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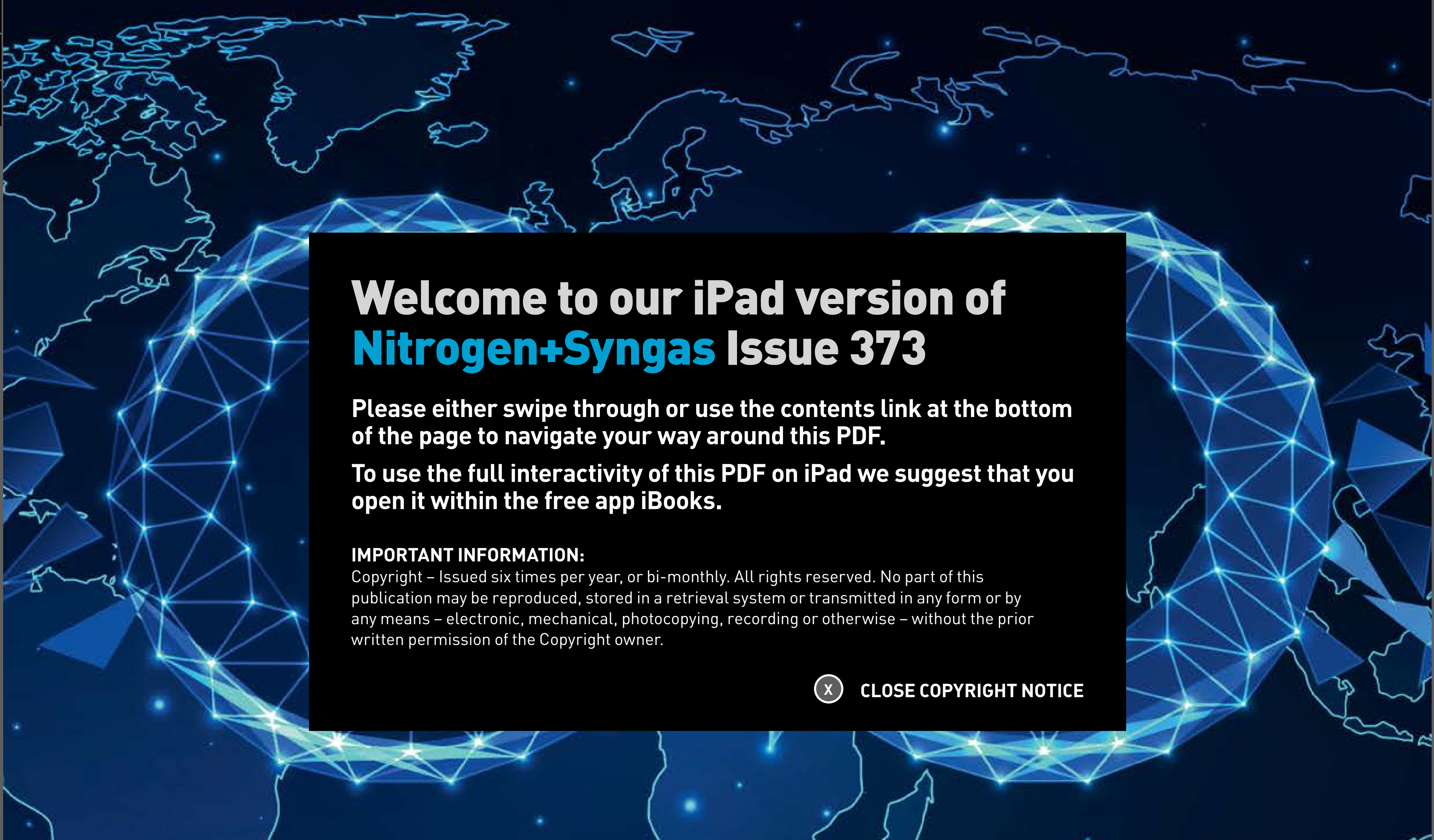

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Middle East nitrogen

CO_2 removal analytics

Sustainable nitric acid/AN production

Waste to methanol

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REGULARS

Middle East nitrogen

The world's largest urea exporting region.

Climate protection

Reducing the environmental impact of production plants.

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Published by:
BCInsight

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Maersk bets on methanol

> **"The question becomes where this methanol will come from..."**

While the past couple of years have seen considerable excitement and momentum concerning the use of blue/green ammonia as a fuel, an announcement in August by Maersk, the largest shipping company in the world, has served once again as a useful reminder that ammonia is not the only candidate molecule. Maersk said on August 24th that it is ordering eight methanol powered vessels from South Korea's Hyundai Heavy Industries at a total cost of $1.4 billion. Each giant ship will have the capacity to carry 16,000 twenty-foot [container] equivalent units (TEUs).

Methanol had already been under consideration as a low sulphur shipping fuel following the tightening of IMO regulations on sulphur content of fuels that occurred in January 2020, and had been reported on in this magazine before (*Nitrogen+Syngas* 347, May/Jun 2017, pp18-20). However, with the prospect of the methanol being made from 'green' hydrogen and waste CO_2, it also has the potential to be a carbon neutral fuel for vessels, and it is in this guise that Maersk is sufficiently convinced about it as a green fuel to be willing to put up one and a half billion dollars. According to the International Energy Agency, in 2019 international shipping was responsible for approximately 2% of global energy-related CO_2 emissions, and the IMO is working to decarbonise the global shipping industry by 2050. While ammonia has been one suggested pathway towards this, green methanol is another.

Maersk's move follows its announcement earlier this year of a methanol-powered 2,000 TEU container ship to be launched in 2023 which will consume 10,000 t/a of green methanol, sourced via Denmark's European Energy and its subsidiary, REintegrate, who will set up a facility to produce carbon neutral methanol for Maersk using solar electricity and "biogenic carbon dioxide". However, the eight new ships – the first one is due to be launched in 2024, and another four in 2025 – will consume even more methanol. As they will replace older, less efficient vessels, Maersk says that once the whole fleet is operational it will save a total of 1 million t/a of carbon dioxide, and presumably consume almost as much green methanol. The question then becomes where this methanol will come from. The REintegrate facility will certainly not be sufficient, and Maersk has left its options open by saying that it "will operate the vessels on carbon neutral e-methanol or sustainable bio-methanol as soon as possible", while building them with dual fuel engines that can also run on conventional low-sulphur marine fuels. Still, the knowledge of a guaranteed market for up to 1 million t/a of green methanol might be a spur to other developers even if Maersk does not take a direct hand in generating the fuel.

Maersk's move is a bold one, but could it be just the beginning? The shipowner has a fleet of over 700 ships, and says that it wishes to maintain a fleet capacity "in the 4.0 to 4.3 million TEU range", of which these ships would represent only 3.2%. The sky – or perhaps rather the sea – could be the limit for green methanol. ■

Richard Hands, Editor

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Price trends

Market Insight courtesy of Argus Media

NITROGEN

East Asian delivered ammonia prices fell for the first time since December 2020, falling $10/t on the week, in line with steadily improving global supply. But few spot cargoes are being agreed on a fixed-price basis with counterparties leaning towards formula-priced agreements until the production outlook has firmed up, particularly from Saudi Arabia. Ma'aden's MPC plant remains offline but there are suggestions it could start in the last week of August, with a vessel nominated to load from Ras al Khair on 24-28 August. An Indonesian spot sale is confirmed for Luwuk-loading, indicating improving availability from the region. Ma'aden re-directed the Egyptian tonnes it bought in early-July at $690/t c.fr to China in mid-August. The cargo had been waiting at RAK as floating storage for around 25 days. It is yet to be seen whether or not this change in sentiment in the east will be replicated in the west, with high feedstock costs in Europe likely to steer sentiment into 4Q.

Recent market developments include improving Indonesian supply, Ma'aden's MPC plant still offline and feedstock costs. Most key demand hubs have covered themselves in September and improving supply may add downward pressure to October pricing. But seasonal demand and high feedstock costs in the west are likely to limit any potential price deterioration.

Urea prices generally fell around mid-August, with demand thin, freight high and the market generally lacking fervour. In China, some short-selling of prills for September loading occurred at prices below $430/t f.o.b. Trade from Algeria, though, was similar to last business at around $449/t f.o.b. Brazil also bucked the trend, with prices rising on steady demand and reaching $480/t c.fr in mid August.

Delay to India's much-anticipated purchase tender and the sense of a fragile market encouraged producers from Egypt to the Middle East to remain largely on the sidelines. Recent market drivers include freight – ocean shipping costs escalated again in mid-August and are likely to continue challenging f.o.b. prices. Indian tenders – or lack thereof – remain a key pillar of support, while natural gas price in Europe reached almost $16/million Btu in mid-August, up another 5% from the previous week.

Clarity on f.o.b. prices will likely follow India's next tender, leading to a fresh wave of buying interest from other regions. Although the recent Indian tender absorbed 1.2 million t of urea, over 700,000 tonnes is due to ship from China, indicating that Chinese urea will continue to provide export market liquidity, despite concerns that Beijing's interventions to restrain cargos would limit availability in the second half of 2021. ■

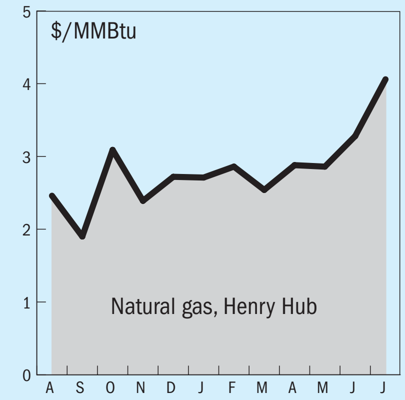
Table 1: **Price indications**

Cash equivalent	**mid-Aug**	**mid-June**	**mid-April**	**mid-Feb**
Ammonia ($/t)				
f.o.b. Black Sea	560-610	485-525	430-470	300-370
f.o.b. Caribbean	540-600	475-525	430-460	290-335
f.o.b. Arab Gulf	590-640	550-610	440-480	290-330
c.fr N.W. Europe	625-680	550-600	490-540	340-420
Urea ($/t)				
f.o.b. bulk Black Sea	390-435	370-435	300-340	300-380
f.o.b. bulk Arab Gulf*	439-470	435-470	320-355	350-380
f.o.b. NOLA barge (metric tonnes)	400-440	445-495	365-405	329-365
f.o.b. bagged China	415-450	400-460	320-355	320-365
DAP ($/t)				
f.o.b. bulk US Gulf	655-667	640-685	572-613	568-600
UAN (€/tonne)				
f.o.t. ex-tank Rouen, 30%N	157	157	157	157

*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



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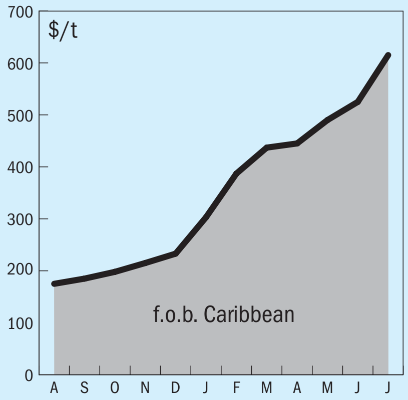
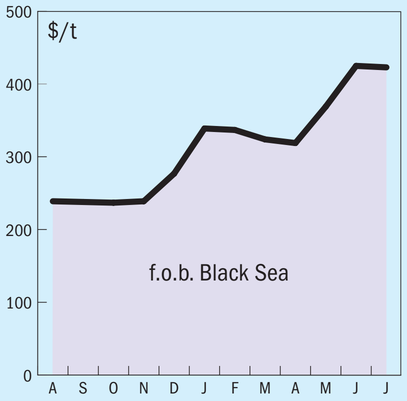
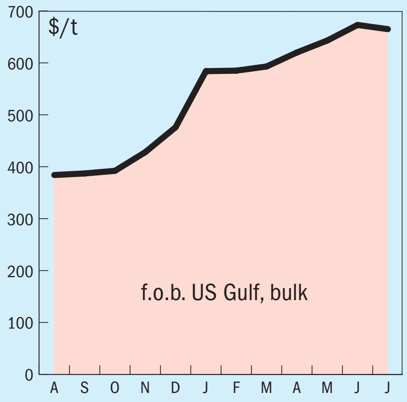


urea



diammonium phosphate



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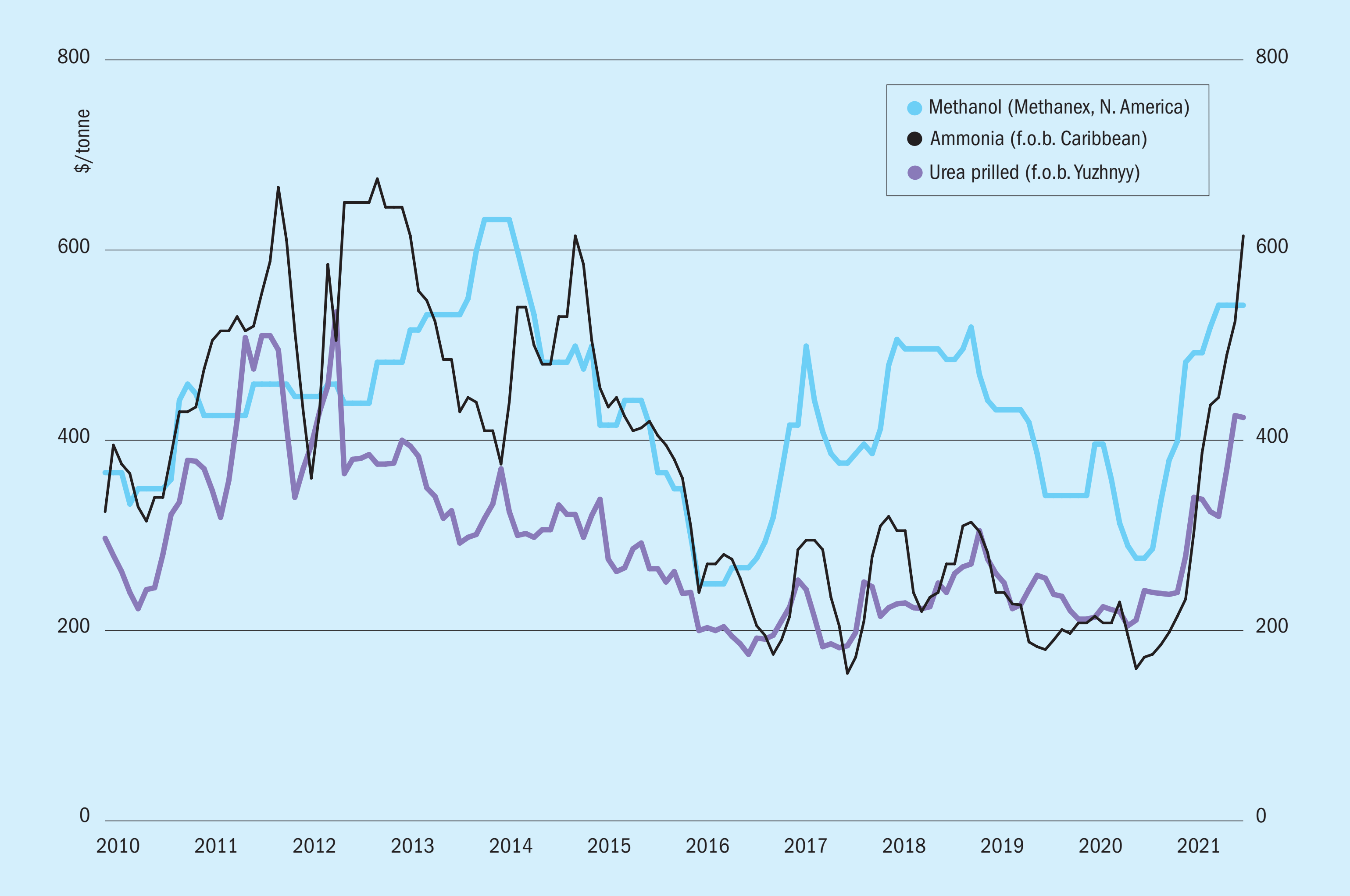
Market Outlook

Historical price trends $/tonne



Source: BCInsight

AMMONIA

- The first half of 2021 has been characterised by tight supply in the ammonia market, exacerbated by plant outages in Europe, Trinidad, Saudi Arabia and Indonesia. At the same time, higher spot demand has fuelled significant price increases in both the eastern and western hemispheres. Low inventories and reduced export availability in the Far East forced Indian phosphate producers and industrial consumers of ammonia to source product from other locations.
- More recently however, supply has been improving, especially from Indonesia. Most key demand hubs have covered themselves in September and improving supply may add downward pressure to October pricing.
- However, feedstock costs remain high in Europe, and the return of seasonal demand will limit the downside potential for ammonia prices, and they are likely to remain at relatively historically high levels for the remainder of the year.

UREA

- Urea buyers played a waiting game during August with many waiting for a new Indian tender by RCF to set prices. Market sentiment was soft, and offered prices steadily declined with the pressure for sellers to find new business, though some Brazilian sales led to a pickup of around $20/t mid-month.
- Availability from China was also a question, with the government and trade associations trying to encourage supplies into the domestic market. However, in spite of high freight rates and the prospects of a urea export tax, Chinese urea exports to end July were reported to be 2.67 million tonnes this year, up 40% on the same period in 2021, with India taking the lion's share. China committed 650,000 tonnes of urea to India in the July tender.
- Hurricane Ida forced the closure of CF Industries' Donaldsonville plant and associated disruptions to supply in the region led to a surge in NOLA f.o.b. prices to nearly $500/st; a nine-year high.

METHANOL

- Asian Methanol prices took a downturn in Asia in July, but increased steadily during August as a number of Chinese methanol plants took turnarounds, tightening supply and leading to an increase in prices. Higher coal prices have also supported higher methanol production costs. Chinese prices were up just over 1% during August, though up more than 60% compared to the same period last year. Prices overall edged upwards towards $400/t for delivered methanol to northeast Asian ports.
- MHTL's shutdown in Trinidad was resolved and the new gas price contract seems to stabilised prospects for supply from Trinidad.
- European supply has taken turnarounds at a number of plants. Thin spot demand was balanced by consistent contract demand, with traded volumes rising. Rotterdam f.o.b. methanol prices were fairly stable at around €425/tonne ($496/tonne). ■

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Nitrogen Industry News

UNITED ARAB EMIRATES

Blue ammonia to Japan

OCI subsidiary Fertiglobe says that it has partnered with the Abu Dhabi National Oil Company (ADNOC), to enable the sale by ADNOC of the first cargo of blue ammonia to Itochu in Japan, for use in fertilizer production. Fertiglobe, a 58% – 42% partnership between OCI and ADNOC respectively, will produce the blue ammonia at its Fertil plant at Ruwais in Abu Dhabi for delivery to ADNOC's customers in Japan. This represent the first production milestone of a planned scale-up of blue ammonia production capabilities in Abu Dhabi, which is expected to include a low-cost debottlenecking program at Fertil. In addition, it was announced in June that Fertiglobe will join ADNOC and sovereign wealth fund ADQ as a partner in a new world-scale 1.0 million t/a blue ammonia project at Ta'Ziz in Ruwais, subject to regulatory approvals. The design contract for this project has been awarded, with a final investment decision expected in 2022 and start-up targeted for 2025. A feasibility study was also agreed in July betweenh the state-owned Japan Oil, Gas and Metals National Corp. (Jogmec), Inpex and JERA as well as ADNOC to explore the possibility of producing 1.0 million t/a of blue ammonia in Abu Dhabi and transporting it to Japan.

Nassef Sawiris, executive chairman of OCI and CEO of Fertiglobe, commented: "I am pleased that Fertiglobe is growing its low-carbon production capabilities in partnership with ADNOC. As a result of decarbonising the feedstock supply, we can materially reduce the carbon intensity of our downstream customers along the value chain and across a wide range of industries. We are pleased to leverage the Fertiglobe and ADNOC platforms to help decarbonise our production and customers' footprints, while creating value to shareholders, a win-win across the board. This project shows that Fertiglobe is on track to become a global leader in low-carbon solutions, leveraging its globally leading position in ammonia."

Masaya Tanaka, COO of Itochu's Power & Environmental Solution Division, said: "We are pleased that Itochu… is contributing to a low-carbon society together with ADNOC. Starting with this trial of blue ammonia for fertilizer applications, we aim to create a wide range of ammonia value chains for existing industrial applications as well as future energy use. By collaborating with ADNOC and Fertiglobe, we expect to initiate and enhance our industrial portfolio in the fertilizer sector while achieving our commitments towards decarbonisation activities in other industries."

Dr. Sultan Ahmed Al Jaber, UAE Minister of Industry and Advanced Technology and ADNOC managing director and Group CEO, said: "Today's announcement builds upon ADNOC's commitment to expanding the UAE's position as a regional leader in the production of hydrogen and its carrier fuels, meeting the needs of critical global export markets such as Japan. Through the expansion of our capabilities across the blue ammonia value chain, we look forward to furthering our legacy as one of the world's least carbon intensive hydrocarbon producers and supporting industrial decarbonisation with a competitive low-carbon product portfolio."

Following the sale to Itochu, ADNOC and Fertiglobe have made other sales to Japanese customers, including Inpex and Idemitsu. The former shipment is due to load in October. ■

Green ammonia in Abu Dhabi

German chemical licensor thyssenkrupp says that it has been awarded a contract to perform a technical study for a new green hydrogen and ammonia project by UAE company Helios. A water electrolysis plant as well as a facility for sustainable ammonia production are planned to be constructed at Kizad in Abu Dhabi, based on thyssenkrupp technology. It will be the first commercial plant to produce CO_2-free green ammonia from renewable resources in the UAE.

The planned facility will integrate thyssenkrupp's green hydrogen and green ammonia technologies, with the first phase set to incorporate a multi-megawatt electrolyser plant and an ammonia production facility with a capacity of 20,000 t/a in the first phase, with the next step being to increase this to 200,000 t/a.

M. K. Saiyed, managing director of Helios, said: "This project is another important milestone in the UAE's shift to a lower carbon renewable energy future. The new facility will produce green ammonia which is an energy carrier that enables easy transportation of renewable energy e.g. via ship. It can also be used as emission-free transport fuel and in the fertilizer and chemical industries."

Sami Pelkonen, CEO of thyssenkrupp's Uhde business unit added: "We are very excited to work together with Helios to support the UAE on its way into a sustainable future. In doing so, we are building both on our innovative technology solutions as well as on thyssenkrupp's regional and local footprint and long heritage as a partner to the region."

UNITED STATES

Nutrien to partner in ship powered by low-carbon ammonia

Nutrien and liquefied gas transportation specialist EXMAR have signed a collaboration agreement to jointly develop and build a low-carbon, ammonia-fuelled vessel. Both partners support the decarbonisation of shipping and the International Maritime Organization's (IMO) greenhouse gas strategy to reduce emissions. Their new collaboration aims to significantly reduce Nutrien's maritime transportation emissions and enable the commercial development of an ammonia-fuelled vessel.

Nutrien says that it has actively been pursuing the development of low-carbon ammonia for more than a decade, and has a total of approximately 1 million t/a of production capability at its Redwater and Joffre Alberta and its Geismar, Louisiana facilities which employs carbon capture and sequestration to reduce the carbon intensity of its ammonia for use as a maritime fuel. When compared to conventional fuels, it is anticipated that the use of Nutrien's existing low-carbon ammonia will achieve a reduction of greenhouse gas emissions of up to 40%. Emissions reductions of up to 70% can be achieved with the development of low-carbon ammonia using proven, scalable, best available technology and permanent sequestration of CO_2.

Under the collaboration agreement, Nutrien and EXMAR aim to select an ammonia engine and supply system manufacturer; select a shipyard capable of building

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an ammonia-powered vessel; use Nutrien's existing low-carbon ammonia supply from Geismar, LA as a fuel; and deploy an ammonia-fuelled vessel as early as 2025.

ITC continues probe into UAN from Trinidad

The US International Trade Commission says that it has determined that there is a "reasonable indication" that US industry is being "materially injured" by imports of urea ammonium nitrate solutions that are allegedly subsidised and sold in the US below market value – so-called 'dumping'. The finding means that the Commerce Department will continue to conduct a separate investigation into whether Russia and Trinidad & Tobago are unfairly subsidising exports of the fertilizer. Preliminary countervailing duty determinations are due on September 23rd, and anti-dumping duty determinations on December 7th.

GERMANY

Clariant expands emissions control capacity

Clariant Catalysts says that it is expanding and enhancing its capacity for emission control catalysts to meet growing global demand, particularly in China. The company has recently commenced operations at an additional, upgraded production facility in Heufeld, Germany, which features state-of-the-art production equipment exclusively dedicated to emission control catalysts, including the EnviCat catalyst range for removal of harmful emissions such as volatile organic compounds, carbon monoxide, nitrous oxide and nitrogen oxide. Production capacity for the catalysts has been increased to enable a volume growth of 100% compared to 2019. The site, which now includes two units, covering a combined area of 1,500 m².

FINLAND

Test programme on ammonia fuelled ships

Maritme technology group Wärtsilä has begun a test programme to pioneer the adoption of hydrogen and ammonia as viable engine fuels in the company's new fuel-flexible combustion engines. Full-scale engine tests have been recently carried out in Wärtsilä's engine laboratory in Vaasa, Finland, to assess the optimum engine parameters for running on these fuels. The company describes the test results as "very encouraging", with one test engine performing very well when running on a fuel with 70% ammonia content at a typical marine load range. Tests were also completed successfully on another engine in pure hydrogen operation. Testing will continue with the aim of defining the most feasible internal combustion engine-based solutions for power plant and marine applications, thereby enabling the transition to a decarbonised future with green fuels.

For the energy market, Wärtsilä expects to have an engine and plant concept for pure hydrogen operation ready by 2025. For the marine market, the company expects to have an engine running on an ammonia blend later this year, and an engine concept with pure ammonia fuel in 2023. In the energy sector, it is anticipated that green hydrogen will deliver 7% of global energy demand by 2050.

Wärtsilä is also developing ammonia storage and supply systems as part of the EU's ShipFC project. The company has already gained significant experience with ammonia from designing cargo handling systems for liquid petroleum gas carrier vessels, many of which are used to transport ammonia. In addition, Wärtsilä will begin testing ammonia in a marine four-stroke combustion engine together with customers Knutsen OAS, Repsol Norway and Equinor at the Sustainable Energy Catapult Centre in Stord, Norway, as part of the Demo2000 project.

EGYPT

Revamp for Abu Qir 3

thyssenkrupp Fertilizer Technology has signed a contract with Abu Qir Fertilizers for the revamp of their Abu Qir 3 urea granulation plant in Alexandria, by 2025, thyssenkrupp Fertilizer Technology will supply the license, the process design package and proprietary equipment. *UFT*® fluid bed granulation will increase the nameplate capacity from 2,000 t/d of urea granules to more than 2,500 t/d. The company says that its proprietary horizontal cross flow scrubbing system minimises urea dust and ammonia emissions. This is achieved by appropriate handling of the exhaust streams from the urea granulation plant and from the urea synthesis plant.

Abu Qir 3 plant, Egypt.

NORWAY

Yara in partnership for Porsgrunn decarbonisation

Yara, Aker Clean Hydrogen and Statkraft are all equal partners in a new company, HEGRA, which has been launched to electrify and decarbonise ammonia production at Yara's ammonia plant at Herøya, Porsgrunn. HEGRA is short for HErøya GReen Ammonia. The decarbonisation project will reduce CO_2-emissions by 800,000 t/a, equivalent to the emissions of 300,000 fossil-fuelled cars, with a timescale of 5-7 years, assuming that sufficient power can be made available to the site and the required public co-funding is in place. It is aimed at meeting the ambitions of the European Commission's 'Fit for 5' initiative, which aims to reduce EU emissions by 55% by 2030. The Norwegian maritime industry is also looking to cut their emissions in half by 2030, and access to emission-free fuels will be key to reach this goal.

AUSTRALIA

Origin and Mitsui in green ammonia tie-up

Australian upstream and utility firm Origin Energy and Japanese shipping firm Mitsui OSK Lines say that they will investigate the prospect of developing a supply chain to support the export of green ammonia from Australia. The joint study is expected to be completed by the end of this year, with any green ammonia export project to supply downstream markets from 2026. Origin is already carrying out a A$3.2 million ($2.3 million) feasibility study into building a 420,000 t/a green hydrogen and ammonia plant for exports at Bell Bay in Tasmania. Mitsui meanwhile says that it has restarted its ammonia transportation business to meet rising demand for cleaner energy, and is joining a project to develop the supply infrastructure for ammonia as a marine fuel in Singapore.

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ETHIOPIA

Ammonia complex for Ethiopia?

Chinese solar panel maker GCL Group says that it plans a plant in Ethiopia to make ammonia using natural gas produced from fields it has been developing under a deal with the local government. It is potentially ultimately looking at 4 million t/a of ammonia production at Djibouti, with the aim of using the ammonia as a carrier for 2.5 million t/a of liquid hydrogen, to be recovered elsewhere, though the initial development is likely to be a 1.0 million t/a ammonia facility. GCL inked a deal with the Ethiopian government in 2013 to develop two gas fields, Calub and Hilala, and to carry out exploration at eight further blocks. The existing fields are expected to produce 3.5 bcm per year of natural gas in the first phase. GCL also plans to build 400,000 t/a of green hydrogen production capacity from renewable power sources, mainly solar power stations in northwestern China, by 2025.

CANADA

Petronas considering blue ammonia project for hydrogen transport

Malaysian state-owned oil and gas company Petronas has initiated a feasibility study into building a $1.3 billion plant in Alberta to export hydrogen to Asian markets as ammonia. The company is partnering Japan's Itochu Corp and a Canadian pipeline company in the study, which is considering a 1.0 million t/a blue ammonia plant using natural gas from Petronas owned fields in British Columbia together with carbon capture and storage. Petronas and Itochu would jointly market the ammonia produced in Asian markets, potentially including thermal power generation in Japan.

UKRAINE

OPZ improves output and returns to profit

Odessa Port Plant (OPZ) says that it produced 409,200 tonnes of urea and 276,100 tonnes of ammonia in the first six months of 2021, with the volume sent to domestic and foreign customers. The company did not provide comparative data but confirmed both urea units and one of its two ammonia plants operated during the January-June reporting period. Of the ammonia, 42,100 tonnes were sold on a commercial basis, while OPZ's transhipment facilities loaded 1.04 million tonnes of ammonia at the Black Sea port of Yuzhnyy, as well as 363,000 tonnes of urea. The state-owned firm also "significantly" increased deliveries to domestic buyers, with nearly 22,000 tonnes of ammonia and 51,000 tonnes of urea moved by rail and road – up 1,200% and 170% year on year, respectively.

The positive performance meant the producer made a profit of Ukraine hryvnia (UAH) 434 million ($16.1 million) in H1 2021, versus a loss of $600,000 over the same period in 2020.

EUROPEAN UNION

Nitrogen producers to bear the brunt of emissions legislation

Fitch Ratings says that nitrogen producers will be the most affected in the fertilizer sector by tighter emission regulations, particularly in Europe, and by closer investor focus. Long-term costs and decarbonisation capex needs will increase, but companies with credible environmental, social and governance (ESG) strategies can offset some pressures.

The European Commission's new 'Fit for 55' climate plan is the latest regulatory proposal that will affect the sector, if approved by the EU Parliament, mostly through the revised terms for the Emission Trading System (ETS), and the introduction of the Carbon Border Adjustment Mechanism (CBAM). This proposal will affect European producers and exporters to the EU, but many countries outside the EU are considering similar regulations. However, the strictest regulatory requirements should come into force outside of our forecast horizon.

Carbon costs for fertilizer producers will rise as a result. Manufacturers' investment needs to adjust their operations and protect their market positioning will also increase, Fitch says. Companies that act first and have credible ESG strategies may be able to mitigate these pressures through access to attractive green financing and an ability to capitalise on first-mover advantages in developing new products and technologies.

Only CF Industries, OCI and Yara have committed to carbon neutrality by 2050, while most other companies' commitments are focused on greenhouse gas (GHG) intensity reduction. Only PhosAgro and ICL have incorporated Scope 3 emissions in their absolute GHG emissions reduction targets. Scope 3 emissions from product consumption account for the largest part of GHG emissions, representing more than 70% of all emissions. These emissions are the hardest to reduce, particularly in developing countries with less advanced agricultural practices. Some companies, including EuroChem and OCP, are yet to publish their emissions data and reduction plans. As investors and policymakers increasingly focus on climate change, we believe fertilizer producers' ESG strategies are lagging behind, especially compared to European oil and gas majors.

Ammonia producers are most affected by the drive to cut emissions as hydrocarbons, mostly natural gas, are used as a feedstock in its production. The nitrogen industry is responsible for about 1% of global CO_2 emissions.

ISRAEL

KBR to license nitric acid plant upgrades for Haifa

KBR says that it has been awarded a nitric acid technology contract by Haifa Group for two of its process plants at Mishor Rotem, Israel. Under the terms of the contract, KBR will provide the technology license, basic engineering design and proprietary equipment for both plants, to deliver a capacity increase of approximately 35% at each plant.

"We are proud to partner with Haifa Group to increase the production capacity of its plants through the use of our proprietary technology and knowhow," said Doug Kelly, KBR President, Technology. "KBR has the industry's leading design for energy-efficient nitric acid production in both mono-pressure and dual-pressure plants, and we look forward to working with Haifa to deliver higher production capacities while lowering plant emissions and operating expenses."

Motti Levin, Haifa Group CEO, said, "This is a strategic initiative that strengthens Haifa's position as a leader in the field of precision agriculture. It will contribute to an increase in agricultural yields while helping maintain an ecological balance. The two nitric acid plants are integral to our expansion plan to double our production capacity in the coming years."

KBR's Weatherly nitric acid technology has been successfully employed in 75 plants worldwide since the 1950's, including approximately 80% of all US nitric acid plants. ■

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UNITED KINGDOM

Government publishes hydrogen strategy

The UK has published its Hydrogen Strategy, setting out the government's ambition to create a low carbon hydrogen sector, with up to one third of the UK's energy consumption being hydrogen-based by 2050. The commitments set out in the strategy unlocks £4 billion of government investment by 2030. The government plans 5GW of low carbon hydrogen production capacity and the establishment of carbon capture, use and storage (CCUS) in four industrial clusters by 2030, as well as blending of hydrogen into the existing gas network and a 'twin-track' approach to hydrogen production, using both electrolytic and CCUS-enabled low carbon hydrogen production in order to scale up production in time to meet the UK's 2030 and 2050 carbon emissions targets.

Green methanol proposal for Scotland

The Global Energy Group has entered into an agreement with Swiss-based Proman Group, the world's second largest producer of methanol, for a feasibility study into the development of a low carbon industrial cluster in the Cromarty Firth, an inlet on the northeast coast of Scotland, north of Inverness. The first fruit of the Cromarty Clean Fuels Project would be a methanol plant at the Nigg Oil Terminal using offshore wind energy to generate hydrogen and local sources of captured carbon dioxide to make the fuel. Proman would become the owner, operator and offtaker of the green methanol production facility, which would include repurposing existing onshore storage at Nigg and export of methanol via the repurposed jetty at the site.

David Cassidy, CEO of Proman, commented: "As a global leader in methanol production we are actively investing and pursuing green methanol projects to further develop methanol's potential as a clean fuel for the future. Working with Global Energy Group in establishing green methanol production in Scotland is an exciting development in our strategy as it combines the necessary requirements of low cost renewable energy and utilises local sources of captured CO_2 to produce green methanol. The UK has proven itself as a world leader in supporting offshore wind, tidal and other clean power generation technologies. Green methanol presents a significant opportunity to bridge the gap from fossil-based to renewable fuels as we move to a lower carbon future and as such the production of and market for 'green' methanol from sustainable sources such as waste, bio-mass or renewable energy is growing and highly scalable."

CHINA

Haldor Topsoe and Yanchang build methanol catalyst facility

Haldor Topsoe and Shaanxi Yanchang Petroleum Co., Ltd have formed a joint venture to locally produce *MK-151+* methanol synthesis catalysts for the Chinese market. Together, the two companies will build a production facility in Shaanxi Fupin in China to produce methanol synthesis catalysts. Topsoe and Yanchang have designed the plant and ordered long lead time equipment and therefore plan on starting up at the beginning of 2022.

"Yanchang is well-positioned in the oil and gas value chain and a very experienced methanol producer. With this joint venture we combine Topsoe's world-leading methanol catalyst technology and Yanchang's outstanding production capabilities to produce our high-performance methanol synthesis catalysts that Topsoe will sell directly to our Chinese customers, enhancing our presence in the Chinese market," says Amy Hebert, Chief Commercial Officer at Topsoe.

Clariant selected for CNOOC

Clariant has been contracted to supply its high-performance methanol synthesis catalyst, *MegaMax 800* by the China National Offshore Oil Corporation (CNOOC) for its 800,000 t/a methanol plant at Fudao in Hainan, based on a Davy production process. It is a reorder following first delivery of the catalyst in 2018. The 2018 charge allowed CNOOC to increase methanol yield by 38,000 tonnes, representing up to $10.8 million in product, as well as reducing total natural gas consumption (feedstock and fuel) by 1.5% on average, with lower wax formation.

Stefan Heuser, senior vice president and general manager at Clariant Catalysts, stated, "The repeat order is a significant achievement for us and further proof of the quality of our unique methanol synthesis catalyst's performance. It is an honour to support CNOOC, one of China's largest oil and gas producers, in enhancing their production, efficiency, and plant reliability."

CANADA

Air Products to build net-zero hydrogen energy complex in Canada

Air Products has announced the development of a net zero hydrogen energy complex at Edmonton, Allberta. This new facility will be based on Haldor Topsoe's SynCOR™ autothermal reforming technology, and capture over 95% of the CO_2 generated for storage underground. Hydrogen-fuelled electricity will power the plant and offset the remaining 5% of emissions at the site. The clean energy complex will help refining and petrochemical customers served by the Air Products Heartland Hydrogen Pipeline to reduce their carbon intensity. The complex will also produce liquid hydrogen for merchant sales and as a clean fuel in the transportation sector. It is expected to come on-stream in 2024.

Canada's clean energy diversification strategy has marked hydrogen as a key enabler for Canada to achieve its goal of carbon neutrality by 2050.

"We are very proud of our collaboration with Air Products, and that our SynCOR™ technology plays a central part in their landmark net-zero hydrogen project. This is not only proof of our ability to deliver efficient hydrogen solutions, it also bears testament to our ability to achieve our vision of being recognized as the world leader in carbon emission reduction technologies by 2024. Our work and this project is a strong contribution to the decarbonisation of fuels and chemicals in Alberta and across the world," said Amy Hebert, CCO at Topsoe.

INDIA

Prime minister Narendra Modi announces National Hydrogen Mission

In his address to the nation on the country's 75th Independence Day, India's prime minister Narendra Modi announced the setting up of the National Hydrogen Mission. Modi said that green hydrogen would play a crucial role in helping the nation take a quantum leap in terms of climate change mitigation, and called upon industry and other stakeholders to make India a global hub for green hydrogen production and export. "This will not only help India to make new progress in the field of energy self-reliance but will also become a new inspiration for clean energy transition all over the world. New opportunities from green growth to the green job are opening up today for our start-ups and youth," he said.

With the government push, India has seen a good number of projects announced both from public and private sectors, including JSW Energy partnering with Australia-based Fortescue Future Industries on green hydrogen for steel making and hydrogen mobility, IndianOil's plans to build India's first green hydrogen plant at its Mathura refinery, and BGR Energy's partnership with Ireland's Fusion Fuel Green on a demonstrator plant for cost-competitive green hydrogen. Industry majors have also formed an India Hydrogen Alliance led by Reliance Industries.

At the same time, India's power and renewable energy minister RK Singh has placed draft plans before the cabinet for the country's refining and fertilizer sectors to switch to renewable 'green' hydrogen feeds. Other energy intensive sectors such as steel and transport are likely to follow. The policy suggests that refiners must have 10% of their hydrogen consumption generated from renewable electricity by the end of financial year 2023-24, rising to 25% by 2030. The comparable figures for ammonia/urea production are 5% and 20%, respectively. India is pursuing some of the world's most ambitious renewable energy targets of 175 GW of renewable energy capacity by the end of 2022 and 450 GW by 2030.

State-owned refiner IOC says that it will build its first commercial green hydrogen plant at the 160,000 bbl/d Mathura refinery in north India, using electricity generated from wind energy in Rajasthan to electrolyse water. The company also says that for the 500,000 bbl/d of new refining capacity that it plans to add by 2024 at its existing Panipat, Barauni and Nagapattinam refineries, it will use clean energy to run operations instead of fossil fuels such as fuel oil, naphtha or natural gas.

Reliance Industries has also announced investments totalling $10 billion over the next three years to build plants that will produce green hydrogen and other forms of clean energy.

CHILE

Ground broken on green hydrogen project

Chile's Highly Innovative Fuels (HIF) consortium has broken ground on a $45 million green hydrogen pilot project to produce methanol and carbon-neutral gasoline and LPG. The Haru Oni project will use hydrogen derived from 3.4 MW of dedicated wind energy to produce green methanol at Punta Arenas in the south of Chile, which will then be used to produce carbon-neutral gasoline and other products. The pilot project, which is due to begin operations next year, will produce 350 t/a of methanol and 130,000 litres/year of gasoline, and is designed to be scaled up in two subsequent stages. A final investment decision is expected next year on a $800 million commercial scale plant with 140,000 t/a of methanol capacity, which would be intended to come on-stream in late 2024 or early 2025. A further final investment decision on a 'world scale' 1.4 million t/a methanol facility is expected in 2023, for start-up in 2026. The HIF consortium includes Italian generator Enel, German engineering company Siemens and Chile's state-owned oil company Enap. The German government has provided financing for the pilot project.

TRINIDAD & TOBAGO

NGC signs gas contract with MHTL

Trinidad's state-owned National Gas Company (NGC) has finally signed a consolidated gas supply contract with Methanol Holdings (Trinidad) Ltd (MHTL), bringing to an end protracted negotiations between the government and Proman, the largest tenant at the Point Lisas Industrial Estate. In a joint statement, issued yesterday, NGC and MHTL said the contract will support operations at the MHTL methanol complex, which includes the 1.9 million t/a M5 methanol plant, one of the world's largest. Proman, via MHTL, owns five methanol plants with a combined capacity of 4 million t/a and an ammonia, urea ammonium nitrate and melamine complex. The company also owns shares in two ammonia plants at the Point Lisas Industrial Estate: Caribbean Nitrogen Company and Nitrogen (2000), as well as a majority stake in DeNovo Energy, which delivers 80 million scf/d to the Point Lisas Estate from the Iguana field.

Previously, each of MHTL's plants was supplied under individual gas sales contracts, but the consolidated gas supply contract is a single contract which will govern the sale of gas to the entire complex. The companies say that this new approach will streamline and enhance contract administration, relationship management, logistics and planning, and give flexibility to MHTL to manage its supply in the most efficient manner.

Managing director of MHTL, Jerome Dookie, welcomed the new gas supply contract, saying: "Today's agreement creates a period of stability that will provide immediate benefit to all parts of the gas value chain and indeed the entire national economy. We are grateful for the sustained efforts of NGC and our negotiating teams throughout this process and for the ongoing support of the Government of Trinidad and Tobago. There is no doubt that this has been a difficult period for our industry, with long-term economic gas supply challenges exacerbated by the global market downturn caused by Covid-19. As the global energy sector begins its lower-carbon transition, we look forward to working with all stakeholders to secure a sustainable and globally competitive future for our national energy industry, capitalising on the world-class skills, infrastructure and capabilities that we have collectively built to date."

UNITED STATES

Methanol plant construction restarts at Geismar

On July 16th Methanex announced the company's restart of construction on its new third methanol plant at Geismar, Louisiana. The company deferred construction on the 1.8 million t/a facility in 2020 due to uncertainty at the beginning of the coronavirus pandemic. In a statement, Methanex president and CEO John Floren said that: "The timing is right to restart construction on our Geismar 3 project as the methanol industry outlook is positive, we have a strong financial position to fund the project and the project has been significantly de-risked and is well positioned to be completed on-time and on budget. Geismar 3 will strengthen our asset portfolio as it will be one of our lowest cost plants, with access to abundant and low-cost natural gas and have one of the lowest CO_2 emissions intensity profiles in the industry."

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Current methanol industry fundamentals are positive as growing methanol demand, low global inventory levels, ongoing industry supply challenges and a rising energy price environment have supported higher methanol prices. Over the medium term, Methanex believes that the industry will need new supply to meet growing methanol demand. It anticipates strong methanol demand growth of approximately 16 million tonnes or 20% (~4% CAGR) over the next five years, compared with just 14 million tonnes of new industry capacity additions over that same period, including Geismar 3. With limited project commitments beyond 2022, industry operating rates will need to increase to meet growing demand.

Methanex said that Geismar 3 is on budget and on-track for commercial operations by late 2023/early 2024, with the total capital costs put at $1.25-1.35 billion.

GERMANY

MAN Andritz Hydro to jointly develop green hydrogen projects

MAN Energy Solutions and Andritz Hydro have signed a strategic framework agreement to jointly develop international projects for the production of green hydrogen from hydro-electric power. This collaboration will begin with a pilot project in Europe, with the companies looking to jointly identify further projects and implement them in the context of the German Federal Government's H2 Global initiative.

Frank Mette, CEO of Andritz Hydro, said, "hydropower is one of the few completely climate-neutral forms of energy, which is capable of providing base load power. We therefore see excellent potential for worldwide expansion – in new construction projects just as much as in repowering. By adding the possibility of producing hydrogen to hydropower plants, we are taking the next step and also making the energy generated there ready for export and storage without restriction. Together with MAN Energy Solutions, we can open up new markets and opportunities for the operators."

MOZAMBIQUE

Security issues plague LNG and downstream developments

Mozambique's ambitions to develop a massive LNG project in the onshore Cabo Delgado province in conjunction with France's Total at a cost of $20 billion is being stymied by on ongoing Islamic State insurgency uprising that is not only threatening to tear the country apart, but could also fuel an economic collapse. It is estimated that more than 2,600 people have been killed and 700,000 have fled their homes since the insurgency, led by ISIS-linked Al-Shabab, began in 2017. In April, Total issued a force majeure on the project and went on to withdraw personnel from the Afungi site. The move throws the project, one of three LNG projects being implemented in the country and the only one that has achieved significant progress, into jeopardy. Before invoking a force majeure, Total had promised to ship the first LNG cargoes in 2024 from its project whose capacity stands at 13.1 million t/a.

US giant ExxonMobil, which is leading the $30 billion Rovuma LNG project, is also said to be considering abandoning the project after pushing back the signing of the final investment decision for its 15.2 million t/a project. Shell has also abandoned a greenfield gas to liquids project, and fertilizer major Yara has cancelled plans to invest in fertilizer and power plants. The one remaining bright spot is the offshore Coral South floating production facility being developed by Eni. The project's progress has been largely untouched by the insurgency and remains on track to begin exports in 2022, with a capacity of 3.4 million t/a.

SOUTH AFRICA

Natref faces sale or closure

Sasol and its joint venture partner Total say that they are considering selling or closing their 107,000 bbl/d Natref refinery at Sasolburg. The firms have concluded that making the refinery compliant with the country's pending Clean Fuel 2 regulations, equivalent to Euro-V (<10 ppm sulphur) would not be financially viable, because current margins do not justify the investment required. South Africa currently operates on much more forgiving Euro-II (<500 ppm) sulphur standards.

Sasol and Total are reportedly exploring options such as converting Natref into a storage and blending facility to supply Sasol's facility at Secunda, which Sasol intends to convert to green hydrogen use to produce sustainable aviation fuels by 2030. The other options would be a sale or closure of the facility. Sasol expects to make a decision on Natref in the next few months. Sasol owns 63% of the Natref refinery, and Total owns the remaining 27%. ■

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People

Former Danish Minister of Climate, Energy, and Gender Equality, **Lykke Friis**, has been elected to the Blue World Technologies' board of directors. The company says that she will support its "journey towards providing a strong green alternative to combustion engines and diesel generators for industries around the world."

"We see her profile as the perfect match for a board position at Blue World Technologies, and we are very much looking forward to our collaboration", said co-founder and CEO of Blue World Technologies, Anders Korsgaard.

Friis holds a PhD in political science from the University of Copenhage and a Master's degree from the London School of Economics. She has served as Senior Researcher and later Head of Research at the Danish Institute for International Affairs, and in 2003 took over as Director for European affairs in the Confederation of Danish Industries (DI). She has also served on the boards of directors of House of Energy, Vestas A/S from 2014-18, and the Rockwool Foundation, as well as being a member of the European Council of Foreign Relations since 2011 (and co-chair since 2019), and president of the Danish Cancer Society.

Speaking about her appointment, Lykke Friis said: "it is now time for Europe, and for that matter, the world, to convert all its ambitious climate goals from paper into action. I am convinced that Blue World Technologies, with a 'ready to go technology', can play a crucial role, not at least in the all-important transport sector.

Haldor Topsoe says that its Chief Commercial Officer (CCO) **Amy Hebert** has left the company "by mutual agreement". Roeland Baan, Tospoe's CEO said in a brief statement: "Amy Hebert has been with Topsoe since 2018, and I would like to take this opportunity to thank Amy for her contribution and dedicated efforts in furthering our commercial offerings. I wish her all the best in her future endeavours." The recruitment process for the next CCO of Topsoe has been initiated.

Borealis has appointed **Leo Alders** as acting CEO of its fertilizers, melamine and technical nitrogen business from 1st September 2021. In his new role, Alders will succeed Rainer Hoefling, who is stepoing down from his role as CEO. Before joining Borealis in 1994 as Engineering & Maintenance Manager, Alders held positions at Philips Electronics, Bayer, and Neste Chemicals. At Borealis, he held several leadership positions in Operations and Process Safety. He was appointed Vice President Base Chemicals in 2018 before taking on his current role of Chief Operating Officer (COO) of Borealis' nitrogen business.

"I am delighted that Leo has been named my successor as CEO of Borealis' nitrogen business," comments Rainer Hoefling. "The combination of long-term expertise, profound understanding of the business, and dedication make him the right person to lead this organisation."

Trinity AgTech has announced the appointment of professor **Michael Lee**, deputy vice chancellor of Harper Adams University, to its Scientific Board. Lee is an expert in sustainable livestock systems, defining their role in ensuring global food security at the same time as protecting environmental health. He graduated with first class honours in Animal Science from the University of Wales, Aberystwyth in 1997 and gained a PhD in ruminant nutrition (protein and energy metabolism) from the University of Aberdeen in 2001.

Speaking on his appointment and the recent launch of the Harper Adams School of Sustainable Food and Farming, of which Trinity AgTech is an inaugural partner, Professor Lee said: "The aim of the new school is to support the agricultural transition that has to take place. The agricultural industry has been phenomenally good at producing vast amounts of food because the focus has been on yields. Now we are aware that we need to farm in a more environmentally sensitive way which will look at that transition from chemical to biological agriculture."

Clariant has announced the appointment of **Tatiana Berardinelli** as the company's new Chief Human Resources Officer and Head of Group HR from August 1st, 2021. She brings over fifteen years of experience in human resources, employee experience and operational excellence, and joins Clariant from PPG Industries in Pittsburgh, USA, where she most recently held the position of Global Head of People Operations. Prior to that, she was global HR Director, Architectural Coatings and North America Region, global HR Director, Automotive OEM and Latin America Region. ■

! The following events may be subject to postponement or cancellation due to the global coronavirus pandemic. Please check the status of individual events with organisers.

Calendar 2021

SEPTEMBER

14-15

Argus Methanol Forum – **virtual event**
Contact: Argus Media Group
Tel: +44 (0)20 7780 4340
Email: conferences@argusmedia.com
Web: www.argusmedia.com/en/conferences-events-listing/methanol-forum

20-23

Sustainable Fertilizer Production Technology Forum – **virtual event**
Contact: CRU Events
Tel: +44 (0)20 7903 2444
Fax: +44 (0)20 7903 2172
Email: conferences@crugroup.com

27-29

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

OCTOBER

2-7 **POSTPONED TO 2022**

Ammonium Nitrate/Nitric Acid Conference, HOUSTON, Texas, USA
Contact: Hans Reuvers, BASF
Karl Hohenwarter, Borealis
Email: johannes.reuvers@basf.com
karl.hohenwarter@borealisgroup.com
annaconferencehelp@gmail.com
Web: an-na.org

NOVEMBER

16-18

39th Annual World Methanol Conference – **virtual event**
Contact: Jake Barrett, IHS Markit
Tel: +1 212 709 1316
Email: Jake.Barrett@ihsmarkit.com
Web: ihsmarkit.com/events/39th-annual-world-methanol-conference/overview.html

DECEMBER

7-9

Argus Green Ammonia – **virtual event**
Contact: Argus Media Group
Tel: +44 (0)20 7780 4340
Email: conferences@argusmedia.com
Web: www.argusmedia.com/en/conferences-events-listing/green-ammonia

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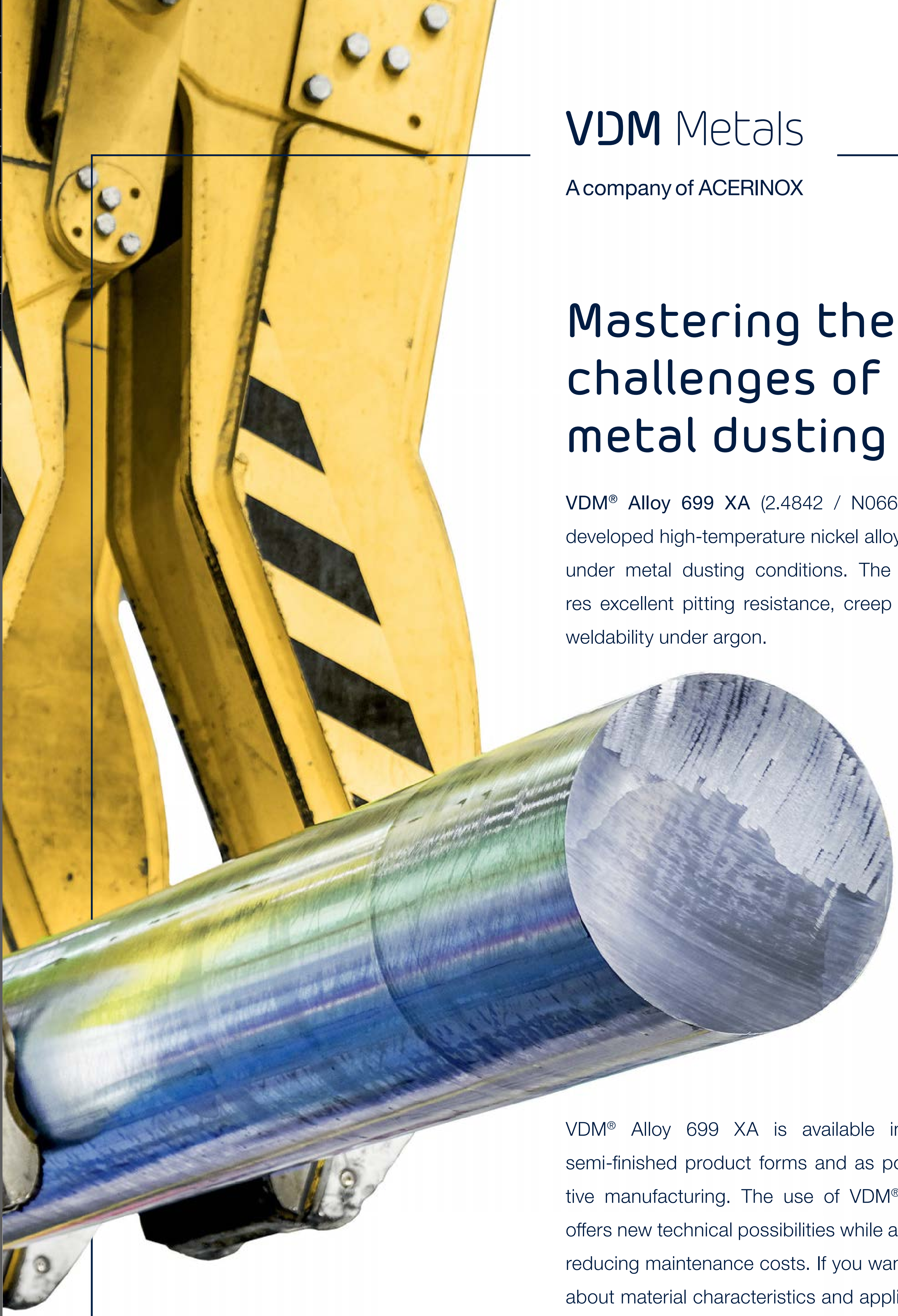


Plant Manager+

Problem No. 62

Biuret build-up in the urea melter

The fact that biuret is toxic to plants has been known for a long time – since the middle of the last century. Very sensitive (pineapple, citrus), moderately sensitive (cereals, legumes) and resistant (conifers) plant species were identified. The maximum concentration of biuret in urea for each species has been established for soil application and foliar application. Most field crops easily tolerate foliar fertilization with urea, which contains 1 wt-% biuret. Potatoes and tomatoes are more sensitive – for foliar feeding of these crops, it is advisable to use urea with an admixture of biuret of no more than 0.5 wt-%. Citrus fruits and pineapples are so sensitive that biuret in urea for foliar feeding should be no more than 0.35 wt-%.

Why is biuret toxic for certain crops?

First, biuret can enter the plant through the root and/or leaf surface. Cell membranes can be permeable to biuret: a small polar molecule without lipophilic moieties can move by simple diffusion.

When entering through the root, biuret moves along the xylem to the leaves; therefore, the concentration of biuret in the aerial part of the seedlings is much higher than in the roots. The main “transporter” of biuret during acropetal movement is transpiration. In foliar application of a solution containing biuret, this substance remains in the tissues of the treated leaves and practically does not move in the plant.

Secondly, biuret enters the plant into the plant slowly: the rate of absorption of biuret is one to two orders of magnitude lower than the rate of absorption of urea. In foliar application, biuret also lags behind urea. Therefore, the symptoms of “poisoning” do not appear immediately: citrus leaves turn yellow only 3-4 weeks after the introduction of carbamide with an admixture of 0.5% biuret.

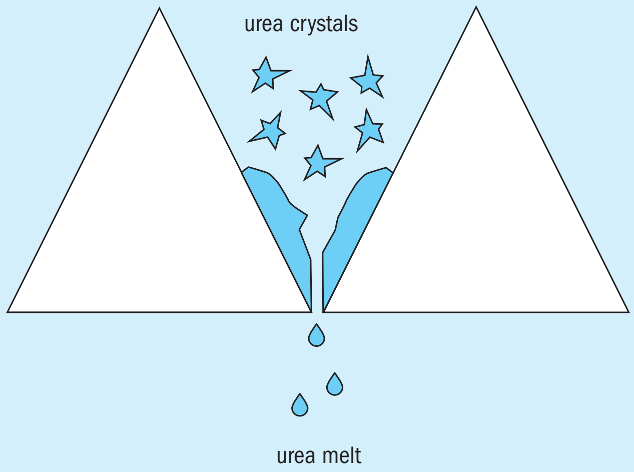
Thirdly, the biuret in the plant is preserved in its original form: plants do not have specialised enzymes to break down this substance. In orange leaves, for example, biuret persists even eight months after spraying.

Most urea plants in the world nowadays produce prills or granules with a biuret figure between 0.8 and 1.0 wt-%. In these plants urea is concentrated by means of a one or two stage evaporation section at low vacuum pressures. The low pressures lead to low operating temperatures which restricts biuret formation.

In the 1960s and 1970s of the last century, several urea plants were built which have been able to produce urea with a low biuret figure. Instead of evaporation, crystallisation technology was applied, making use of the difference in crystallisation temperature between urea and biuret.

The urea crystals produced contain hardly any biuret and some plants sell these crystals for high value pharmaceutical or food applications. However, to convert the crystals into prills or granules suitable for fertilizer application, typically the crystals are remelted and sent to a prilling tower or granulation section. The melter is the cause of some formation of biuret leading to a biuret content of some 0.3 to 0.5 wt-%.

Lance Gerdeman of Nutrien in the United States kicks of this round table discussion: We operate a crystalliser to produce low biuret prills. The unit was constructed in 1970 by C&I Girdler in Ohio, United States. The dried urea crystals are pneumatically conveyed to the top of the prill tower, pass through a cyclone separator, and fall to two parallel melters. The melters are rectangular in shape, have a bank of triangular tubes heated by 160 psig steam, and a rake to spread the crystals across the tube bank. The bottom vertices of the triangular tubes have a small gap that allows the liquified melt to flow through while preventing any crystals from passing through (see diagram below). We struggle with stagnant areas along the edges of the tube bank where the urea sits for long enough to polymerise to biuret/triuret and builds up in large chunks requiring annual cleaning. The solids are fairly insoluble in steam condensate so mechanical removal is typically required which is time consuming and hazardous (confined space entry, very challenging work environment).



I am interested if others have experience with chemically dissolving biuret/triuret solids, perhaps to eliminate the need for mechanical removal.

I am also curious to know if others could share what type of melter technologies they are using for prill units using crystallisers?

Mark Brouwer of UreaKnowHow.com in the Netherlands replies: I know the following melters:

1. Same principle but with round tubes instead of triangular.
2. Small vessel with heater and circulating pump. You could also consider flushing with urea melt which is very effective at dissolving urea polymers

Prem Baboo from Dangote Fertilizers in Nigeria shares his valuable experiences: The biuret problem seems to be in the head tank level and outlet temperature of the melter. Sometimes the head tank level shows erratic when at maximum level. If the problem with the melter is stagnant areas, this can be rectified during a shutdown. In my opinion a melter should have no stagnant areas. I also think the biuret level can be controlled by the temperature: You are using 160 psi pressure steam, the saturation temperature at this pressure is 188°C which is very high. The temperature required for steam is 145-150°C which means 55-60 psi is sufficient for the melter. However, in case you are using a pressure let down valve in the steam line please realise the let down is isentropic expansion. The following points may be helpful to control biuret levels:

- level of head tank (minimum);
- temperature of the melter;
- melter outlet condensate should be removed with a condensate pot with control valve to maintain the level in the pot (do not use a trap);
- the stainless steel rods between the melter steam tubes (replace any eroded rods)
- the biuret may be removed in the slurry stage i.e, centrifuge into the mother liquor. Steam condensate (DM water) can be increased in the centrifuge slurry to separate the biuret into the mother liquor.

Muhamad Reda of Pupuk Kujang in Indonesia shares also his interesting views: In our old plant (Kujang 1A) using TR-CI urea process technology by TEC in Japan we have a similar case. To remove the solid biuret/triuret/urea solid during turnaround we used caustic soda (NaOH) liquid 40% concentration. We fill up the melter with steam condensate until almost full then add 3-5 t NaOH then boil it (using the steam coil inside the melter). Continue boiling with NaOH for eight hours minimum. You can boil it with condensate only before and after caustic-boiling to rinse the melter. The procedure was successful, resulting in a clean melter, ready to inspect with no need for mechanical cleaning. ■

This series of discussions is compiled from a selection of round table topics discussed on the UreaKnowHow.com website. UreaKnowHow.com promotes the exchange of technical information to improve the performance and safety of urea plants. A wide range of round table discussions take place in the field of process design, operations, mechanical issues, maintenance, inspection, safety, environmental concerns, and product quality for urea, ammonia, nitric acid and other fertilizers.

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Middle East nitrogen exports

The new KIMA plant, Aswan, Egypt.

PHOTO: STAMICARBON

Although the stranded gas boom that led to the construction of the region's nitrogen capacity in the 1980s-2000s may be largely over, the Middle East remains the largest nitrogen exporting region in the world.

During the 1990s and 2000s, the Middle East, particularly the Arabian Gulf, became the favoured destination for new investment in ammonia and urea capacity. With access to the markets of both India and, via the Suez Canal, Europe, plentiful and cheap natural gas supplies and a favourable investment climate, national oil companies, sometimes partnered by western producers and investors, developed a large and efficient export-oriented nitrogen industry, based on what was often then regarded as "stranded" natural gas, with limited alternative values and, in the case of oil-associated gas, potentially negative costs associated with flaring. Low, fixed gas prices were the norm, with good margins for ammonia and urea producers.

The region still has the legacy of this capacity, and as a result remains the largest exporting region for ammonia and urea. However, the rapid development of the international gas market, as pipelines and liquefied natural gas (LNG) terminals have proliferated, and the equally rapid urbanisation of the region, requiring more power and more gas to generate that power, have both complicated the regional dynamics. Gas availability has fallen and prices – while often still controlled for existing projects – have risen sharply for new developments.

While the region as a whole is still gas rich, as Table 1 shows, and claims 38% of the world's natural gas reserves, most of that is concentrated in two countries; Iran and Qatar. Elsewhere a number of countries, including Kuwait and the UAE, have moved into gas deficit, even though the UAE still exports LNG from Das Island, off Abu Dhabi.

Table 1: **Middle Eastern gas industries, 2020, billion cubic metres/year**

Country	Production	Consumption	Imports	Exports	Reserves
Bahrain	16.9	16.9	-	-	75
Egypt	**64.9**	**58.9**	**-**	**6.0**	**2,100**
Iran	**244.2**	**223.6**	**-**	**20.6**	**32,000**
Iraq	10.8	19.9	9.1	-	3,500
Kuwait	18.4	23.5	5.1	-	1,700
Oman	**36.3**	**25.0**	**2.8**	**14.1**	**700**
Qatar	**178.1**	**41.1**	**-**	**128.6**	**24,700**
Saudi Arabia	113.6	113.6	-	-	6,000
UAE	62.5	69.3	14.5	7.7	5,900

Bold *indicates a country in surplus, red a country in gas deficit.*

Source: BP

Barriers to growth

Rising gas consumption ended the era of cheap gas in the Middle East. Demand growth was driven by low, subsidised gas prices which were intended to spur economic growth and encourage energy-intensive industrialisation. But the countries were a victim of their own success as low gas pricing and a young demographic profile moving into the region's rapidly growing cities led to demand increases year on year of up to 6-7% in some countries, while at the same time, low prices meant low or negative returns on gas exploration and development, discouraging the exploitation of new resources. In several countries, such as Kuwait and Saudi Arabia, gas production has also been tied to associated oil production, with OPEC oil quotas limiting volumes of gas that could be recovered as well. In Saudi Arabia and the UAE this has led to the development of large non-associated sour gas fields, which have been technically challenging and hence expensive. Increasingly, therefore, countries in the region are having to look at their long-standing policies of subsidising gas pricing, and this has made building new gas-based industrial capacity more difficult.

Political troubles have also loomed large for the region, such as the upheavals of the 'Arab Spring' that led to political instability in Egypt and the collapse of Syria and Yemen into civil war. Saudi Arabia and some of the other GCC states have tried to sanction Qatar in 2017 for its alleged support of terrorism, although an accommodation was reached earlier this year and restrictions are being eased. Meanwhile, the lingering fallout from the US intervention in Iraq in 2003 and the ongoing dispute with Iran over its nuclear energy and nuclear weapons programmes have also encouraged investors to look elsewhere to find a home for their money.

More recently, the increasing focus on reducing global carbon emissions has put the entire future of fossil fuel-based chemical production into some doubt. With an eye both to this and the region's abundant availability of solar energy, there are now many pilot projects in the region looking at the production of 'green' or 'blue' ammonia.

For the time being, however, regional production will remain largely gas-based and, in the absence of any significant local demand for fertilizer, the Middle East will continue to be a dominant force in world ammonia and urea markets.

Saudi Arabia

Saudi Arabia continues to expand its gas production as part of a plan to replace oil burning in power stations with gas and renewables and to become a net gas exporter by 2030 by expanding unconventional gas production, possibly including shale gas production from the Jafurah basin, east of the Ghawar field (Baker Hughes estimates the country's gas shale resources at 18 tcm). Some of this is coming from sour gas fields, processed at gas plants like Fadhili. At the moment, however, there are no plans for additional downstream urea/methanol output.

Saudi Arabia remains the world's fifth largest urea exporter, with 4.4 million t/a of domestic urea capacity, most of it in the hands of Safco, the Saudi Arabian Fertilizer Company, at its al Jubail site, although there has been no new capacity built since the delayed start-up of Safco V in 2015. Instead, Saudi Arabia has been diversifying into phosphate production over the past two decades, and mining company Ma'aden has built three large new ammonia plants (the third is due to begin operations in early 2022), but these are aimed at feeding mono- and diammonium phosphate production at the Ras al-Khair phosphate hub on the east coast, north of Jubail. These plants have at times provided some merchant ammonia capacity in between the start-up of the ammonia plants ahead of the associated DAP plants, but there is no long-term increase in net ammonia or urea capacity planned at present.

Bahrain

Bahrain's Gulf Petrochemical Industries Co (GPIC), which has 450,000 t/a of ammonia and 650,000 t/a of urea capacity at Sitra, has long looked to expand production at the site, but has been hampered by lack of gas availability from its mature and declining fields. However, in 2018 Bahrain announced the discovery of the Khaleej al-Bahrain field, its largest oil and gas find since 1932, off the island's west coast, which is estimated to contain at least 80 billion barrels of tight (shale) oil, and the Pre-Unayzah gas field, where reserves may be as high as 10-20 tcf. With production at the former due to begin at the end of 2022, plans for expansion of Sitra have moved back onto the front burner, and last year Saipem was awarded two feasibility studies to look at either a 15% increase in ammonia, urea and methanol production at Sitra at an estimated cost of $390 million, via debottlenecking and efficiency increases, or the construction of a new large-scale ammonia/urea plant with a capacity of 726,000 t/a of ammonia and 1.1 million t/a of urea respectively, which is expected to cost between $1.65-2.2 billion.

Egypt

Egypt went on a considerable capacity building spree in the 1990s and 2000s, ending up with major complexes at Alexandria (AlexFert and Abu Qir), Damietta (El Delta and MOPCO) and Suez (EBIC and EFC). There is also the 650,000 t/a Helwan plant near Cairo, and there has also been replacement of old capacity at KIMA at Aswan in the south of Egypt, which began operations in 2019. In total, this brings Egypt's urea capacity to 6.9 million t/a, with production running at 93% in 2019, and turning Egypt into the largest exporter of urea in the region after Qatar.

Like Saudi Arabia, Egypt has also begun expanding domestic phosphate production, and there is another new fertilizer complex under development at Ain Sokhna to include 440,000 t/a of ammonia, 380,000 t/a of urea and 300,000 t/a of calcium ammonium nitrate (CAN) capacity, due for completion in 2022.

Oman

There are two nitrogen producers in Oman. The first complex, built in 2005, is operated by the Oman India Fertilizer Company (OMIFCO), a joint venture between the Oman Oil Company and two Indian fertilizer cooperatives, the Krishak Bharati Cooperative and the Indian Farmers Fertilizer Cooperative. It operates two ammonia-urea trains with a total capacity of 1.7 million t/a at Sur (debottlenecked to 1.9 million t/a). There is also the privately owned Sohar urea plant at Sohar, completed in 2009, with a further 1.2 million t/a of capacity.

Oman is continuing to develop gas fields and expand its LNG export capacity, but some expansions are to balance declines in mature fields. No new nitrogen capacity is currently foreseen.

Qatar

Qatar has the world's third largest gas reserves, via its huge offshore North Field, and has turned itself into a gas superpower over the past two decades, focusing mainly upon gas exports, via the Dolphin pipeline to the UAE, and especially via the huge LNG export complex at Ras Laffan at the northern tip of the peninsula. Until 2020, when it was overtaken by Australia, Qatar was the world's largest LNG producer and exporter.

On the nitrogen side, Qatar is also the world's second largest exporter of urea, after Russia. The Qatar Fertilizer Company has a large complex at Mesaieed with six ammonia and urea trains with a total capacity of 3.8 million t/a of ammonia and 5.6 million t/a of urea, the most recent of which came

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on-stream in 2012. Fertilizer giant Yara was originally a 25% stakeholder in Qafco, and this lasted until 2020, when it was bought out by Qatar Petroleum, whose holding was then merged into Industries Qatar. The latter has said that it intends to make investments to keep the plants operating efficiently – some are of considerable vintage – but there are no plans for new capacity. Indeed, for several years from 2008 Qatar maintained a virtual moratorium on new North Field gas-based developments, with the sole exception of the Barzan LNG development, although continuing delays to that project mean that it only began initial production in April 2021. Qatar has now ended the development moratorium and is looking to expand LNG capacity once more, with the aim of increasing output by 40% to 110 million t/a by 2026. In August this year Spain's Tecnicas Reunidas was awarded the EPC contract for the North Field expansion.

Iran

Across the Gulf, and sharing the giant North Field with Qatar (Iran calls this the South Pars field), Iran has the largest gas reserves in the world. The country embarked upon a major development programme for its gas reserves in the 1980s and 1990s, and then began another development spurt in the mid to late 2000s. The latter however became mired in difficulty due to disagreements with the US and its allies over Iran's nuclear programme. The subsequent sanctions regime made transfers of money and equipment/technology difficult and on occasions impossible, and Iran's development of several large new ammonia/urea complexes has stalled. Nevertheless, some of the projects continue to inch forward, with Shiraz 3 completed in 2016 and Pardis in 2018. Last November Iran announced the final mechanical completion of the 1.1 million t/a Lordegan urea plant. Any relaxation of sanctions could fairly quickly bring a considerable amount of Iranian capacity back onto the international market.

Kuwait

Kuwait's lone foray into syngas-based industries was the Petrochemical Industries Corporation (PIC), which operated three ammonia-urea trains at Shuaiba. However, ongoing shortages of natural gas – Kuwait became an importer of LNG in 2009 – led to the production gradually being shut down. The last urea train ceased operation in 2018. Although Kuwait has reserves of gas in the Jurassic formation, it uses a lot of natural gas for enhanced oil recovery (EOR) and there are no plans for any further downstream petrochemical developments.

UAE

The UAE's nitrogen production is in the hands of ADNOC Fertilizers, at Ruwais in the west of the country, where there are two ammonia-urea trains, the first becoming operative in 1983, the second in 2013, with a combined capacity of 2.1 million t/a. ADNOC bought out Total's share of the fertilizer business in 2018, and in 2019 entered into a partnership with OCI; Fertiglobe, to trade fertilizers worldwide and look at further development opportunities.

The UAE is a major gas consumer via the megacities of Abu Dhabi and Dubai, but the Emirate of Abu Dhabi holds all of the oil and gas reserves. The UAE imports natural gas along the Dolphin pipeline from Qatar, but also exports LNG from the Das Island terminal. Abu Dhabi has announced its intention to become self-sufficient in gas by 2030 by expanding its non-associated sour gas production from the existing Shah field, as well as new onshore and offshore developments at Bab, Hail and Ghasha.

Table 1: **Middle East urea production and trade, 2019, million t/a**

Country	Production	Consumption	Imports	Exports
Bahrain	0.71	-	-	0.71
Egypt	6.46	1.76	-	4.70
Iran	6.15	4.02	-	2.13
Iraq	0.17	0.35	0.16	-
Kuwait	-	-	-	-
Oman	3.33	0.09	-	3.24
Qatar	5.78	0.28	-	5.50
Saudi Arabia	4.52	0.30	-	4.22
UAE	1.91	-	-	1.91
Total	**29.04**	**6.80**	**0.16**	**22.41**

Source: IFA

Consumption

The region's nitrogen demand is relatively small, with an estimated consumption of about 7 million t/a of urea in 2019, most of this coming from Egypt and Iran, as shown in Table 2. The Middle East is largely an arid region, and the development of its agricultural sector has been hindered by many factors such as small farm sizes, weak infrastructure, soil deterioration, and water scarcity. Although some growth in this is foreseen over the coming years, the region is likely to remain a huge net exporter for the foreseeable future.

Green and blue ammonia

Perhaps the most striking development of the past year or so have been the number of project proposals for 'blue' and 'green' ammonia production; the former using exhausted oil and gas reservoirs for carbon capture and storage, the latter using mainly solar-based renewable energy to electrolyse water for hydrogen production.

As noted in our News section (see page 8), Fertiglobe is looking to build 1.0 million t/a of blue ammonia capacity at Ruwais for sale to Japan, while there is a 20,000 t/a green ammonia pilot plant planned at Kizad. Oman has talked of 10 million t/a of green ammonia by 2038, beginning with a 790,000 t/a wind and solar powered plant at Duqm with construction scheduled for next year. NEOM in Saudi Arabia plans 1.2 million t/a of green ammonia production from 2025. Sabic already claims to have sent a 'blue' ammonia shipment to Japan, and is looking at further conversion of existing capacity to blue production.

Further announcements are sure to follow, and the region certainly has a winning combination of high solar incidence and many exhausted oil and gas wells that can be used for carbon capture and storage, as well as experience at dealing with the corrosive effects of carbon dioxide on pipework. While the region's natural gas boom may be running down, green and blue nitrogen capacity may provide a boost for future development. ■

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Damage to the port of Beirut following the August 2020 explosion.

PHOTO: MEHR NEWS AGENCY/WIKIMEDIA COMMONS

Ammonium nitrate after Beirut

The ammonium nitrate explosion in Beirut in August 2020 has once again focused minds upon the potential risks associated with the chemical.

It is now just over a year since the terrible explosion in the port of Beirut that killed over 200 people and injured over 5,000 others, and devastated the heart of the city. Over 2,700 tonnes of ammonium nitrate fertilizer had been impounded from an unsafe transport ship moored in the port and transferred to a dockside warehouse. However, there it languished for seven years while legal cases related to the ship and its cargo dragged on, with customs officials and courts swapping letters but no move made to transfer the cargo to a safer location. Eventually, it is believed that sparks from welding ignited the AN, and the subsequent fire further denatured the product until it finally detonated.

The tragic incident is of course merely another in a series of high profile ammonium nitrate accidents that include a similar explosion at the port of Tianjin, China in 2015, which killed 173 people, and the fire and explosion at West, Texas in 2013, where 15 where killed. Once again it placed an unwelcome spotlight upon the industry and how AN is stored and used.

A number of countries announced reviews into current storage and handling practises for ammonium nitrate. By and large these appear to have found no serious concerns. The sole upshot in New Zealand appeared to be the removal of AN from a storage site at Sawyers Bay near Dunedin to Macraes, 90 km away, closer to a mine site where it was used. In Australia, Orica faced questions about the storage of AN at Orica's Kooragang Island site near Newcastle, NSW, though the company insists that it meets all safety requirements. Australia is in the process of drafting an Explosives Bill, which went for public comment earlier in the year, in order to streamline and rationalise what had been old and slightly disparate state-based regulations on authorisation and licensing of the industry, and it touches on 'Security Sensitive' AN (defined as AN mixtures with >45% AN by weight), but this is largely a harmonisation exercise.

China

One of the most notable consequences of Beirut has been a proposed tightening of ammonium nitrate regulations by the Chinese government. Following the explosion, the Chinese government set in train a new round of safety inspections on hazardous chemicals, focusing on ports, wharves, warehouses, and chemical industrial zones. Permissible inventory levels were lowered and many AN producers were forced to idle production – Chinese AN producers are now allowed to only store 1-3 days' of production on-site.

In May 2021 China's Ministry of Emergency Management published a draft circular on stricter safety control of ammonium nitrate to solicit comments. The comment period ended in June 2021. The ministry noted in its circular that the draft has been developed to enhance the safety control over the production, use, etc. of ammonium nitrate, in direct response to the explosion in Beirut. It proposes stricter licensing criteria for construction projects involving ammonium nitrate; projects not complying with occupational safety laws and other rules will be denied a license. It also sets tighter national limits for chloride ion and organic compound content in AN products, and specifies that solid AN must be stored in isolation from other chemicals in accordance with Section 6.5 of the Rule for Storage of Chemical Hazards. Regarding sale and use, ammonium nitrate producers and sellers must obtain a civilian explosive sale license to be allowed to sell or purchase it. There is also to be stricter supervision by government bodies; if a government body for emergency management finds that a company producing or dealing with ammonium nitrate does not meet the production safety requirements, it will suspend or revoke the company's production license. There is also a quantity limit on export sales.

Regulatory gaps

One of the issues that Tianjin and Beirut has exposed is the status of ports, which can be legal 'twilight zones'. Ships carrying dangerous materials fall under the jurisdiction of the International Maritime Organisation's (IMO's) Dangerous Goods Code (IMDG Code), a product of the 1960 Safety for Life at Sea Convention, updated most recently in January 2021. However, there is currently no standardised legislation for ports across the globe, and implementation of existing standards can be extremely patchy, as Beirut showed. Since the end of the Lebanese civil war in 1990, Beirut's port has been managed autonomously by a Temporary Committee which does not report to any government agency. This led to the back-passing between courts and customs officials over the AN shipment.

The UN Office for Disaster Risk Reduction has published various frameworks for national risk reduction, most recently the Sendai Framework. However, a law to implement such a risk reduction body has been stuck in the Lebanese parliament for 20 years. If Beirut was primarily a regulatory failure, as with the West, Texas disaster it has highlighted the need for better coordination between bodies with responsibility for enforcing regulations on safe chemical storage and handling. ■

BASF's ammonia plant at its Ludwigshaven site, Germany, where ammonia has been made for over 100 years.

PHOTO: BASF

2021 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 virtually on 30 August to 2 September 2021.

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. Attendees to the symposium, who include plant safety personnel, plant managers, and process engineers representing a spectrum of nitrogen fertilizer based industries, amongst others, share technological advances and discuss strategies for improving plant safety, maintenance, and management. This year's virtual event – the first in the organisation's history – included about 250 engineers from more than 30 countries and 75 companies.

Clean ammonia

This year's keynote speech; 'Clean ammonia: scaling up for new opportunities', was presented by Trevor Brown, executive director of the Ammonia Energy Association (AEA), who advocated for ammonia's responsible use in a sustainable energy economy. According to the International Renewable Energy Agency (IRENA), by 2050, about 70 million tonnes of current ammonia capacity will either be shut down or have been converted from fossil to renewable inputs. But about 500 million t/a ammonia capacity could be developed using available renewable energy sources. The prediction is that demand for clean ammonia will grow in industries such as fertilizer, maritime fuel, as a hydrogen carrier and as a fuel for electric power generation.

A number of low carbon ammonia projects are already under way. Already announced low carbon ammonia revamp projects include:

- CF Industries – 600,000 t/a including at Billingham, UK;
- OCI Beaumont – 365,000 t/a;
- ADNOC, Ruwais: 1 million t/a;
- PAU Sulawesi: 660,000 t/a;
- SAFCO, Al-Jubail: 1 million t/a; and
- Nutrien, North America: 450,000 t/a.

In addition to these, there are green ammonia electrolysis-based pilot projects at: Yara Pilbara (Engie); Fertiberia; Yara Sluisil; Yara Porsgrunn: and CF Donaldsonville, and new mega ammonia renewable projects announced for:

- Asian Renewable Energy Hub (Australia): 9.9 million t/a, 16 GW wind+solar.
- Svevind (Kazakhstan): 15 million t/a, 45 GW wind+solar.
- Aman (Mauritania): <20 million tonnes, 30 GW wind+solar.
- Al Wusa (Oman): <10 million tonnes, 15 GW wind+solar.
- Western Green Energy Hub (Australia): 20 million tonnes 50 GW wind+solar.
- Grand Inga Dam (DRC): >20 million tonnes, 40 GW hydroelectric.

Safety incidents

This year's key safety-related papers were:

Failure of a hot walled ammonia synthesis converter

The ammonia plant was shut down for a turnaround, and as part of the risk-based inspection (RBI) programme, an inspection was performed in and around the shell and nozzle welds of the second synloop converter. Indications of hydrogen assisted cracking (HAC) were found between the man-way nozzle top head and bottom inlet/outlet nozzle. The root cause investigation concluded that the cracking phenomenon resulted from a combination of nitriding at the inner surface and hydrogen-induced embrittlement. The nitride inner layer was prone to cracking when taking the equipment in and out of service and acted as a crack initiation point. Moreover, the hydrogen charged material exhibited a lower threshold stress resistance factor and a higher crack propagation rate with respect

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to uncharged material. The usage of a high strength material (3Cr type compared to 2.25Cr) also increased the stress level at the cracked areas.

The following preventive actions have been planned: adjustment of inspection planning for all converters, ensuring that time of flight diffraction (TOFD) and phased array ultrasonic testing (PAUT) are performed to find cracks in all orientations; and the establishment of minimum pressurising temperature (MPT) curves for all converters and adjustment of operating procedures if required.

Failure of ammonia synthesis converter internals

A complete failure occurred on the inlet and outlet expansion joints for the first bed interchanger in an ammonia synthesis converter. The direct cause of the failure was the overpressure of the converter during start-up. To prevent a reoccurrence, the following recommendations were made:

- Minimum stop of 15% on one of the quench valves.
- Installation of DCS indications with alarms for the differential pressure between the inlet and outlet of Interchanger #1.
- Installation of an automated converter pressurisation scheme to provide a controlled and well measured system by which the converter is pressurised during a startup.
- To properly sample for moisture prior to introducing gas into the converter, the start-up procedure will be altered to ensure sampling is performed on the discharge of the synthesis gas compressor.

Failure of a high-pressure steam superheater header

The outlet header of a high-pressure steam superheater located in the convection section of a primary reformer failed catastrophically, leading to significant damage to surrounding equipment and extended plant downtime. The failure occurred despite using materials in compliance with the ASME code. The failure of the HP steam superheater was a major event that resulted in an unplanned and extended plant outage and could have been much more serious. Stress relaxation cracking of austenitic alloys has been recognised for some time. The use of these alloys appears to have become more common since the turn of the century due to the relative reduction in price compared to ferritic materials of similar strength. This has led to an increase in the number of reported stress relaxation failures. The ASME code has recognised this problem for alloy 800H pressure vessels built to ASME Div. VIII, and introduced a post-weld heat treatment for design temperatures above 1000°F (538°C). Such heat treatments are not required for other austenitic alloys unless cold work strain and design temperature limits are exceeded.

The experience from this event suggests it is inadequate to avoid in-service stress relaxation limits. It is considered that requirements for post-weld heat treatments of new builds using austenitic alloys at elevated temperatures should be considered.

For existing applications, the need for inspection to ensure freedom from cracking is important. The plant had a risk-based inspection system in place. However, stress relaxation cracking had not been identified as a possible damage mechanism due in part to compliance with the ASME code and the relatively low operating temperature. This experience has raised the awareness of stress relaxation cracking as a potential damage mechanism, and inspection tests have been introduced to monitor susceptible plant equipment. The lessons learned from this incident have resulted in significant changes to the risk management of stainless-steel components operating at elevated temperatures in all Methanex facilities.

This has introduced additional problems related to non-destructive inspection. The sound portion of the seam weld in the HP superheater outlet header and the equivalent weld in the inlet header were inspected for damage using ultrasonic methods. These inspections reported cracking was also occurring in these welds. Subsequent investigation found minimal damage. It is thought that beam bending of the ultrasonic wave due to microstructural variations was responsible for the false interpretation that weld root cracking had occurred. These false-positive results have led to ongoing investigations into ultrasonic testing procedures to improve the sensitivity and reliability of these methods.

Failure and field repair of urea reactor shell rupture

The outer shell of a multi-layered urea reactor ruptured while the plant was in operation. The plant made an emergency shutdown, samples were collected, and an investigation was carried out to establish the root cause of the failure.

Urea reactors are usually vertical pressure vessels with either a mono-wall, multi-layer, or multi-wall construction. Because of the corrosive nature of the medium, the interior surface of the vessel is lined with corrosion-resistant materials. The inside surface of the reactor showed signs of corrosion on the long liner seam, circumferential joints, and buttering welds (old cleat removal area). During the air test, weep holes were blocked due to the solidification of carbamate in the leak path. The air test was performed after the weep holes were cleared leakage in the long liner seam. Corrosion attack was observed on the dummy shell layer and first shell layer in the vicinity of the liner leakage.

Lessons learned:

- Approved contractors should perform liner fabrication and welding.
- Liner welding should be performed using fixtures to restrict the lifting of the liner during welding and creating excessive air gaps.
- The optimum weld sequence should be developed to reduce the liner shrinkage during installation.
- The weld process parameters and filler wire selection should be optimised to restrict the heat input during pass partition plate welds.
- All attachments on the liners shoud be full penetration welds.
- Vent holes should be inspected and verified as open following the erection of lined vessels and also during each turnaround.
- As the process licensor specifies, periodic quality checks for the weep tube leak detection system are mandatory.

Explosion inside HP urea reactor

A urea plant was operating for decades when during a restart, an abnormality was observed in the form of a rumbling sound not heard before. No actions were taken at that time, and the reactor was operated as normal with barely any difference in operational parameters. Upon opening of the reactor during a planned turnaround, however, it was observed that all of the trays were displaced from their supports and deposited in the bottom of the reactor. Most of the trays were heavily deformed.

A root cause analysis found that an explosion must have occurred between the 3rd and 4th tray during start-up with sufficient force to displace all the trays from their supports, depositing them in the bottom of the reactor. The analysis found that the most likely cause was the formation of a combustible mixture that exploded due to self-ignition or due to ignition caused by a static discharge. Before this occurrence, no scenarios were recognised which could lead to such an incident.

The scenario described only occurs when inerts get the chance to accumulate in combination with high hydrogen content in the carbon dioxide. To prevent the recurrence of this incident in the future, the following measures were planned:

- A hydrogen analyser has been installed in the carbon dioxide feed to the reactor.
- The start-up and shut down procedures have been adapted to prevent the accumulation of hydrogen.
- The vent valve will not be fully closed anymore during these periods to allow inerts to be vented to the downstream sections.
- All personnel will be instructed regarding the risks of inert accumulation in general, especially during start-up and shut down activities.
- All work instructions have been adapted to reflect the findings and to avoid this scenario from occurring again.

Corrosion under insulation

Corrosion under insulation (CUI), despite being very well known, is responsible for significant maintenance costs in the process industry. There is no doubt that CUI threatens the safe operation of our installations, but with a change in organisational culture that drives continuous improvement using standard work protocols, CUI can certainly be controlled. For sites without an established CUI inspection program, a significant initial effort and capital will be required to develop and execute new inspection processes. This case clearly shows that this is an effort worth making.

Mitigations:

- The use of thermal insulation for services that required insulation just for personnel protection was stopped
- Improved practices around the preparation of metal surfaces prior to application of the coating and the selection of coating for new insulation applications and repairs.
- Use of piping for rigging and support during maintenance activities was abandoned to prevent damage to insulation
- Insulation craftsmanship and caulking methods were reviewed
- The operations team will incorporate annual insulation surveys to identify insulation deficiencies and prevent water ingress by repairing insulation damages.
- Repositioning of supports and brackets where insulation is replaced and avoiding couplings under insulation lagging
- Begin use of organic coatings on carbon steel equipment and use of aluminium foil for protecting stainless steel

Round table

On the Symposium's fourth and final day, a round table session was held, with topics which included an ammonia pump failure that led to two fatalities; changing a tank's outlet manifold with a passing isolation valve; a safety park in Brunei; reforming furnace tube failure resulting in fire outside the box; 1.5 million years of Safurex operation; and incidents and near misses in ammonia plants.

Next year's symposium will be in Chicago, from 12th-15th September 2022.

CO_2 removal system analytics

Arun Murugan and **Mike Antony** of FITIRI and **Venkat Pattabathula** of SVP Chemical Plant Services discuss the COORS Analytics system for more accurate prediction of the performance of a CO_2 removal system.

The level of CO_2 in the atmosphere is now over 410 ppm, yet when the authors were in chemical engineering classes in late 1970s, we used a value of 330 ppm. Such an increase by human activities in so short a span of time and the consequent weather calamities of recent years has pushed humanity to think about this existential threat. Any technology which can remove CO_2 from the atmosphere or industrial waste gas or flue gas streams will thus be one of the most critical technologies in the years ahead. Furthermore, CO_2 removal systems play a critical role in industrial chemical production such as the manufacturing of ammonia, hydrogen, LNG and in natural gas purification plants.

CO_2 removal systems are designed and their performance predicted using chemical engineering techniques such as McCabe and Thiele diagrams and other analytical models. But actual performance of the system varies from plant to plant even with the same design. We call this a ‘personality trait’ for CO_2 systems – no two plants behave the same way, due to too many design and operating variables. It is simply impossible to correlate the performance to engineering equations and analytical models. A CO_2 removal system with its own ‘personality’ is thus an ideal engineering problem for data analytics and artificial intelligence.

COORS Analytics stands for CO_2 (COO) Removal System Analytics. With COORS, we can accurately predict the performance of a system when operating parameters are changed, and we can predict optimum operating parameters for a new or modified plant.

CO_2 removal processes

There are number of technologies available for CO_2 removal using both physical and chemical solvents. The amine-based solvent aMDEA has emerged as the leader among all technologies based on ease of operation, control of corrosion and overall energy consumption. Different technologies used in CO_2 removal systems mainly vary in the solvent used. Hot potash systems, Catacarb, Vetrocoke, Selexsol, Rectisol, GV Vetrocoke, MEA, DME, aMDEA, Sulfinol, propylene carbonate etc are some of the most popular in the industry. In almost all systems, CO_2 is first absorbed in a solution in an absorption tower with trays or packed beds at high pressure and low temperature, and then the solution is recovered by stripping in a regeneration tower at low pressure and high temperature.

Some of the various removal processes are as follows:

1. **Water scrubbing:** The oldest method, water scrubbing, is practically abandoned in many plants. The CO_2 is absorbed in water under pressure and the water is regenerated by a release in pressure. Most of the energy contained in the high pressure water is recovered by a hydraulic turbine which, along with an electric motor, drive the high pressure water pump. Although this method is simple and inexpensive, hydrogen is dissolved along with the CO_2 and therefore the H_2 loss is appreciable, amounting to 1.5-2.5% when the scrubber is operated at 7.2 bar. Several schemes were proposed for recovering hydrogen, but this required additional equipment and increased investment that couldn’t be justified via the value of the hydrogen recovered.
2. **MEA absorption:** The first generation of single-train plants often used a monoethanolamine (MEA) solution with a high demand of low-grade heat for solvent regeneration. With corrosion inhibition systems, the amine strength could be raised and solvent circulation reduced, saving heat and mechanical energy.
3. **Selexol:** This process uses polyethylene glycol dimethyl ether as a solvent, which is stable, non-corrosive, not very volatile, but has a rather high capacity to absorb water. For this reason, a relatively dry gas is required, which is achieved by chilling.
4. **Rectisol:** This process seems to be the prime choice in partial oxidation plants, and is very versatile and allows a number of different configurations.
5. **Sulfinol:** The Sulfinol process uses a mixture of sulpholane and di-isopropanolamine (DIPA). The Sulfinol solution is replaced by others due to the high cost of solvent loss and usage of heavy metals as corrosion inhibitors.
6. **Hot potash systems:** Commercial hot potash systems differ in the type of activator used to increase the reaction rate between the CO_2 and the solvent. The activators enhance mass transfer and thus influence not only the regeneration energy demand but also the equipment sizing. The various hot potassium solvents are as follows:
   - The Catacarb process, with amine and borate as the activator.
   - The Giammarco-Vetrocoke process with glycine and various ethanolamines as the activators.
   - The Benfield Loheat process with DEA as the activator. Many variations in the flow sheet are operating in different applications. A simplified flow diagram of the Benfield process is shown in Figure 1.

   Benfield technology uses hot potassium carbonate as the absorbent. There are hundreds of installations of Benfield systems around the world. When CO_2 is absorbed, the carbonate is converted to bicar-

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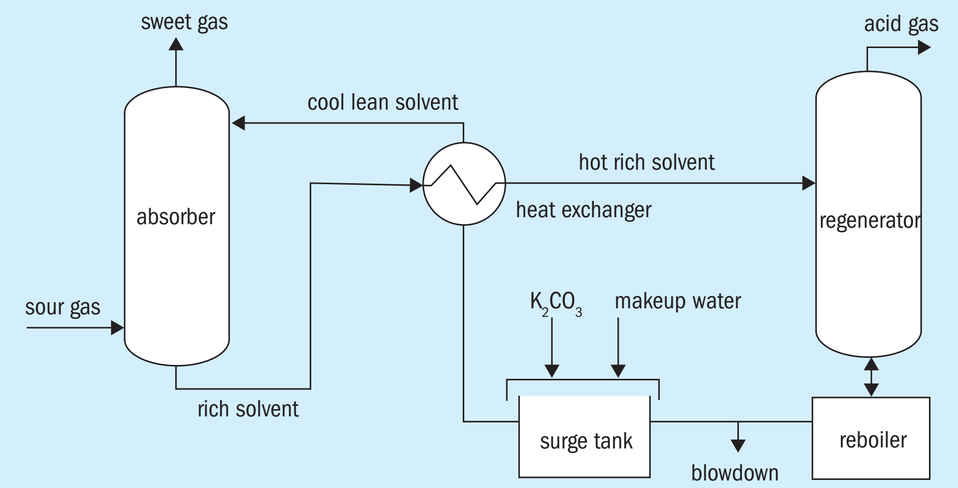
Fig. 1: **Benfield basic process schematic**



Source: *FITIRI*

bonate and therefore this system is a chemical absorption. The Benfield system offers very stable operation, but the solution loaded with CO_2 is very corrosive and therefore needs a corrosion inhibitor. Benfield uses pentavalent vanadium (V^{5+}) as a corrosion inhibitor, and when it undergoes the corrosion inhibition reaction it is reduced to tetravalent vanadium (V^{4+}). The solution also uses DEA as the promoter.

The process contains a gas absorption step and a carbonate regeneration step. Potassium carbonate (K_2CO_3) is the alkali in the absorption solvent. K_2CO_3 reacts with CO_2 and H_2S in the absorber tower, forming bicarbonate (HCO_3^{-1}) and bisulphide (HS^{-1}). This reaction enables the solvent to dissolve significantly more CO_2 and H_2S than is possible with pure water. This rich solvent is then steam stripped of the absorbed CO_2 and H_2S in the regeneration tower. The regenerated solvent is recycled back to the absorber after energy recovery using heat exchangers.

7. **aMDEA:** A leading process today is the BASF's activated methyl diethanolamine (aMDEA) with a special activator. Because of the low vapor pressure of aMDEA, the solvent losses are at a minimum. The CO_2 binds much less strongly to MDEA than to MEA and hence requires less energy for regeneration. Many MEA solvent systems were revamped by swapping the solvent without a need to change the process equipment.

Case study

The plant chosen for the study was Incitec Pivot Ltd's (IPL) Gibson Island ammonia plant (part of a larger fertilizer complex) in Brisbane, Australia. The plants at this site produce ammonia, urea, granular ammonium sulphate, and liquid CO_2. The Gibson Island Product Distribution Centre dispatches approximately 550,000 t/a of fertilizers to IPL customers. The site also has a 160 t/d liquid carbon dioxide plant that supplies half the liquid CO_2 in Queensland, and is the main source of CO_2 in carbonated soft drinks in Queensland and northern New South Wales.

CO_2 removal at Gibson Island

The IPL Gibson Island plant uses the BASF aMDEA process, which offers energy efficient and reliable operation using an activated MDEA solvent for CO_2 absorption. The activator accelerates the rate of CO_2 absorption and is considered to be a quasi-physical absorption system.

Though COORS analytics can predict the performance of different related flow sheets under aMDEA system, we use a more popular flow diagram with lean and rich solutions, one stage flash, process and steam reboilers and regenerator overhead condenser and reflux systems.

Process gas exiting the low temperature shift converter (LTS) is first cooled to just above its dew point using the LTS outlet desuperheater, DSHT602. The gas then passes through the aMDEA reboilers, E602A and E602B. Here heat is transferred to the aMDEA solution and most of the steam in the process gas condenses as the temperature drops. The mixture of process gas and water then passes to the hot condensate separator, T602, where the water formed in the E602s is separated from the process. Gas from T602 passes through a further cooling stage provided by the condensate preheater E674, and the gas cooler E603, operating in parallel. Here the rest of the steam in the process gas condenses.

Gas from T603 passes through to the aMDEA absorber, D602, where it is counter-currently contacted with aMDEA to allow absorption of the CO_2. This allows for almost complete removal of the CO_2 in the gas stream. After passing through D602, the process gas passes through a water wash tower D604 to ensure that no aMDEA or other material carryover has occurred. The wash tower overhead separator T619 is positioned downstream of D604 to ensure that all liquid carryover is collected prior to the process gas passing into the methanation section; aMDEA is an expensive chemical and this way the losses are minimised.

COORS

As noted above, no two CO_2 removal systems behave the same way in practice. The objective of the study was thus to predict the performance of the system when operating parameters are changed, and also to find the optimal performance parameters for a plant given the limiting conditions of operating parameters. We also aimed to develop a model that could predict the optimum operating parameters for a new or modified plant.

We use all available data collected by field operators, DCS data from historians, lab and online analysers. If the plant has Fitiri's *PlantMS*, it can automatically upload and store all required data. The design parameters are used for reference and control. The list of data collected include feed gas composition (percentage methane, ethane, propane by volume); gas heating value; absorber (D602) temperatures, including aMDEA and gas in and out, lean solution flow; aMDEA circulation; absorber delta P; process gas to absorber composition (only available every two months; stripper (D601) tray temperatures; gas temperatures exiting the water wash tower (D604); gas inlet and outlet temperatures at the methanator (R605); and aMDEA and gas temperatures in and out of the reboilers (E602a and b).

Since the methanator delta T can explain the amount of CO_2 and CO coming out of the absorber we decided to use this as the target variable, and since CO partial pressure is negligible, we can say this is essentually the amount of CO_2 present in the gas coming out of absorber.

Lab data includes absorber inlet and outlet gas compositions (hydrogen, argon, nitrogen, methane, CO, CO_2 percentages and H_2:N_2 ratio).

Methodology

The COORS methodology differs from traditional simulation and calculative methods by using a machine learning approach. Machine learning is an application of artificial intelligence (AI) that provides systems with the ability to automatically learn and improve from experience without being explicitly programmed. Machine learning focuses on the development of computer programs that can access data and use it to learn for themselves. The process of learning begins with observations or data, such as examples, direct experience, or instruction, in order to look for patterns in data and make better decisions in the future based on the examples that we provide.

The primary aim is to allow the computers to learn automatically without human intervention or assistance and adjust actions accordingly. Supervised machine learning algorithms can apply what has been learned in the past to new data using labeled examples to predict future events. Starting from the analysis of a known training dataset, the learning algorithm produces an inferred function to make predictions about the output values. The system is able to provide targets for any new input after sufficient training. The learning algorithm can also compare its output with the correct, intended output and find errors in order to modify the model accordingly.

Such an approach will help us to identify a more accurate and real-time model which is much closer to the actual performance of the CO_2 removal system in the plant, since it is based on real-time operational data rather than simulated or expected data.

Analytical models

Within the field of machine learning, there are two main types of tasks: supervised, and unsupervised. The main difference between the two types is that supervised learning is done using a 'ground truth', or in other words, we have prior knowledge of what the output values for our samples should be. Therefore, the goal of supervised learning is to learn a function that, given a sample of data and desired outputs, best approximates the relationship between input and output observable in the data. Unsupervised learning, on the other hand, does not have labeled outputs, so its goal is to infer the natural structure present within a set of data points. In both regression and classification, the goal is to find specific relationships or structure in the input data that allow us to effectively produce correct output data. Supervised learning is typically done in the context of classification, when we want to map input to output labels, or regression, when we want to map input to a continuous output. Common algorithms in supervised learning include logistic regression, naive bayes, support vector machines, artificial neural networks, and random forests.

The problem we are trying to solve here is a good use case for a supervised learning regression model. The popular algorithms for this are linear regression and random forest. The function in a linear regression can easily be written as:

$$y = mx + c$$

while a function in a complex random forest regression seems like a black box that can't easily be represented as a function. Generally, random forests produce better results, work well on large datasets, and are able to work with missing data by creating estimates for them.

Linear regression

This is one of the most widely known modeling techniques. Linear regression is usually among the first topics which people pick while learning predictive modeling. In this technique, the dependent variable is continuous, independent variable(s) can be continuous or discrete, and the nature of the regression line is linear. Linear regression establishes a relationship between a dependent variable (y) and one or more independent variables (x) using a best fit straight line (also known as regression line). It is represented by the equation

$$y= (a+b) x + e$$

where a is the intercept, b is slope of the line and e is the error term. This equation can be used to predict the value of target variable based on given predictor variable(s).

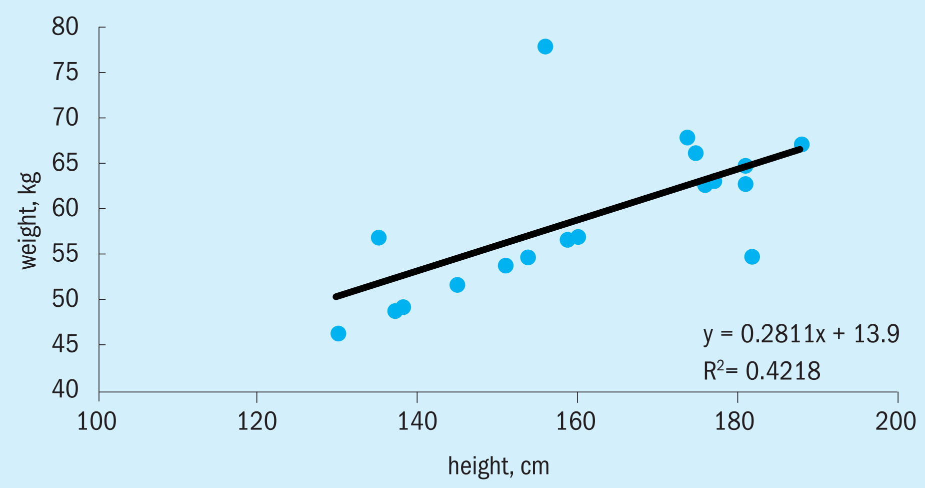
The difference between simple linear regression and multiple linear regression is that multiple linear regression has more than one independent variable, whereas simple linear regression has only one independent variable. Now the question is: how do we obtain the best line fit?

Random forest

Decision trees are great for obtaining non-linear relationships between input features and the target variable. The inner working of a decision Tree can be thought of as a bunch of if-else conditions. It starts at the very top with one node. This node then splits into a left and right node – decision nodes. These nodes then split into their respective right and left nodes. At the end of the leaf node, the average of the observation that occurs within that area is computed. Most bottom nodes are referred to as leaves or terminal nodes.

Random forest is an ensemble of decision trees. This is to say that many trees,

Fig. 2: **Linear regression example**



Source: FITIRI

Fig. 3: **Random forest model**

Source: FITIRI

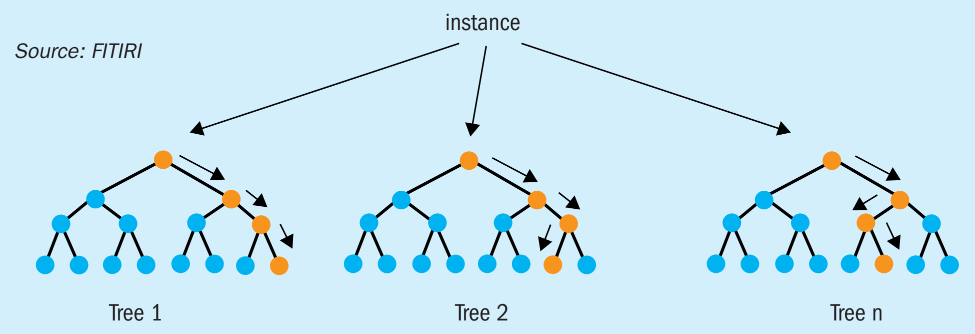
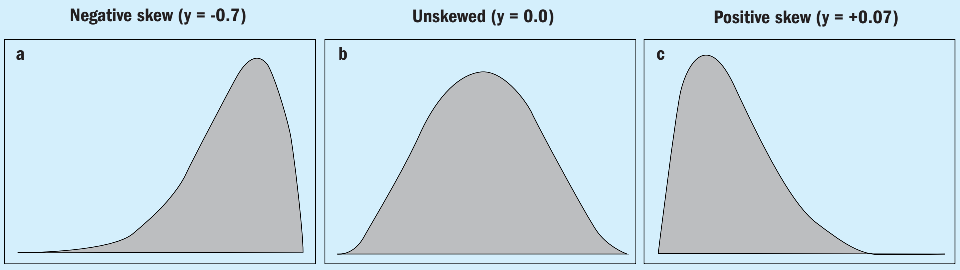


Fig. 4: **Skewness**



Source: FITIRI

Table 1: **Skewness results for data**

Parameter	Unit	Skewness
NG heating value	Pascals	1.155768
MDEA TO D602	°F	0.573944
MDEA EX D602	°F	-2.251146
GAS TO D602	°F	0.163269
GAS EX D602	°F	0.527680
GAS EX D604	°F	0.315303
MDEA CIRCULATION	1,000lb/h	-1.595290
D602 CO2 ABSORBER	In H_2O	-0.959836
D601 overhead	°F	-0.070354
D601 TRAY 8	°F	0.672454
aMDEA CO$_2$ STRIPPER TRAY 4	°F	-0.516321
D601 MDEA STRIPPER	Psig	-1.596106
MDEA EX E602A	°F	-0.866957
MDEA EX E602B	°F	-1.919872
GAS EX E602B	°F	-2.477090
D601 upper DP	Psi	-1.842998
D601 Diff. Pressure	Psi	1.055181
GAS EX E602A	°F	-1.320231
EX DSHT602 after R604	°F	-0.323659
MDEA RFX PUMP DISCHRG	1,000lb/h	-0.217363
D601 STRIPPER INLET	°F	-2.511602
Methanator dT	°F	0.186981

Source: FITIRI

constructed in a certain "random" way form a random forest. Each tree is created from a different sample of rows and at each node, a different sample of features is selected for splitting. Each of the trees makes its own individual prediction. These predictions are then averaged to produce a single result. The averaging makes a random forest better than a single decision tree and hence improves its accuracy and reduces overfitting. A prediction from the random forest regressor is an average of the predictions produced by the trees in the forest.

The random forest model is very good at handling tabular data with numerical features, or categorical features with fewer than hundreds of categories. Unlike linear models, random forests are able to capture non-linear interaction between the features and the target. The random forest model is a type of additive model that makes predictions by combining decisions from a sequence of base models. More formally we can write this class of models as:

$$g(x) = f0(x) + f1(x) + f2(x) +\ldots$$

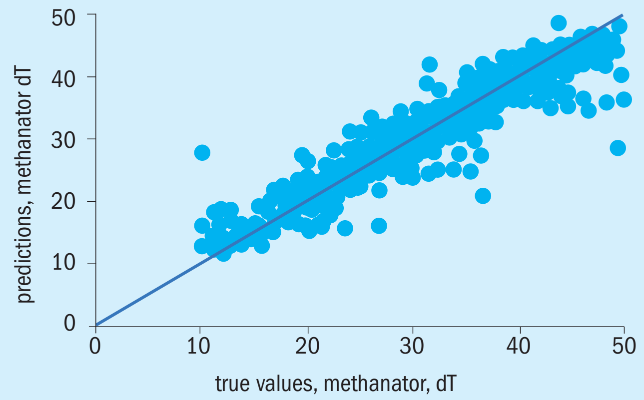
where the final model g is the sum of simple base models fi. Here, each base classifier is a simple decision tree.

Operational data correlations

We were able to get 30,000 readings for each parameter of the CO$_2$ removal system. However, we got only 38 readings for the gas composition of the absorber inlet process gas, and there is no flow meter for this inlet gas. This means we cannot directly compute the amount of CO$_2$ to be removed (absorber inlet flow x % CO$_2$ in the inlet gas). This quantity is one the most important parameters in evaluating the CO$_2$ removal system performance.

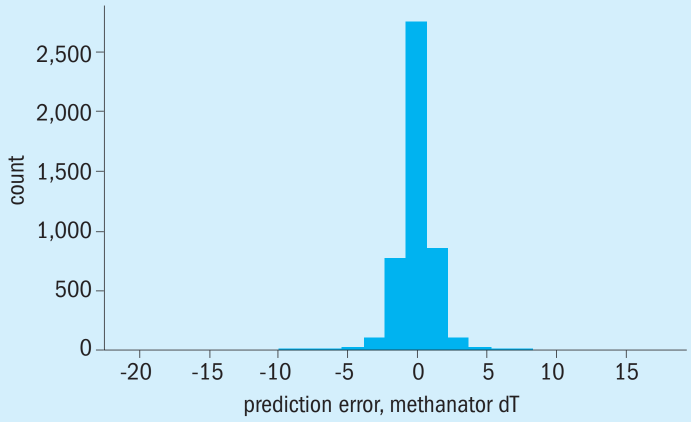
We therefore calculated this load in an indirect way: we used the feed natural gas flow to the primary reformer and calculated the carbon amount from natural gas analysis. Each carbon atom in the feed gas will create one molecule of CO$_2$ in the absorber inlet, minus the small amount of CO exiting the LTS. This can be a powerful tool to determine the CO$_2$ load into the absorber. However, the gas analysis may not be available on an hourly basis, so this can be assumed to be the same between monthly analyses without introducing too much error. Furthermore, if the calorific value of the natural gas is available, this can be used in place of the gas composition.

Fig. 5: **Accuracy of prediction (for methanator temperature differential)**



Source: FITIRI

Fig. 6: **Prediction error (for methanator temperature differential)**



Source: FITIRI

LTS outlet CO concentration generally tends to stay the same and changes gradually with LTS catalyst activity. If you have an LTS CO slip online analyser, that would be ideal, but even if you only have this analysis done in the lab once per month or so, it will still be acceptable; this small CO concentration does not introduce much error in the total CO_2 load. We already have the feed gas flow data for every two hours and the LTS outlet analysis for CO.

The great thing about analytics is that we need to only identify the critical parameters, or their equivalent parameters and the system will correlate and find the relation. The corresponding correlation and the prediction will be as accurate as inputting the original parameter. We do not need to convert the fed gas analysis into carbon numbers and subtract the LTS CO etc, we just feed the gas analysis, feed gas flow and LTS outlet CO concentration and the model will do the rest.

In the same way, the absorber outlet CO_2 slip is also critical. Absorber outlet CO_2 (CO_2 slip) is the main objective parameter of a CO_2 removal system. Most plants have online analysers for continuous measurement. If it is not measured on a continuous basis, we can also use methanator delta T, since it will be correlated to CO_2 slip for a known LTS CO slip. The methanator delta T is the sum of CO that is methanated to CH_4 and CO_2 that is methanted to CH_4. Both these reactions are exothermic. The predictability of the rise in temperature is very accurate as both reactions are using dry gases and the gases involved in heat rise calculation are mainly ideal gases such as H_2 and N_2. We can also see this in the COORS model output showing one on one correlation to CO_2 slip.

After removing high correlation variables, we got a good set of highly significant variables.

Skewness

A data is called skewed when a curve appears distorted or skewed either to the left or to the right, in a statistical distribution. In a normal distribution, the graph appears symmetrical – meaning the number of values on the left side of the mean is same as to the right side (Figure 4). Our skewness result was as shown in Table 1.

Data normalisation

During start up and shutdowns the delta T of the methanator tends to be negative or very small. Since these are not an accurate representation of the performance of the absorber and stripper and the system as a whole, dT values below 10 degrees were removed from the dataset. Also, values above 65 degrees were removed. This helped to significantly improve the accuracy of the model.

Similarly, natural gas heating value less than 37, stripper exit temperatures below 300°F, stripper inlet temperatures less than 214°F and more than 360°F were removed. This helped to create a dataset with minimal skewness and outliers.

Standard scaling was performed on the data such that its distribution will have a mean value of 0 and standard deviation of 1. Given the distribution of the data, each value in the dataset will have the sample mean value subtracted, and then divided by the standard deviation of the whole dataset.

In machine learning models, we use a portion of the data to build the model and the rest of the data to test the model. In COORS we used 75% of the data for training the model and 25% for testing the model.

Results and predictions

The model yielded an accuracy of 96.85 % and a mean absolute error of 0.92 degrees (Figure 5). Our prediction error provided a nice bell curve around 0 (Figure 6).

A random set of data for 15 readings were selected for prediction with the machine learning model we have built with the data provided to us. The results for the sample data gave very satisfactory results, with a mean percentage error of 1.8%.

Multiclass models also generate an independent feature importance vector for each class. Each class's feature importance vector demonstrates which features made a class more likely or less likely. The results from this study showed that aMDEA circulation was the most important variable, with aMDEA stripper pressure in D601, gas temperature exiting D604 and aMDEA temperature exiting E602a also scoring highly.

Conclusions

We were able to predict the methanator delta T within the range of +/- 0.92°F. Since this is directly related to the amount of carbon dioxide coming out of the removal system, we were able to accurately identify the parameters that affect the amount of CO_2 and also their impact on the system efficiency. We identified aMDEA circulation as the most critical parameter that the plant operations should keep in mind to bring down the CO_2 levels in the methanator. These results were achieved through data analytics and machine learning approach rather than though traditional calculations or simulations. ■

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Sustainable nitric acid and ammonium nitrate production

By utilising state-of-the-art technologies, nitric acid and ammonium nitrate producers are able to reduce the environmental impact of their production plants and make a key contribution to climate protection.

Nitric acid plants are a significant producer of nitrogen oxides (NOx) and nitrous oxide (N_2O) emissions that have a radical impact on the environment, contributing to acid rain, the greenhouse gas (GHG) effect and ozone layer depletion. In the production of nitric acid, the main combustion product during the oxidation of ammonia over platinum gauzes is nitric oxide (NO), that is further oxidised to nitrogen dioxide (NO_2), which reacts with water in the absorber to form nitric acid.

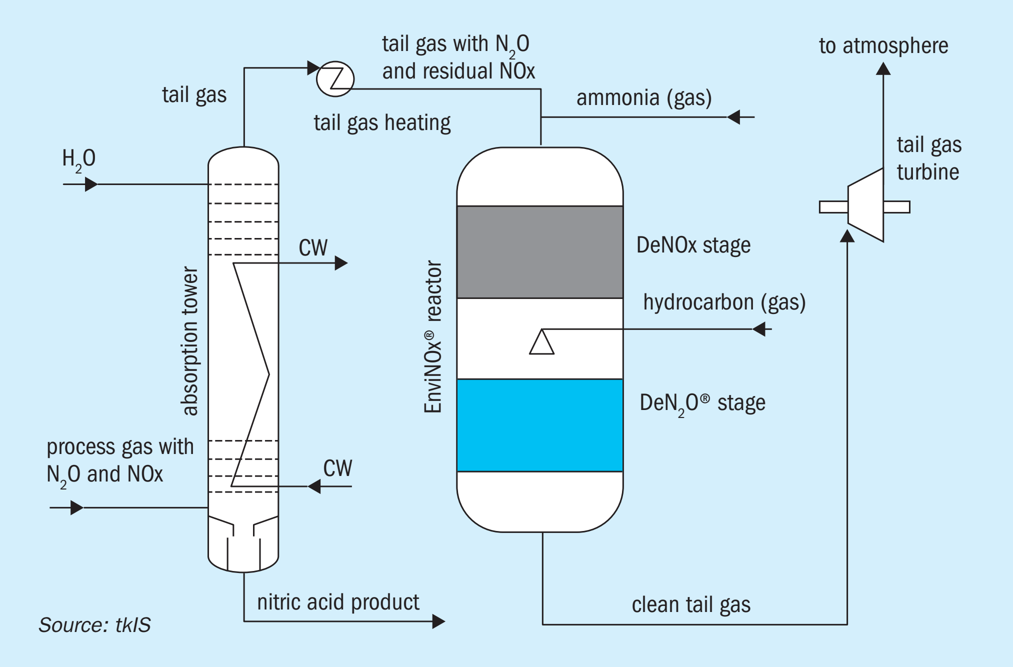
Unfortunately, the process also generates unwanted nitrous oxide (N_2O) which passes unchanged through the plant and enters the atmosphere in the plant's tail gas. Some residual NOx, not turned into nitric acid, is also emitted with the N_2O. While limits on NOx emissions have long been in force because of concerns about acid rain and smog, N_2O emissions have not been subject to effective restrictions until fairly recently, but are now recognised as the powerful climate killer it truly is.

Nitrous oxide (N_2O) is a potent greenhouse gas, 265 times worse than carbon dioxide, due to its longevity in the earth's atmosphere and its infrared radiation absorption properties. Emissions of N_2O have made nitric acid plants one of the world's largest sources of greenhouse gas emissions amongst industrial manufacturing facilities.

Emission rules and limits adopted by different countries are quite varied: NOx emissions are normally regulated in all countries worldwide, but emission limits in developing countries can be as much as 100 times higher than in stricter jurisdictions. As regards N_2O, most countries do not impose any emission limits. Only about a quarter of the nitric acid plants worldwide enforce a programme to reduce nitrous oxide emissions. Many of these nitric acid plants are located in Europe, where emissions trading supports plants to reduce their emissions.

N_2O/NOx abatement technologies are available to solve both emission problems.

Fig. 1: **Typical arrangement of an EnviNOx® NOx and N_2O abatement system for nitric acid plants**



Source: tkIS

thyssenkrupp EnviNOx® abatement process

The thyssenkrupp EnviNOx® abatement process provides an effective solution to reduce both NOx and N_2O emissions. It is an end-of-pipe technology because it is installed in the waste gas stream of the plant and thus entails no risk of product contamination, production loss or fouling of equipment (Fig. 1). Its multiple installations in nitric acid plants worldwide show N_2O removal rates of 99% and above, and elimination of NOx down to nearly zero ppm. It is also a highly practical solution as abatement of both pollutants can be combined in a single reactor vessel.

Operators can gain advantage from installing an EnviNOx® system as a greenhouse gas emission reduction project under any emission trading scheme.

Using thyssenkrupp's wealth of experience and expertise the solutions can be optimised for particular process conditions

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and temperature ranges. With this proven technology to remove harmful greenhouse gases, thyssenkrupp is helping nitric acid plant operators make a key contribution to climate protection.

Use of green ammonia

In addition to the use of an abatement technology, further reduction of greenhouse gas emissions can be achieved by using green ammonia. Using green ammonia for nitric acid production, results in a much smaller carbon footprint. By partly replacing the process air in the nitric acid plant by the oxygen which is an otherwise unused by-product of the water electrolysis, or by adding this oxygen stream the plant can be significantly increased in capacity and efficiency.

Nowadays the syngas-based industry is under increased pressure, driven by low product prices on the one hand and higher environmental standards on the other hand. Producers are faced with increasing CO_2 quotas or politically driven greenhouse gas reduction programs, which have caused several plant shutdowns in established markets such as China. The key objectives for the syngas industry are obvious – further increase production to serve market requirements driven by a growing world population and increasing wealth, but find process solutions with the lowest carbon footprint. The solution to stop climate change is the reduction of greenhouse gas emissions.

In order to achieve these ambitious long-term goals, different measures can be taken such as improvements in energy efficiency, an increased share of renewable energy, carbon capture and increased carbon utilisation.

Sustainability and energy efficiency are two of the key drivers for thyssenkrupp Industrial Solutions AG (tkIS). tkIS offers key elements which are important for more sustainable production processes with the target to reduce GHG emissions:

- Green hydrogen production based on alkaline water electrolysis technology provided by thyssenkrupp's Uhde Chlorine Engineers (tk-UCE) being a Joint Venture of tkIS and Industrie De Nora either as standalone solution or as revamp option.
- Application of this to ammonia, methanol or other hydrogen-based production processes like synthetic natural gas (SNG, by methanation) and Fischer-Tropsch synthesis.
- Catalyst-based N_2O emission reduction in nitric acid plants by EnviNOx® technology.

Fig. 2: JSC Navoiyazot nitric acid plant.

Casale nitric acid and ammonium nitrate plants

Casale is able to provide the full production line from nitric acid (HNO_3) to ammonium nitrate solution (ANS) in compliance with the most stringent emission and liquid waste regulations. The following Uzbek case study provides an example that shows that emission reduction programmes are being progressively applied even in countries where no local emissions limits on N_2O are imposed.

Uzbek nitric acid case study

In 2020, Casale completed an EPC project for a new 1,500 t/d nitric acid plant based on the dual pressure technology for JSC Navoiyazot in Uzbekistan (Fig. 2). Casale's scope of work extended beyond the nitric acid production unit to include all the required utilities such as the start-up boiler, nitric acid storage tanks, cooling water facilities, demi water unit and the water treatment plant.

Casale provided JSC Navoiyazot with an innovative combination of know-how and technological solutions for the 1,500 t/d new nitric acid plant (based on the Casale NA2000™ process scheme), as well as an effective emission abatement system.

The JSC Navoiyazot nitric acid plant has been designed to reduce emissions in line with limits imposed by the client: NOx <50 ppmv, NH_3 <5 ppmv, N_2O <50 ppmv. These limits are more severe than the Uzbek limit requirements. The actual reductions achieved exceeded by far any expectations as the abatement system was able to achieve N_2O and NOx slip lower than 10 ppmv and 25 ppmv respectively.

The JSC Navoiyazot catalytic system consists of the combined integration of secondary and tertiary abatement. Different catalyst arrangements can be provided depending on client requirements and emissions limits.

The burner basket design in JSC Navoiyazot is made with the provision to accommodate enough deN_2O secondary catalyst to ensure substantial N_2O abatement underneath the gauzes. The Casale tertiary catalyst, named GPRN20, is then installed directly upstream of the tail gas expander, where it operates at 430°C to ensure the decomposition of both the residual N_2O slipping from the secondary catalyst and NOx residue from the absorber (Fig. 3).

Besides catalyst, no specific reactant is required for the DeN_2O reaction since N_2O dissociation is promoted by temperature in the presence of the NOx that is naturally present in the tail gas, according to the following reaction:

$$2N_2O \rightarrow 2N_2 + O_2$$

NOx is decomposed by ammonia gas that is mixed with the tail gas upstream of the catalyst bed and reacts over catalyst according to the following SCR reactions:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

Special operating procedures and control loops are implemented in the Uzbek plant to achieve the emissions targets and ensure the accurate feeding of ammonia

Fig. 3: Loading of tertiary catalyst.

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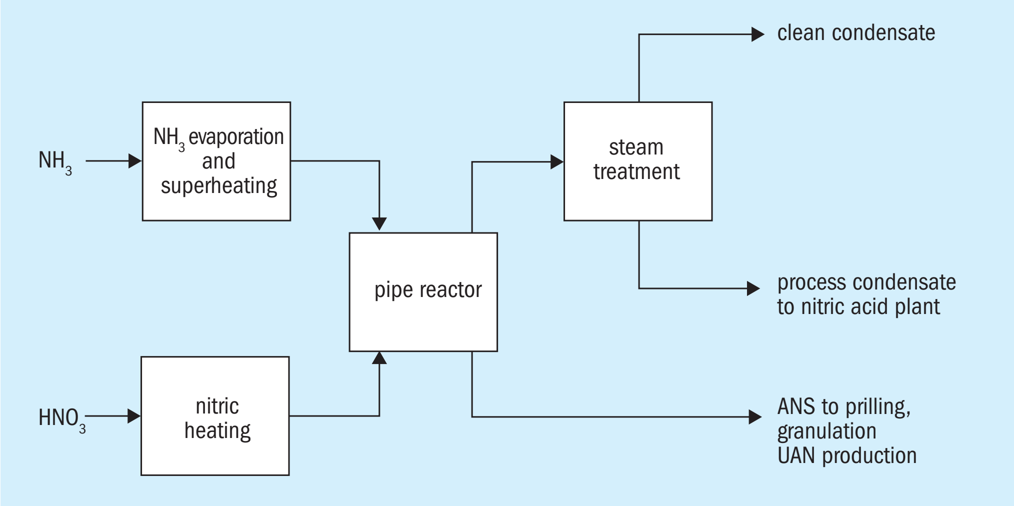
Fig. 4: **Casale ANS process**



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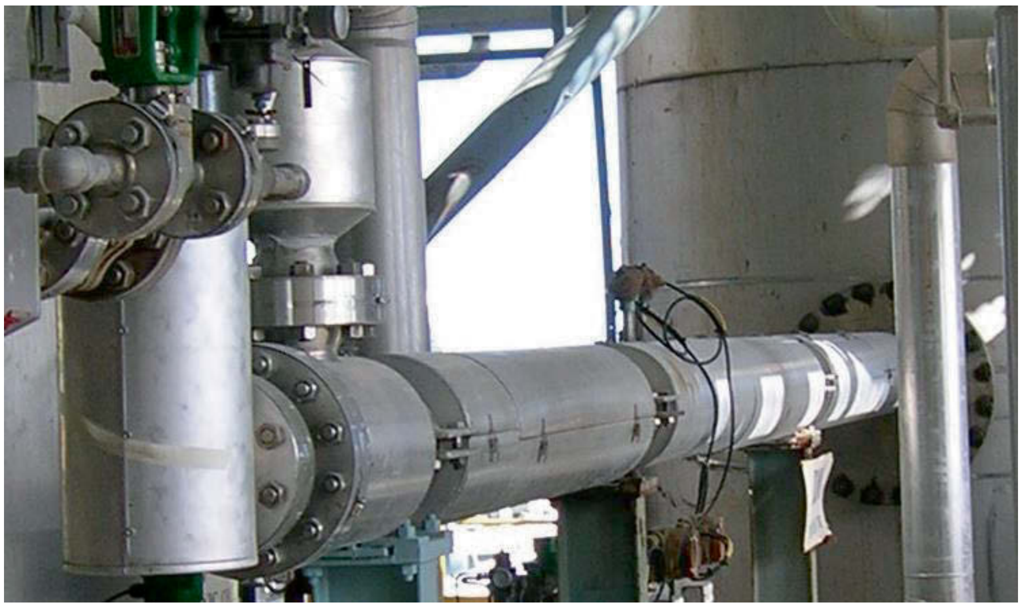
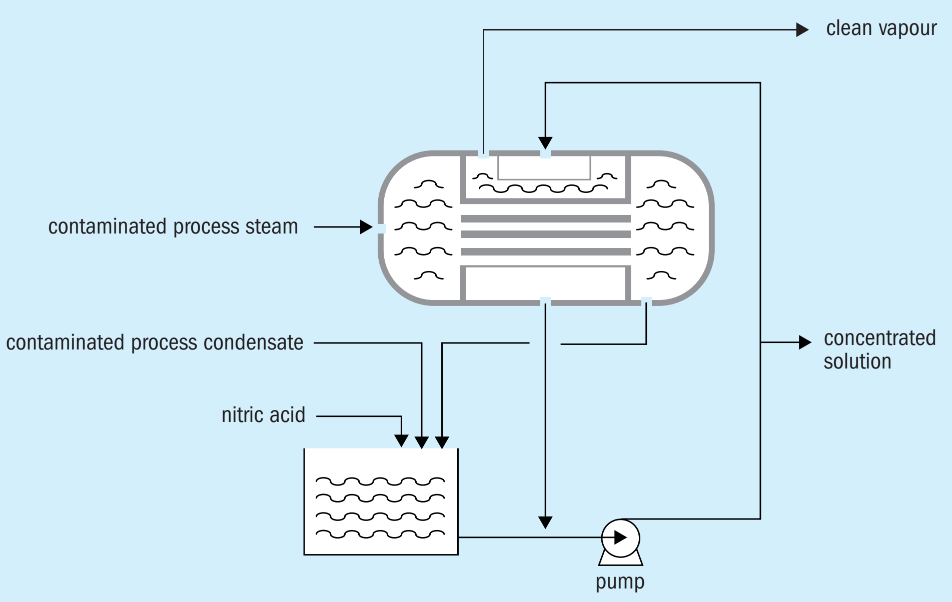


PHOTO: CASALE

Fig. 5: Casale pipe reactor.

Fig. 6: **Casale Purifier Exchanger**



Source: Casale

to the tertiary catalyst to avoid ammonia slip or overdosing. Ammonia slippage is minimised (concentration below 2 ppmv is achieved) to ensure that ammonium nitrate is not formed during start-up preventing unsafe operations. In addition, NOx concentration in the tail gas is kept below the limit of stack plume visibility during normal operation as well as during start-up.

The pressure drop of the entire tertiary abatement system has been limited to less than 120 mbar ensuring a proper gas distribution across the catalyst thanks to the optimised design.

The proposed tertiary catalyst GPRN20 is industrially proven in a large variety of similar application and worldwide successfully applied with a record of long and trouble-free performances.

Casale has long experience in the design of catalytic reactors, mainly in ammonia synthesis, that has also contributed to its achievements in nitric acid applications:

- maximum abatement efficiencies with low emission levels;
- optimal gas distribution within the catalyst bed to ensure longer service life;
- reduced pressure drops over the reactor and minimized compressor energy loss.

Feedback after several years of continuous operation from another nitric acid plant commissioned by Casale and adopting the same GPRN20 as tertiary catalyst was extremely positive, having recorded almost 98.5% N_2O conversion and NOx emissions lower than 10 ppmv.

Thanks to the remarkably high N_2O conversion, the tail gas treatment system provided by Casale was potentially able to ensure a shorter return of investment due to the higher carbon trading payback.

Casale ammonium nitrate solution process

Casale's know how in designing ammonium nitrate plants dates back to the early 1980s, when the first ammonium nitrate plant was started-up in France by Grande Paroisse. Since then, Casale has designed more than 40 ammonium nitrate units with capacities ranging from 250 to 2,000 t/d.

Ammonium nitrate solution (ANS) is produced by the reaction of ammonia with nitric acid, which is strongly exothermic:

$$HNO_3 + NH_3 \rightarrow NH_4NO_3$$

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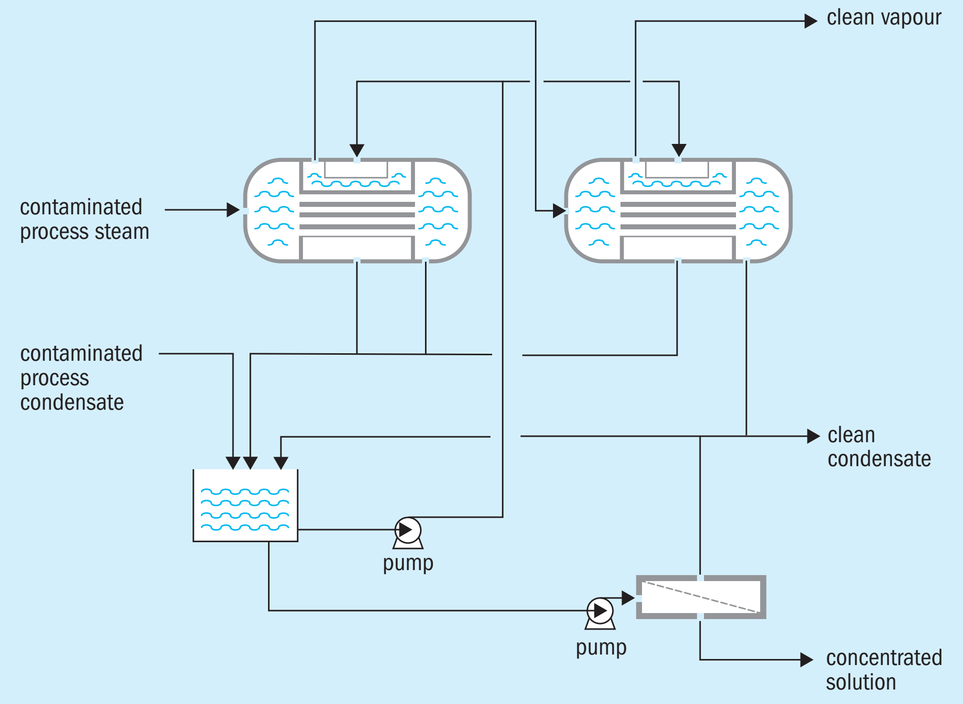
Fig. 7: **Two Purifier Exchangers in series**



Source: Casale

The main goal is to optimise the process to make the best use of the released energy and to obtain the highest ANS concentration possible. This is the base concept for the pipe reactor (Fig. 4), the distinctive Casale ammonium nitrate solution technology named AN2000™, where neutralisation operates at nearly atmospheric pressure and maximises the use of the generated heat to achieve a high ANS concentration.

The heart of the process is the pipe reactor, where raw materials are efficiently mixed and react to produce ANS (Fig. 5). The formation of ammonium nitrate occurs almost instantaneously, releasing a significant amount of heat that is used to partially vaporise the water fed with the nitric acid. The resulting ANS product flashes into a separator, where ANS is collected at the bottom and the vaporised water is released as process steam.

The AN2000™ pipe reactor design has undergone a series of improvements to accommodate a large range of operational requirements, while maintaining the simplicity and easy maintenance as well as the following advantages.

Safety

Safety is of paramount importance in ammonium nitrate solution production. In a pipe reactor, raw materials are mixed in an extremely small space, eliminating the need for large reaction volumes which would exacerbate the consequences of an uncontrolled decomposition. For example, the reaction volume required by a 2,000 t/d ANS plant is 0.2 m^3 for the pipe reactor versus a threshold value of 20 m^3 for a conventional neutraliser process.

Low capex

The process is extremely simple, thus requiring relatively few items of equipment as well as a limited footprint area. In addition, because it is an atmospheric-pressure process, it has the major benefit of a minimised capital cost.

Start-up and shutdown

Thanks to the limited reaction zone volume, the plant can be started up to from scratch to nominal capacity in less than 30 minutes. Shutdown is almost immediate once the raw material feed valves are closed.

Condensate purification

The AN2000™ pipe reactor process is intrinsically designed to have a low contaminated liquid stream (< 30 ppmw) but can be easily upgraded to a no waste effluent discharge plant.

The AN2000™ process and effluent treatment is relatively simple: steam released from the pipe reactor separator contains traces of ammonia, nitric acid, and ammonium nitrate, which are removed in a venturi scrubber, and a cyclonic column. Process steam can be further purified to the most stringent limits without requiring any external energy stream using the Casale Purifier Exchanger.

This Purifier Exchanger re-evaporates part of the process condensate in the shell side through the condensation of the process steam from the cyclonic column in the tube side (Fig. 6).

This simple operating step makes it possible to concentrate the contaminants in a single stream while the clean stream is purified up to a level (<30 ppmw) allowing it to be reused as DW or cooling water make-up within the fertilizer complex.

The concentrated condensate stream is then partially reused internally in the cyclonic column and the resulting amount is recycled to the absorption tower of the nitric acid unit. In this way it is possible to prevent environmental impact from the ammonium nitrate solution plant.

The typical mass ratio between the clean and concentrate condensates is 2:1 respectively, ensuring a substantial reduction of the waste liquid, resulting in more economic management of the liquid effluents.

In some cases, this latest option may not be viable in the client complex set-up, e.g. when the nitric acid plant is not available at the site or the nitric acid produced has a dual use as raw material for fertilizers and chemicals preventing the recycle of the concentrated condensate. To overcome such issues, the purification capacity can be doubled by installing two Purifier Exchangers in series (Fig. 7) to boost the clean steam generation, additionally combined with a reverse osmosis package to further improve recovery of the concentrated condensate stream.

In this way, the concentrate condensate can be reduced to an amount suitable for internal reuse in the ANS scrubbing and cyclonic unit, making the entire ANS plant virtually a no liquid effluent plant.

The AN2000™ pipe reactor process is also intrinsically designed to have no gaseous emissions since the steam generated is fully condensed either as heating steam for the raw materials or in the Casale Purifier and later in a cooling water condenser, with substantially no vapour streams released to the atmosphere. ■

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

Waste to methanol

Johnson Matthey and MyRechemical have formed an alliance to commercially develop waste to methanol technology. In this article, two different approaches to waste disposal and chemical production are analysed: a post combustion scenario with waste incineration and hydrogenation of the CO_2 recovered from flue gas to produce methanol, and a precombustion approach with waste gasification followed by conversion of synthesis gas into methanol.

Reduction of greenhouse gas (GHG) emissions in the industrial sector to mitigate climate change is a major challenge facing the global industrial and scientific community. Efforts and action in this community are underway through transformation of carbon-based fossil energy to a zero carbon footprint, the so-called energy transition.

This approach is re-shaping energy production by exploring more sustainable routes based on increased share of renewable energy, less intensive use of fossil resource, introduction of the circular economy concept, application of carbon capture in conventional process as well as measures aimed at increasing process efficiency.

A more sustainable use of resources has also been supported in the last few years by the European Commission (EC) through a policy stating that waste management should be improved and transformed into sustainable material management with a view to promoting the principles of the circular economy, enhancing the use of renewable energy, and providing new economic opportunities (EU Directive, 2018)[1]. In this regard many accomplishments have already been achieved, as demonstrated by several ongoing projects aimed at valorisation of non-conventional feedstock such as solid, gaseous, or liquid waste source.

Arcelor Mittal completed construction of the first commercial plant in Europe aimed at re-use of the waste gases emitted from steelmaking for ethanol production. This plant will produce 80,000 million litres per year of ethanol[2].

Fulcrum has developed a commercial scale project to enable the conversion of municipal solid waste into low-carbon renewable transportation fuels, including jet fuel and diesel. This process combines gasification technology with Johnson Matthey (JM) and British Petroleum's (BP) Fischer-Tropsch (FT) technology to produce renewable transportation fuels. Before feeding the system, municipal solid waste is pretreated to remove recyclable products and other material not suitable for processing. The resulting syngas then enters the FT process followed by upgrading step to a transportation fuel[3].

The above-mentioned examples demonstrate how the concept of a circular economy is already in motion and is currently reshaping many industries with the aim of waste valorisation.

Focusing on municipal solid waste (MSW), the current processes for residue plastics and the dry fraction of MSW, commonly known as refuse derived fuel (RDF), are mainly based on thermal valorisation for power and heat production followed by disposal in landfill. Although the efficiency of modern incinerators has increased, incineration does not recover any carbon or hydrogen, instead these components are fully oxidised to CO_2 and water and discharged in diluted form into the environment through flue gas. Because of the resulting high GHG emissions, waste disposal is under the spotlight and carbon capture solutions are being investigated to mitigate the emissions from incinerators, to provide a more sustainable approach.

Huttenhuis et al.[4] described an application of carbon capture and utilisation (CCU) at Twente incineration plant, where carbon dioxide (CO_2) captured from flue gas is used for mineralisation. The CO_2 is converted, through sodium carbonate, directly into sodium bicarbonate (SBC). The resulting SBC slurry is directly utilised at the waste to energy (WTE) plant to purify the flue gas stream before it is released to atmosphere. The new SBC plant produces 8,000 tonnes of SBC annually by capturing 2,000 tonnes per year of CO_2.

To the authors knowledge, besides Twente, there are only three other WTE plants with integrated carbon capture, in Norway (Klemetsrud CHP), Japan (Saga City) and the Netherlands (AVR)[5]. In Japan, an alkaline aqueous amine technology for CO_2 capture has been utilised on the incinerator and the captured CO_2 is used for local crop cultivation and algae culture formation. This waste incineration plant captures 10 t/d of carbon dioxide.

The AVR plant was designed to capture and liquefy 60,000 t/a of CO_2 to be used mainly for the greenhouse agriculture industry.

The waste incineration plant at Kelmetsrud in Oslo is integrated with a carbon capture system having a capacity of around 400,000 t/a of CO_2. Unlike the other mentioned applications, the plant in Klemetsrud will be a carbon capture and sequestration (CCS) facility, where it is foreseen that CO_2 will be permanently stored in the North Sea.

The CCS raises some doubts about its real effectiveness, due to the availability of geological storage sites, as well as the unknown behaviour of the CO_2 when stored in these sites[6]. CO_2 utilisation has also been explored as a valid alternative to carbon storage, for example, looking at the direct application of CO_2 for food preservation, beverage carbonation, fire extinguishers, supercritical extraction, and dry ice production. All these applications account for only a fraction of the potential CO_2 volume resulting from the wide application of the CCU concept. The reuse of captured carbon for chemicals production would therefore expand the application of CO_2 utilisation application.

The main drawback of CO_2 capture from flue gases is the resulting energy penalty of this approach. As a result, the efficiency of the WTE plant once integrated with CO_2 capture drops by 8-12%[7].

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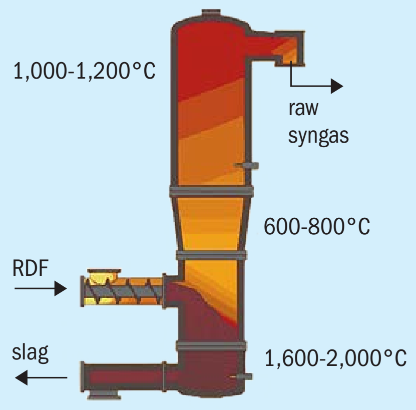
Table 1: **Typical elementary composition of PW and RDF and relevant LHV values**

Component	RDF	PW
Wet basis		
C, wt-%	33-38	47-61
H, wt-%	4-5	5-7
O, wt-%	16-18	14-20
N, wt-%	0.2-1.0	0.2-0.5
S, wt-%	0.02-0.15	0.02-0.3
Cl, wt-%	0.8-1.5	0.8-1.5
Moisture, wt-%	17-21	5-9
Inert, wt-%	17-25	7-20
LHVwet, MJ/kg	14-16	21-24

Source: MyRechemical

Fig. 1: **High temperature gasification reactor**



Source: MyRechemical

A different, less energy intensive approach for carbon capture from waste disposal is a precombustion scenario using waste gasification. Conversion of waste into a syngas, which is different from a flue gas stream, allows the efficient conversion of hydrogen (H_2), carbon monoxide (CO) and CO_2 directly into chemicals, therefore avoiding the energy intensive step of CO_2 capture.

Once purified, the syngas resulting from waste gasification, may be suitable for conversion into a wide range of chemicals like methanol, hydrogen, synthetic methane, ethanol, and their derivatives products[8-10].

Methanol is a good candidate for CCU as it has applications in both chemicals and fuels. As a fuel, methanol shows excellent combustion properties: although characterised by around half of the gasoline energy density, it has a higher octane number accounting for a more efficient combustion. Furthermore, there is a renewed interest towards sustainable methanol production, linked to the Renewable Energy Directive which promotes the use of advanced and/or carbon recycled fuel, such as fuel produced from non-fossil fuel feedstocks like waste or biomass.

RDF, the unsorted fraction of MSW, and the unrecyclable fraction of sorted plastic waste, in compliance with the so-called waste hierarchy, are all eligible for the waste-to-chemical processes due to their high calorific value.

An agreement is in place between Johnson Matthey and MyRechemical to commercially develop waste to methanol technology. MyRechemical is a company dedicated to waste to chemical solutions and is a subsidiary of NextChem, which is itself a subsidiary of Maire Tecnimont, and is a company specialising in energy transition technologies.

In this article, two different approaches to waste disposal and chemical production are analysed: a post combustion scenario with waste incineration and hydrogenation of the CO_2 recovered from flue gas, and a precombustion approach with waste gasification followed by conversion of synthesis gas into methanol.

Due to the characteristics of the feedstock, both approaches face a shortage of hydrogen, and therefore require external hydrogen addition via water electrolysis. The two cases are analysed from a technical and environmental viewpoint.

Waste as sustainable feedstock

One of the routes where the energy transition is moving is the investigation of sustainable feedstocks as a substitute for conventional fossil-based fuels. It is well known that a chemistry based on non-fossil fuel feedstock generally has higher feedstock and processing costs compared to conventional fossil fuel feedstocks. This aspect must be properly taken into account by policies put in place by government to effectively promote the energy transition. The increase of feedstock cost when moving from natural gas to a biobased feedstock can result in a cost increase of up to 60 times[11]. In this context, waste is a very interesting feedstock as it is available at a negative price, the so-called gate fee. Compared to natural gas, waste represents a more diverse feedstock with respect to its composition and requires a robust and reliable technology to manage the heterogeneous nature of the waste as well as the poisons to downstream catalysts. This will generally increase the capex intensity of the plant but in the end is predominantly offset by the gate fee. The latter may vary from one country to another as a direct consequence of the local disposal facility and depending on the type of waste (MSW, hazardous waste, RDF, etc)[12]. This therefore results in competitive production costs for selected chemicals[13].

MSW, RDF and plastic waste (PW), due to the high content of carbon and hydrogen, may be considered an alternative and sustainable feedstock to be used as a substitute for conventional fossil fuels[14]. Typical compositions for the types of waste mentioned above are listed in Table 1. As shown by the elementary composition, carbon content may vary in the range 30-60 wt-%, while hydrogen may vary in the range 4-7 wt-%.

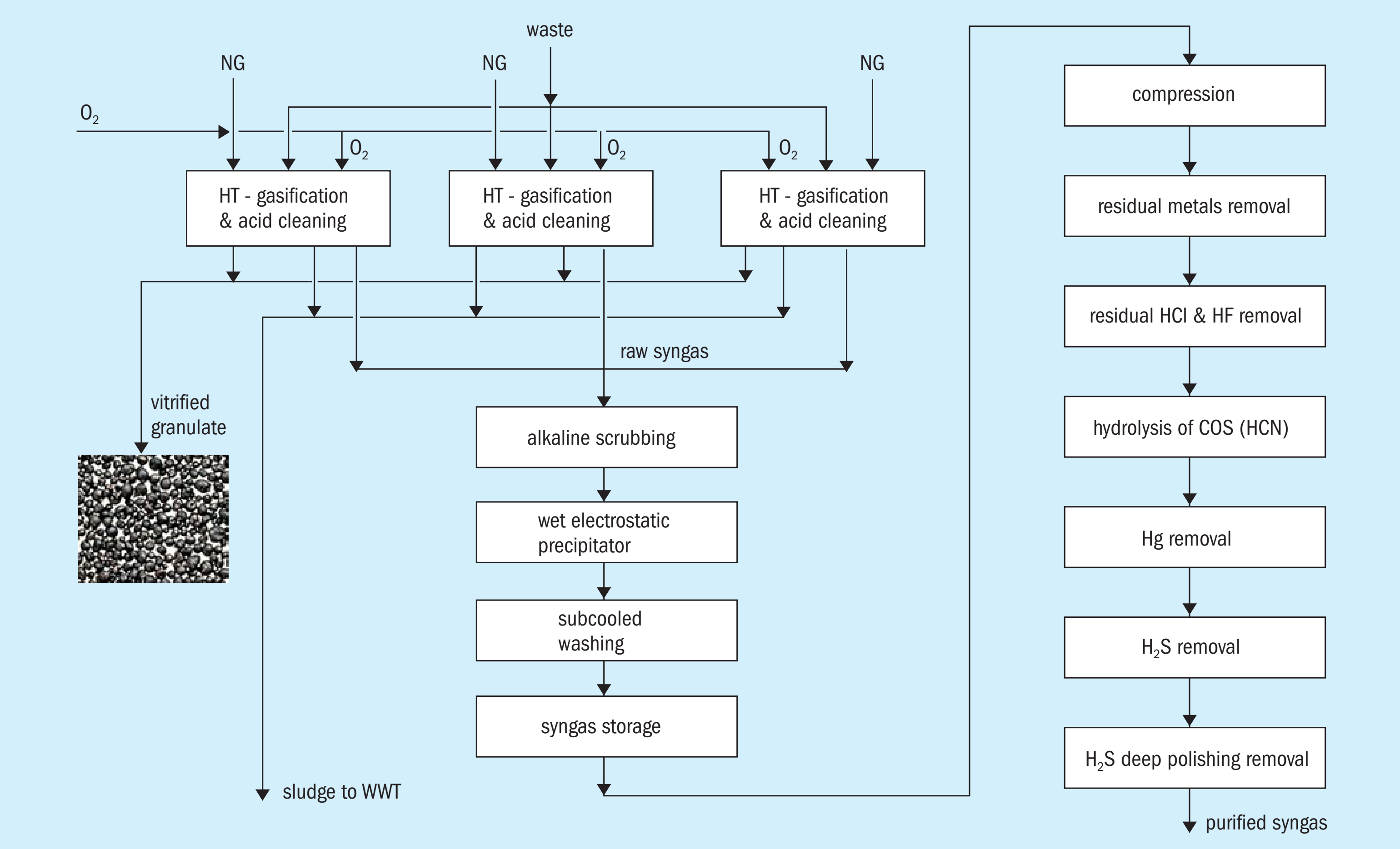
Looking at the huge availability of waste, about 2 billion tonnes/annum of waste is currently produced globally and 3.4 billion tonnes is foreseen by 2050 because of the expected increase of population and GDP[15]. It is therefore necessary to rethink waste as a resource rather than a problem.

Waste to chemical route

Direct carbon conversion through gasification

The proposed gasification technology allowing the conversion of waste into chemicals is based on a high temperature gasification process carried out under a pure oxygen environment. This is different from a thermo-valorisation technology based on a full oxidation path, and the partial oxidation reaction performed during gasification allows the conversion of feedstock into a syngas having a high content of H_2 and CO. The temperature profile along the reactor

Fig. 2: **Block scheme: Gasification and syngas purification**



Source: MyRechemical

is a key parameter for assuring good syngas quality. A schematic view of the gasifier reactor is shown in Fig. 1.

The gasifier reactor may be divided into three sections: the bottom melting zone (1,600°C), where exothermic reactions and the melting of inert compounds takes place; the intermediate gasification zone (600-800°C), where low oxygen-content promote partial oxidation reactions; the top stabilisation zone, where a further addition of auxiliary fuel and oxygen lead to an increase of temperature (1,100°C) ensuring tar degradation and full decomposition of organic molecules as well as inhibition of pollutant compounds such as dioxins and furans.

The above-described temperature profile is controlled through multiple injection points of oxygen and auxiliary fuel along the reactor. The temperature profile assures full conversion of feedstock into a gaseous and solid product: a high value syngas rich in H_2, CO and free of char, tar, dioxins, and furans is discharged from the top of reactor and an inert vitrified material is discharged from the bottom[16]. The high temperature in the melting zone allows the inert components of waste, minerals and metals to be discharged in a granulated and vitrified state, carbon free. Depending on local legislation, this material can be valorised into cement, ceramics, or used in the construction industry.

The syngas yield and relevant composition are mainly affected by the LHV value and C/O ratio: higher LHV results in higher syngas yields as well as higher content in terms of CO an H_2 and lower concentration of CO_2[17]. The syngas produced contains mainly CO, H_2, CO_2 and other minor components such as volatile metals and any particles carried over with the syngas, which require a dedicated pretreatment before being fed to the synthesis section.

Fig. 2 shows a block diagram of the gasification section, preliminary cleaning, and syngas purification section. The hot syngas exiting the gasifier is routed to an evaporative quench, where the temperature is quickly reduced to 85-90°C by direct injection of water. Such rapid cooling, although wasting the high temperature heat contained in the syngas, freezes the chemical composition achieved at high temperature, and avoids any undesired reactions during cooling. The resulting liquid-gas mixture exiting the quench is routed to a sedimentation tank. This unit allows the collection of a concentrated sludge at the bottom of the tank which is continuously removed from the system and sent to waste water treatment, while the clairified water is directly reused in the quencher. The sedimentation tank works under low pH conditions (pH 1.5-3) to promote the migration of volatile metals into the liquid phase, mainly as chlorides. The syngas exiting the sedimentation tank is routed to an acidic column that further promotes the removal of metals.

Syngas exiting from the acidic columns of each gasification train is collected and sent to a common section comprising an alkaline scrubbing column, wet electrostatic precipitators (WESP) and subcooling washing. Water streams collected from the bottom of the washing columns are sent to the wastewater treatment unit to remove any potential pollutants.

The gasifier operates at slightly above atmospheric pressure, which results in the pressure at the end of cleaning section being a few mbar. A compression section is therefore required to route the syngas to the downstream section. To balance the flow rate and pressure fluctuations resulting from the gasifier operation, a gas

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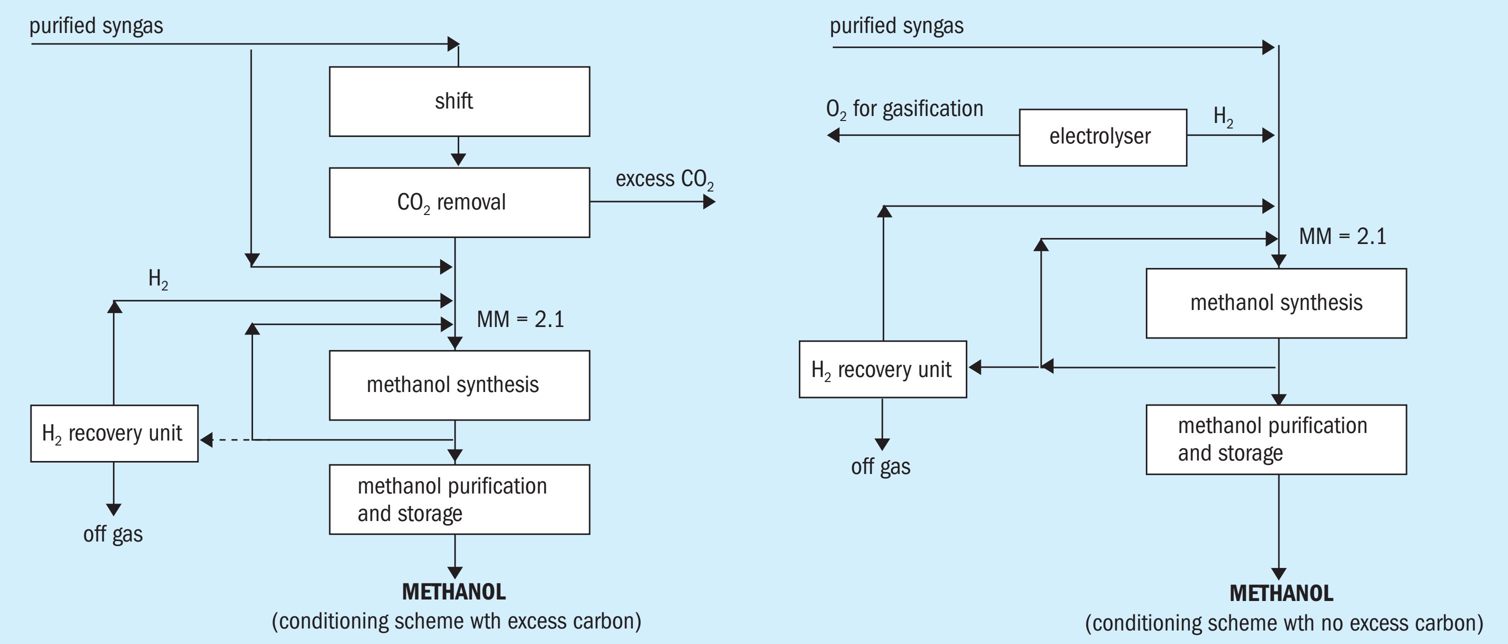
Fig. 3: **Block diagram of conditioning section: scheme with excess carbon and scheme with no excess carbon**



Source: MyRechemical

holder is installed before feeding the syngas to the compression step.

The cleaned syngas resulting from the multiple scrubbing stage still contains sulphur compounds, mainly in the form of H_2S and COS, together with residual chlorine, HCN, and traces of Hg. The compressed syngas is routed to the purification section involving the following step: removal of residual dust and metals, removal of HCl, hydrolysis of the COS and HCN, H_2S removal through an oxy-reduction system and a final polishing step based on zinc oxide absorbents to reduce sulphur content down to ppb as required by the catalyst required for the downstream methanol synthesis.

The high temperature regime and the use of a waste as feedstock, requires a dedicated maintenance program aimed at preventing damage to refractory materials and avoiding excessive fouling along the quench wall and sedimentation. To mitigate reduced syngas production due to the requirement for two shutdowns per year for each gasifier for maintenance, the plant is designed with multiple gasification trains operating in parallel so that when one gasification train is down for maintenance the other two lines are kept operating at maximum capacity to ensure continuous operation with minimum turndown.

Table 2: **Purified syngas composition resulting from waste gasification**

Component	Value
H_2, mol-%	39.1
CO, mol-%	42.6
CO_2, mol-%	12.8
H_2O, mol-%	0.4
N_2, mol-%	4.8
CH_4, mol-%	0.21
Arg, mol-%	-
H_2S, ppm	0.01
COS, ppm	0.1
HCN, ppm	0.1
HCl, ppm	0.1
Hg, ppm	-
PM, ppm	-

Source: MyRechemical

The purification procedure delivers a syngas suitable to be fed to a catalyst-based process like the synthesis of methanol. To optimise the syngas composition to produce methanol, an additional step is required to balance the ratios of H_2, CO and CO_2. This ratio is called the methanol module (MM). The MM is calculated using the following formula and has a target value of 2.1:

$$MM = \frac{(H_2 - CO_2)}{(CO + CO_2)} = 2.1$$

The latter is directly linked to the stoichiometry of methanol synthesis.

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad \Delta H^0_{298K} = -90.64 \text{ kJ/mol}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad \Delta H^0_{298K} = -49.47 \text{ kJ/mol}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta H^0_{298K} = -41.17 \text{ kJ/mol}$$

The purified syngas composition from waste gasification of a reference waste feedstock with a calorific value of 16 MJ/kg is listed in Table 2.

The resulting MM is in the order of 0.5, therefore the syngas requires shifting to increase the H_2 content, followed by a CO_2 removal step to increase the MM. This approach provides a syngas with the correct MM, with the excess carbon removed in the form of pure CO_2.

To avoid any CO_2 emission in situ, an external source of hydrogen may be added to balance the excess carbon. Looking at a pressurised electrolyser as source of hydrogen, further integration may be achieved by reusing oxygen coproduced by the electrolyser to sustain the gasification reaction as shown in Fig. 3. The design based on H_2 addition will allow for full utilisation of the carbon and hydrogen contained in the waste, excluding minor losses linked to off gas streams, for the replacement of the air separation unit (ASU) with the electrolyser and for the removal of the shift and CO_2 removal units.

Fig. 4 shows a block diagram of a waste to methanol plant based on the gasification of approx. 192,000 t/a of waste.

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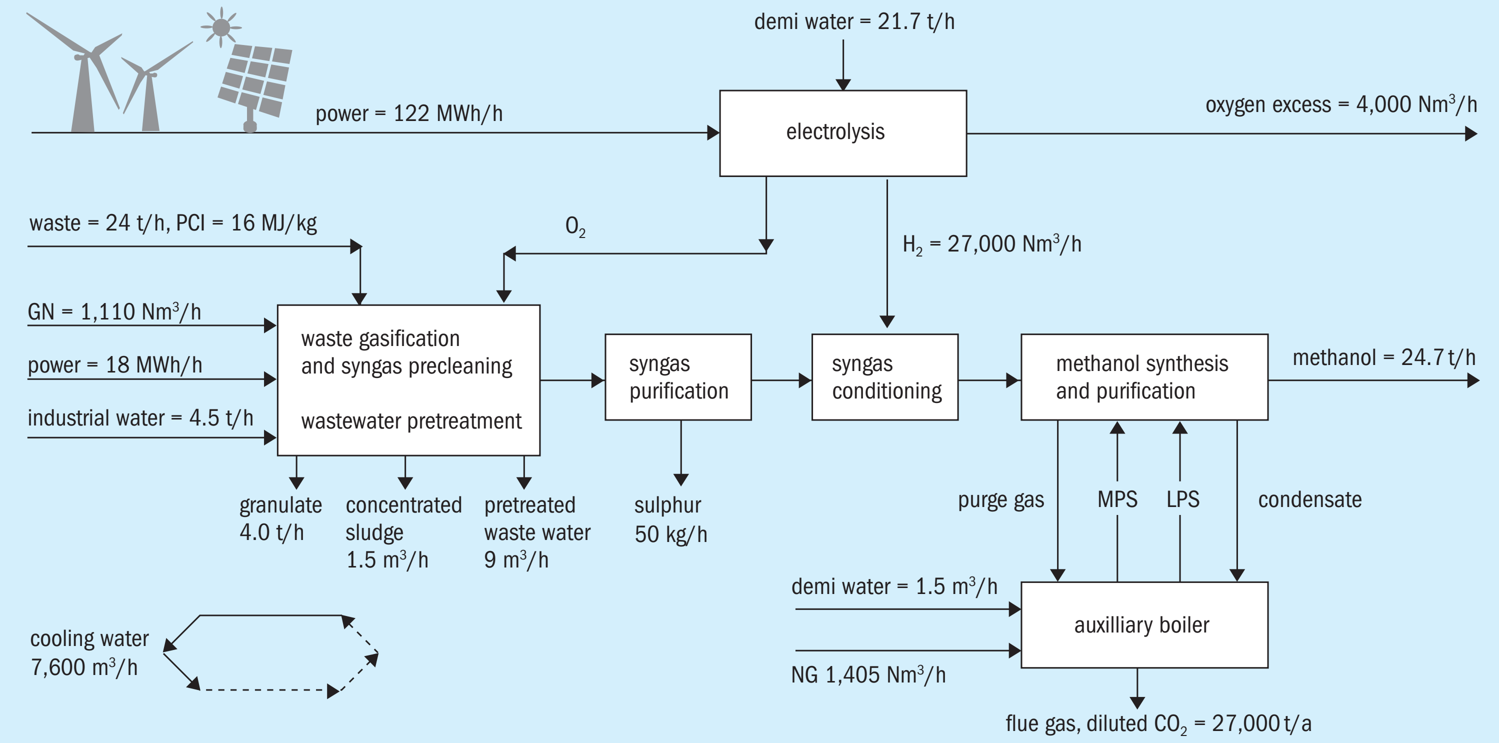
Fig. 4: **Block diagram of methanol production via waste gasification integrated with electrolysis**



Source: MyRechemical

The waste gasification route coupled with electrolysis designed to balance the shortage of hydrogen and to meet the oxygen requirement for gasification, allows the production of around 198,000 t/a of methanol. A supply of around 27,000 Nm³/h of hydrogen is needed to achieve a MM equal to 2.1. Such hydrogen capacity accounts for an oxygen production that fulfils the gasification requirements as well as providing an excess of around 5.8 t/h of oxygen, which can be sold as well used in the auxiliary boiler to increase combustion efficiency. A specific electrolysis consumption in the order of 4.5 kWh/Nm³ has been considered to also take into account the power for hydrogen compression.

This route accounts for a specific CO_2 production in the order of 0.136 ton CO_2/t waste with an external hydrogen requirement in the order of 1,093 Nm³ H_2/t waste. The overall power requirements are around 5.6 MWh/t methanol, where 88% of this power is utilised by the electrolyser.

Indirect carbon conversion through incineration and carbon capture

Applying the concept of CCU to waste incinerators means the conversion of captured CO_2 from flue gas into methanol by direct reaction with hydrogen produced from electrolysis.

The candidate processes for post-combustion CO_2 absorption must work under the following conditions:

- low CO_2 partial pressure, due to near atmospheric pressure of flue gas, with CO_2 concentrations in the order of 10-15 vol-%. Solvents active at low pressure are those with higher reaction energies which result in the highest regeneration energy;
- environment contains oxygen and contaminants such as NOx and SOx that can cause solvent degradation and corrosion due to the formation of degradation products;
- negligible pressure drop otherwise operating costs related to gas compression from atmospheric value would increase too much;
- flue gas is generally available at high temperature and must be cooled to minimise solvent degradation and vaporisation losses and to maintain good absorber efficiency.

An industrial technology referenced for CO_2 capture from flue gas has been selected for the following comparison. It is based on a proprietary, amine-based aqueous solution of a sterically hindered amine, blended with an amine-based rate promoter to enhance the kinetics of CO_2 absorption[18].

The CO_2 recovery plant consists of three main sections: the flue gas quencher, the absorber for CO_2 recovery and the stripper for solvent regeneration.

The flue gas is extracted by a blower from the offsite stack and fed to the flue gas water quencher, where it is cooled down to 45°C or lower. The lower flue gas temperature increases the efficiency of the exothermic CO_2 absorption reaction and minimises volatilisation and thermal degradation losses of the solvent.

The quencher must be designed not only to cool the flue gas but also to remove various impurities such as SOx, NOx and dust. Depending on the flue gas composition, a pre-treating section can be requested upstream of the quencher. The flue gas in the absorber comes into direct contact with the solvent where CO_2 is absorbed. To reduce amine loss the absorber column is equipped with a washing section.

The clean flue gas then moves up into the washing section of the absorber, where it is further cooled to maintain the water balance within the system and to remove vaporised solvent. The sweet flue gas is sent out to the atmosphere through a stack provided at the top of the CO_2 absorber.

The CO_2-rich solvent is heated recovering heat from the hot lean solvent coming from the bottom of the regenerator. The heated rich solvent is then introduced into the upper section of the stripper, where it comes into contact with stripping steam to be converted back into lean solvent. The stripping section is powered by low

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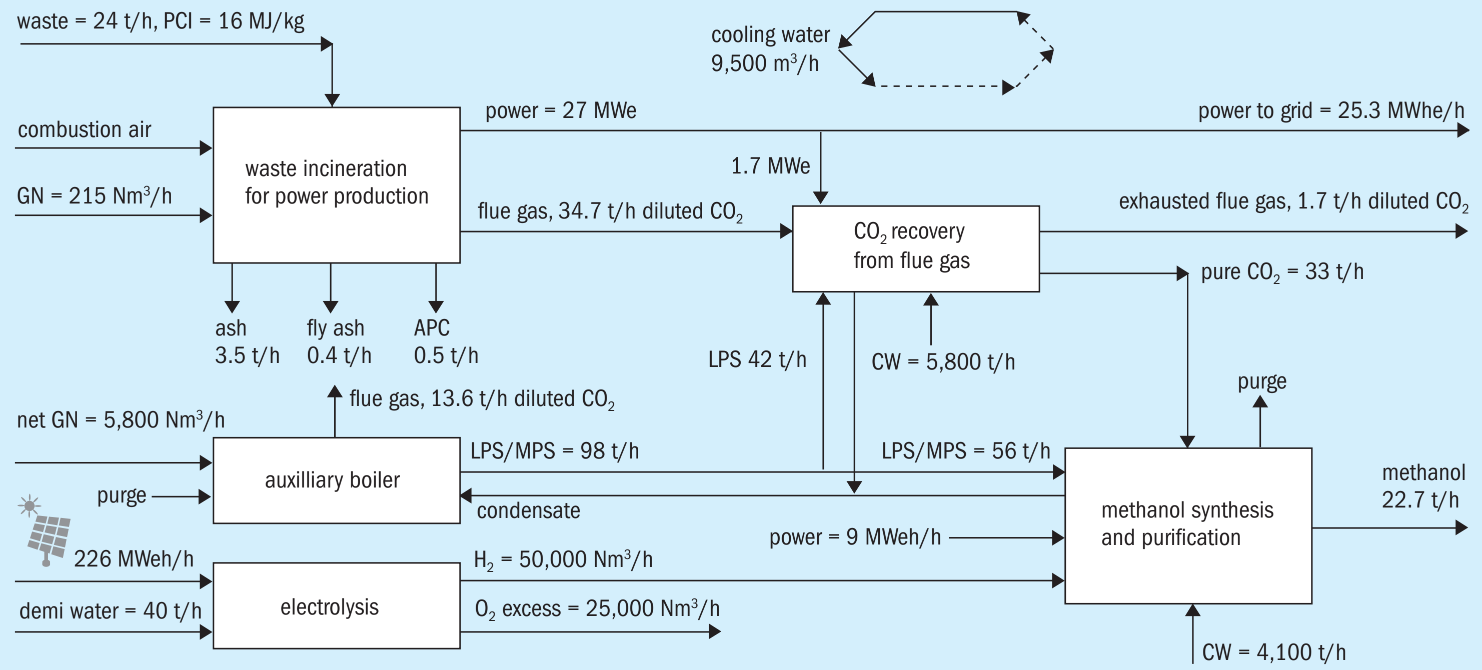
Fig. 5: **Block diagram of methanol production via waste incineration integrated with carbon capture and electrolysis**



Source: MyRechemical

Table 3: **Utilities consumption of CO_2 removal technology from flue gas**

Utilities		
Steam consumption (3.5 barg):	1.3-1.5	t/t CO_2 recovered
Cooling Water (DT=10°C):	170	t/t CO_2 recovered
Electricity:	35-40	kWh/ton CO_2 recovered

Source: MyRechemical

pressure steam (LPS). The recovered CO_2 is available at a slightly higher than atmospheric pressure thus requiring a compression to be converted into methanol.

The utilities consumption of the CO_2 removal package has been taken from literature as reported in Table 3[19].

Fig. 6 is a block diagram of methanol production based on waste incinerators combined with CO_2 recovery from flue gas and hydrogen supply via water electrolysis.

The incineration route integrated with CO_2 capture from flue gas and electrolysis to balance the hydrogen deficit, allows the production of around 182,000 t/a of methanol. A supply of around 50,000 Nm³/h of hydorogen is needed to achieve the stoichiometric conversion of CO_2.

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad \Delta H^0_{298K} = -49.47 \text{ kJ/mol}$$

Looking at the methanol section, the hydrogen requirement is higher in the incinerator than the waste-based gasification scheme due to the stoichiometry of direct CO_2 conversion into methanol, which wastes more hydrogen, since one mole of water is produced for every mole of methanol in the conversion of CO_2 to methanol, but that is not the case for the conversion of CO to methanol.

Such hydrogen capacity accounts for an oxygen productivity that in a conventional incinerator cannot be valorised otherwise moving from an air combustion towards an enriched air waste combustion or oxycombustion[20].

The incinerator route accounts for emissions of around 122,000 t/a, equivalent to 0.672 t CO_2/t waste with external hydrogen requirements in the order of 2,083 Nm³ H_2/t waste. Based on the assumption of an electrolysis consumption of around 4.5 kWh/Nm³ of H_2, the overall net power requirement, deducting the power directly produced from waste, results in around 9.96 MWh/t methanol.

Results and discussion

The two routes described coupling waste disposal and methanol synthesis result in different figures in terms of methanol production, utilities consumption and CO_2 emission. A direct comparison is shown in Table 4.

The first section of both schemes accounts for waste disposal. Due to the different operating conditions characterising the two technologies, the co-products/by-products from gasification and incineration will be different. Thanks to the high operating conditions adopted in the bottom of the gasifier, inert components are discharged as granulate, fully vitrified and carbon free. This product, in contrast to the ash collected in the incinerator, does not require additional pretreatment, it is a non-leachable material and can be considered a co-product instead of a by-product or waste. In both schemes, gas cleaning produces a waste rich in metals: a concentrated sludge in the gasification scheme and ash resulting from the air pollution controller (APC) in the incinerator.

Assuming that all required steam is produced from a dedicated boiler instead of diverting it from steam cycle associated to the incinerator, the incinerator scheme emits overall 3.9 times more t CO_2/t methanol than the gasification-based scheme.

Extending the analysis to indirect CO_2 emissions, for instance taking into account GHG emissions associated to power production, the incineration-based scheme accounts for a higher specific consumption that would imply higher emissions. Due to the high power consumption of electrolysis, the general hypothesis is to have a fully or highly decarbonised grid, otherwise any electrolysis application would dramatically alter the carbon footprint of the overall process.

Conclusion

In compliance with EC directives to promote the concept of waste as a resource, two different technologies to produce methanol from waste have been investigated and compared: a precombustion scenario, based on waste gasification and syngas conversion to methanol through electrolytic H_2 addition (Scheme A) and a post combustion scenario based on waste incineration, CO_2 capture from flue gas and hydrogenation to methanol through electrolytic H_2 (Scheme B).

From a technical point of view the gasification-based scheme accounts for a higher yield in terms of t MeOH/t waste with a lower requirement for hydrogen from electrolysis. External hydrogen supply is 85% higher in the incinerator than in the waste-based gasification scheme due to the stoichiometry of direct CO_2 conversion into methanol, requiring two moles of hydrogen compared to one for CO conversion.

The resulting methanol from both cases, according to the Renewable Energy Directive, would be recognised as a carbon recycled fuel produced from a waste feedstock. In proportion to the biogenic content of the waste, a fraction of the methanol produced may be eligible as an advanced biofuel, attracting a premium price. Moving from waste to biomass feedstock would further increase the market price of the resulting methanol.

Waste gasification provides an efficient route for the production of methanol from recycled carbon carbon, disposing of waste and with a negative carbon footprint. The integration with water electrolysis under the scenario of a fully decarbonised grid, maximises carbon conversion into methanol. ■

Table 4: **Methanol production scheme comparison: Gasification versus incineration**

	Scheme A Gasification Based	**Scheme B Incinerator Based**
Waste feedstock, t/a	192,000	192,000
Methanol production, t/a	197,600	181,600
CO_2 emission (through flue gas), t/a	27,000	122,000
Inert granulate, t/a	32,000	-
Ash/fly ash, t/a	-	31.200
APC, t/a	-	4.000
Concentrate sludge, t/a	12,000	-
O_2 to battery limits, M Nm³/a	32.5	200
Main utilities		
Power electrolysis, MWh/t MeOH	4.94	9.96
Overall net power, MWh/t MeOH	5.67	9.24 (*)
Natural gas, Nm³/t MeOH	102	265
Demi water, m³/t MeOH	0.94	1.76
Cooling water, m³/t MeOH	308	440

(*) Net value considering power delivered at battery limits.

Source: MyRechemical

References

1. Directive (EU) 2018/851 of the European parliament and of the council of 30 May 2018. Amending directive 2008/98/EC on waste. L 150/109. Official Journal of the European Union. 14.6.2018. Available at https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32018L0851&from=EN
2. Ancelor Mittal. Towards a circular economy breakthrough: Our partnership with LanzaTech. Available at:https://corporate.arcelormittal.com/news-and-media/our-stories/our-partnership-with-lanzatech.
3. Fulcrum BioEnergy (fulcrum-bioenergy.com). Accessed August 2021.
4. Huttenhuis P., Roeloffzen A., Versteeg G., The 8th Trondheim Conference on Capture, Transport and Storage CO_2 Capture and Reuse at a Waste Incinerator. Energy Procedia 86, 47-55 (2016).
5. Kearns D.T.: Waste-to-energy with CCS: A pathway to carbon-negative power generation. 2019 Perspective. Available at Waste-to-Energy-Perspective_October-2019-5.pdf (globalccsinstitute.com).
6. Carbon capture: A mixed picture | Waste Management World (waste-management-world.com). Accessed August 2021.
7. Wienchol P., Szle A., Ditaranto M.: Waste-to-energy technology integrated with carbon capture: Challenges and opportunities. Energy Volume 198, 1 May 2020, 117352.
8. Iaquaniello G., Salladini A.: A process and relating apparatus to make pure bio-methanol from a syngas originated from wastes gasification. WO 2018/134853 A1.
9. Iaquaniello G., Centi G., Salladini A, Palo E., Perathoner S.: Waste to chemicals for a circular economy. Chemistry A European Journal. DOI:10.1002/chem.201802903
10. WO 2017/134691. Antonetti E., Iaquaniello G., Salladini A.: A carbon neutral process and relating apparatus to produce urea from municipal or industrial wastes with zero emissions.
11. Bomgardner M.: Renewables firms focus on cost squeeze. Chemical Engineering News, Volume 94, Issue 18 (May 2, 2016).
12. European Commission. Best Available Techniques (BAT) Reference Document for Waste Incineration (2018).
13. Iaquaniello G., Centi G., Salladini A., Palo E., Perathoner S., Spadacini L.: Waste-to-methanol: Process and economics assessment. Bioresource Technology 243, 611-619 (2017).
14. Salladini A., Agostini E., Borgogna A., Iaquaniello G.: Chapter 11 – Waste feedstocks for sustainable chemicals and fuels. Catalysis, Green Chemistry and Sustainable Energy. Edited by Angelo Basile, Gabriele Centi, Marcello De Falco, Gaetano Iaquaniello. Volume 179, Pages 7-524 (2019).
15. World Data Bank. What a waste. [Internet]. Available from: https://datatopics.worldbank.org/what-a-waste/trends_in_solid_waste_management.html [Accessed: 2021-01-27]
16. WO 2018/066013. Iaquaniello G., Spadacini L., Salladini A., Antonetti E.: Method and equipment to produce a syngas from wastes, preferably industrial or municipal wastes and their deliverables.
17. Salladini A., Borgogna A., Spadacini L., Pitrelli A., Annesini M.C., Iaquaniello G.: Methanol production from refuse derived fuel: Influence of feedstock composition on process yield through gasification analysis. Journal of Cleaner Production, Volume 235, 20 October 2019, Pages 1080-1089 (2017).
18. KM-CDR Process Mitsubishi CO_2 Capture Technology, Mitsubishi Heavy Industries Ltd
19. Okuzumi N. et al.: CO_2 recovery unit for surplus urea production, Mitsubishi Heavy Industries Ltd, Asia Nitrogen 2012 International Conference.
20. Wienchol P., Szle A., Ditaranto M.: Waste-to-energy technology integrated with carbon capture, challenges and opportunities. Energy 198, 117352 (2020).

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A flexible tool for methanol synthesis

MegaZonE™ is a newly introduced layered loading technology for boiling water-cooled reactors used for methanol synthesis. This new concept is one of the latest results of the long-standing collaboration between Air Liquide Engineering & Construction and Clariant Catalysts to improve the methanol process flowsheet and optimise catalyst performance in the complete reactor system.

S. Osborne, H. Schwarz, N. Ringer and S. Reitmeier from Clariant Catalysts.

Clariant has been producing industrial catalysts for methanol production for well over 40 years. However, Clariant's efforts to continuously improve the catalyst performance are not limited solely to catalyst formulation, but also focus on the overall process and how the catalysts can be optimally utilised in the complete reactor system.

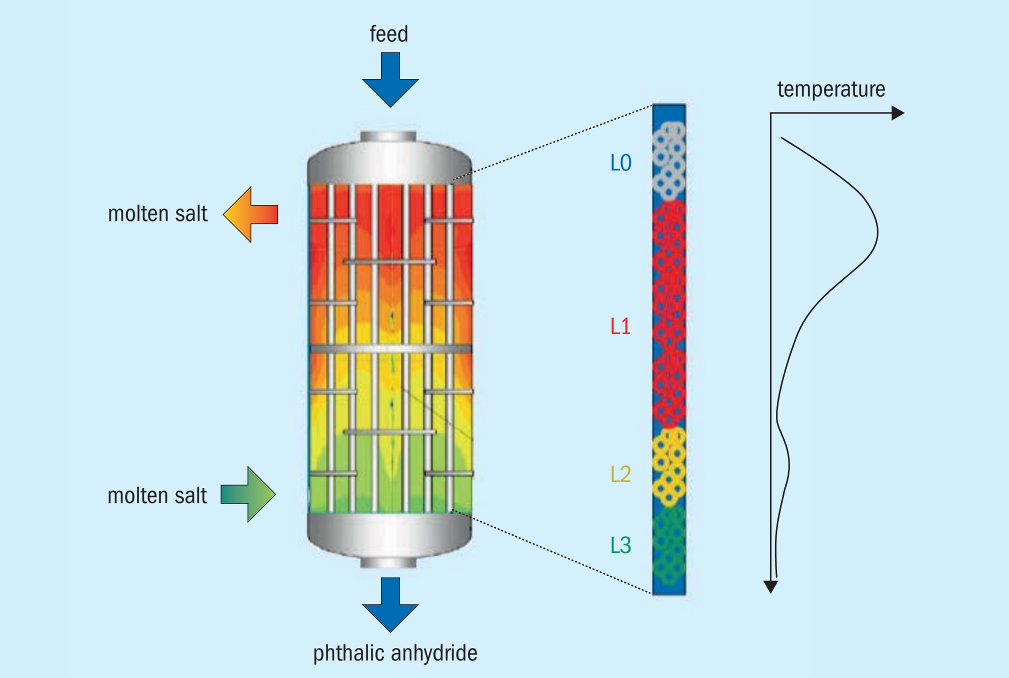
A cooperative relationship

Since the early 1970s, Air Liquide Engineering & Construction and Clariant Catalysts have been in a strategic collaborative partnership which has led to many innovations over the last 50 years.

One of the main goals in Clariant's catalyst development has been to enable Air Liquide to achieve their future design goals as they continue to innovate and optimise their methanol process flowsheet.

In parallel, Clariant has been developing new catalyst generations such as the MegaMax® 700, 800 and 900 series. The development of innovative plant designs along with state-of-the-art catalysts is enabling producers to further maximise production at reduced total costs and increasing lifetime. Another result of the long-standing collaborative relationship with its partner Air Liquide is Clariant's newly introduced layered loading concept called MegaZonE™.

Fig. 1: **MegaZone™ in selective oxidation applications**



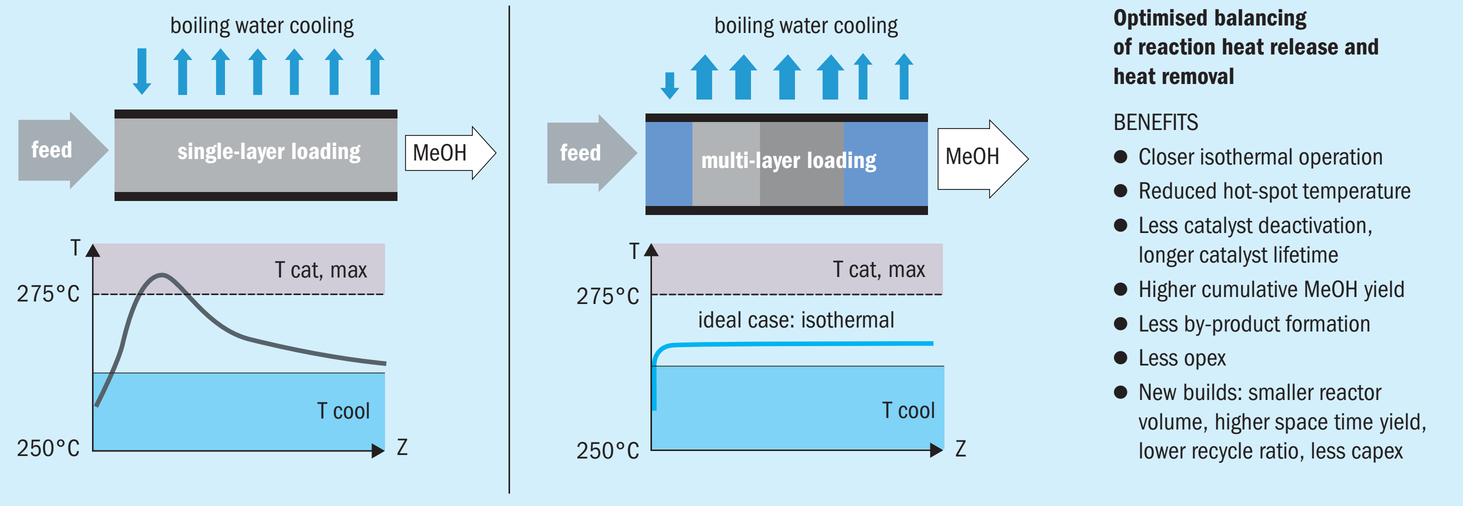
Source: Reference 8: O. Richter, Jahrestreffen Reaktionstechnik 2017

The concept

The Air Liquide reactor systems (water- and gas-cooled reactor designs) are already the benchmark for per pass conversion and heat management. Customarily, the reactor tubes are loaded with a single catalyst type only. However, Clariant is involved in various commercial application areas and speciality sectors that employ catalysts where different loading schemes are applied. Two relevant examples are the Phthalimax® series of catalysts used for phthalic anhydride production and the FAMAX® series for formaldehyde production. These are selective oxidation reactions utilising tubular reactors with catalysts in the tubes and a cooling medium on the shell side for temperature management, resembling the boiling water methanol reactor concept (Fig. 1). Both applications have been optimised over the years and benefitted dramatically from the use of multi-layer catalyst loadings. For these applications, a layered loading scheme is nowadays a standard approach and considered state-of-the-art. Each of the applications uses specially tailored catalyst layers that may incorporate different catalyst shapes, activity levels, and selectivities. The concept allows optimisation of the reaction rates over the reaction path, which improves the temperature profile and selectivity. It is particularly critical in these systems to control the peak or hot spot temperature as it can lead to premature aging, severe by-product make, and even the possibility of runaway reactions[2,3,4,5].

In the methanol reactor, peak reaction temperatures and reaction profiles also need to be considered to optimise

Fig. 2: **Temperature optimisation across reaction zones via multi-layered loading**



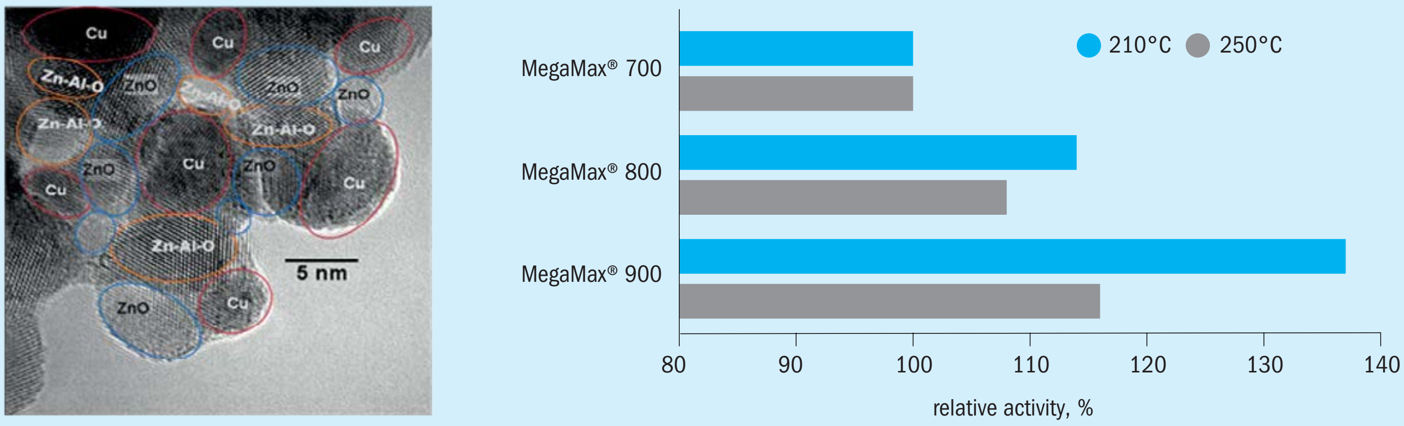
Optimised balancing of reaction heat release and heat removal

BENEFITS

- Closer isothermal operation
- Reduced hot-spot temperature
- Less catalyst deactivation, longer catalyst lifetime
- Higher cumulative MeOH yield
- Less by-product formation
- Less opex
- New builds: smaller reactor volume, higher space time yield, lower recycle ratio, less capex

Source: Clariant

Fig. 3: **HR-TEM image of $CuO/ZnO/Al_2O_3$ catalyst[7] and evolution of MegaMax® catalyst generations**



Source: Clariant

the overall process efficiency. In contrast to the selective oxidation applications, for which hot-spot reduction is the major target, Clariant's investigations focused on the possibility of improving the utilisation of the catalyst volume in the methanol reactor over the catalyst lifetime, i.e., increasing space-time yield and catalyst lifetime.

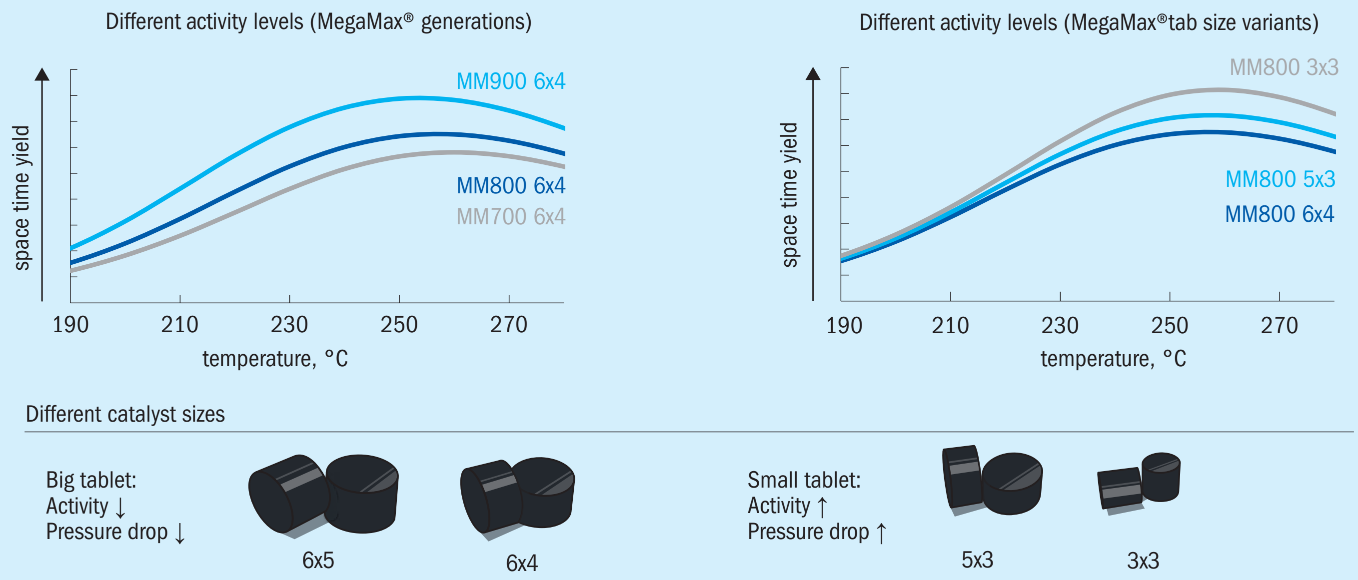
Based on the success in selective oxidation applications, it was felt that there would also be potential benefits when applied to methanol synthesis. The challenge was trying to determine the true potential. Several years ago, Air Liquide and Clariant initiated a cooperation with the University of Erlangen to perform an initial scoping study of the concept. It involved some detailed computational examination of multi-level layered loadings as applied to a methanol reaction system. The results were very promising and showed that it was possible to achieve more effective utilisation of the catalyst volume through multi-level layering. This data provided the confidence leading to the decision to proceed and further investigate and exploit the concept on a commercial scale.

Thus, what is the goal, and why is a layered loading concept of potential benefit in the boiling water-cooled style of methanol reactor? Fig. 2 illustrates a potential advantage of a layered loading which was conceptionally derived from the initial scoping study and then further evolved over the past years.

In the scenario depicted in Fig. 2, the scheme on the left shows a traditional steam raising reactor loaded with a single highly active catalyst layer. The desire is to maximise yield and ultimately provide the longest life possible. Much like in the previous selective oxidation type reactor, the incoming reactive gas, in the presence of a highly active catalyst, can result in high reaction rates with a corresponding rapid increase in the temperature. The ability of the reactor to remove this heat and reduce the peak temperature is a function of the reactor heat transfer and the temperature of the water/steam on the shell side. Unfortunately, this relatively high reaction rate can result in high peak temperatures, which can lead to an increased rate of deactivation and by-product formation, not to mention potential equilibrium limitations.

Ideally, it would be better to try and smooth out the profile to reduce the peak, resulting in a net lower average, more ideal temperature profile. By incorporating multiple layers of catalysts with specific properties related to reaction rates, heat transfer, selectivity, etc., it becomes possible to better control this overall temperature and reaction profile.

Fig. 4: **Different activity levels according to catalyst generation and catalyst size**



This can then yield a closer to isothermal operation, reduced hot spot, resulting in lower catalyst deactivation, higher cumulative methanol yield, lower by-product formation, ultimately resulting in reduced opex and higher lifetime yields. The benefit of increased lifetime yields achievable by using a customised arrangement of only two catalyst layers is described in detail based on a modelling case study in the following sections (see Figs 8 and 9).

For new plant builds, the concept can be further exploited, potentially leading to reduced reactor volume, higher space-time yields, lower recycle ratio, and hence reduced capex.

MegaMax® methanol catalyst portfolio as a basis for MegaZonE™

Clariant is well known for its syngas catalyst portfolio, and in Air Liquide's methanol process Clariant's copper-based methanol catalyst (i.e., the MegaMax® series) is well established as a basis for their design. An extensive research effort and scientific collaboration helped unveil the intimate interplay of Cu, Zn, and Al and understand the fundamental kinetics of the Cu/ZnO/Al_2O_3 system, as illustrated in high-resolution electron microscopy images (Fig. 3 left)[7]. Consequently, this allowed Clariant to improve the catalyst preparation route and the production process resulting in continuously increasing intrinsic activities from one catalyst generation to the next (Fig. 3 right).

To serve the concept of MegaZonE™ and allow rapid "in-silico" screening, Clariant has developed a catalyst library[8]. This allows the simulation of various MegaZonE™ setups (consisting of tailored layers of different catalyst shapes and/or catalyst generations) in a methanol loop model developed jointly with Air Liquide (see Fig. 4). The catalyst model is based on a sophisticated heterogenous pellet model and uses a proprietary kinetic mechanism. In the MegaZonE™ concept, each layer can thus be attributed with a different function depending on the targets or boundary conditions of the reactor design (i.e., pressure drop, methanol yield, catalyst lifetime, by-products). Moreover, the overall process model allows simulations at an industrial scale and concurrent performance optimisation.

Clariant and Air Liquide developed modelling tools to predict the performance of a methanol reactor loop employing MegaZonE™ over the full lifetime of the catalyst. These modelling tools are continuously validated and improved based on pilot plant data and industrial feedback.

Model and concept validation with pilot plant

One of the strengths of Air Liquide's experts is in generating data in a pilot plant and translating the data into a form that can be used to scale up results. To support these efforts, Air Liquide utilises a process development unit (PDU) which consists of a single reactor tube with a steam jacket, two separators at different pressure levels, and a recycle loop to feed unconverted gas back to the inlet of the reactor as depicted in Fig. 5. The single reactor tube translates directly to industrial-scale, multi-tubular tube-bundle reactors.

The comparison of one of the experiments and the respective modelling results are shown in Fig. 6. It shows that the temperature profile and the conversion obtained from the model are in line with the experimental observations. Therefore, the experiments confirm the validity and accuracy of the model developed by Air Liquide with the support of Clariant.

Catalyst deactivation in industrial processes

Deactivation is unavoidable in commercial methanol plants, so an industrial catalytic process cannot be designed or optimised without considering catalyst aging over the lifetime. Therefore, understanding and predicting catalyst deactivation behaviour is crucial to determine the lifetime yield and catalyst turnover. Based on the temperature profiles of commercial plants, an activity profile can be deduced using an optimisation approach. As can be anticipated, the result is a sigmoidal activity profile (Fig. 7, right) as a function of the normalised reactor dimension. In addition, routine evaluation of actual plant data by Clariant's Applied Catalyst Technology (ACT) personnel allows Clariant to refine and update its models, ensuring excellent simulation accuracy.

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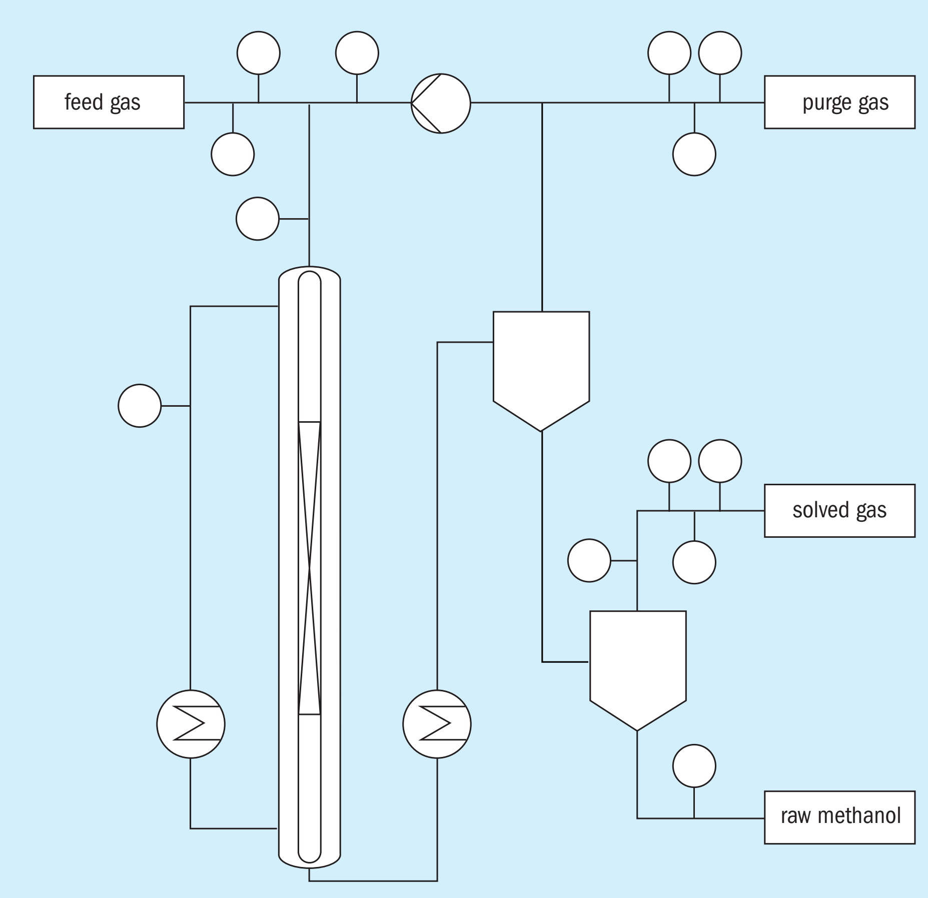
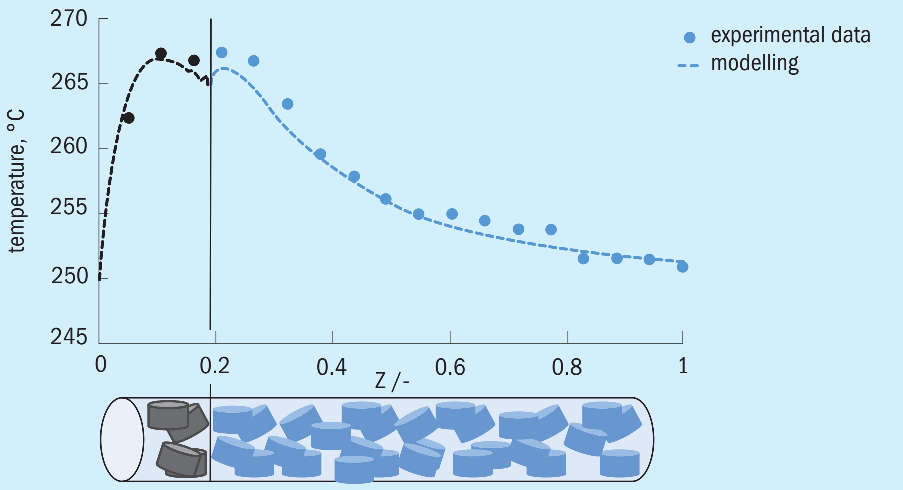
Fig. 5: **Air Liquide's process development unit**



Source: Reference 10: Layer Management for Methanol Process

Fig. 6: **Pilot plant experimental results for MegaZonE™ and validation of model predictions***



Pilot plant	Experiment	Model
T_{max}, °C	267.3	266.9
T_{out}, °C	250.9	251.3
$X_{CO,\ pp}$, %	81.5	81.6
$X_{CO_2,\ pp}$, %	32.2	31.2

** In this experiment, the top 20% of the reactor was filled with a different catalyst than loaded at the bottom.*

Source: Clariant/Air Liquide

Concept for commercialisation

Commercialisation is envisioned through refill solutions that could meet the constraints of existing facilities and stepwise exploit the potential of the MegaZonE™ concept. The first MegaZonE™ reference has been in commercial operation since August 2018. In this case, the successfully achieved target was to optimise pressure drop in the gas-cooled reactor of a large-scale MegaMethanol™ plant. However, the main objective of MegaZonE™ for refill cases, besides pressure drop optimisation, is a longer lifetime of the catalyst and more accumulated methanol production over the lifetime (lifetime yield).

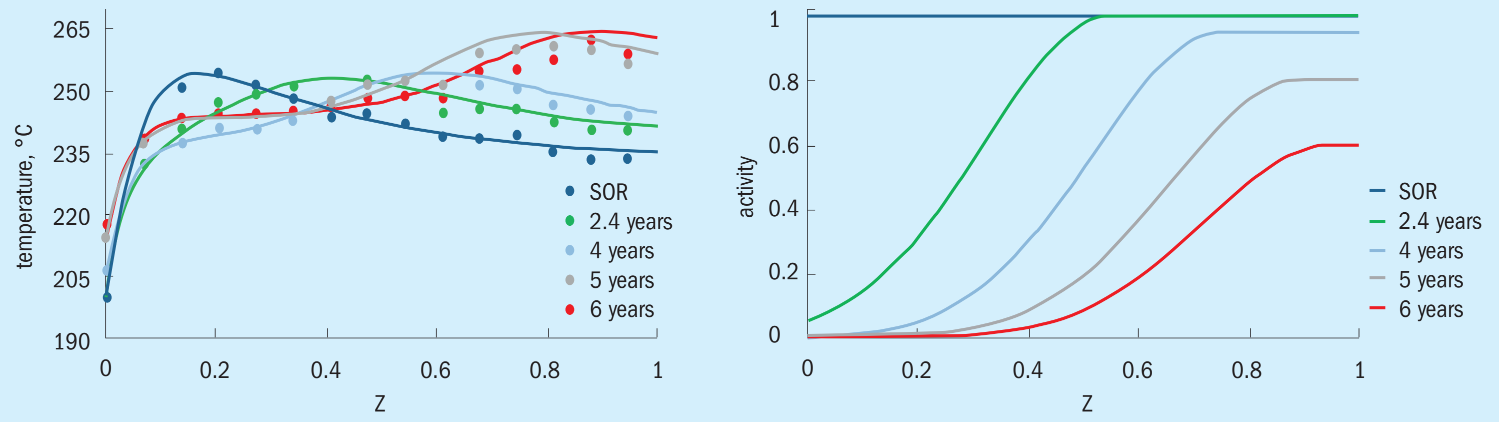
When evaluating MegaZonE™ for existing methanol processes, one of the critical factors to be considered is the pressure drop. Pressure drop can be a significant constraint to equip plants with MegaZonE™, and it will impact the operating conditions of the whole synthesis loop. Therefore, the aim is to find a solution to improve the methanol production by using the MegaZonE™ concept within the design restriction of pressure drop. Case studies were taken into consideration to evaluate the benefit of MegaZonE™ on existing plants. All plant-specific constraints (i.e., pressure drop, recycle compressor, steam temperature...) are considered in the simulations, and an optimum solution for the specific plant is developed. In most methanol plants, recycle ratio, reaction temperature, and loop pressure in the methanol synthesis loop are increased over time to compensate for the deactivation of the catalyst. With MegaZonE™, the loop efficiency would be increased, thus the loop could be operated at milder conditions, particularly at start-of-run and through the life of the charge. This would result in increased energy efficiency and extended catalyst lifetime. If more synthesis gas can be made available, MegaZonE™ would even be a solution for further increased capacity.

As highlighted earlier, the benefits of MegaZonE™ will ultimately be exploited in Air Liquide's future design for grass-roots plants, resulting in lower capex and opex costs.

Modelling case study

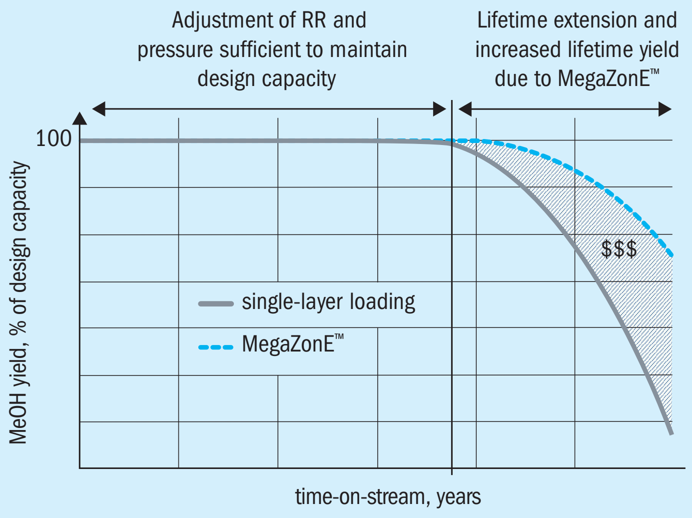
Based on the validated model and the commercial deactivation behaviour, it is possible to make reliable lifetime yield predictions and optimise the reactor layout. In a modelling case study, a significant benefit in achievable methanol yield could be shown,

Fig. 7: **(Left) Temperature and (Right) activity profile over the reactor length in commercial reactors for different times-on-stream**



Source: Clariant/Air Liquide

Fig. 8: **Prediction of methanol yield over the lifetime for single-layer loading vs. MegaZonE™**



- Greater benefit is realised towards end-of-run operation due to more active catalyst being layered at the bottom of the reactor.
- This opens the possibility to extend the operation further.

Source: Clariant

especially at end-of-run (EOR) when local deactivation of the catalyst layers becomes important and the per pass conversion decreases (schematically shown in Fig. 8). This opens the possibility to extend the operation lifetime and contributes significantly to the lifetime production of the catalyst. However, it should be considered that under typical plant operation with regular adjustments of operating conditions, e.g., RR or pressure, to keep methanol productivity close to 100% of design capacity, the benefits of MegaZonE™ will be less obvious at start-of-run (SOR) and middle-of-run (MOR). Here catalyst activity is typically so high that per pass conversion is limited by thermodynamic equilibrium, and overall plant conversion is close to 100% also in a single catalyst loading scenario. The real benefit of MegaZonE™ can be seen when proceeding from MOR to EOR when adjustments of the operating conditions in a single catalyst loading scenario could no longer compensate for the deactivation effects. The benefit on lifetime yield achievable is visualised in Figs 8 and 9.

A specific study was performed for a plant proposal where a significant amount of optimisation studies and examination of different layered loading concepts was examined. It was important to adhere to design limits related to maximum make-up gas flow, compressor capacity, loop pressure, and overall pressure drop in the study (Fig. 9). The graph on the left shows the simulated performance of the single-layer concept compared to the MegaZonE™ optimised loading. As noted in the previous general example, the benefit is not particularly large in the early part of the charge's life but does depend on specifics related to reactor heat transfer and loop constraints. After approximately three years on-stream, however, there is a noticeable production rate differential. This differential would appear sooner if poisoning mechanisms were higher. The chart on the right thus shows the incremental production associated with the MegaZonE™ loading versus the single layer loading. The potential benefit is quite significant in terms of both the total volume of additional methanol produced and the potential for lifetime extension between turnarounds. In the example, it could yield a total additional cumulative production level of over 30,000 tonnes by year 5.

Catalyst loading technology

Depending on the generation of the reactor, the traditional Air Liquide water-cooled reactors consist of 4,800 to 8,000 tubes per reactor with a loaded height ranging from 7 to 10 m long. Normal loading procedures are relatively simple and involve pouring the catalyst onto the tube sheet. Newer loading methods developed by Clariant's Applied Catalyst Technology (ACT) team also incorporate a cassette loading system capable of achieving higher loaded densities with more uniform packing characteristics. These methods, however, were only applicable to standard single-layer loadings so far.

When implementing the MegaZonE™ layered loading catalyst system, it is necessary to ensure that all tubes are loaded uniformly in density and height. To accomplish this, it was also necessary to develop loading methods able to accurately load two or possibly more different layers of catalysts into the reactor tubes. This must not only be done accurately but also fast to avoid excessive additional downtime for the loadings. By leveraging extensive loading

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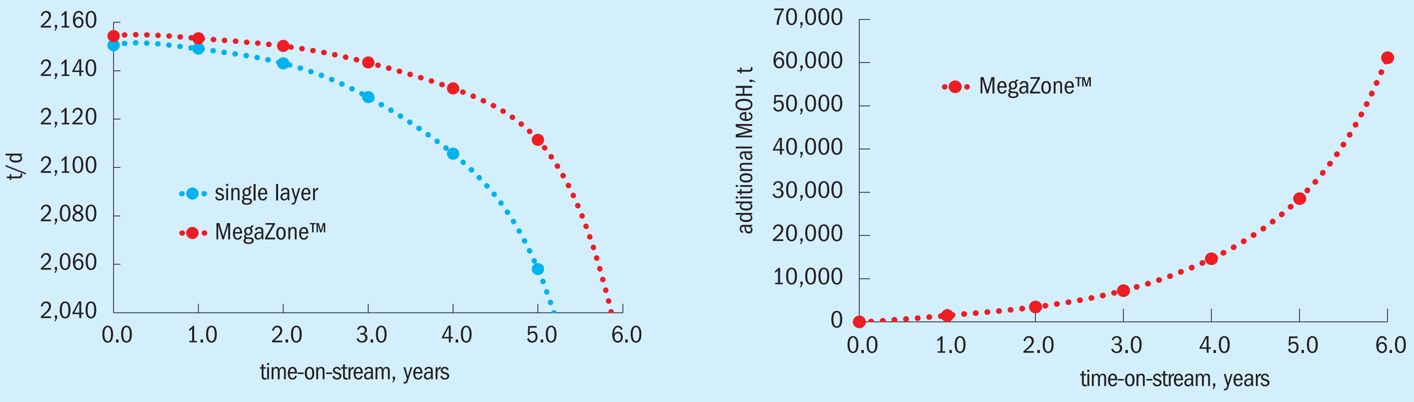
Fig. 9: **Comparison of simulation results for MegaZonE™ versus single layer loading in plant modelling example**



Source: Clariant

experience and customised loading equipment for multi-layer oxidation catalyst systems combined with expertise in single catalyst loading for methanol reactors, it was possible to develop and test new concepts. Based on the specific requirements for the layered loadings, it was further necessary to consider multiple methods adjustable to the reactor configuration and necessary loaded heights needed.

By adapting the oxidation catalyst loading technologies and developing innovative specialty equipment, it was possible to design and then test the systems in Clariant's pilot-scale reactor system. The result of further fine-tuning is a set of loading systems flexible enough to handle all loading requirements and able to achieve both uniform loading densities but also outage variation typically under 50 mm for different layer configurations. These approaches then ensure that the catalyst is loaded optimally for performance and also time efficiency.

MegaZonE™ commercial implementation

Apart from the initial loading in August 2018 referenced earlier, the concept has now been successfully implemented in two other world-scale Air Liquide water-cooled reactors. Both plants were loaded and started up in early May of 2021. In both cases, the operating conditions and process/equipment constraints were carefully reviewed in the proposal stage to develop the best layering option given system limitations and maximise the overall benefit. Since start-up, both plants have performed as expected concerning overall conversion and pressure drop expectations. At one site, the enhanced activity of the Clariant catalyst MegaZonE™ loading has enabled further loop optimisation resulting in a substantial production rate and loop efficiency increase at the same time on-stream. Clariant continues to trend the performance and expects to see an increased benefit with additional time on-stream.

Conclusion

Clariant and Air Liquide have been collaborating in methanol synthesis for many decades and have successfully investigated the possibility of improving the interplay and overall performance of catalyst and the reactor system. The development of MegaZonE™ for methanol synthesis is another example of successful cross-market technology transfer and joint-development between an engineering company and a catalyst provider working in close collaboration. The potential of MegaZonE™ can be seen as a game-changer for current methanol producers and in the future for more compact and resilient designs. By utilising the rigorous modelling tools and expertise related to loading, operation, and optimisation within Clariant's Applied Catalyst Technology group, the ideal solution for each application can be ensured. This combined catalyst and technology approach allows for a vast range of tailormade refill options and process optimisation to improve the catalyst usage in all existing units (for example, debottlenecking). Furthermore, in the context of a circular economy, different feed sources such as stranded gas, unused syngas capacities, and CO_2-rich gases, MegaZonE™ is a flexible tool to offer optimised methanol synthesis set-ups for a wide range of specific plant configurations. ■

References

1. Schlichting H., Hackel P.M., Wurzel T., patent WO 2011/101081 A1, Process for preparing methanol.
2. Gueckel C., Dialer H., Estenfelder M., Pitschi W., patent WO 2006/092305 A1, Method for producing a multi-layer catalyst for obtaining phthalic anhydride.
3. Estenfelder M., Zaino R., patent WO 2010/076246 A1, Improved process for oxidation on fixed catalytic bed of methanol to formaldehyde.
4. Estenfelder M., Zaino R., patent WO 2010/076246 A1, Improved process for oxidation on fixed catalytic bed of methanol to formaldehyde.
5. Marx R., doctoral thesis, Clausthal University of Technology, Kinetics of the selective oxidation of o-xylene to phthalic anhydride (2012).
6. Freund H.J., Frind R., Henkel T., Kaiser M., Schuhmann T., Seuffert W., Werner S., patent WO 2018/149811 A1, Reactor and method for maximizing methanol yield by using catalyst layers.
7. Behrens M. et al., J. Am. Chem. Soc., 135:6061 (2013), Performance improvement of nanocatalysts by promoter-induced defects in the support material: methanol synthesis over Cu/ZnO:Al.
8. Henkel T., doctoral thesis, Technical University of Munich (2001), Modellierung von Reaktion und Stofftransport in geformten Katalysatoren am Beispiel der Methanolsynthese.
9. Richter O., Jahrestreffen Reaktionstechnik 2017 – Annual Meeting on Reaction Engineering, Selective oxidation of o-xylene to phthalic anhydride.
10. Layer Management for Methanol Process, Lecture at DGMK conference "Circular economy – A fresh view on petrochemistry" (2019).

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Latest catalyst provides more methanol for longer

Johnson Matthey's latest methanol synthesis catalyst, KATALCO™ 51-102, was introduced in 2018 to offer improved catalyst stability and therefore higher end-of-life activity and extended lifetimes than conventional methanol synthesis catalysts. Since launch, KATALCO 51-102 has been successfully installed in two methanol plants and a third is planned for later in the year. In this article Johnson Matthey provides an update on the proven performance of KATALCO 51-102 during lab and pilot scale testing as well as in customer plants. The application of catalysts made using the KATALCO 51-102 technology for methanol synthesis via new 'green' routes, such as using captured and purified CO_2 in conjunction with 'green' hydrogen, is also discussed.

Y. Cui, A. Fish, P. Glen, N. Macleod, N. Mistry, M. Nicholson, S. Roloff-Standring, D. Sheldon, M. Garcia from Johnson Matthey.

Many catalysts have been developed and successfully commercialised by JM (previously ICI) since the development of the original copper-based industrial catalyst and low-pressure process back in the mid-1960s. Detailed understanding of the sintering mechanism and the role of the structural promoters in the CuZnAl catalysts has led to the development of KATALCO™ 51-102[1], which was introduced in 2018. KATALCO 51-102 offers higher sustained activity over time compared to any of its predecessors. The improved performance was achieved via the addition of a stability promoter to the formulation. This change to the formulation is relatively minor and has no impact on further catalyst characteristics such as selectivity, strength, or attrition resistance.

Although not discussed in detail in this article, the structural 'backbone' of the catalyst is also crucial to a long, stable catalyst life without significant increases in pressure drop. Simply 'adding more copper' to increase activity can have a detrimental effect on pellet stability and JM's formulation and manufacture is carefully designed to avoid issues with pressure drop increase in service. This is unchanged between KATALCO 51-102 and previous generations.

Synthesis of methanol from CO_2 (potentially captured directly from the atmosphere or from streams that would otherwise be emitted to the atmosphere) and hydrogen streams is attracting much attention and presents some additional challenges to the catalyst. In contrast to traditional syngas streams, the higher CO_2 leads to high concentrations of water in the process, putting additional demands on the catalysts' hydrothermal stability. JM's conventional catalysts have demonstrated lives of around four years and stable performance in such duties, but materials developed using the same scientific principles as KATALCO 51-102 demonstrate further advantages in such conditions.

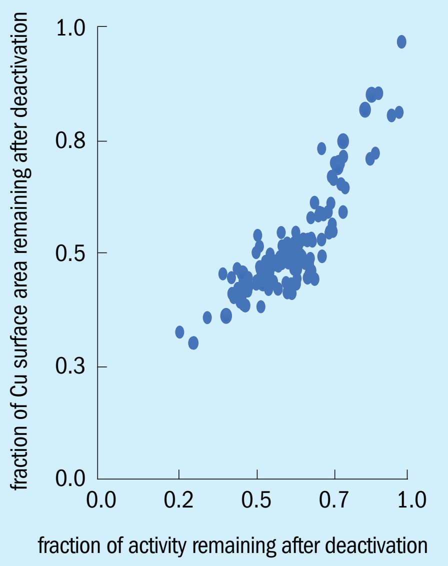
In this article the properties and benefits of KATALCO 51-102 are reviewed and evidence is provided of its proven performance at lab and pilot scale testing as well as in customer plants, since its launch in 2018. The performance of catalysts made using the same technical principles as KATALCO 51-102 under CO_2 to methanol conditions is also discussed.

Methanol synthesis catalyst deactivation

The deactivation of a catalyst over time ultimately determines the catalyst life and end-of-run plant rate. The two main mechanisms that drive the deactivation of copper-based catalysts used in the synthesis of methanol are sintering and poisoning, sintering being the dominant process in the majority of applications. It is generally accepted that the activity of a methanol synthesis catalyst is directly proportional to the active surface area, which is that of metallic copper. Other factors in the catalyst may also play a role in defining the activity, such as copper-zinc interactions[2,3], however, the degree of copper dispersion is universally accepted as one of the main descriptors for catalyst activity. Therefore, as a general rule, a good methanol synthesis catalyst requires high copper surface area, which is achieved by having small nanoparticles of copper, typically 2-10 nm. In order to reach a reasonable lifetime cycle and the desired productivities in a plant, these nanoparticles should be as stable as possible. However, the small copper crystallites present have a high surface to volume ratio and most of the copper atoms occupy high energy surface sites. There is therefore a significant thermodynamic driving force towards sintering; small particles become larger in order to reduce this surface energy[4]. Moreover, the relative low melting point of copper makes this metal prone to sintering, since at the temperatures required for methanol synthesis the copper atoms can become mobile.

As sintering requires the physical movement of atoms or clusters, it is an activated process and therefore the rate of sintering will increase with increasing temperature. Temperature is, in fact, one of the dominant variables leading to sintering, although other factors such as gas composition may also be important. The rate of sintering and therefore deactivation of methanol synthesis catalysts normally follows an exponential decay, in which the rates are faster at the start of life of the catalyst, when the copper surface area is the highest, and slows down as copper crystallites become larger and the driving force for sintering decreases. For the greater part of the catalyst operating life, the catalyst activity is significantly lower than that of the fresh material. Once the activity is too low to maintain the required level of productivity, a catalyst change-out will be required. There is therefore a significant incentive to have a stable catalyst, such as KATALCO 51-102, which minimises the impact of thermal sintering and thereby improves the productivity and life of methanol synthesis catalysts.

Fig. 1: **Change in catalyst activity with copper surface area**

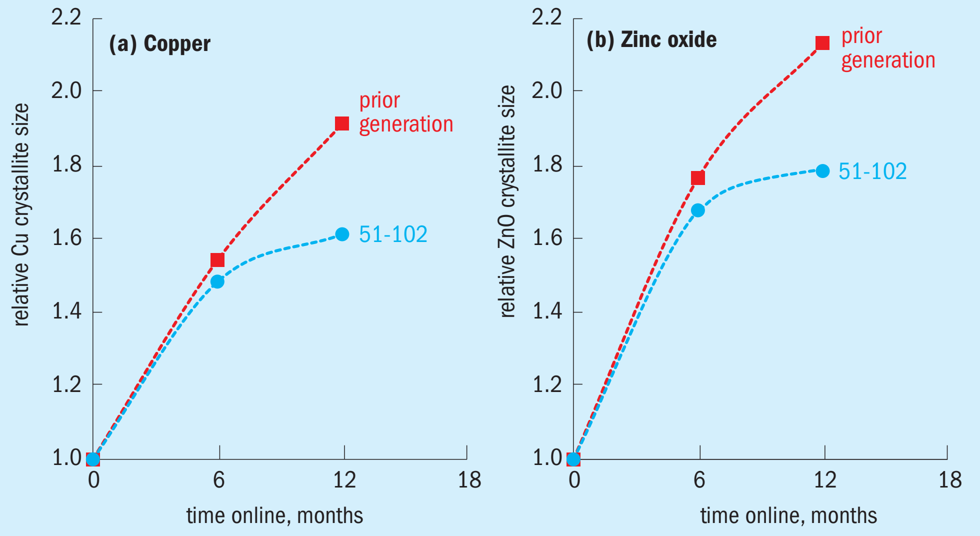


Source: Johnson Matthey

The science behind KATALCO 51-102

Most industrial methanol synthesis catalysts are composed of copper, zinc and aluminium. The current generation of KATALCO 51-series methanol synthesis catalysts also contains magnesium. Copper oxide is the main component (~64 wt-%) and is the active phase upon reduction to metallic copper; the reduction is carried out in situ in the methanol converter before the charge is brought into service. The dispersion of copper is directly related to the activity of the catalyst as reflected by the relationship between copper surface area and remnant activity shown in Fig. 1.

Fig. 2: **Relative crystallite size for copper (a) and zinc oxide (b) with time online**



Source: Johnson Matthey

While a high initial activity is desirable, the retention of activity/copper dispersion over time is far more important. Zinc oxide (ZnO) and aluminium oxide (or alumina, Al_2O_3) are included in the formulation with the main purpose of stabilising the copper phase. The alumina also gives physical strength to the pellets of catalyst.

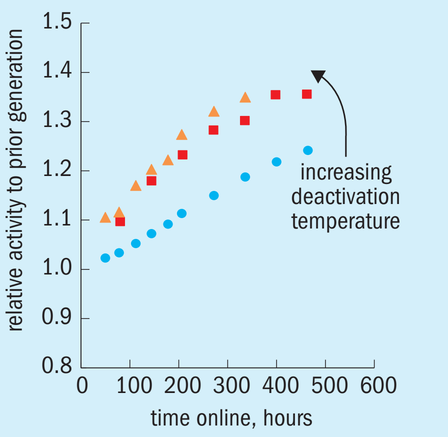
There is a close interaction between copper and zinc, which starts during the manufacturing of the methanol synthesis catalysts. During the precipitation process a mixed copper-zinc hydroxycarbonate phase is formed as an intermediate, that upon decomposition to oxides by heating, generates small copper crystallites in close contact with small zinc oxide crystallites that help to stabilise the copper. Zinc oxide also acts as a sulphur guard, to provide further protection in case of sulphur slipping through the purification section and reaching the methanol converter. It also helps neutralise acid sites and stabilise the alumina phase. Acid sites may promote the formation of dimethyl ether (DME) via dehydration of methanol, affecting the selectivity of the catalyst. The alumina phase is stabilised by zinc via the formation of zinc aluminate during service, which is a more hydrothermally stable phase than alumina.

Magnesium oxide (MgO) is incorporated to maximise the initial dispersion of copper and therefore boost the initial activity of the methanol synthesis catalysts. The increase in copper surface area in Mg-containing copper-based catalyst can be of the order of 20% versus a Mg-free variant.

A detailed understating of these complex multicomponent catalytic systems at start-of-life and during service has led to a new optimised and patent pending formulation[5], in which a small amount of a fifth component, silica, is added as a stability promoter. This new formulation is commercialised as KATALCO 51-102, which provides improved activity in service via a higher retention of initial copper surface area over time when compared with the conventional CuZnAlMg systems.

The addition of SiO_2 slows down the rate of copper and zinc sintering. As mentioned above, zinc crystallites of similar size to those of copper are fundamental in stabilising the copper phase. This is better exemplified in Fig. 2, where the relative crystallite size of copper and zinc oxide with time online are shown for KATALCO 51-102 in comparison with a Si-free formulation. In the next section the superior performance of KATALCO 51-102

Fig. 3: **Relative activity for 51-102 during accelerated deactivation tests at different temperatures**



Source: Johnson Matthey

Fig. 4: **Loss in intrinsic activity during accelerated deactivation tests**

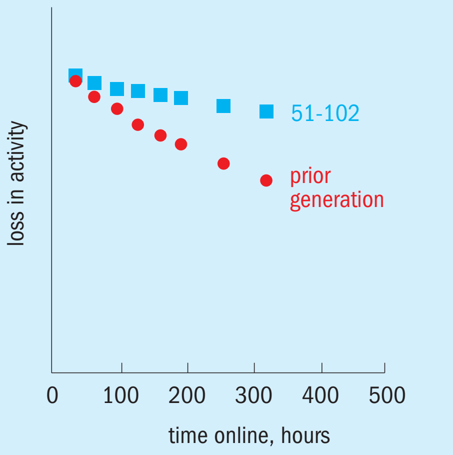


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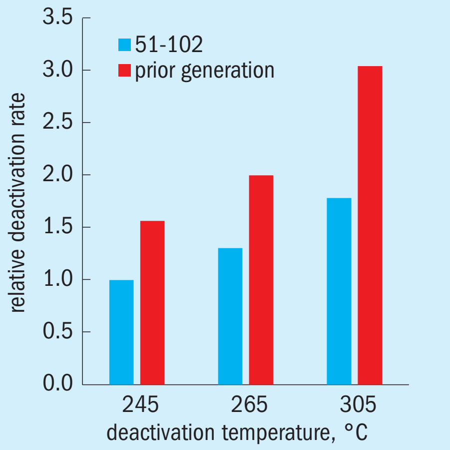
Fig. 5: **Relative catalyst deactivation rate at different temperatures**



Source: Johnson Matthey

over time is analysed, proving the benefits expected due to stabilisation of the active component.

KATALCO 51-102 performance

KATALCO 51-102 has been extensively evaluated, during its development and after launch for quality purposes. Approaching 100 batches of KATALCO 51-102 have been manufactured since 2018, all presenting the expected performance in terms of activity over time as well as pellet robustness and integrity.

Lab testing

Lab testing protocols have been specially developed by our R&D team to evaluate the long-term performance of KATALCO 51-102, which is the key benefit of this new product. Methanol synthesis catalysts may be online for many years, however, lab testing of catalysts for such long periods of time is impractical and economically unfeasible. It is therefore paramount to accelerate the deactivation of the catalyst in a controlled manner during lab testing to predict the long-term performance of the catalysts. The deactivation of the catalyst can be accelerated during lab testing by increasing the temperature above the operating temperature expected for methanol synthesis; this temperature should be such that the sintering of the copper is accelerated, but the mechanism of sintering should not be affected. In other words, the activation energy for sintering when using accelerated deactivation conditions should be the same as that when the material is subjected to milder deactivation conditions. Testing protocols for accelerated deactivation that fulfil that criterium were defined and validated by carrying out tests at several deactivation conditions in JM's accelerated aging rig. Deactivation models that predict the performance of KATALCO 51-102 at different plant conditions were also developed, which enable the link between the accelerated aging results and the real-world performance.

The accelerated aging rig is a multi-reactor laboratory-based automated microreactor system that was designed to evaluate the effect of sintering upon the deactivation of methanol synthesis catalysts in the absence of poisons. A set of data for KATALCO 51-102 from the accelerated aging rig at different accelerated deactivation conditions is shown in Fig. 3. The data set is shown in terms of relative activities over time online for KATALCO 51-102 vs. a prior generation catalyst. All the relative activities shown in Fig. 3 are above unity at any time, indicating that methanol is made faster over KATALCO 51-102 than with the prior generation catalyst. These relative activities increase over time at all conditions as a result of KATALCO 51-102 being more stable than the prior generation catalyst. The stability benefit is better reflected in Fig. 4, where a smaller loss in activity over time at a set of accelerated deactivation conditions can be seen for KATALCO 51-102 than for the prior generation material.

It is worth pointing out that the stability benefit of KATALCO 51-102 vs. the prior generation catalyst is greater as the deactivation conditions are harsher, as shown by larger relative activities as the deactivation temperature is increased (Fig. 3). This is due to a lower dependence of the deactivation rates on deactivation conditions for KATALCO 51-102 in comparison to the prior generation catalyst, as reflected by the relative deactivation rates at different deactivation temperatures in Fig. 5.

As a standard part of the JM quality assurance and control procedure, all batches of KATALCO 51-102 are carefully sampled and analysed for the key properties that define the performance of the catalyst such as chemical composition, density, impurity levels, copper surface area and strength (among others); all these properties are part of the specifications of the product and the defined values must be met. Moreover, a significant number of batches are randomly selected and further tested for reduced crush strength, activity/stability and a second measurement of copper surface area, to further corroborate the relationship between the established specifications of the products and their catalytic performance. The performance of KATALCO 51-102 batches has been consistent and clearly shows the stability benefit over the prior generation catalyst, as reflected by the relative activities for the randomly selected samples shown in Fig. 6, measured after subjecting the catalysts to accelerated deactivation conditions for a defined period of time.

The strength, attrition resistance, shrinkage on reduction, mass loss on reduction, copper loading and zinc loading for KATALCO 51-102 are comparable to the prior generation of catalysts from the KATALCO 51-series, these properties are not changed by the small addition of silica to KATALCO 51-102. While the addition of silica has not caused any change to

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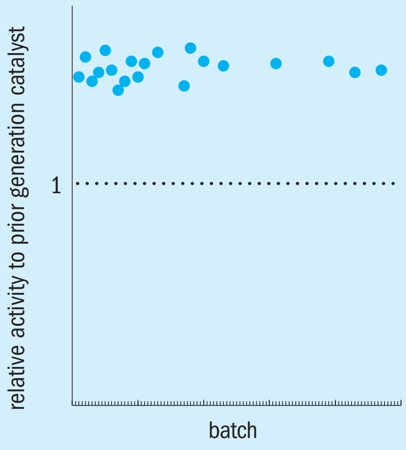
Fig. 6: **Relative activity for 51-102 after accelerated deactivation test**



Source: Johnson Matthey

the physical properties of the catalyst pellets, work on pelleting during the development of KATALCO 51-102 has helped JM improve the strength of a number of products, as shown by the increase in mean horizontal crush strength (MHCS) for catalysts from the KATALCO 51-series in Fig. 7.

The formation of by-products during the synthesis of methanol is unavoidable, however, the selectivity of the catalysts from the KATALCO 51-series is very high and only very small amounts of higher oxygenates are typically formed. KATALCO 51-102 was extensively studied for by-product formation via condensate collection and on-line gas chromatography (GC) analysis in JM's testing units. The selectivity of fresh KATALCO 51-102 is comparable to that of the prior generation catalyst from the KATALCO 51-series, as shown by the by-product distribution for the main oxygenates detected in the gas phase during reaction conditions (Fig. 8). KATALCO 51-102 is as highly selective as all the catalysts from the KATALCO 51-series, the addition of silica (SiO_2) to the formulation has not impacted the levels of by-product formation or its distribution. In particular, silica does not affect the formation of DME (dimethyl ether; Fig. 8 and Fig. 9), which could have been impacted by changes in acid sites in the new Si-containing formulation, since DME is formed via dehydration of methanol on the acid sites of the catalyst. The formation of alkanes is also not impacted by the addition of silica to the formulation.

The formation of most of the by-products during the synthesis of methanol is kinetically limited and therefore increases with temperature. As the methanol synthesis catalyst deactivates over time online and the temperatures in the converter are ramped-up to compensate for the loss in activity, the formation of by-products is expected to increase accordingly. However, the selectivity achieved with KATALCO 51-102 is likely to be improved over prior generation catalysts due to the slower deactivation and consequently slower ramp-up of temperature.

Pilot scale testing: methanol side-stream unit

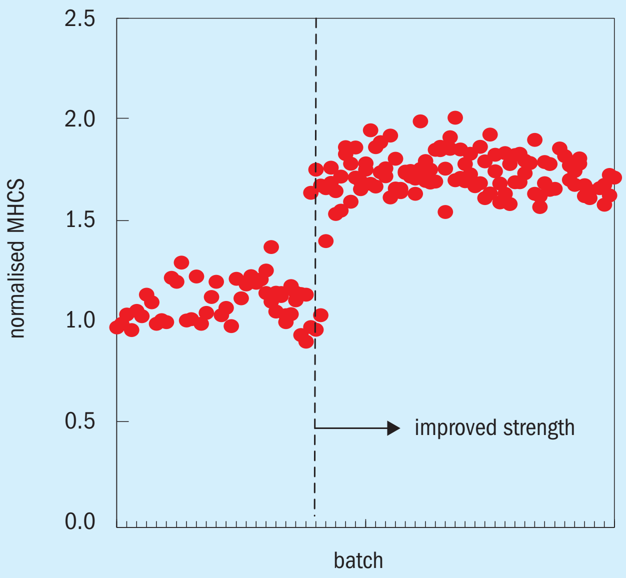
As part of the development and post-launch evaluation of KATALCO 51-102, this product has been tested for long periods of time (6-12 months) at real plant conditions in JM's methanol side-stream unit. The methanol side-stream unit is attached to a customer's plant; a small fraction of the converter feed in the plant is directed to the unit. JM is grateful that the side-stream unit is currently hosted by Proman USA Pampa Plant, Texas. This unit has six pairs of adiabatic converters that expose the catalyst to plant conditions in real time. Reactors may be withdrawn at different intervals to assess the catalyst activity after different lengths of time online. The reactors can be boxed up and shipped to our facilities under an inert atmosphere to avoid re-oxidation of the copper component before catalysts are analysed.

Fig. 10 shows the relative activity for KATALCO 51-102 vs. a prior generation catalyst installed in the same reactor pair for six and 12 months. KATALCO 51-102 was 1.30 and 1.70 times more active than the prior generation catalyst after six and 12 months online in the side-stream unit, respectively. These results from the side-stream unit are in line with the performance of KATALCO 51-102 in customer plants, as exemplified in the next section.

Industrial references

The first industrial reference for KATALCO 51-102 was a 25 tonne (27.5 short ton) charge installed in a tube cooled converter at Proman USA Pampa Plant, which is operating on average at 120% of design capacity. This charge was brought online in early November 2018 and has been

Fig. 7: **Normalised mean horizontal crush strength for KATALCO 51-series catalyts**



Source: Johnson Matthey

Fig. 8: **Catalyst selectivity comparison**

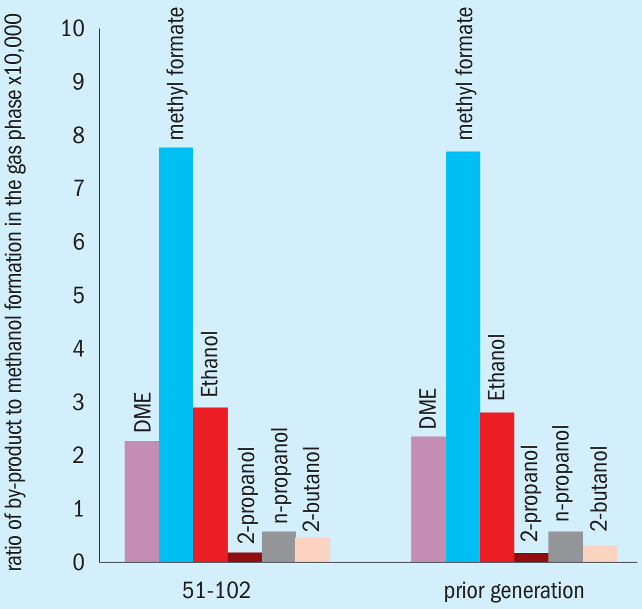


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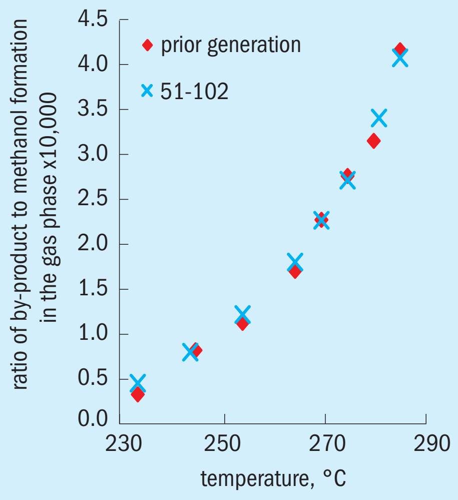
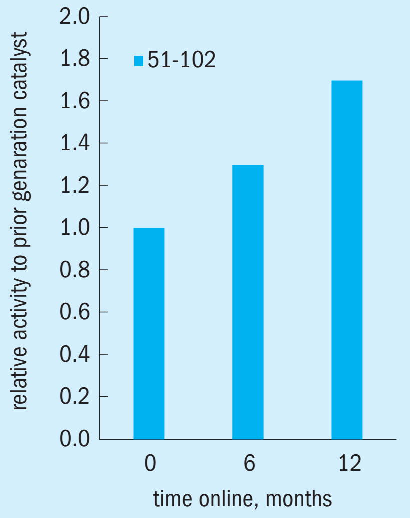
Fig. 9: **Selectivity to DME**



Source: Johnson Matthey

Fig. 10: **Relative activity for 51-102 in methanol side stream unit**



Source: Johnson Matthey

running without issues since then. The KATALCO 51-102 charge has demonstrated a substantial improvement in activity retention over time with respect to the prior generation catalyst, as can be seen in Fig. 11, where the activities at start of life are similar to those for the prior generation catalyst and then decrease at a much slower pace. The stability benefit is even clearer when plotting this set of data in terms of relative activity (Fig. 12), which shows a relative activity of around 1.6 after 24 months online. As mentioned in the previous section, the relative activities for the KATALCO 51-102 charge at Proman USA Pampa Plant are in line with the relative activities measured in the methanol side-stream unit (Fig. 10).

Consistent with lab data for by-product formation on KATALCO 51-102 (Fig. 8), the ethanol production at Proman USA Pampa Plant with the KATALCO 51-102 charge has shown no significant differences in ethanol formation when compared to the previous charge of a prior generation catalyst, as seen in Fig. 13.

After the successful performance of KATALCO 51-102 at Proman USA Pampa Plant, a second charge of KATALCO 51-102 has also been installed in a larger methanol plant and a third charge is planned to be installed later this year. The second charge of KATALCO 51-102 has been loaded in a world scale methanol plant, operating at high rates; at the time of writing the plant has been online for just over six months and the performance is slightly above expectations at start of life and substantially above the performance of the prior generation catalyst from the KATALCO 51-series (see Fig. 14; relative activity to prior generation catalyst is around 1.3-1.4 at 6 months online). The third charge will be installed in a methanol plant with a capacity of over 1,600 t/d.

CO_2 hydrogenation to methanol

Methanol is a key product in the chemical industry, and it is currently mostly produced from fossil fuels. The production and subsequent use of methanol generates emissions in the region of 0.3 gigatons of CO_2 per annum, approximately 10% of the total for all chemicals[6]. Nowadays there is a growing concern about global climate change due to emissions from carbon intense processes and that has intensified the search for ways to 'green' our activities. Global megatrends are accelerating towards net zero emissions and we all should play a role in this. In this context, CO_2 hydrogenation to methanol can be part of the pathway to eventually achieve the decarbonisation of the chemical and transport sectors.

Catalysts from the KATALCO 51-series are already being used successfully in these applications. To name an example, our catalyst is in use for the production of renewable methanol using hydrogen from electrolysis of water and captured CO_2. The catalyst has been successfully operating in one cycle of more than five years and it is now in the third year of the second cycle.

Methanol synthesis is an equilibrium limited reaction and therefore a recycle is essential to maximise the production of methanol and make the process economically feasible at large scale. Therefore, the actual operating partial pressures of CO_2 for the production of green methanol are not

Fig. 11: **Catalyst performance at Proman USA Pampa Plant**

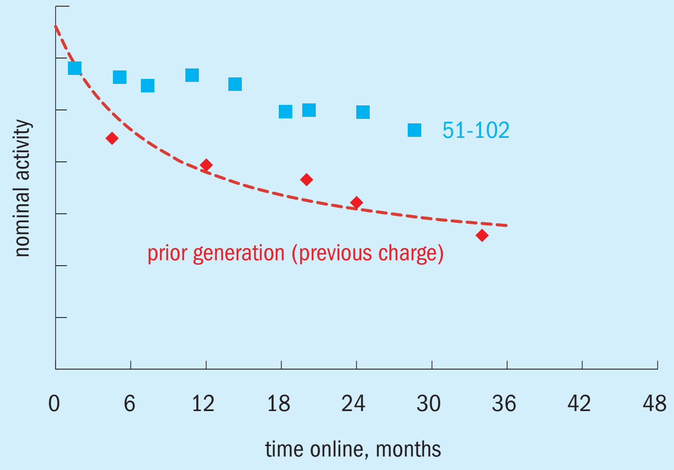


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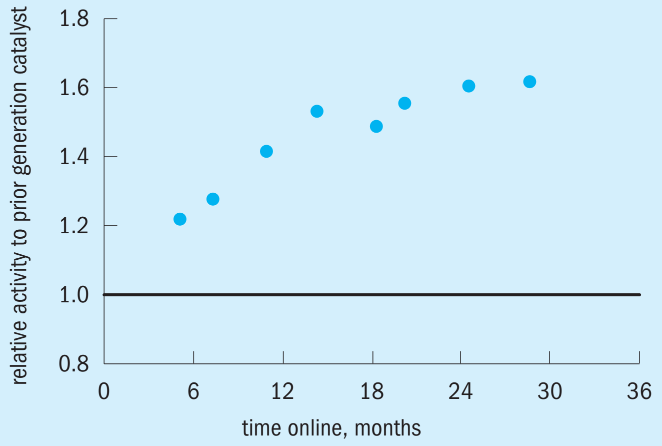
Fig. 12: **Relative activity for 51-102 at Proman USA Pampa Plant**



Source: Johnson Matthey

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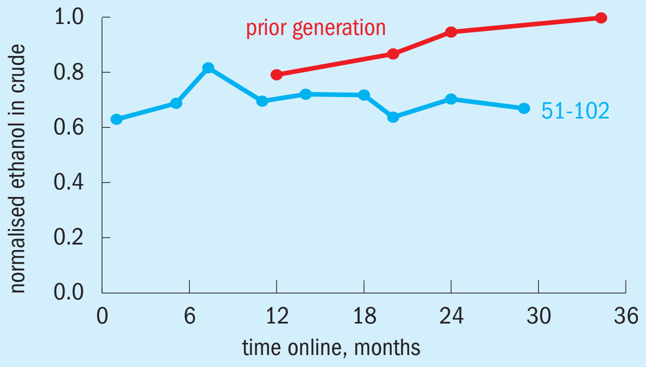
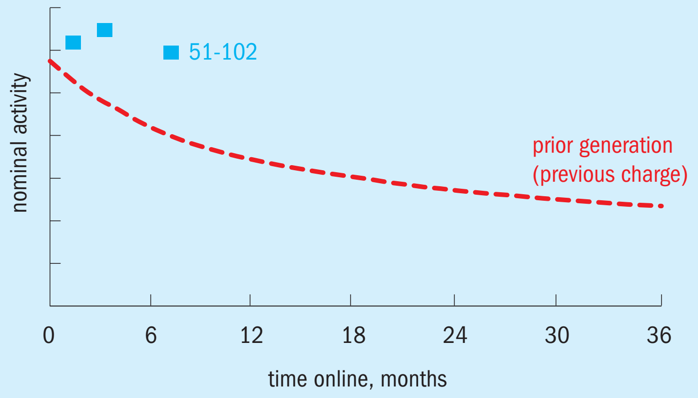
Fig. 13: **Normalised ethanol production with 51-102 at Proman USA Pampa Plant**



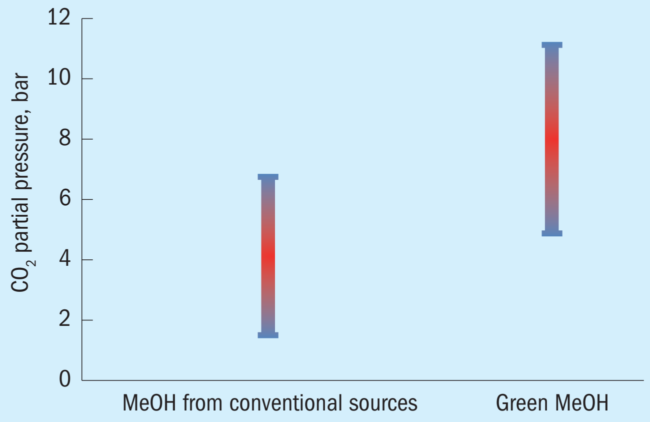
Source: Johnson Matthey

Fig. 14: **Catalyst performance at 2nd industrial reference**



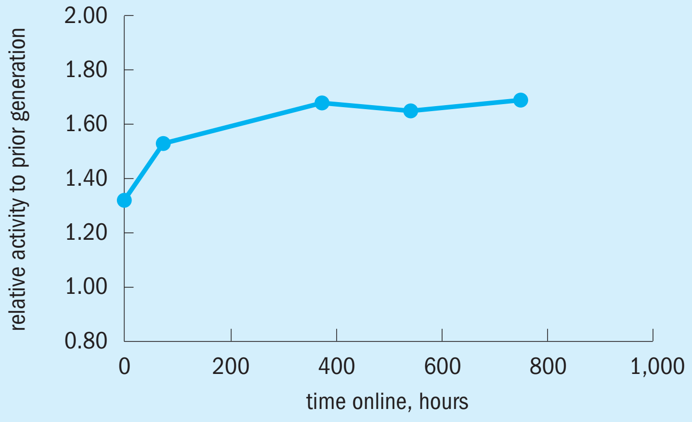
Source: Johnson Matthey

Fig. 15: **Typical CO_2 partial pressures in the methanol converter**



Source: Johnson Matthey

Fig. 16: **Relative activity for a Si-promoted catalyst during accelerated deactivation test at relevant conditions for green methanol production**



Source: Johnson Matthey

massively higher than those observed during the production of methanol from conventional sources (see Fig. 15). However, these will still lead to a larger formation of water and it is beneficial to use an even more hydrothermally stable catalyst made using Si as a stability promoter in these duties. Relative activities for a Si-promoted catalyst to a prior generation material are shown in Fig. 16. This data set was acquired during an accelerated deactivation test at conditions relevant for green methanol production. This curve shows how catalysts made using this technology are more stable and perform better than the prior generation materials in this duty, yielding large benefits for plants using CO_2 as a feedstock.

Conclusions

KATALCO 51-102 is the latest methanol synthesis catalyst developed and commercialised by Johnson Matthey. It offers higher sustained activity over time compared to any of its predecessors which is obtained via a small addition of silica to the formulation. This tailored modification to the recipe has no significant impact on other important catalyst performance metrics such as selectivity, strength, or attrition resistance, however, the effect on the stability of the catalyst over time is remarkable. The improved stability over time for KATALCO 51-102 has not only been proven by extensive testing at lab and pilot scale, but also in commercial methanol plants. All the evidence to date points to significant value generation for customers in terms of additional methanol make over the normal catalyst life, plus potential increased time between change-outs. A typical 3,000 t/d plant switching to KATALCO 51-102 could make an additional 2.5% methanol over four years, worth $9 million in extra margin (assuming $100/t margin). An extra year on the change-out cycle would be worth a further $0.8 million per year. A more stressed or revamped plant could generate even more value. Additionally, the technical developments that are intrinsic to KATALCO 51-102 will also yield major benefits for 'green' methanol plants utilising CO_2 as a feedstock. ■

References

1. Garcia M., Glen P., Mistry N., Nicholson M., Roloff-Standring S., Macleod N.: IMTOF 2019.
2. Kuld S., Thorhauge M., Falsig H., Elkjaer C.F., Helvig S., Chorkendorff I., Sehested J., Science 352 (2016) 969.
3. Behrens M., Studt F., Kasatkin I., Kühl S., Hävecker M., Abild-Pedersen F., Zander S., Girgdies F., Kurr P., Kniep B-L., Tovar M., Fischer R.W., Nørskov J.K., Schlögl R.: Science 336 (2012) 893.
4. Macleod N. and Fitzpatrick T., IMTOF 2013
5. Patent Application WO2020212681A1
6. IRENA AND Methanol Institute (2021), Innovation Outlook: Renewable Methanol, International Renewable Energy Agency, Abu Dhabi, 2021

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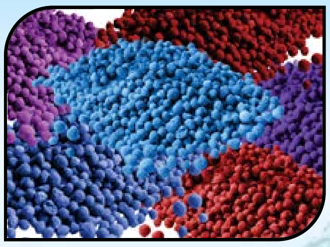

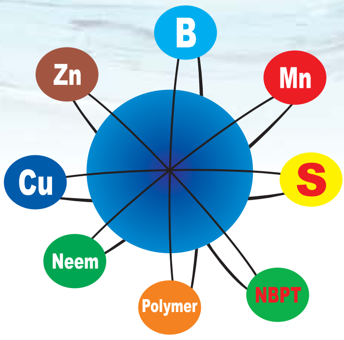
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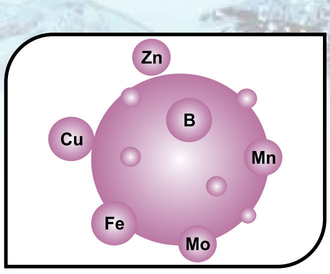
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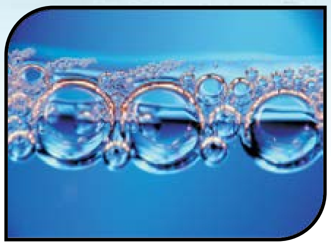

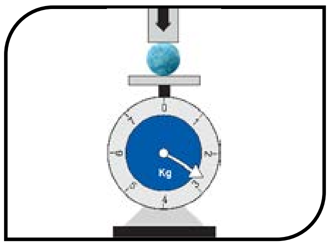

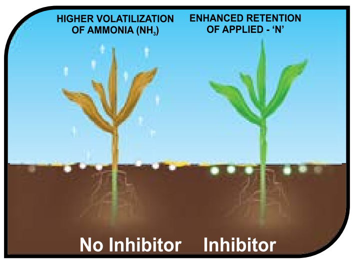
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