped to maximise ammonia production).

Key benefits

MAC²4000™ offers major capital cost benefits for the producer. Compared to independent new methanol and ammonia units, sized for the same capacities, the coproduction design strategy allows the installation of a single syngas generation section and the sharing of utilities and the operating and production facilities. Furthermore, the exploitation of hydrogen from the methanol plant leads to a proportional reduction of the ammonia plant front-end equipment size. The CO_2 injection in the methanol synloop is convenient for maximising the methanol production. Optionally, the design can be customised in order to balance carbon dioxide with ammonia, enabling total conversion of the ammonia to urea, thereby maximising urea production.

Key technologies

Key technologies of the MAC²4000™ process include:

- Casale reactors: pre-reformer, high temperature shift, low temperature shift, IMC methanol converter and ammonia converter;
- high-efficiency secondary reformer;
- ejector ammonia wash system;
- ammonia loop waste heat boiler.

MAC²4000M™ process

MAC²4000M™ technology for the coproduction of ammonia and methanol is based on a front-end section based on pure steam reforming and sized for the methanol unit capacity (see Fig. 3).

The methanol unit is characterised by a high efficiency synthesis section installed with a Casale plate-cooled IMC reactor. Product final purification is performed in a distillation section based on a two or three-column design depending on the methanol plant capacity and energy efficiency targets.

The composition of the syngas from steam reforming is not optimal for methanol synthesis as it contains an excess of hydrogen (from downstream of the synthesis reactions) which must be purged from the synthesis loop. This hydrogen-rich stream, typically recycled as fuel to the primary reformer, can be more efficiently used for the synthesis of ammonia: a PSA unit is provided to recover hydrogen from the methanol synthesis loop purge which is sent to the ammonia plant (syngas compressor suction).

At the same time the ASU provides the nitrogen necessary for the ammonia synthesis.

The ammonia unit, for both warm and cold ammonia production, consists of a synthesis loop and refrigeration section only and is based on the Casale patented 3-bed ammonia synthesis converter with two internal interchangers.

The coproduction process is suitable for single line plants with an overall capacity of up to 4,000 t/d with an ammonia production of up to 25% of the overall production. MAC²4000M™ technology can also be applied, as a general concept, for the revamping of existing plants. Similar, to the revamping of an ammonia plant, the revamping of a methanol plant with the MAC² concept is reversible depending on market indicators.

Key benefits

MAC²4000M™ offers major capital cost benefits for the producer. Compared to independent new methanol and ammonia units, sized for the same capacities, the coproduction design strategy allows the omission of the entire ammonia plant front end and sharing of utilities and the operating and production facilities.

Optionally, the design can be customised to recover the necessary CO_2 from primary reformer flue gases, in order to balance carbon dioxide with ammonia, to enable total conversion of the ammonia to urea, thereby maximising urea production.

Key technologies

Key technologies of the MAC²4000M™ process include:

- Casale reactors: pre-reformer, IMC methanol converter and ammonia converter;
- ammonia loop waste heat boiler.

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Decarbonisation of ammonia and methanol

Industry focus on technologies to reduce the carbon intensity of ammonia and methanol production has been intensifying. In this article thyssenkrupp Uhde, Proton Ventures, Toyo Engineering Corporation, Stamicarbon, BD Energy Systems and KBR report on some of their latest technology developments towards decarbonisation.

THYSSENKRUPP UHDE

Clean energy based on fossil fuels – blue ammonia solutions

This article introduces the blue ammonia process and technology as a method based on natural gas or other fossil resources with avoidance or reduction of CO_2 emissions. Blue ammonia options for new plants and the retrofit of existing plants from grey to blue are presented.

Blue ammonia is attracting more and more attention as, in addition to traditional ammonia demand, there is an emerging additional market for ammonia as an energy and hydrogen carrier. After shipment of ammonia as energy carrier, hydrogen can be released by the cracking of ammonia at the final destination. Blue ammonia technology plays an important role in the transition phase from grey to green ammonia providing the required additional capacity.

Challenges and potential in ammonia production

Ammonia has a worldwide production of roughly 180 million t/a. 80% is used for fertilizer production, and 20% is used for other applications. Around 20 million tonnes are traded and the infrastructure for that is well established.

To date, the prime interest in ammonia has been for its nitrogen content for the production of nitrogen fertilizers. The other element in ammonia however, hydrogen, is the base chemical of the future, replacing oil and gas.

Hydrogen can be easily produced by using renewable energy via water electrolysis, completely free of carbon dioxide emissions. It allows us to store and transport renewable energy and use the hydrogen for a variety of industry sectors.

However, in this vision there are a number of issues that need to be addressed, such as:

- building up a renewable energy infrastructure;
- intercontinental transportation of hydrogen.

Building up a renewable energy infrastructure is the basis for "green" development. However, it will take time to increase the capacity, time which is not available because action is needed now along with social, political and commercial drivers such as:

- increasing CO_2 taxes;
- shrinking renewable energy costs;
- new greenhouse gas reduction targets;
- and finally social pressure.

Therefore, despite all movements to green products and processes blue and green products will co-exist, with the focus on blue products in the transition phase. Blue ammonia will be primarily installed where gas is available at relatively low cost.

The other big issue is intercontinental energy transportation. For liquid hydrogen transportation, hydrogen losses and high power consumption for cooling are critical. In addition, there is no infrastructure for long distance shipping available. That's where ammonia comes into play: It is easy to transport, it has a higher energy density than hydrogen, and global trade is already established. For this reason, ammonia is considered as the most important energy carrier to be globally traded in the future.

Options for reduction of CO_2 emissions

Basically, there are two alternative processes for the production of hydrogen from natural gas:

- First, there is steam methane reforming (SMR), where reforming of natural gas takes place inside catalyst-filled tubes, and the heat to drive the reaction is supplied by combustion of gas in a furnace box and heat transfer into the tubes. The flue gas from the furnace is used to preheat the inlet streams and to superheat steam.
- The alternative process is autothermal reforming, where the necessary heat for reforming is supplied by combustion of a portion of the feedstock inside the process vessel. A separate fired heater is utilised to preheat the inlet streams of the autothermal reformer (ATR).

In both concepts there are two CO_2 emission points:

- The first emission point is in the reforming section, consisting of the reformer flue gas or the flue gas from fired heater. These streams usually contain only a small fraction of CO_2, the rest is mostly nitrogen, residual oxygen, water vapour, and other impurities.
- The second emission point is in the purification section of the process, where the CO_2 is separated from the process gas. This stream is much larger, usually with a CO_2 purity of more than 99%. It is this stream, therefore, that is often used for urea production.

At both emission points the CO_2 is available at low pressure.

The CO_2 emission can be reduced by capturing the CO_2 and sending it to a sink. If the CO_2 emission is largely reduced, the ammonia is called "blue ammonia", but there is no unique definition of this term. In principle, two options exist:

- **Carbon capture and utilisation, CCU:** Using CO_2 for downstream applications by production of other sustainable products and thus permanently avoiding its emission into the atmosphere. Unfortunately, not many possibilities exist.
- **Carbon capture and sequestration, CCS:** Compressing the CO_2 and storing it permanently underground in a suitable geological formation.

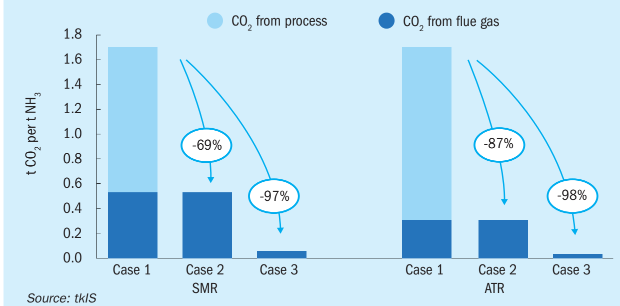
The overall emission for SMR and ATR is similar (around 1.7 t CO_2 per t NH_3 for a typical modern plant), but the split of the CO_2 emissions between the reforming section and the process differs.

When avoiding CO_2 emissions one can define three cases with different degrees of emission reduction, as illustrated in Fig. 1:

- **Case 1/base case:** No reduction of emission, two emission points as listed above.
- **Case 2:** Carbon capture and export (either CCU or CCS) of the CO_2 from the purification section of the process. CO_2 removal is already provided as part of the standard ammonia process. Therefore, the export of CO_2 can be accomplished with low effort by providing an additional export blower or compressor for downstream use. In this way, in the SMR case, the CO_2 emission can be reduced by almost 70%, and even more in the ATR version.
- **Case 3:** Case 2 plus CCU or CCS of the CO_2 from flue gas. For this option more effort is required because first a unit for removal of CO_2 from the flue gas has to be provided in order to be able to send the CO_2 to the export compressor or blower as in Case 2. Technologies for CO_2 removal from flue gas are available from thyssenkrupp Uhde and others. 90% removal of the CO_2 from flue gas is reported as a typical figure, giving a total CO_2 emission reduction of 98%, however, this figure can be increased if desired.

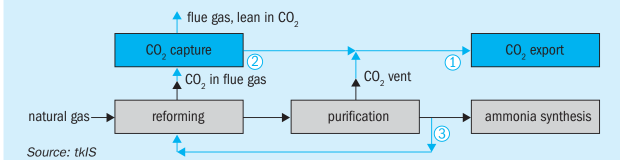
For ATR, Uhde offers an alternative and more cost-effective process to reduce the CO_2 emission further than the figures shown for Case 2. The fired heater is provided with hydrogen-rich fuel gas which is

Fig. 1: **CO_2 emission per tonne of ammonia produced for steam reformer and autothermal reformer**



Source: tkIS

Fig. 2: **Conversion of an existing ammonia plant to a blue plant. Grey/black: existing; blue: added**



Source: tkIS

diverted from the process (pre combustion solution). This increases the size of the front end but avoids the installation of an additional flue gas scrubbing unit (post combustion solution).

In any case, for the application of ammonia as an energy carrier the demand will be so high that only large ammonia plants will make sense, and for those there is a cost advantage for an ATR plant over a steam reformer plant.

Retrofits of existing plants

Existing plants can be retrofitted to lower their CO_2 emission. As shown in Fig. 2 they also possess the same two CO_2 emission points as described above.

Many of the existing plants in the fertilizer industry use the process CO_2 for urea production. That means, Case 2 (as defined above) is not an option for them. Urea production for fertilizer does not qualify as CCU because the CO_2 is only temporarily bound in the urea molecule. It is released to the atmosphere as soon as urea is applied to the field and decomposes.

Case 3 is an option. A CO_2 recovery unit can be retrofitted if a destination for the CO_2 can be found. Only certain types of geology permit the permanent storage of CO_2. Further, it has to be considered that the cost of CO_2 sequestration infrastructure is far higher than the that of the equipment for capturing and exporting the CO_2.

Summary

There is an emerging additional market for ammonia as an energy and hydrogen carrier. Blue ammonia will play an important role in the transition phase. The ammonia process has two CO_2 emission points: While capture from the process gas is standard, capture from flue gas is relatively new, but technologies are available.

For new blue ammonia plants, Uhde offers an optimised and cost-effective process, making use of autothermal reforming (ATR) allowing for more than 90% emission reduction without the need for an additional flue gas CO_2 removal unit.

Existing ammonia plants can be retrofitted with a unit to recover CO_2 from flue gas in order to lower the CO_2 emission and to lower the CO_2 footprint of its products which can lead to a competitive advantage. ■

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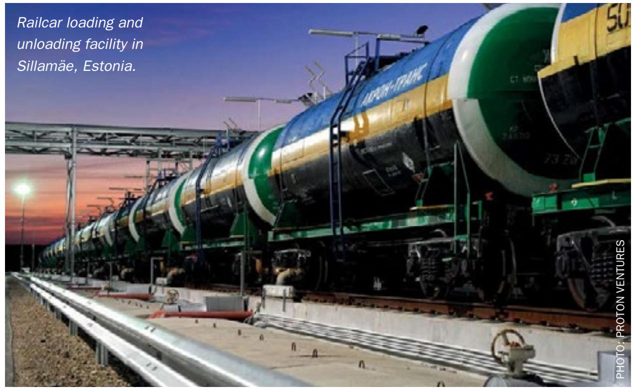
PROTON VENTURES

Providing engineering solutions for the ammonia economy

Kevin Rouwenhorst



Railcar loading and unloading facility in Sillamäe, Estonia.

PHOTO: PROTON VENTURES

Proton Ventures is an engineering solutions provider in the (green) ammonia industry. The company was founded in 2001 by former CEO Hans Vrijenhoef, who had previously been the plant manager of a now defunct ammonia plant in Rozenburg, The Netherlands. Even in the early days, Hans already had the vision to use ammonia as a zero-carbon fuel and hydrogen carrier. About 20 years later, this vision is taking shape with weekly announcements of green ammonia production plants.

Proton Ventures has its fair share of projects in this emerging landscape. These range from scoping studies, feasibility studies, FEEDs (front end engineering designs), and EPC (engineering, procurement, and construction) projects. One of the distinguishing strengths of Proton Ventures is its technology agnostic approach as system integrator, which allows Proton Ventures to select the most suitable licensors and original equipment suppliers (OEMs) for the specific project.

Green ammonia production

Green ammonia production has been a key focus throughout the two decades of Proton Ventures' existence. Instead of focusing on world-scale ammonia plants producing up to one million tonnes per annum, Proton Ventures has historically focused on modular ammonia plants with a production capacity in the range 3-60 t/d of ammonia. This allows ammonia plants to be located next to modular electrolysers combined with solar PV and wind capacity. The modular approach allows for improved flexibility of the overall ammonia plant.

Recently, Proton Ventures was selected as the EPC contractor for a 4 t/d green ammonia pilot plant (GAPP), to be built at the OCP Group chemical complex in Jorf Lasfar, Morocco. This pilot facility will consist of both an alkaline electrolyser and a PEM electrolyser for hydrogen production, compressed hydrogen storage, nitrogen purification with a PSA system, and a Haber-Bosch ammonia synthesis loop. Another key aspect of the project is the emulator that can simulate electricity profiles from anywhere around the world. This facility is an important step towards scaling up to large-scale green ammonia facilities. The facility will be operated by the Mohammed VI Polytechnic University, thus producing future engineers who have already had experience and training in the green ammonia industry as part of their formal studies.

In addition, Proton Ventures is active within the TransHydrogen Alliance, which aims to produce ammonia in areas with abundant solar and wind resources, such as Brazil and Morocco, with subsequent transport and cracking of ammonia to hydrogen in Rotterdam, the Netherlands. Here the aim is to produce ammonia at a larger scale, e.g., up to 1 million tonnes per annum. The benefit of the TransHydrogen Alliance is that production and utilisation are coupled, ensuring supply while keeping the system cost as low as possible.

The above projects are mainly based on available technology. However, Proton Ventures also works on innovative solutions for ammonia synthesis, such as novel electrolyser technologies and improves ammonia synthesis technologies. Improving hydrogen production via electrolysis is key, as hydrogen production typically accounts for at least 90% of the energy input for ammonia production. Proton Ventures recently performed a feasibility study with Supercritical and Scottish Power for integrating more energy efficient and high-pressure electrolysers with a Haber-Bosch ammonia synthesis loop. Furthermore, Proton Ventures has aided the development of the Battolyser from a university laboratory to a standalone company. The Battolyser is a combination of an iron-nickel battery and an alkaline type electrolyser. Within the EU project ARENHA, Proton Ventures has also patented a low-pressure ammonia synthesis technology that can significantly improve the single pass conversion.

Ammonia storage and handling

Some of the largest projects executed by Proton Ventures are its refrigerated storage tanks in Estonia (BCT) and Bulgaria (Agropolychim), which are among the largest operating ammonia storage tanks in Europe. For example, the two tanks in Estonia each have a capacity for 30 kilotonnes of refrigerated ammonia at -33°C. The tanks are double containment storage tanks complying with modern safety standards. The facilities in Estonia also consist of railcar loading and unloading systems, a marine loading arm facility, and four UAN tanks of 20 kilotonnes each.

The global trade of ammonia is set to expand over the coming decade, as the use of ammonia as a shipping fuel, stationary fuel, and as a hydrogen carrier is taking off. In light of these developments, Proton Ventures has been selected as the EPC contractor for new ammonia storage capacity.

Proton Ventures complies with state-of-the-art requirements for new ammonia storage tanks, even when these are located in desert areas where temperatures sometimes exceed 50°C. Recently, a FEED+ engineering package was completed for a new ammonia export terminal in the United Arab Emirates. An example is a special main discharge bottom valve for inherent safety. Intermittent flaring and an interconnecting bridge between the two storage tanks with a combined staircase optimise the capital investment, spatial utilisation and simplicity. Furthermore, the refrigeration system design is optimised for hot climate operations and a low operational cost.

Nitrogen oxide emissions

When ammonia is utilised as a fuel or for nitric acid production, nitrogen oxide emissions must be mitigated. NOx emissions are mainly a local issue, causing eutrophication. On the other hand, nitrous oxide (N_2O) emissions cause global warming, with a GWP (global warming potential) equivalent to 298 times that of carbon dioxide.

Nitrogen oxide emissions can be mitigated by reacting nitrogen oxides with ammonia in an SCR (selective catalytic reduction) system, resulting in the production of unharmful atmospheric dinitrogen and water. Within the EU, most nitric acid plants are equipped with such SCR systems, nearly eliminating N_2O emissions from these plants. Around the rest of the world, this is not yet standard practice, implying it is low hanging fruit in the global effort to decarbonise.

Proton Ventures was contracted as EPC contractor by Kavala Fertilizers in Greece for DeNOx and N_2O reduction with an SCR system at a nitric acid plant. This DeNOx system saves about twenty thousand tonnes of carbon dioxide equivalent emissions annually, while meeting the most stringent nitrogen oxide emission standards. The SCR system has also eliminated the yellow plume from the nitric acid plant.

Such SCR systems can also be used for ammonia conversion for energy applications, such as gas turbines and maritime engines. In fact, various gas turbines that are currently fed with hydrocarbons, such as natural gas, have already installed an SCR system, thus already handling ammonia onsite.

Hydrogen production

As ammonia will become more abundant as an energy vector, its use as a hydrogen carrier is set to increase. Ammonia cracker facilities for hydrogen production are currently being considered in various northern European ports, such as Rotterdam and Wilhelmshaven. Proton Ventures has performed various studies on ammonia cracking for clients and remains active within various research consortia. Centralised ammonia cracker solutions for pure hydrogen production are functionally very similar to natural gas processing plants for hydrogen production. Alternatively, decentralised ammonia cracker solutions are currently being developed, which do not always require full conversion and purification of the hydrogen, thereby improving the energy efficiency of the system and the cost.

To consolidate the solution for ammonia cracking, Proton Ventures is currently building its high-pressure ammonia cracking testing facility at the high-pressure laboratory at the University of Twente, the Netherlands. This is critical to validate the operational performance under industrially relevant conditions, while also allowing to test novel cracker concepts. The next aim is to build a commercial pilot for ammonia cracking, before moving to world-scale hydrogen production facilities. This is necessary, as performance in terms of ammonia feedstock utilisation is key for the cost of produced hydrogen. The ammonia feedstock cost can account for over 90% of the total levelised cost of hydrogen from ammonia cracking. Thus, ensuring minimal ammonia feedstock utilisation is paramount.

PHOTO: PROTON VENTURES

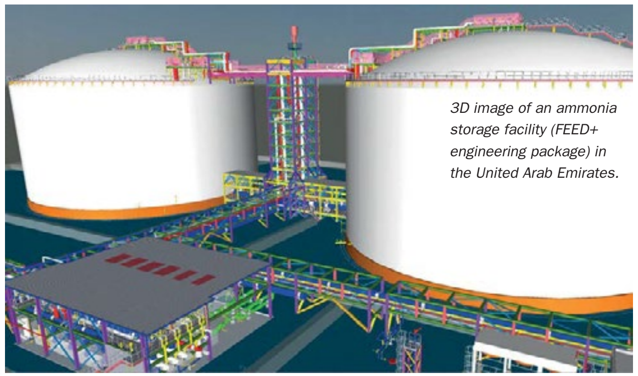
Founder and former CEO of Proton Ventures, Hans Vrijenhoef speaking at the NH3 Event in 2022.

Leading by example

The ammonia economy will likely become a reality soon. Various decarbonisation projects for existing ammonia plants have already been realised, with newbuilt green ammonia plants under construction. Various consortia are commercialising ammonia energy solutions.

Proton Ventures has been at the forefront of these discussions with the initiation of the NH3 Event in 2017, which was the first European conference focused on low carbon ammonia production, as well as its utilisation as low carbon fertilizer, zero-carbon fuel, and hydrogen carrier. The conference boasts a strong industrial presence, as well as various excellent academic speakers. On the 8th and 9th of June 2023, the NH3 event will be held for the sixth time, returning to its iconic venue: Diergaarde Blijdorp in Rotterdam, the Netherlands.

Twenty years ago, even five years ago, few believed in ammonia as an energy carrier. Throughout its two decades of existence, Proton Ventures has established itself as an engineering solutions expert in the green ammonia landscape. With the same passion, the team continues to serve its customers with ammonia solutions. ■



3D image of an ammonia storage facility (FEED+ engineering package) in the United Arab Emirates.

IMAGE: PROTON VENTURES

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TOYO ENGINEERING CORPORATION (TOYO)

TOYO expands into clean and renewable energy

Michiko Nakajo

Toyo Engineering Corporation (TOYO) is a leading international engineering contractor and is expanding its business field to clean and renewable energy towards the realisation of a carbon-free society. In the 1960s, TOYO had its own ammonia process and had licenced it to customers. However, in 1968, based on detailed investigations of a large-scale ammonia plant design, TOYO decided to have a general license agreement with KBR, the global leading ammonia process licensor. In 1969, TOYO built and commissioned its first 1,000 t/d ammonia plant by integrating its own experience and know-how in designing ammonia plants with the KBR process. To date, TOYO's experience in ammonia plant projects, including plants based on its own and KBR processes, amounts to 86 projects.

Conventionally, ammonia has been produced from fossil fuels such as natural gas, and most of it has been used for the purpose of chemical fertilizers. In response to the global trend toward carbon neutrality, in recent years ammonia, which burns CO_2-free, has been attracting attention as a new fuel that supports energy security. In addition to expanding the use of ammonia as a low-emission fuel, there is a demand to develop a low-carbon ammonia process.

Responding to this movement, JGC Holdings Corporation (JGC), a global engineering company headquartered in Yokohama, Japan, and TOYO signed an alliance agreement on 26th April 2022 with the aim of speedily demonstrating to ammonia fuel business operators enhanced proposal capabilities and competitiveness by combining the JGC's extensive record of constructing process plants in regions such as Australia and the Middle East with the TOYO's extensive track record and technical expertise in ammonia production plants. This agreement covers all activities from integrating efforts from the conceptual stage to EPC. Through the expanded use of ammonia fuel, the two groups will contribute to the realisation of a decarbonised society.

Ammonia Alliance Japan

As mentioned above, JGC and TOYO formed an alliance named Ammonia Alliance Japan (AAJ) in April 2022 to realise a zero-carbon society by utilising ammonia as a fuel (Fig. 1).

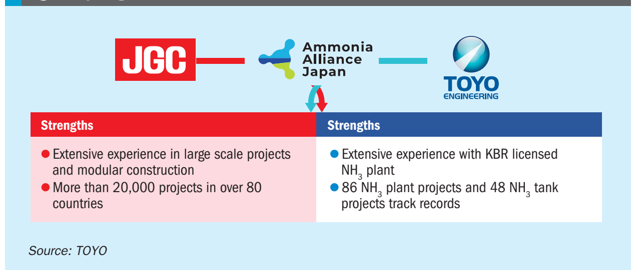
In October 2020, the Japanese government declared its goal of realising carbon neutrality by 2050. Ammonia fuel shows promise as a decarbonised fuel for power generation, marine transportation, etc. The government has therefore set expanded implementation targets of 3 million tonnes per year as of 2030 and 30 million tonnes per year as of 2050. Accordingly, various companies and organisations both in Japan and overseas have launched initiatives aimed at the manufacturing, transport and use of ammonia fuel.

An alignment of the Japanese government and companies is expected to play a key role in the ammonia fuel business in the future. JGC and TOYO will jointly pursue business operations and project execution related to the evaluation, planning, engineering, procurement and construction of ammonia fuel manufacturing-related facilities around the world, including for overseas companies, and contribute to the future of ammonia fuel.

With the aim to establish a supply chain for ammonia, AAJ, as a global leading engineering contractor, is offering the following solutions with the goal of achieving a decarbonised society:

- Reduce construction risk by modularisation
- A 3,000 t/d 3D model and construction basis of proven design has been developed
- Ready to deliver based on deep experience and study
- Benefit from economies of scale by enlarging plant capacity
- Offering a design of 6,000 t/d ammonia production plant with single equipment throughout the flowsheet
- Ready for front-end engineering design (FEED)
- Maximise quality, control and delivery (QCD) level by leveraging the existing facility
- Connect electrolyser and utilise unused production capacity
- Earn "Renewable Energy (RE) & Green Ammonia Certificate" and swap with other plants

Fig. 1: Synergetic effect of JGC and TOYO for ammonia fuel business

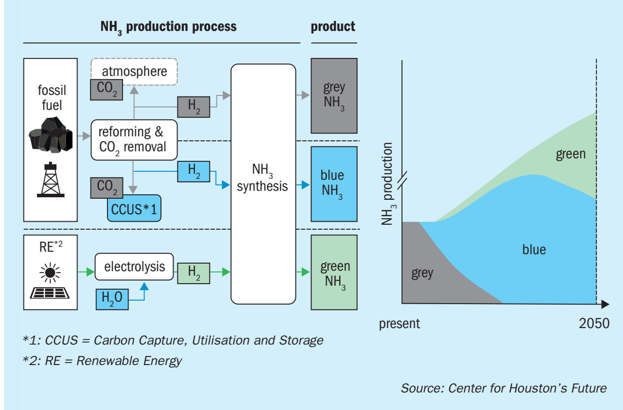


Source: TOYO

Low-carbon ammonia

Conventional ammonia produced from fossil fuels such as natural gas is called "grey ammonia", while low-carbon ammonia, in which CO_2 emissions are reduced in the production process are often referred to as "blue ammonia" and "green ammonia", depending on the production process and the degree of reduction in CO_2 emissions. In this article, blue ammonia is defined as ammonia produced from fossil fuels where the CO_2 emissions generated in the production process are sequestered by carbon capture and storage (CCS), carbon capture and utilisation (CCU), or enhanced oil recovery (EOR). Green ammonia is defined as the ammonia synthesised from hydrogen produced by water electrolysis using renewable energy, such as solar, wind, hydro, geothermal, and biomass power.

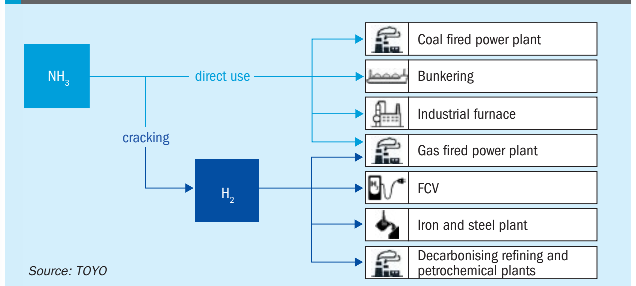
Fig. 2: Comparison of ammonia production processes (left) and production forecast for grey, blue and green ammonia production (right)



*1: CCUS = Carbon Capture, Utilisation and Storage
*2: RE = Renewable Energy

Source: Center for Houston's Future

Fig. 3: Versatility of ammonia



Source: TOYO

Fig. 2 shows a simplified process flow diagram and chart showing the production forecast for grey, blue and green ammonia up to 2050. As mentioned before, blue ammonia is a kind of derivative of grey ammonia, still using the conventional steam reforming process but with added CCS or CCU. The hydrogen production for green ammonia, on the other hand, replaces the conventional steam reforming process with electrolysis using renewable electricity, which has a relatively high cost to split water into hydrogen and oxygen. In addition, green ammonia still has several other issues that need to be resolved, for example:

- the energy efficiency of electrolysis is only 70 to 80%; and
- renewable power sources such as solar and wind fluctuate which adds to ammonia production costs.

Blue ammonia is able to cost-effectively supply the large volumes of low-carbon ammonia required to fulfil the new demand for clean fuel in the short term, and it is expected that the large-scale value chain from the Middle East and/or North America to Asia will be built. For green ammonia, on the other hand, local small-scale value chains will be built first in regions such as Europe. After 2030, green ammonia production, for instance in the Middle East, will be increased, where solar generated power is low, and green ammonia will be exported.

Ammonia can be used in many sectors and for many different purposes. To date, it has mainly been utilised in the field of nitrogen fertilizer. However, there is current interest in ammonia being utilised as a fuel directly for coal-fired power plants, bunkering, industry furnace or gas-fired power plants, or used indirectly as a hydrogen resource, which is produced by ammonia cracking technology, for gas fired power plants, fuel cell vehicles (FCV) or iron and steel plants (see Fig. 3).

The infrastructure for ammonia transportation, such as marine transportation, land transportation and storage, already exists and is in commercial operation. In contrast, liquefied hydrogen is extremely expensive to produce and transport as it requires cooling to a very low cryogenic temperature, is challenging to contain and lacks the required transport infrastructure. In the case of methylcyclohexane (MCH), which is a hydrogen carrier composed of liquid made by the chemical reaction of hydrogen to toluene, it can be used in the existing petroleum infrastructure because of the liquid phase with petroleum-like characteristics. However, its costs are higher than ammonia since much larger volumes of material need to be transported per unit of hydrogen delivered. This is summarised in Table 1.

Blue ammonia process

The blue ammonia process consists of the conventional ammonia production facilities and the additional system for CCS or CCU. Although it is more costly than a conventional ammonia process due to the extra facilities, the unit production cost of ammonia can be reduced to a reasonable level by increasing the capacity, due to economies of scale. Currently the largest ammonia plant licensed by KBR with a single converter (and all other equipment) is operating at 3,000 t/d; KBR has already completed the design for 6,000 t/d in a single train, named AMMONIA 6000® and has verified all major equipment with vendors. Fig. 4 shows the process flow diagram of the KBR PurifierPlus™ Blue Ammonia process.

Globally, there is currently no common definition for blue ammonia or hydrogen for example the definitions stipulated by several organisations in different regions currently refer to the amount of CO_2 emission. KBR has an extensive line-up of ammonia processes to meet the CO_2 emissions requirements stipulated by any of these definitions. Fig. 5 compares CO_2 emission rates for KBR's ammonia processes: (I) conventional steam methane reformer (SMR) and auto thermal reformer (ATR); (II) KBR Purifier™; (III) KBR PurifierPlus™; (IV) PurifierPlus™ + H_2 recycle; (V) PurifierPlus™ + CO_2 removal; and (VI) O_2 ATR.

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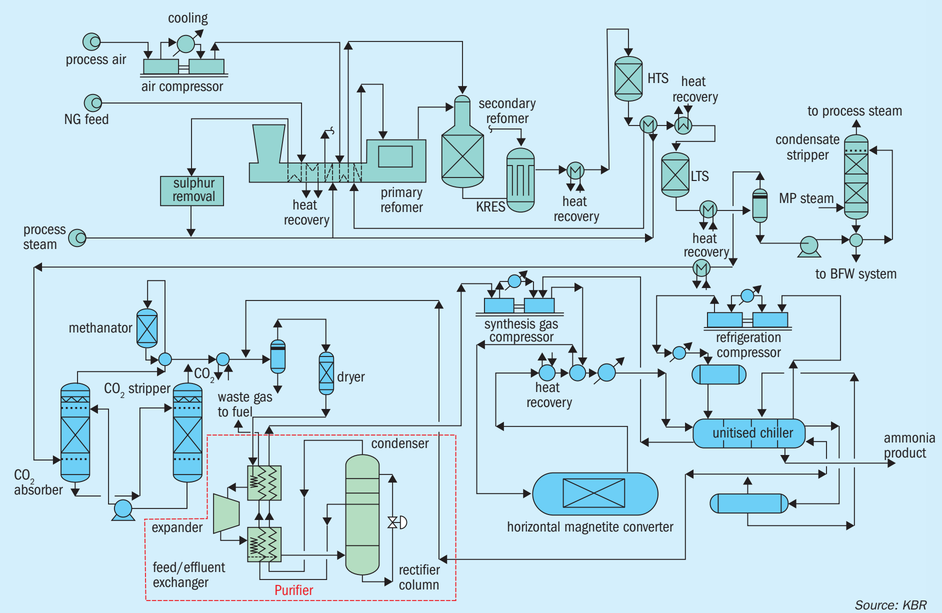
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33

Table 1: **Comparison of ammonia and hydrogen carriers**

	Ammonia (Direct Use)	Hydrogen carrier		
		Ammonia	Liquefied hydrogen	Methylcyclohexane (MCH)
Heating value	Good 9.41 MJ/Nm³	Excellent 10.88 MJ/Nm³	Excellent 10.88 MJ/Nm³	Excellent 10.88 MJ/Nm³
Condition in transportation	Proven -33°C	Proven -33°C	Under development -253°C	Proven normal temperature
Efficiency in transportation	High 121 kg H_2/m³	High 121 kg H_2/m³	Medium 70.6 kg H_2/m³	Low 47.3 kg H_2/m³
Cost to Japan*	Lowest	Low approx. 5.5 USD/kg H_2	High approx. 7 USD/kg H_2	Medium approx. 6 USD/kg H_2

**Cost of delivering hydrogen or ammonia produced via electrolysis from Australia to an industrial customer in Japan in 2030, IEA "The Future of Hydrogen".*
Source: TOYO

Fig. 4: **KBR PurifierPlus™ process flow diagram**



Source: KBR

Carbon dioxide in flue gas and process gas is emitted from the ammonia plant, and either one or both should be recovered to reduce the emission rate. CO_2 in process gas is already recovered by the conventional process (I); the CO_2 recovery rate is approximately 60-65%. For KBR's Purifier™ process (II), the CO_2 recovery rate for the process gas is up to 70-75%. KBR's PurifierPlus™ applying KBR's proprietary technology, Kellogg Reforming Exchanger System (KRES™) as well as the Purifier (III), is the most environmentally friendly, cost-effective, energy-efficient and reliable ammonia technology and can improve the CO_2 recovery rate up to approximately 80%. Note that the primary reformer for this process is 60% smaller than that required for a conventional ammonia process which not only yields capex and opex benefits but also reduces CO_2 emissions. The KBR PurifierPlus™ process is not a conventional SMR process since its primary reformer is 60% smaller, hence it may be termed a "mini-SMR + ATR without ASU" process.

If a CO_2 recovery rate of more than 80% is required in line with the latest regulation or a definition at that time, PurifierPlus™ with hydrogen recycling (IV) should be applied. In this process, hydrogen produced in the reforming section is utilised as fuel for the SMR, therefore, the amount of CO_2

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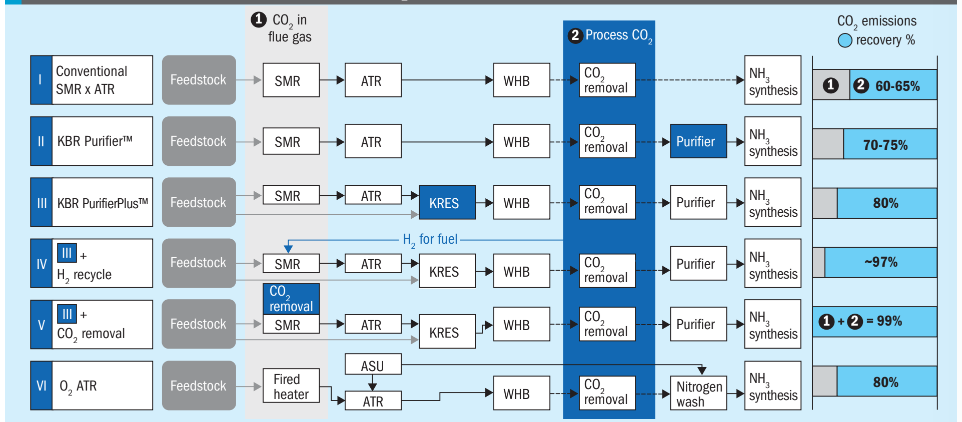
Fig. 5: **Ammonia production processes and their CO_2 recovery rate**

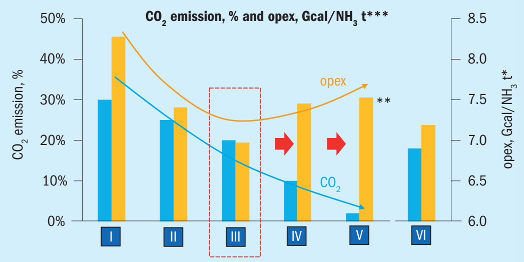


KBR SMR in Case III is 60% smaller than required for a conventional ammonia process.

Source: TOYO

Fig. 6: **CO_2 emission % and opex for each ammonia process**

- I Conventional SMR
- II KBR Purifier™
- III KBR PurifierPlus™
- IV Fuel by surplus syngas **(opex increases)**
- V Flue gas CO_2 recovery **(opex increases)**
- VI O_2 ATR (reference)

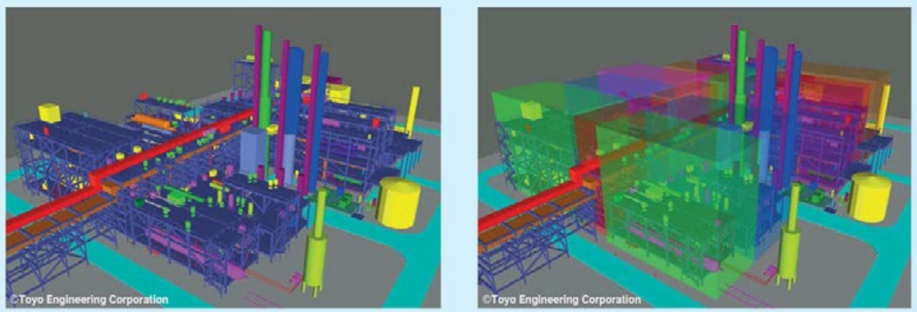


Notes:

* Opex (Gcal/t NH_3) is calculated based on methane feedstock/ fuel and CO_2 emission rate. It is typical rate only.
** Energy efficiency for flue gas CO_2 recovery as typical 2.6 GJ/t CO_2.
*** CO_2 from CO_2 compression is not included.

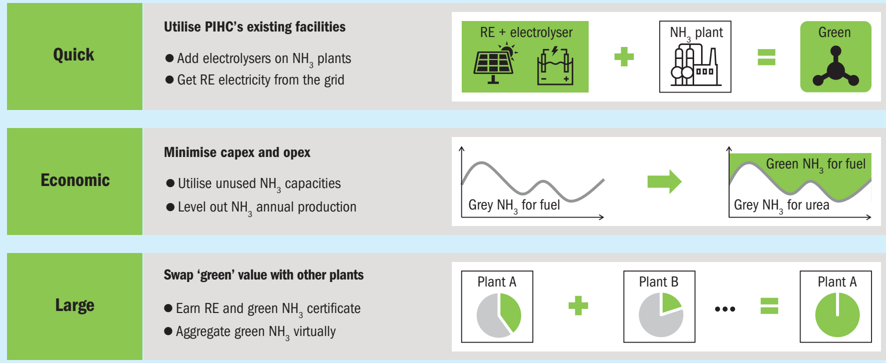
Source: TOYO

Fig. 7: **Modularisation study for a 3,000 t/d ammonia plant**



Source: TOYO

Fig. 8: **Plans to turn grey ammonia to green ammonia in Indonesia**



Source: TOYO

contained in the flue gas decreases accordingly. The recovery rate will increase up to 97% in this case. A 99% CO_2 recovery rate can be achieved by deploying PurifierPlus™ with a small CO_2 post combustion carbon capture unit (V). Finally, for the O_2 ATR case (VI), the CO_2 recovery rate is not 100% because of the associated fired heater that is required. In addition, CO_2 emissions from the air separation unit (ASU) should also be considered if renewable energy is not used for the ASU. The CO_2 recovery rate for this process is 80%, which is lower than the process using PurifierPlus™ with hydrogen recycling (IV).

In AAJ's opinion, blindly chasing CO_2 recovery rate is meaningless because the opex to achieve the high recovery rate increases, therefore, it is crucial to consider the balance between opex and a suitable recovery rate. AAJ regards the KBR PurifierPlus™ process (III) as the optimum process option when considering the best balance. In this case, even if the recovery rate needs to increase in the future by due to new regulations, it can be easily achieved by using the hydrogen recycling concept (IV). The balance between CO_2 recovery rate and opex is shown in Fig. 6.

Modularisation

Aiming for ammonia production cost reduction, the modularisation of an ammonia production plant with a capacity of 3,000 t/d has been evaluated (Fig. 7). Modularisation can be a cost-effective approach, especially in regions with high labour costs, such as North America or Australia. In addition, the design of 6,000 MTPD ammonia plant, which might require the modularisation concept, has already been completed and is ready for FEED.

Using a modular assembly enables AAJ to be flexible for the design and provides an engineering solution that facilitates the successful management of EPC, regardless of the project size, scope or location. By fabricating key components in a controlled environment, it is possible to minimise risk, improve quality and stabilise field construction costs, which are typically high and variable. Modularisation also facilitates plant start-up because piecemeal checkouts can be made in a controlled environment. Since modularisation requires careful planning before moving forward and many facets should be considered to make project execution effective, sufficient time should be allocated to assess the various options and to bring all the elements of modularisation together.

AAJ can provide cost certainty to its clients by integrating planning, modularisation know-how, and tightly managing project execution.

Feasibility study for green ammonia

A green ammonia process consists of an ammonia synthesis process with electrolyser facilities, such as water electrolysis, hydrogen gas holders, and storage.

TOYO received an award from the Ministry of Economy, Trade and Industry (METI), Government of Japan and started a feasibility study for green ammonia production in Indonesia, in collaboration with Pupuk Indonesia Holding Company (PIHC), a government enterprise in Indonesia, and Pupuk Iskandar Muda (PIM), a subsidiary company under PIHC.

During the feasibility study, TOYO studied the feasibility of green ammonia production in Indonesia at the existing fertilizer plants owned and operated by PIM, and established a plan for their optimal development, taking into consideration the selection of an appropriate renewable energy power source, effective measures to deal with the fluctuation of renewable energy power supply, etc. TOYO constructed the fertilizer plant for PIM in the 2000s. Utilising its experience and knowledge, TOYO developed a competitive green ammonia production facility by minimising modifications to the existing plant in the most optimum way. In addition, the future decarbonisation of other fertilizer plants under PIHC by applying a similar scheme is also included in the feasibility study (see Fig. 8).

Ammonia is an essential global commodity mainly used for nitrogen fertilizers, and also emerging as a zero-carbon fuel and as a hydrogen carrier for international trade of carbon-free energy. As a technology-orientated contractor, TOYO and JGC have always endeavoured to improve plant efficiency and to reduce plant life cycle costs and will contribute to a carbon-free energy future through the expanded use of blue and green ammonia. ■

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STAMICARBON

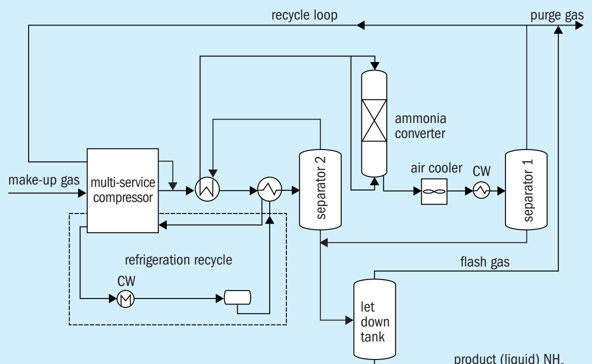
Powering ammonia synthesis with renewable energy sources

Deepak Shetty

Climate change can only be beaten if society stops emitting greenhouse gases. To do this, we need to cut emissions from as many sectors as possible and generate the electricity we need using renewable energy sources. As wind and solar energy have inherent fluctuations in availability, integrating renewable energy sources into our grid is a big challenge. Water electrolysis, a patented and proven technology for producing green hydrogen, is the best way to solve this problem by utilising the electrical energy from renewable plants. As hydrogen has a very low energy density, it needs to be stored at high pressures and, on its own, cannot solve many of the world's challenges.

Ammonia has a higher energy density than even liquid hydrogen. This makes ammonia a good source of bunker/shipping fuel and perfect for green chemicals on an industrial scale, especially with the necessary infrastructure to carry ammonia already in place. With its use in fertilizers, green ammonia is a prime candidate for any country to produce local fertilizers and industrial green chemicals using renewable power and substitute the import.

Fig. 1: **Typical process flow diagram for Stami Green Ammonia**



Source: Stamicarbon

Stami Green Ammonia in fertilizer production

The Stami Green Ammonia technology differs in the synthesis gas pressure (approximately 300 bar) compared to other conventional ammonia technologies. According to the principle of chemical equilibrium, the synthesis of ammonia is favoured at low temperatures and high pressure due to an exothermic reaction and reduction in the number of moles. The high-pressure ammonia synloop at the heart of the technology has been customised to make the most efficient plant design at a small scale, especially with green feedstock. This setup is more favourable, due to the high purity of the synthesis gas feedstock that has a higher partial pressure of reactants. In addition, there are hardly any inerts present within the process, which means that the conversion per pass of the reactor is higher. This results in a high concentration of ammonia at the outlet of the converter. As a result, purging is also minimised. Due to the phase property of ammonia at high pressure, this design choice allows the majority of ammonia that is synthesised to be condensed with the cooling water, eliminating the need for a multistage refrigerating compressor or multistage chiller where a single-stage refrigeration cycle is sufficient. As a result, the plant operates with a single proven and reliable electric-driven multiservice reciprocating compressor. The minimal equipment needed for plant operations leads to substantial capex savings – an important consideration for small-scale applications. Furthermore, due to the high pressure, ammonia synthesis requires a very small catalyst volume.

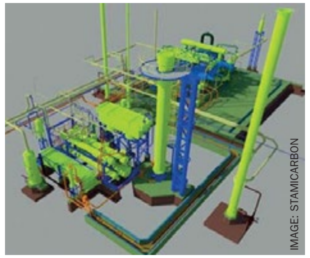


Fig. 2: Typical 3D model of a Stami Green Ammonia Plant.

The Stami Green Ammonia technology configuration (Fig. 1), characterised by a modularised approach and thus perfect for small-scale facilities, is the first of its kind, based on proven technology. The operating reference plants are based on natural gas which has been adapted to make-up gas produced via a green route. This technology is especially suitable for the decentralised production of green ammonia utilising a renewable source of energy. The plant is fully flexible in managing the intermittent nature of renewable energy if that is required. The technology package is available in tailored capacities for small-scale plants in the range of 50 to 500 t/d of ammonia production but can be scaled upwards. The plant has a lean and compact design (Fig. 2). A capacity of 300 t/d ammonia production has a footprint of approximately 50 x 40 m, including the compressor building. It utilises about 130-140 MW of power, depending on its capacity.

Stamicarbon's technology package offers a competitive solution for local production on a small scale. It can be applied in combination with its existing (mono-pressure and dual-pressure) nitric acid and urea technologies, moving from grey ammonia to green ammonia-based fertilizers to produce green nitrate fertilizers. In combination with the use of recycled or recovered CO_2, it reduces the carbon intensity of urea fertilizer production.

The technology has four recently commissioned operating references based on natural gas. This is the strongest technology reference in a small-scale range that makes a sound basis for further development of the future small-scale ammonia plant concept.

The technology includes the following key features:

- high capex efficiency;
- strongest reference base with five small-scale plants in operation;
- lean, compact and modularised design;
- high plant reliability thanks to a multi-service reciprocating compressor;
- compliance with the highest environmental standards;
- dedicated operator training simulator available;
- access to digital solutions, such as a process monitoring tool;
- agnostic to upstream water electrolysers and can be integrated with Stamicarbon's nitric acid and urea technologies.

Green ammonia for a greener future

By 2050 the world's population will grow to nearly 10 billion people. Also, by 2050 hundreds of countries will have to achieve their targets of net-zero emissions aligned with the Paris Agreement. Ammonia acts as a building block for nitrogen fertilizers and plays an important role in providing optimal plant nutrition, yet it is responsible for 1% of the world's greenhouse gas emissions. Powering ammonia synthesis with renewable energy sources thus becomes a significant step towards more sustainable fertilizer production. The Stami Green Ammonia technology aims to serve as a gateway to carbon-free and futureproof ammonia production and a solution for the production of smart, sustainable, renewable feedstock for nitrogen-based fertilizers. ■

BD ENERGY SYSTEMS

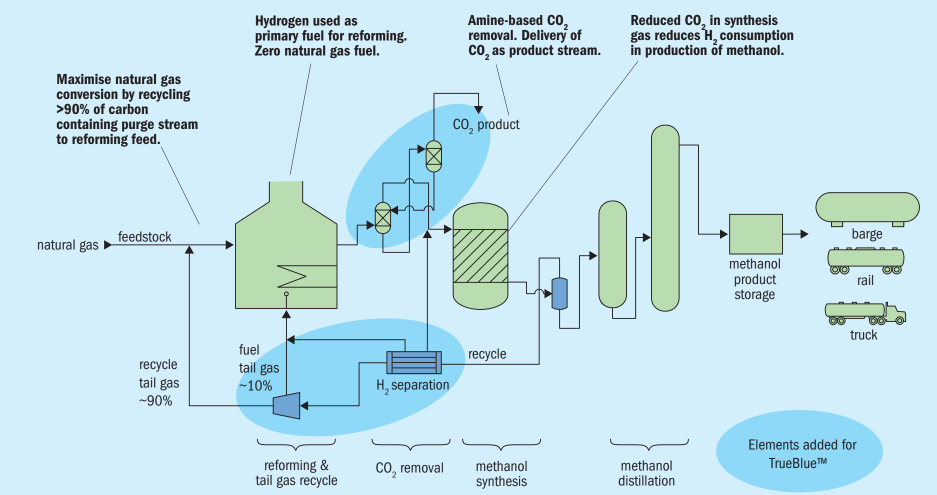
New low carbon methanol production approach

Dan Barnett

BD Energy Systems LLC introduces TrueBlue Methanol™, an innovative low carbon emission steam methane reformer (SMR) based methanol production process to the industry. This process utilises proven techniques to achieve greater than 90% reduction in the emission of CO_2 from the stack of the SMR furnace while producing methanol with an overall energy consumption that is favourably competitive with even the newest operating SMR-based methanol plants. The TrueBlue™ process can be implemented not only on grassroot and relocated methanol plants but as an upgrade to many existing methanol plants for any natural gas fed process configuration.

This process delivers a product CO_2 stream using an amine-based CO_2 removal system placed upstream of the methanol synthesis reactor. Doing so reduces the consumption of hydrogen in the methanol synthesis process, resulting in greater hydrogen availability for SMR fuel. Removal of hydrogen from the synthesis loop purge stream recovers hydrogen for use as SMR fuel, and recompression of the carbon containing tail gas allows recycle of most of the tail gas to the SMR feed. This recycle results

Fig. 1: **The BDE TrueBlue Methanol™ process**



Source: BDEnergy Systems

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in more complete conversion of incoming natural gas feed to synthesis gas and use of hydrogen as the primary fuel effectively reduces SMR stack gas CO_2 emissions to a very low level.

This article presents key flowsheet elements of the TrueBlue™ process and an overall performance contrast of the BDE process with conventional natural gas fed SMR-based methanol plants.

Worldwide methanol production[1] is largely based on the use of natural gas feed with ~65% of total methanol production based on natural gas, ~35% based on coal, and less than 1% currently based on renewables. Achieving significant reductions in atmospheric CO_2 emissions from natural gas-based methanol production is made possible with the approach outlined here.

Conventional SMR-based methanol production

For the purposes of comparison, the "conventional" SMR-based methanol plant is defined in general terms as one having a modern high efficiency SMR, an "isothermal" methanol synthesis reactor, and combustion of the synthesis loop purge gas in the SMR. Overall energy consumption of a conventional SMR-based methanol plant is in the range of 27.0-28.0 million Btu of total energy (LHV basis) per short ton of high purity methanol product. Total energy here is based on total natural gas, feed plus fuel, as well as net electric power import for the methanol plant and associated utility units.

Use of natural gas (96-97% methane) as feed results in the production of more hydrogen than required for methanol synthesis. This excess hydrogen is typically purged from the methanol synthesis loop and burned as fuel in the SMR. This reduces the make-up natural gas fuel required for the SMR; however, required natural gas fuel makeup remains in the 7-8% range in terms of total required heat release. Further, the hydrogen containing purge gas from the methanol synthesis loop also contains methane, carbon monoxide and carbon dioxide. Considering only the SMR fuel, not including fuel to a gas fired boiler or a gas turbine, the emission of CO_2 to atmosphere is in the range of 0.35-0.36 weight CO_2/weight methanol product. So, for a 2,000 t/d conventional methanol plant, the SMR stack gas CO_2 emissions would be in the range of 700-720 t/d (255,500 to 262,800 t/a).

BDE TrueBlue Methanol™ production

The BDE TrueBlue Methanol™ plant design is also SMR-based with several significant additions when compared with the conventional plant. First, the SMR front end includes the use of pre-reforming and convection section reheat of pre-reformer effluent to effectively shift a portion of the required reforming reaction duty from the radiant section to the convection section.

Second, an amine-based CO_2 removal system is added immediately upstream of the synthesis gas compressor to reduce the proportion of CO_2 feeding to the methanol synthesis reactor. This effectively reduces the quantity of hydrogen consumed in the production of methanol, reducing the amount of reaction water produced, which enables recovery of that hydrogen for use as SMR fuel.

$$CO + 2H_2 = CH_3OH + heat$$

(2 mol H_2 consumed/mol CH_3OH produced)

$$CO_2 + 3H_2 = CH_3OH + H_2O + Heat$$

(3 mol H_2 consumed/mol CH_3OH produced)

Third, purge gas from the methanol synthesis loop is routed to a pressure swing adsorption (PSA) unit to separate out a major portion of the hydrogen remaining in that stream for use as fuel. The tail gas from the PSA unit, containing CH_4, CO_2, CO, inert components, and unrecovered H_2, is recompressed to allow recycle of approximately 90% of the tail gas back to the SMR feed stream. Approximately 10% of the PSA tail gas is routed to SMR fuel to limit the accumulation of inerts in the synthesis gas. The recovery of hydrogen as described, along with the small PSA tail gas flow are enough to supply all the fuel required for the SMR, reducing the natural gas firing of the SMR to zero. The recycle of approximately 90% of the carbon containing components of the purge achieves more complete conversion of incoming natural gas feed to synthesis gas.

These added elements extract CO_2 from the plant as a product stream while reducing the SMR stack gas emissions of CO_2 by 90-93% when compared with a conventional plant.

Overall energy consumption of the BDE TrueBlue™ methanol plant remains in the range of 27.0-28.0 million Btu of total energy (LHV basis) per short ton of high purity methanol product. Total energy here is based on total natural gas feed with zero natural gas fuel, as well as net electric power import for the methanol plant and associated utility units.

With the use of hydrogen as the primary fuel and make-up fuel being a portion of the PSA tail gas, there is no need for natural gas fuel firing.

Compared to conventional SMR-based plants, considering only the SMR fuel, not including fuel to a gas fired boiler or a gas turbine, the emission of CO_2 to atmosphere is in the range of 0.032-0.035 weight CO_2/weight methanol product. So, for a 2,000 t/d conventional methanol plant, the SMR stack gas CO_2 emissions would be in the range of 64-70 t/d (23,400 to 25,600 t/a), and the CO_2 product stream is in the range of 636-650 t/d.

The TrueBlue™ process effectively converts the stack CO_2 emissions of a conventional plant to a CO_2 product stream.

Comparison with alternative carbon capture methods

The BDE TrueBlue Methanol™ production process achieves 90+% reduction in SMR stack CO_2 emissions by reducing carbon containing components in the fuel gas through use of "pre-combustion" CO_2 removal and recycle of a high percentage of the carbon containing tail gas to the feed. There are other processes that utilise a combination of pre-combustion and post-combustion CO_2 capture that can achieve a comparable overall level of CO_2 capture. However, the post-combustion capture techniques for low pressure flue gas can be troublesome with respect to degradation of the absorbent solution, the corrosive nature of those solvents, and reduced efficiency of absorption in a low-pressure application.

The elements added for the TrueBlue™ process are well proven, while the SMR design must be designed specifically to accommodate firing of 98% hydrogen fuel, and a higher extent of pre-reforming compared to a conventional SMR-based plant. ■

Reference

1. International Renewable Energy Agency – Innovation Outlook Renewable Methanol (2021).

KBR

KBR clean ammonia technologies

R. Bernat, E. Stylianou and H. Larsen

The world is facing a massive challenge in the race for decarbonation to combat climate changes and to limit global warming to 1.5°C as per the Paris Agreement. This journey towards net zero in 2050 requires double digit trillion dollars investment in technologies and infrastructure for low carbon fuels and electrification.

Ammonia is predicted to play a major role in this journey, as a clean fuel on its own or as a carrier of hydrogen. The ammonia demand is therefore expected to increase significantly, with CAGR around 4% up to 2050. The majority of this ammonia is expected to be produced via renewable power and electrolysis, often designated green ammonia, but a significant share will be produced via reforming of fossil fuels and carbon capture, often designated blue ammonia.

As a technology provider for ammonia technology for more than 75 years, KBR has actively and continuously enhanced the technical features of its ammonia technology. These technical innovations and improvements have enabled owners of KBR-designed ammonia plants to obtain consistently safe, reliable and cost-effective operation. Today, that same proven technology is being applied to deliver the most efficient solutions for blue and green ammonia, hydrogen as well as ammonia cracking (see Fig. 1).

Blue ammonia

KBR's blue ammonia process is based on its PurifierPlus™ technology which incorporates KBR's proven Purifier™ and KRES™ (KBR Reforming Exchanger) technologies to generate ammonia with high energy efficiency, high reliability, low capex, and low opex, all while capturing up to 99% of the unit's overall CO_2 output.

The sources of CO_2 in the ammonia unit are from the primary reformer fuel combustion, and from the conversion of natural gas into hydrogen in the process system. To reduce the overall generation of CO_2, the KBR Purifier™ technology allows for mild primary reforming, through the use of excess air in the secondary reformer, which is associated with a reformer radiant duty reduction of 30% in comparison with conventional schemes. When combined with a KRES™, there is a further reduction in radiant duty of 20-30%, for a total reformer duty reduction of 50-60% versus conventional designs. This radiant duty reduction leads to much lower CO_2 generation in the ammonia unit, as well as significantly lower generation of CO_2 in the furnace fuel system.

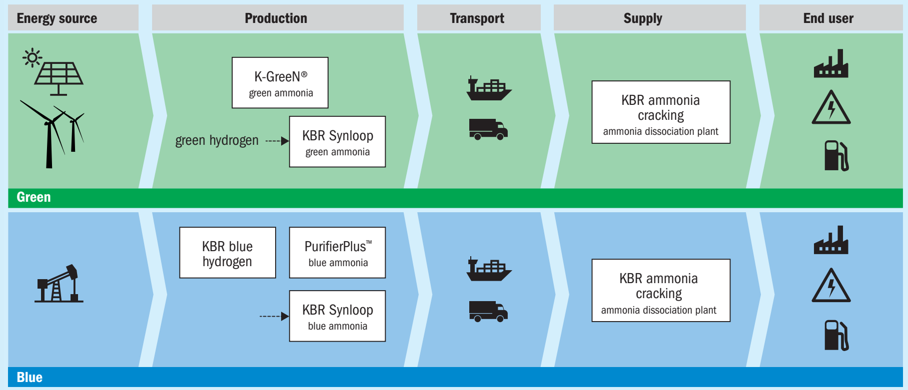
These unique features of the PurifierPlus™ technology, will allow the recovery of up to 80% of the generated CO_2 without any modifications to the PurifierPlus™ process, and this proven technology is therefore an excellent platform for a staged investment that by subsequently applying a syngas recycle as reformer fuel or adding a Post Combustion Capture Unit (PCCU) will be able to increase the CO_2 capture up to 97% and 99% respectively.

The basic PurifierPlus™ technology and the two options for either syngas recycle or a PCCU are shown in Figs 2-4.

In all three process schemes, the inherently better chemistry of a SMR-based process vs. that of an oxygen-based process, described via the R number (R number is used to describe the composition of the syngas produced $R = H_2\text{-}CO_2/CO+CO_2$) leads to the lowest generation of CO_2 per tonne of NH_3 produced.

In the KBR PurifierPlus™ process, R = ~2.2 whereas in ATR processes R = ~1.85. The lower the R number, the more CO_2 and CO the process will produce which is not advantageous when the desired product is NH_3 with no carbon content.

Fig. 1: **KBR Low-carbon technologies**



Source: KBR

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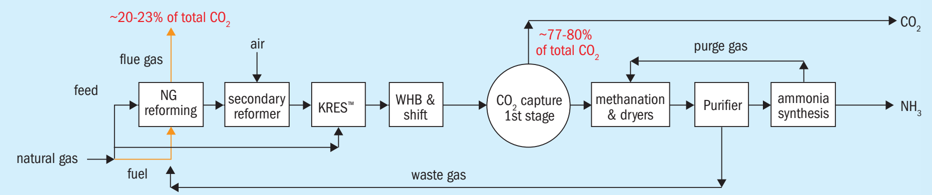
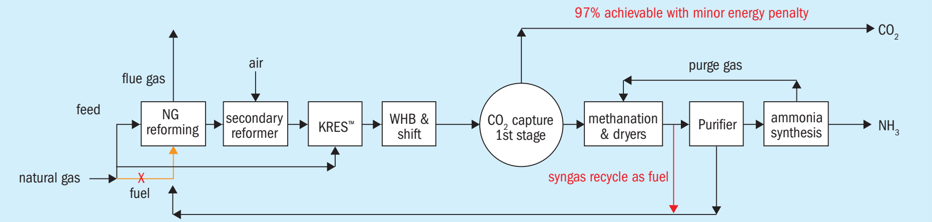
Fig. 2: **KBR PurifierPlus™ technology**



A conventional ammonia process recovers around 65% of CO_2 produced, whereas the KBR PurifierPlus process recovers 80% (and produces less total CO_2 since it consumes less gas).

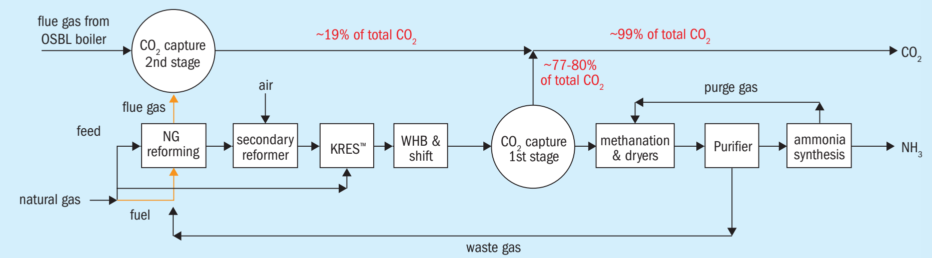
Source: KBR

Fig. 3: **KBR PurifierPlus™ technology with syngas recycle as reformer fuel**



Source: KBR

Fig. 4: **KBR PurifierPlus™ technology with PCCU**



Source: KBR Reformer is 60% smaller than in conventional reforming, hence the PCCU is also designed correspondingly smaller.

Consequently, the natural gas consumption in the KBR PurifierPlus™ process is lower and coupled with a limited need for OSBL support units, this further reduces the overall CO_2 emission when considering the total emission combining scope 1, 2 and 3 of CO_2 emissions.

Green ammonia

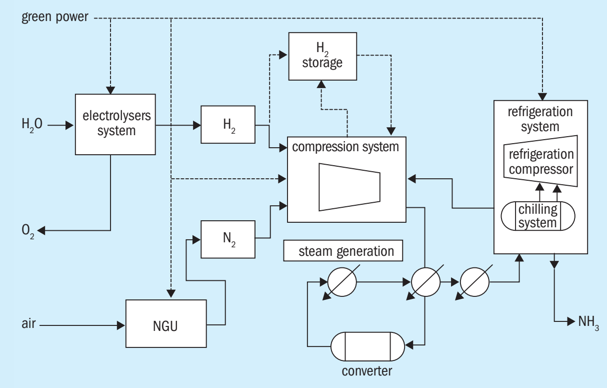
A global shift from grey ammonia in the direction of green requires a technological response to maintain safe and stable operation of the plants as well as to maximise the ammonia production and to increase revenue for the plant operator. Intermittency and fluctuations of renewable energy generation sources delineate increase of responsiveness and flexibility of both electrolysis systems as well as the ammonia synthesis loop itself.

KBR have developed K-GreeN®, a complete solution from renewable energy to green ammonia (Fig. 5). Part of the development comprises technological advantages in the ammonia synthesis loop that allow the plant to be turned down to lower capacities as well as having greater flexibility to ramp it up and down.

Additionally, KBR has developed an advanced process control system for green ammonia that minimises the fluctuations of the process conditions and allows the utilisation of available renewable energy to be maximised. It combines current, forecasted as well as historic weather data with proper management of hydrogen and electricity storage levels. Moreover, it includes electrical grid cooperation and optimises electrical energy sourcing by dynamically responding to variable pricing (e.g., own behind the meter sources, PPA, spot price, etc.). Use of the advanced process control system further stabilises plant operation, minimises mechanical wear of auxiliary equipment, smooths out ramp-up and ramp-down curves and prevents plant outages. This, combined with the most efficient and reliable ammonia technology of KBR, maximises the product output and income for plant operators.

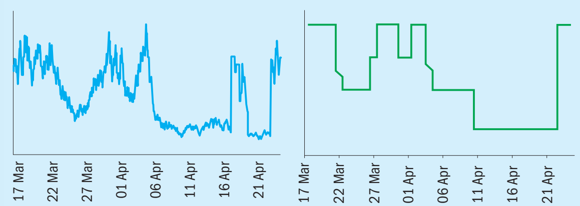
Fig. 6 shows an optimisation case study of the advanced process control system. In the left figure a fluctuating energy feed is presented. This is a typical energy profile that can be expected from a renewable energy source. Usually, even if a grid connection is present, it is not enough (or not cost-effective) to maintain the same level of green ammonia production. Furthermore, if grid power is not generated from renewable energy sources, then the ammonia produced is not from a low-carbon source. Some developments are also planned as off-grid plants, where maintaining stable operation would be required without the capability of receiving external support in terms of grid power. KBR advanced process control systems allow the plant to be optimised from the first concept phase making sure that the equipment is properly sized for the specific project and allows the plant to maintain its stable operation throughout the whole period of operation.

Fig. 5: **K-GreeN® – KBR green ammonia solution**



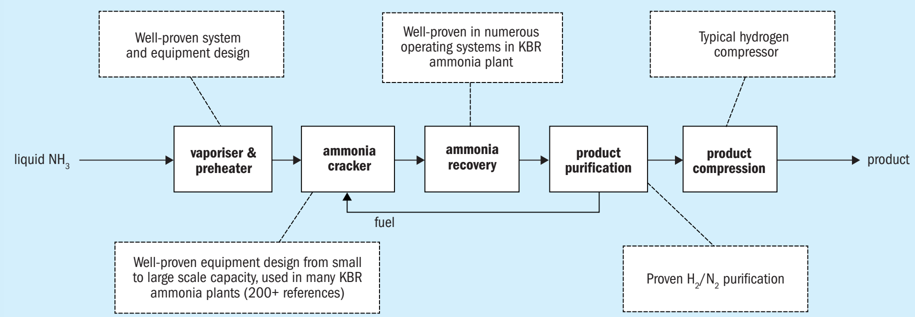
Source: KBR

Fig. 6: **Renewable energy profile and corresponding optimised operation of the plant based on KBR advanced process control**



Source: KBR

Fig. 7: **Simplified block flow diagram for the KBR ammonia cracking unit**



Source: KBR

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Ammonia cracking

Low carbon hydrogen is earmarked as the sustainable fuel of the future while green/blue ammonia offers a flexible, high energy density solution for storage and distribution, utilising existing and reliable infrastructure. The advent of ammonia cracking technology, dissociating green/blue ammonia back into low carbon hydrogen, completes the missing link in the roadmap to sustainability, enabling the production of low carbon ammonia where the renewable energy or natural gas resources are abundant with the ability to supply low carbon hydrogen in locations with high demand but low availability of natural resources to produce it.

Leveraging on decades of ammonia technology experience, KBR is continuing its pioneering journey with KBR Ammonia Cracking technology, to address customer demand and complete the green ammonia value chain offering. KBR has successfully developed a competitive ammonia cracking technology, high efficiency and able to meet stringent environmental requirements on carbon emissions (whether from blue or green ammonia feedstock), targeting moderate to very large-scale capacity green hydrogen production.

Today, this technology is available in the market serving a different purpose. The installed units are fully electricity driven, very small capacity and operate at equilibrium-favoured conditions (low pressure, high temperature). Whilst these units serve the installed purpose, they are not suitable for what the market is looking for in the energy transition.

As a technology powerhouse with decades of know-how in process design and extensive experience in equipment design, coupled with market proven capability to scale-up and commercialise new technology, KBR can offer different routes for technology scale-up and commercialisation.

Fig. 7 shows a typical simplified block flow diagram for the KBR ammonia cracking unit.

KBR is focusing its developments on the following areas:

- **Catalyst:** Partner with world-leading catalyst suppliers and consider both conventional proven and novel catalysts.
- **Reactor:** Use well-proven reactor design using decades of reactor design know-how from successful operation now applied to ammonia cracking application.
- **Flow scheme:** Fully developed flowscheme with high energy efficiency and hydrogen yield. The flow scheme is optimised and tailored to client and project specific requirements to minimise the levelised cost of cracked hydrogen production.

Table 1 outlines the typical performance of the unit.

Table 1: **Typical performance of the KBR ammonia cracking unit**

	Specification
Typical efficiency, % [HHV out / (HHV in + power)]	80-85
Hydrogen product specification	
Hydrogen purity, %	75 to 99.97+
Ammonia content, ppmv	as low as < 0.1
Water content, ppmv	as low as < 1
Delivery pressure	as per client requirement
Hydrogen capacity	
Small scale (demo plant), t/d	5-40
Medium scale, t/d	40-200
Large scale, t/d	200-1,200

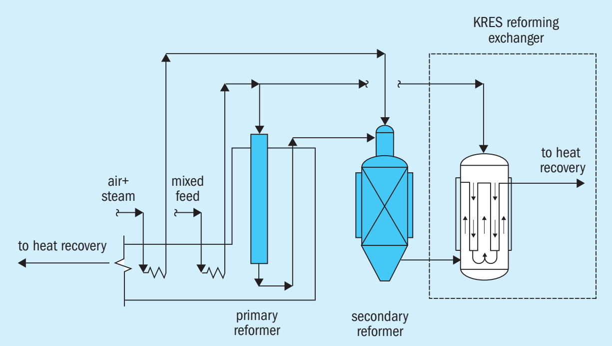
Source: KBR

Table 2: **KBR clean ammonia projects**

Project	Capacity, (t/d)	Location	Type
OCI Beaumont	3,000	US	blue
NeuRizer	1,600	Australia	blue
Monolith	930	US	blue
Undisclosed	3,000	US	blue
Undisclosed	3,000	MEA	blue
ACME	300	Oman	green
NEDO/JGC	4	Japan	green

Source: KBR

Fig. 8: **KRES™ Reforming**



Source: KBR

Flexibility and scale

The first KBR Purifier™ plant was started up in 1966, and since then more than 40 Purifier™/PurifierPlus™ ammonia plants have been built worldwide, providing a highly optimised and proven platform for blue ammonia projects, with lowest energy consumption (below 6.30 Gcal/t) and highest service/online factors, with up to 6,000 t/d ammonia capacity in a single line layout.

This vast experience has been imbedded in the KBR K-GreeN® solution and contributes to the flexibility and scale offered for green ammonia projects as well.

The unique features of the KBR Purifier™/PurifierPlus™ process alongside continuous equipment optimisations, also result in low capex independently of whether the carbon capture is done via the scheme in Fig. 3 or Fig. 4, as the two schemes result in the same capex.

KBR clean ammonia technologies provide the platform for a highly competitive levelised cost of ammonia (LCOA), with an unmatched large scale option for completing the hydrogen value chain via KBR ammonia cracking technology.

Grassroot clean ammonia projects

KBR is already involved as technology provider for several major blue and green ammonia projects in various stages of project completion. In addition to the list shown in Table 2, KBR is working with multiple clients for earlier stage assessment of both revamp and grass root plants well above the 3,000 t/d capacity.

Revamps

For existing ammonia plants, a significant step towards improved CO_2 footprint would naturally require sequestration options or usage of the emitted CO_2. Some revamp options could be:

- Existing process CO_2 removal unit could be revamped for efficiency and energy improvements.
- A PCCU could be added to the steam reformer.
- Natural gas consumption could be lowered by adding a heat exchange reforming unit like KRES™ (Fig. 8) lowering the steam reformer duty with up to 20% and thereby also CO_2 emissions from the stack correspondingly.

KBR is working with multiple partners on further advancements in CO_2 capture technologies and usage of the CO_2 captured. This is vital as advancement in CO_2 capture technology and usage thereof, will be the key to lowering the carbon footprint of existing assets that today have no or limited carbon capture.

Commitment to deliver

The motto of KBR is to deliver, and this promise is carried into the space of clean ammonia technologies, delivering already a wide range of solutions through the whole value chain.

KBR is working closely with many partners in the entire value chain leading to a range of low carbon fuels, to ensure that solutions are adapted to meeting the requirements needed, while also strongly committing to providing reliable and efficient new sustainable solutions.

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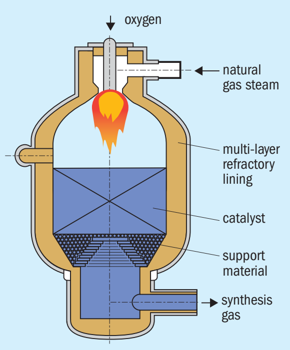
An experience of secondary reformer refractory casting

Refractories are heat resistant materials used in high temperature processes to protect industrial equipment such as utility boilers, heaters, and ammonia primary and secondary reformers against heat and chemical attack. In this article **Hasan Akbari** of Kermanshah petrochemical Industrial company (KPIC) reports on experiences of different stages of refractory casting in the secondary reformer of an ammonia plant, located in Kermanshah province of Iran (KPIC – Phase II). The pouring operation was carried out in three stages and each section was cast nonstop for a period of three days in total.

The secondary reformer is an integral part of the synthesis gas generation in a conventional ammonia plant. The three main processes taking place in the secondary reformer are: mixing of air and process gas, combustion of hydrocarbons, and methane conversion by steam methane reforming over the catalyst bed.

The role of the secondary reformer reactor is to produce and adjust the amount of hydrogen and nitrogen gases. The process gas leaves the primary reformer through the transfer line and enters the secondary reformer at the top through the combustion chamber, where it is mixed with process air. The processes taking place in the combustion chamber liberate heat which raises the temperature of the product gases from the primary reformer. The partially oxidised gas passes through the catalyst zone to produce the hydrogen. Combustion of the process gas with air produces a gas temperature of 1,100-1,200°C in the upper section of the secondary reformer. Because the reforming reaction of methane absorbs heat, the temperature decreases as it passes through the catalyst and finally the reformer gases leave the secondary reformer through the outlet nozzle at the bottom of the reactor. Fig. 1 shows a schematic view of a secondary reformer[1]. The inside of the secondary reformer is lined with insulating refractory to optimise energy use. The insulating refractory reduces the rate of heat flow through the walls of the furnace, keeping the temperature of the outer side of the shell below 110°C. Use of high purity, low silica alumina bubble castable has been accepted as insulation for hot pressured hydrogen lines. The shell must also be water jacketed to prevent failure due to overheating[2].

Fig. 1: Schematic view of secondary reformer[1]



Source: KPIC

Refractory material

Refractories are inorganic, non-metallic, porous and heterogeneous materials composed of thermally stable mineral aggregates, a binder phase and additives. The principal raw materials used in the production of refractories are: oxides of silicon, aluminium, magnesium, calcium and zirconium and some non-oxide refractories like carbides, nitrides, borides, silicates and graphite.

Environment, temperature, and the materials in contact with the refractory are some of the operating factors that determine the composition of refractory materials. Important properties of refractories are: chemical composition, bulk density, cold crushing strength (CCS), permanent liner change (PLC), abrasion resistant and grain size. Refractories can be classified on the basis of chemical composition and the methods of manufacture or physical form.

Classification of refractory based on chemical compositions

Acid refractories

Acid refractories are those which are attacked by alkalis (basic slags). These are used in areas where slag and the environment are acidic. Examples of acid refractories are silica (SiO_2) and zirconia (ZrO_2).

Neutral refractories

Neutral refractories are chemically stable to both acids and bases and are used in areas where slag and the environment are either acidic or basic. Common examples of these materials are: carbon graphite, chromates (Cr_2O_3), and alumina.

Basic refractories

Basic refractories are those which are attacked by acid slags but stable to alkaline slags, dusts and fumes at elevated temperatures. Since these do not react with alkaline slags, these refractories are of considerable importance for furnace linings where the environment is alkaline, for example non-ferrous metallurgical operations. The most important basic raw materials are magnesia (MgO), dolomite (CaO*MgO) and chromite.

Chemical characteristics of the furnace process usually determine the type of refractory required. Theoretically, acid refractories should not be used in contact with basic slags, gases and fumes, whereas basic refractories can be best used in an alkaline environment. Actually, for various reasons, these rules are often violated.

Classification based on physical form

Refractories are classified according to their physical form; these are the shaped and unshaped refractories. The former is commonly known as refractory bricks and the latter as "monolithic" refractories. Shaped refractories are those which have fixed shape when delivered to the user. Unshaped refractories are without definite form and are only given shape upon application. These are categorised as plastic refractories, ramming mixes, castable, gunning mixes, fettling mixes and mortars[3].

Table 1: **Thermomechanical properties of castable and dome brick refractory**

	After drying at 110°C	After heating at 1,730°C
Bulk density, kg/m³	>2,850	...
Cold crushing strength, kg/cm²	500-800	600-750
Modulus of rupture, kg/cm²	120-170	160-200
Liner change, %	negligible	-0.5

Source: KPIC

Table 2: **Refractory technical data**

Temperature service, °C	1,815
Type	hydraulic
Grain size, mm	0-6.5
Water required for pouring, %	8-10
Dry castable required, kg/m³	2,800
Chemical composition, % Al_3O_3 CaO	 93-95 4-6

Source: KPIC

Secondary reformer and its refractory at KPIC

The secondary reformer at KPIC is a vertical vessel with an external jacket and with a maximum working pressure of 41.6 bars. The operating temperature of the reactor is different in different section and varies between 1,277°C and 650°C from top to bottom section. The reactor height is 19,351 mm and the maximum and minimum diameter of vessel varies from 3,780 to 1,120 mm. The design thickness of the internal refractory is between 275 mm and 400 mm and the required weight of refractory was estimated to be 125 t. The reactor has an internal dome brick that supports the weight of the internal catalyst.

The type of refractory used in the secondary reformer was high alumina castable (shell area) and brick (dome brick area) with a blended mixture of tabular alumina and low iron calcium aluminate binder. The physical properties of the refractory are shown in Tables 1 and 2.

Properties of refractories

The most important properties of refractories to be checked according to the datasheet were chemical composition, bulk density, cold crushing strength, and permanent liner change. Preparation, drying and firing of test specimens were performed according to API 936.

- Cold crushing strength is the maximum applied load per unit area that the refractory material will withstand. The test was carried out in accordance with ASTM C133.
- Density is calculated at room temperature by dividing refractory weight by refractory volume in unit kilograms per cubic meter.
- Permanent liner change is the expansion or contraction that remains in a shaped refractory product that is heated to a specific temperature for a specified time and then cooled to ambient temperature. The test was carried out in accordance with ASTM C1134.

Material qualification

Before packaging the refractory material at the manufacturer site, all of the abovementioned necessary tests were performed. Other tests such as abrasion loss, workability index according to the data sheet were not applicable. An inspector directed sampling, preparation and witnessed the testing. The number and size of specimens for the required tests is shown in Table 3.

Specimens were dried and fired according to the following procedure:

- Oven dry: hold for 12 hours minimum at 104°C to 110°C in a dryer.
- Oven fire: heat at 170°C/h maximum to 815°C, hold for five hours at 815°C and then cool at 280°C/h maximum to ambient.

Table 3: **Number and size of test specimens**

Test	Number	Sample size
Cold crushing strength	3	50 mm × 50 mm × 50 mm
Permanent liner change	1	50 mm × 50 mm × 50 mm
Density		crushing cubes or liner change bars (before their target test)

Source: Xxxx

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Fig. 2: View of welded anchor bolts and their cellulose acetate caps.

PHOTOS: KPIC

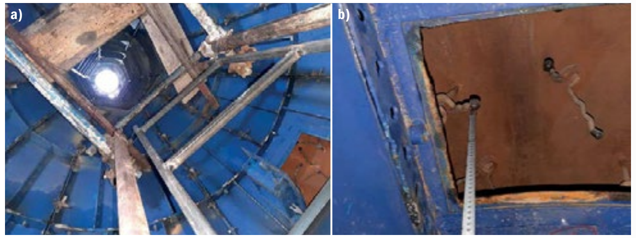

Fig. 3: Internal forms assembled and measurement of lining thickness from pouring holes before casting.

After checking the experimental results with the product datasheet, the raw refractory material was accepted.

Vessel preparation for refractory casting

All activities before casting of refractory that involved checking of anchor bolts, internal forms, cardboard installation and surface cleaning were carried out as detailed below.

Anchor bolt check

The refractory lining is fixed by anchors with cellulose acetate caps. The purpose of these anchors is to strengthen the refractory. All of the anchors were installed at the shop of the manufacturer and were visually checked again at site. The material of construction of the anchors was SS330 and was approved by PMI test. A hammer test had also been used to test the mechanical strength of the welding. All anchors were checked by the vessel fabricator to ensure that the anchor pattern was followed, the anchor welds were sound and none of the anchors were bent out of position. The anchor caps were installed at the site and checked visually (Fig. 2).

Formwork assembly

Prior to assembling metal formworks, cardboard had been wrapped around some internal surfaces such as nozzles and the dome skirt. The next step was to assemble the formworks in the reactor. The formwork installation proceeded from bottom section to top section, step by step. The connection between the separate parts of the formworks was bolted construction with mineral oil coated on the outside surface of the forms to facilitate their removal from the shaped refractory surfaces. The metal forms were stiffened by jigs in the middle section at different heights to prevent deformation and movement due to the vibration and pressure of the refractory material being cast. Pouring holes were installed peripherally to execute refractory casting by a flexible hose. The pouring holes were installed so that the maximum drop in pouring does not exceeds 3 m. From these openings, the thickness of the lining is measured and then, the arrangement of the metal forms was approved. The forms in the top section were installed after casting the bottom and middle sections of vessel (Fig. 3).

Requirements for casting of refractory

Before installation, it was very important to plan the execution of work. First, it was necessary to make sure that all materials and equipment were available. According to refractory manufacturer advice, the ambient temperature and the temperature of the surface onto which the refractory is installed, should be between 16°C and 25°C. Since the refractory was poured during winter, in the cold weather season, it was necessary to heat the water artificially until the operation was complete. It was also very important to use only potable water, containing no salts or foreign substances so, Chemical analysis according to recommended procedures was therefore carried out to check the suitability of the water quality. Checking the manpower and necessary equipment and tools was another step towards issuance of the permit. Required tools and equipment for installation included a crane, diesel generator, horizontal mixers, vibrator, thermometer, heater, and flexible hose in sufficient numbers.

Mock-up test

A mock-up sample was prepared before casting into the vessel to simulate the most difficult pieces of the installation work, including mixing, handling and associated quality control requirement. The refractory thickness, anchors, anchor pattern and the vibration method were in accordance with the actual installation job. Refractory cast in the mock-up piece cured at least 24 hours prior to stripping the forms. Visual inspection of the refractory showed an acceptable surface with minor cavities and some minor cracks that were less than 0.5 mm wide. The mock-up test highlighted some effective parameters which helped to improve the quality of work. Mixing time, mixing temperature, water temperature and vibration method were four important parameters that received a lot of attention during the main work (Fig. 4).

The sample was also broken and inspected visually at its cross section before carrying out all of the necessary tests according to Table 3 and checking with the datasheet that the results were acceptable.

Mixing Procedure

Prior to installation, some bags of castable refractory were inspected for any signs of hydration. Castable refractory was mixed with a ratio of 7.5-10% by weight of water using a paddle horizontal type mixer before charging into the hopper (Fig. 5).

Optimum water percentage was an important parameter to ensure adequate strength and to avoid cracking during the dry out procedure. The mixture and water temperature were checked by a laser thermometer. The acceptable range for both water and casting mixture was 16-37°C and was maintained by adding hot or cold water. According to mixing instructions, the raw refractory was mixed in the dry state and then sufficient water was added gradually. Mixing continued for two to three minutes after completion of refractory and water addition. The refractory was poured within 20 minutes from the time of preparation and mixing to avoid the material from losing its workability and ease of flow (Fig. 6).

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Fig. 4: Mock-up test a) General view of mock-up sample and cutting the form after casting; b) Side view of sample.

Fig. 5: a) Puddle-type mixer; b) Arrangement of four used puddle mixers.

Before casting, the "ball in hand" Test according to ASTM C860 was used to determine the correct consistency[5]. Sufficient water should be added to allow the castable to hold together in a ball when "bounced" in the palm of the hand. If too dry, the ball will break up into a crumbly mass; if too wet, it will slump through the fingers. This "bouncing" in the hand should impart a slight glistening to the surface of the ball of concrete but there should be no appreciable transfer of water and cement to the palm (Fig. 7).

Pouring procedure

The casting was executed in three stages, bottom, middle and top section. The refractory mass of the sections was 16, 80 and 14 t respectively. Important equipment and accessories for casting of the refractory were: two cranes, four mixers, internal scaffolding, flexible hose and chute, hopper, internal light, load speaker interphone and a water drum. The layout of the equipment for refractory casting is shown in Fig. 8.

The different stages of pouring are described below.

A hopper was installed on top of the manhole flange of the reactor and flexible hose and a chute were set in the opening of the bottom section forms to initiate casting.

Castable refractory was transferred to the top of the vessel by crane and drained into the hopper and then through the flexible house and chute into the opening of the forms. During casting and before the refractory reached the bottom of the window (opening) being used, the lower window was closed and the next higher level window was used.

After pouring a batch of refractory, the worker responsible for vibration began vibration internally and externally for 30 to 40 seconds to consolidate the material being cast and to eliminate air bubbles. Close attention is required during vibration to prevent segregation of refractory material and the formation of air bubbles. It is important that the internal vibrator is not removed too quickly which can leave voids in the lining.

By raising the level of casting refractory in the forms, the flexible hose had to be cut according to the height of the pouring holes height to ease setting the chute into the pouring window (Fig. 9).

During the casting two production refractory samples prepared by standard dimensions were tested, e.g., for density, PLC and CCS (Fig. 10). The results of the tests are shown in Table 4.

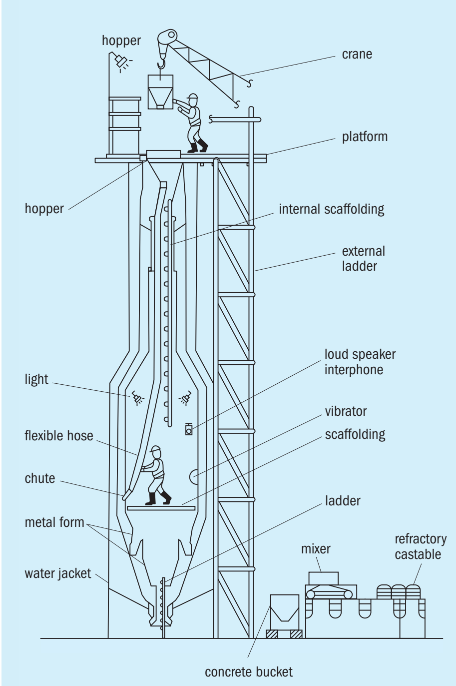
Curing of Refractory

After pouring the refractory and for bond formation in the new monolithic installed refractory, the curing process was carried out for a minimum of 24 hours at 10°C to 32°C according to manufacturer's recommendations and before stripping the forms. The curing temperature of the vessel was maintained by an electrical heater.

Fig. 6: a) Measuring the temperature of water; b) Pouring refractory into the hopper.

Fig. 7: Checking the mixture at site.

Fig. 8: **Schematic view of refractory casting at the site[6].**



Source: KPIC

Fig. 9: a) Draining the casting material into the opening of forms through a flexible hose and chute; b) Internal vibrator via the window opening.

Removing the forms

After casting and curing the refractory, all forms were removed and the entire internal surface was checked visually. Observations showed some distributed cavities with a maximum depth of 3 mm and also some cracks that were less than 0.2 mm wide. In some locations such as the form's window and seams between separate parts of the metal forms there were projections of refractory that were removed by grinding to a smooth surface.

Dome brick installation

Before dryout, internal dome brick was installed consisting of 12 layers (A,B,C,D,E,F,G,H,I,L,M,N). The skew section of the dome consists of three layers (A,B,C) (168 bricks) and the rest of the bricks were laid on the dished section of the dome (259 bricks). Bricks were laid carefully in each layer and cardboard of the same thickness as the mortar thickness was put into the joint spaces of the bricks to check the adjustment of every layer. After assurance of the correct position of the bricks, they pieces of cardboard were removed one by one and replaced with mortar. After placing the three layers of bricks in the metal support (A, B, C), wooden beams and probes and polystyrene forms were set in the bottom section of the reactor. Initially, 22 wooden probes and 9

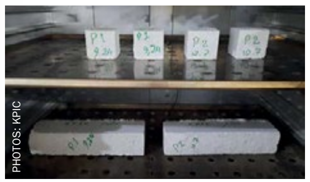


Fig. 10. Placing samples in the heater.

Table 4: **Components modelled in simulation**

	After dry out
Bulk density, kg/m³	>2,820
Cold crushing strength, kg/cm²	>900
Liner change, %	-0.1

Source: KPIC

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1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33

Fig. 11: a) View of polystyrene forms; b) Installation of dome bricks; c) View of wooden beams and probes; d) Final dome brick from bottom view.

wooden beams were installed in the bottom section and fixed to each other with nails, plywood sections were then laid on the probes and beams and finally polystyrene forms were placed on the plywood in the correct positions. Installation of the remaining layers (D,E,F…N) commenced after setting the polyester forms and wooden structures After installation of the last brick (M), wooden beams and probes and polystyrene forms were carefully disassembled and removed via the bottom manholes (Fig. 11).

Dryout

The combined efforts of refractory manufacturer, installer and dryout contractor will result in optimal refractory performance. The dryout process is necessary to reduce the quantity of water in the concrete that may cause undesired reaction like "alkaline hydrolysis". This operation is carried out at the end of the refractory installation and after the curing. Dryout of refractory linings is carried out by applying heat under controlled conditions using high velocity burners. The products of combustion are exhausted through a suitable opening located at the unit outlet.

Thermocouples and burner

Before dryout was started, sufficient temperature measuring devices were installed on the refractory surface using a high temperature resistant glue to monitor the temperature throughout the area to be dried. Accurate drying control requires the correct location of thermocouple probes and efficient heating apparatus. Nine thermocouples probes (type k) were placed 12 mm away from the lining surface.

Direct flame impingement on the refractory surfaces was not allowed so the

Fig. 12: View of burner and its fan in the bottom manhole.

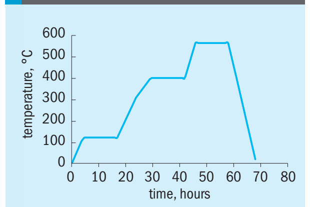
burner was installed via the bottom manhole to avoid damage caused by overheating the refractory, dome brick and other components. The volume of air passing through the lined equipment was checked that it was sufficient to avoid saturation before it reached the outlet. According to the refractory manufacturer recommendations, the minimum blower capacity should be 60 m^3 per hour for each square metre of burner and burners should have a capacity of at least 50% excess air at the maximum intended firing rate[6]. The burner fuel was LNG, which was supplied by a special truck to a LNG storage tank that had all of the required safety devices and had been certified by a valid institute (Figs 12).

Dryout sequence

The procedure for heating and cooling the refractory was carried out according to the following steps:

- Ignite the air heater burner at minimum load and adjust to obtain an initial heat up rate of 27°C/h (for about 5 hours) up to 120°C maximum.
- Hold the temperature of 120°C for 12 hours minimum.

Fig. 13a: **Dryout diagram**



Source: KPIC

- Increase the temperature at 27°C/h up to 315°C.
- Increase the temperature at 17°C/h up from 315°C to 400°C.
- Hold this temperature for 12 hours minimum.
- Increase the temperature at 40°C/h up to 565°C.
- Hold this temperature for 12 hours minimum.
- Cool down the equipment gradually (about 55°C/h) to ambient temperature.

Before start of operation, the position of all internal thermocouples and their distance from the refractory surface was checked. The sensed temperature of every nine thermocouples was plotted by a calibrated recorder in a single graph. The temperatures could also be seen digitally on the recorder (Fig. 13).

According to thermal calculations from the refractory designer, the maximum temperature of external surface of reactor should not exceed 113°C. The maximum temperature of the external water jacket that was monitored by thermometer reached 111°C at the bottom section where the inside burner has been installed and on other sections its maximum value was 75°C, therefore there were no hot spots on the external surface of the vessel during the dry out process.

Inspection after dryout

All of the refractory surface was inspected visually after dryout. According to procedures, cracks wider than 2 mm were considered defect and needed to be repaired. A hammer test with a ball-point machinist hammer also took place when the refractory material has taken its final set. When defective areas were encountered (voids or dry-filled spaces), a dull sound would be heard. Voids or hollow sounding areas

Fig. 13b: Temperature recorder of thermocouples[7].

larger than 150 x 150mm and any soft or "dry fill" areas that reduced the effective lining thickness by more than 25% of the original thickness or more than 13 mm were considered defect and required repair. The maximum width of cracks after dryout were less than 2 mm. The maximum depth of cracks was also checked with a wire of 0.6 mm that was less than 5% of total thickness of refractory. The hammer test also did not show any defects on the refractory surface (Fig. 14).

Fig. 14: Measuring the width of cracks after dryout.

Visual inspection of the refractory after dryout revealed that there was a thin layer of soot (carbon layer) in the top section of the vessel (the surfaces after dome brick) but there was no soot on the dome brick or the region under the dome brick. Checks by process and inspections teams concluded it was due to incomplete combustion from the burner during dryout. According to API 571 only sulphur is harmful for refractory, so the inspection team did not believe the carbon would influence the refractory surface. In the opinion of process team and because of the operation conditions of the reactor temperature >1,000°C and pressure >40 bars), this layer will be burned and vanish in the commissioning step. In addition, the internal surface of the refractory was cleaned of remaining soot as much as possible.

After ending the dryout process, the graph of all the thermocouples was checked and compared with the accepted procedure. Because the position of thermocouples 1, 2 and 3 were near the burner flame, the maximum temperature of 800°C had been reached. However the criteria for temperature was based on thermocouples 4, 5, 6, 7, 8 and 9 which had been positioned on top of dome brick and had minor differences with each other during the heating process.

Conclusion

The secondary reformer has an important role in the ammonia production. The function of the refractory lining in the reactor is to reduce the rate of heat flow through the walls of reactor. The assembly and adjustment of internal forms, mixing of material with water, pouring the refractory, curing and dryout of the refractory, dome brick installation and performing the required tests during this process are effective parameters to achieve a good quality of installed refractory. Refractory insulation at KPIC was performed in three steps. Lasting three days in total. Dryout was performed using an LNG burner according to an accepted graph. Inspection of the internal surface of the refractory showed that cracks after dryout were in the allowable range and acceptable.

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