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Number 363
January | February 2020

nitrogen+syngas

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Nitrogen + Syngas 2020 Conference, The Hague, Netherlands

Feedstock pricing and marginal producers

Methanol routes to a lower carbon footprint

Reforming catalyst developments

NITROGEN+SYNGAS
ISSUE 363
JANUARY-FEBRUARY 2020

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Cover: *Glass roof of central station, The Hague in the Netherlands.*
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Eliminating CO_2 emissions from methanol production.

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A new focus

> **The way to tackle this is via more efficient use of nitrogen fertilizer.**

At the time of writing this editorial, the World Economic Forum was having its usual annual meeting in the Swiss resort of Davos. Prior to this year's meeting, as usual the WEF had produced its annual Global Risks Report to serve as a talking point for the meeting. While some of the risks were as usual political and economic, from proliferation of weapons of mass destruction and the "retreat from multilateralism" to growing inequalities of wealth in the developed world and "domestic political polarisation", for the first time in the organisation's history, the top five global risks in the report ranked by likeliness – which looks at potential global pitfalls over the next 10 years – were environmental. Perhaps with the pictures of Australia's bush fire season fresh in their minds, the 750 experts ranked extreme weather events as the most likely, but climate change, biodiversity loss and sustainability in agriculture all ranked highly.

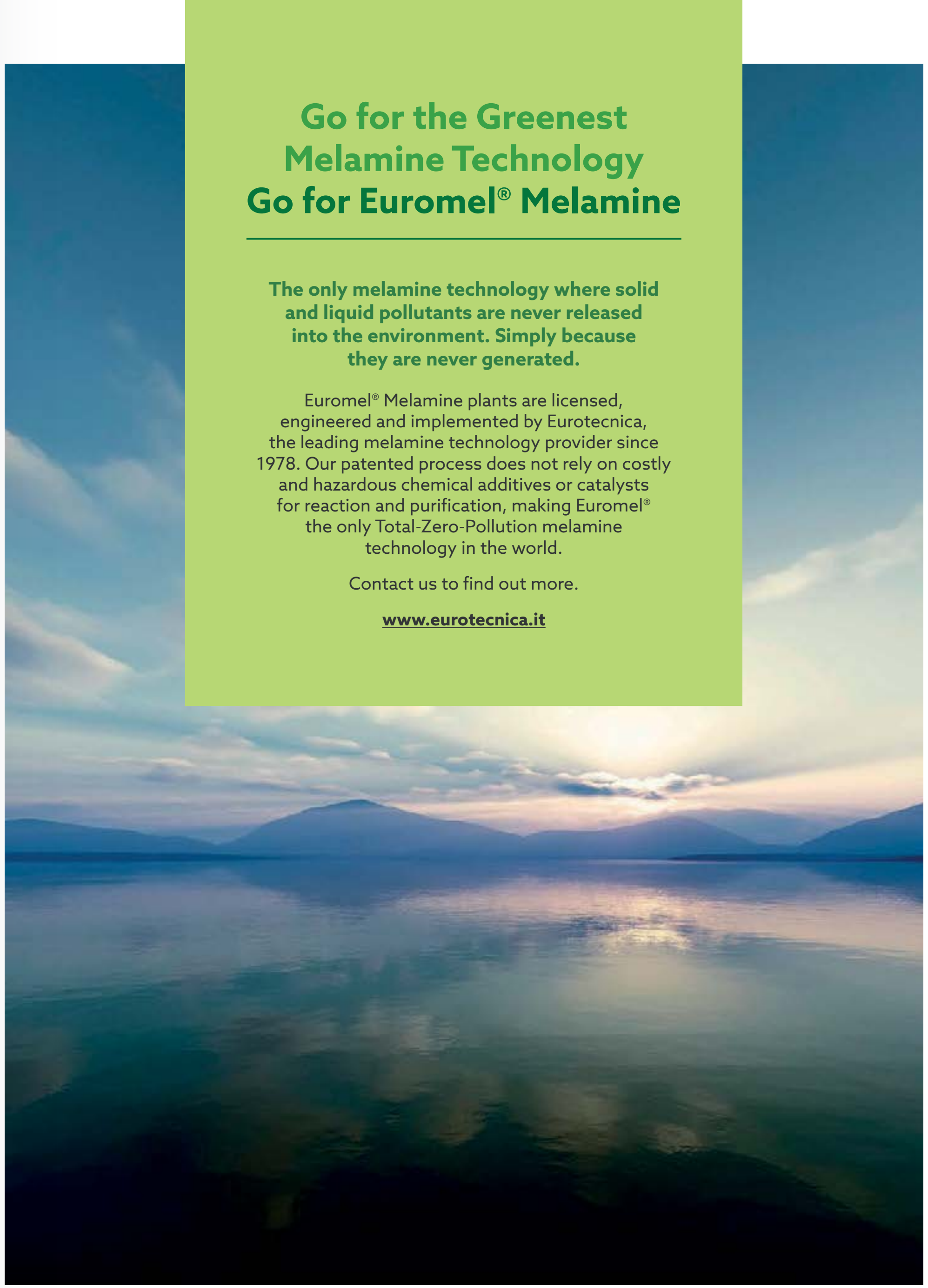
The nitrogen and syngas industries of course have a role to play in helping to tackle these challenges facing humanity in the 21st century. On the production side, the rapidity of advances in the generation of electricity from renewable sources, and in particular the falling cost of electrolysis, is leading to serious consideration of ammonia production from hydrogen generated by water electrolysis or gasified biomass and even, as we reported in our previous issue, the potential use of ammonia or methanol as 'energy carriers' from large solar or wind arrays to point of need/use. In this issue, several advances in low carbon methanol production are discussed, from thyssenkrupp's electrolysis-based process to BASF's 'carbon free' methanol process, recycling CO_2 back into methanol formation. As described on page 41, Johnson Matthey has also, via the process scheme it developed for the proposed NWIW methanol plant in Washington State, designed ways of incorporating renewable electricity into conventional production, lowering emissions from turbine trains and other mechanical parts of the plant.

But production is only part of the issue; on the consumption side, nitrate leaching into water courses and over-application of fertilizer are also major issues that need to be addressed, and excess nitrogen applied to fields is also a source of nitrous oxide emissions to air. In the UK, agriculture was responsible for 69% of all N_2O emissions in 2017. In March last year, during the closing plenary session of the fourth meeting of the UN Environment Assembly (UNEA), delegates adopted a resolution calling for "a coordinated and collaborative approach to sustainable nitrogen management". The resolution recognised "the multiple pollution threats resulting from anthropogenic reactive nitrogen, with adverse effects on the terrestrial, freshwater and marine environments and contributing to air pollution and greenhouse gas emissions", and highlighted ways to better manage nitrogen. UNEP followed this up in October 2019 with the so-called "Colombo declaration", which pledged to reduce nitrogen waste by 50% by 2030.

The way to tackle this is via more efficient use of nitrogen fertilizer, and nutrient use efficiency (NUE) has become an area of focus for farming and industry bodies worldwide. The International Fertilizer Industry Association (IFA) has also moved on this topic, and in December staged a session on nutrient management at last year's UN COP25 Climate Change Conference. This year, in early February, IFA is launching a Global Stewardship Conference with the backing of its agriculture, communications and public affairs, and safety health and environmental committees.

The advancement of these issues onto the agenda at Davos is a harbinger that these things are being taken seriously at the highest levels (with perhaps one or two notable exceptions), and surely a sign of things to come for the nitrogen and syngas industries as we move into the third decade of the 21st century. ■

Richard Hands, Editor



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Price trends

MARKET INSIGHT

Alistair Wallace, Head of Fertilizer Research, Argus Media, assesses price trends and the market outlook for nitrogen.

NITROGEN

With 3Q 2019 seeing slowly rising ammonia prices, the fourth quarter of the year saw prices beginning to flatten out, and then some price declines due to oversupply and weak demand, before the end of 2019 saw the market rebalancing itself, with supply outages in Australia and Trinidad removing excess tonnage from the market. This reversed a two-month weakening price trend. The November contract price for Tampa was agreed up $5/t and Trinidad ammonia was priced at $220/t f.o.b., with Yuzhnyy trading $10-15/t higher. Southeast Asian sales were reported above $260/t f.o.b. for November. The December Tampa price fell $10/t and Trinidad spot fell by the same amount to $210/t f.o.b. The January Tampa price rolled over, as did the Baltic ammonia price.

A poor application season in the US has lowered near-term ammonia demand, while Moroccan import growth is expected to be disappointing, as OCP, the main producer, reduces its output of granulated MAP/DAP. Conversely, concerns over the rate of supply from North Africa has left Yuzhnyy suppliers largely sold out for January and February. Overall the market looks balanced, so any further supply interruptions, particularly in the Middle East, could see some sharp price movements upwards. C.fr values are likely to be bolstered by higher bunker costs and rising time charter rates.

The urea market was predominantly bearish during the fourth quarter, due mostly to a lack of demand. European buyers stayed out of the market, while the Brazilian safrinha corn planting season was delayed. Prices in Brazil eventually bottomed out at around $230/t c.fr, a $50/t fall since September. In Australia and Asia, dry weather and low crop prices also hindered demand. The one bright spot for producers was India, which held several significant tenders in 4Q, stabilising the market after three months of decline. This led to small price rises in China and Egypt. However, US prices continued to trade at a discount for much of the period. Supply for the full year 2019 was boosted by another 2 million tonnes of Chinese exports compared to 2018, while Black Sea urea shipments also rose by around 100,000 tonnes/month. This coincided with reduced import demand in Asia and zero demand growth elsewhere.

With all of the urea in place to cover awards in India, the Asian market is turning bearish. Traders are starting to sell short again. A price recovery in the US still looks vulnerable to incoming cargoes. The outlook is flat to bearish with low Asian demand likely to drag down Middle East urea prices. West of Suez is firmer, but likely to come under pressure too. ■

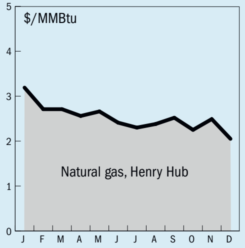
Table 1: **Price indications**

Cash equivalent	**mid-Dec**	**mid-Oct**	**mid-Aug**	**mid-June**
Ammonia ($/t)				
f.o.b. Black Sea	210-225	225-233	195-215	200-210
f.o.b. Caribbean	200-215	193-210	170-190	175-190
f.o.b. Arab Gulf	220-235	230-250	190-205	200-215
c.fr N.W. Europe	250-281	250-285	225-265	230-265
Urea ($/t)				
f.o.b. bulk Black Sea	203-220	225-240	245-260	250-266
f.o.b. bulk Arab Gulf*	238-250	244-260	256-270	285-295
f.o.b. NOLA barge (metric tonnes)	225-240	245	230	248
f.o.b. bagged China	252-270	263-280	277-295	285
DAP ($/t)				
f.o.b. bulk US Gulf	268-294	294-303	313-326	346-349
UAN (€/tonne)				
f.o.t. ex-tank Rouen, 30%N	199	200	197	205

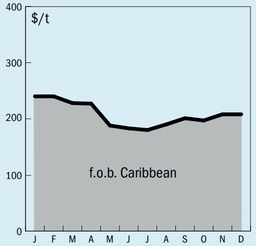
Notes: n.a. price not available at time of going to press.
*n.m. no market   * high-end granular*

END OF MONTH SPOT PRICES

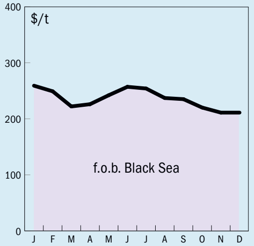
natural gas



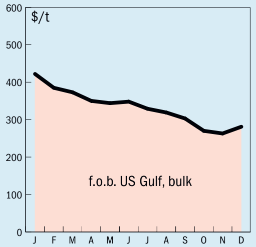
ammonia



urea

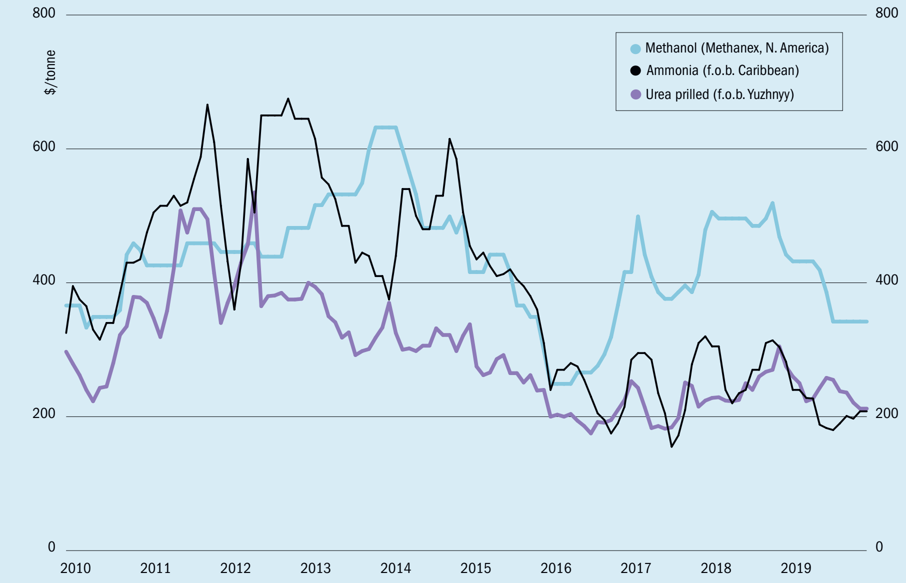


diammonium phosphate



Market Outlook

Historical price trends $/tonne



Source: BCInsight

AMMONIA

- US agricultural demand is expected to pick up in 1Q 2020, and farm inventories are low.
- There are higher freight costs due to the onset of the new IMO regulations which may put a premium on domestic capacity and delay any production cuts made in response to low pricing in both the US and European markets. Both regions are also buoyed by continuing low natural gas prices; 40% down in Europe in 2019 compared to 2018, and 20% down in the US. The US has seen ammonia imports fall as domestic capacity rises.
- Russian ammonia exports are up, rising by around 500,000 tonnes in 2019 compared to the previous year, helping to counter the removal of Iranian tonnage, which was down 60% in 2019 due to renewed US sanctions.
- More demand is expected from OCP in Morocco for ammonium phosphate production.

UREA

- Agricultural demand is expected to generally pick up in 2020 following a poor year in 2019, with spring corn planting requiring significant tonnages. Overall demand is forecast to be 200,000 t/a up in 2020.
- However, urea stocks are comparatively high in the US after last year's disappointing application season, and end of year applications were also down due to poor weather.
- Indian buying has so far supported the market, with record rainfall helping to boost demand last year. India received 3.7 million tonnes in 4Q 2019 and so far has contracted for 700,000 t in 1Q 2020. Indian urea imports were up 34% in 2019.
- China however has more urea available due to falling coal prices and a favourable dollar exchange rate which have helped importers to turn around the country's long-term decline in urea exports, for now.

METHANOL

- Methanol markets will see more new capacity this year. In Iran, two new plants are expected to come onstream, at Bushehr and Pars, each with a capacity of 1.65 million t/a. In spite of US sanctions, Iranian deliveries into China are expected to increase.
- This comes on top of additional tonnage expected from Russia and Trinidad – the latter from the new Caribbean Gas Chemicals unit, scheduled for 1H 2020.
- Chinese MTO production has been running at record levels, helping to absorb some of the excess, and production outages in southeast Asia have also helped, but new conventional olefins production in Asia may squeeze Chinese MTO producers going forward, in spite of new MTO capacity coming onstream, and reduce Chinese demand for methanol.
- Overall methanol markets look bearish for 2020. ■

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Nitrogen Industry News

NETHERLANDS

Tecnimont and Stamicarbon celebrate 10th anniversary

Maire Tecnimont and its urea licensing subsidiary Stamicarbon celebrated the 10th anniversary of Tecnimont's purchase of Stamicarbon from DSM at Limbricht Castle in the Netherlands. The event, attended by Stamicarbon employees and the management of both companies, was an opportunity for the companies to reflect on the past ten years, as well as future developments and opportunities. From Maire Tecnimont's point of view, it has enabled them to become a leading technology provider for urea production, and strengthened the group's identity as a major technology licensor and EPC contractor for fertilizer plants. Stamicarbon was able to broaden its value proposition thanks to effective synergies with the group's sister companies, while leveraging Maire Tecnimont's network to expand its international footprint.

Speaking at the event, Pierroberto Folgiero, CEO of Maire Tecnimont said: "Innovation is the result of vision and investment, but to take off, it needs know-how and human capital, two qualifications that Stamicarbon has always had. The future driver for innovation and transformation of the group will be digitalisation, where we were able to make a step forward by acquiring the company Protomation, specialised in information technology with an extensive portfolio in the fertilizer sector. The acquisition also brought growth to Stamicarbon, as we were able to expand our portfolio of products and services (e.g. by including Basic Engineering) to accelerate our growth."

Pejman Djavdan, CEO of Stamicarbon said. "In order to keep feeding a growing population we will focus, together with the group, on sustainable intensification of agriculture with fertilizers. This means that production of fertilizers needs to be optimised to keep less impact on the environment and to be based on renewable energy sources. But also new technologies have to be developed to make fertilizers more efficient and effective. A challenge that we and Maire Tecnimont will work on." ■

AUSTRALIA

Burrup fertilizer plant moving ahead

Perdaman Industries, which is developing the US$4.5 billion Burrup fertilizer project in northwest Australia, says that it has now received the backing of the local Murujunga Aboriginal Corporation (MAC), and can proceed to planning and environmental approvals. The agreement will see Perdaman contributing more than $11 million over the estimated 25 year life of the project to MAC, which represents the Yinjibarndi, Yaburara, Mardudhunera and Wong-Goo-Tt-Oo peoples. The funding is partly for support and preservation of indigenous art and culture, including the Burrup Peninsula's extensive rock art, which has been submitted for World Heritage status, and about which there were concerns that emissions from the plant could degrade the petroglyphs.

Perdaman is planning to build a 2 million t/a ammonia-urea plant, exporting finished product via the nearby port of Dampier. The Burrup Peninsula is already home to the Yara Pilbara Fertilisers ammonia plant, and the Yara Pilbara Nitrates ammonium nitrate plant, which is currently nearing completion. Once planning and environmental approvals are complete and project finance in place, which Perdaman anticipates being complete in 1H 2020, construction can begin, with completion expected by the end of 2023 and commercial production beginning in 2Q 2024.

PHOTO: URALCHEM

Uralchem's Dmitry Konyaev (second from right) at the signing ceremony in Angola.

ANGOLA

Uralchem in joint venture fertilizer project

Uralchem has signed a memorandum of understanding with Angola's Grupo Opaia SA for the development of a joint venture ammonia and urea complex. The signing ceremony was attended by Dmitry Konyaev, deputy chairman of Uralchem's board of directors and Agostinho Kapaia, president of Grupo Opaia SA. The proposed project is a 1.2 million t/a ammonia-urea unit, with cost put at $1.2-1.3 billion, with bank financing to be arranged by Uralchem. The projected on-stream date for the complex is 2023. Uralchem will be responsible for all issues related to the design and construction of the plant and sale of the products, while Grupo Opaia SA will be responsible for approvals and documentation, securing gas supply and selecting a suitable site.

Speaking at the ceremony, Dmitry Konyaev said that the existing problems in Africa related to food, logistics and technology can be solved only if there will be support from individual countries, as well as from development institutions, governments and the business community. He stressed that Uralchem is ready to offer not only mineral fertilizers, but also digital solutions for farmers, as well as agricultural consulting services.

POLAND

KBR technology selected for nitric acid plant

KBR has been awarded a contract to license its proprietary Plinke Magnac technology to produce high concentration nitric acid at Grupa Azoty's Tarnow site in Poland. KBR will provide basic and detailed engineering design, equipment, and related advisory services for the plant, which will be built adjacent to an existing plant that was also supplied by KBR (via its takeover of Weatherly Inc), and which been in operation since 1998. Magnac technology is used to produce 98.5 wt% high concentration nitric acid from fresh, weak nitric acid.

Grupa Azoty is a leader in the fertilizer and chemical market in Poland and one of the key players in Europe. It is the second largest EU-based manufacturer of nitrogen and compound fertilizers, as well as a range of other products, including melamine, caprolactam, polyamide, oxo-alcohols, plasticisers and titanium white.

"This contract reinforces KBR's existing relationship with Grupa Azoty," said Doug Kelly, KBR President, Technology Solutions. "We are proud to deliver well-proven solutions that will enable Grupa Azoty to achieve its business expansion goals safely, reliably and efficiently."

INDIA

Ramagundam plant aiming for March commissioning

Ramagundam Fertilizers and Chemicals Ltd (RFCL) says that it expects to complete commissioning of its urea plant at Ramagundam and begin commercial urea production by the end of March. The gas supply pipeline from Kakinada is now operational and the plant's flare stack was recently commissioned. The plant will be the first of the previously closed state-owned fertilizer plants, in this case run by the Fertilizer Corporation of India Ltd, which are being revamped and upgraded and brought back on-line as part of the government's attempt to reassert Indian self-sufficiency in urea production. RFCL was incorporated in 2015 as a joint venture between National Fertilizers Ltd (NFL) and Engineers India Ltd, which both have a 26% stake, the Fertilizer Corporation of India Ltd and the government of Telangana, both with 11%, the Gas Association of India Ltd (14.3%) and the HTAS Consortium (11.7%). The plant's new foundation stone was laid by India's prime minister Narendra Modi in August 2016.

KBR, Stamicarbon to supply technology for Talcher ammonia-urea project

KBR has secured a contract for its ammonia synthesis technology from Wuhuan Engineering Co., Ltd for the Talcher fertilizer unit, as part of the benchmark coal-to-urea project in India. Under the terms of the contract, KBR will provide the technology license and basic engineering design, catalyst, and proprietary process equipment for the plant, based on KBR's ammonia synthesis technology.

The project is part of the Government of India's efforts to increase domestic urea capacity for fertilizer production, reducing India's reliance on imported urea and fertilizer. At present, there are no operational coal gasification based urea plants in India. Wuhuan is the EPC contractor for Talcher Fertilizer Limited (TFL), a joint venture of Indian public sector companies formed to complete the project.

"We are proud to be part of this significant project in India," said Doug Kelly, KBR President, Technology Solutions. "KBR's ammonia synthesis process will deliver flexibility, reliability, and cost competitiveness to Talcher for years to come."

Stamicarbon have been awarded the license for the associated urea plant. The company says that this project is a strategic milestone, as it marks 40 years of Stamicarbon's presence in the Indian market. Stamicarbon will deliver the process design package for a 3850 t/d urea melt and prilling plant, featuring a pool condenser design. The complete synthesis section will be carried out in *Safurex*® stainless steel. The commissioning of the plant is expected in 2023.

IndianOil to collaborate on DEF bulk dispensing

IndianOil has signed an agreement with Cummins Technologies India Pvt Limited for bulk dispensing of IndianOil's diesel exhaust fluid (DEF) urea solution, branded as *IOC ClearBlue*, in their advanced engines with SCR (selective catalytic reduction) systems. Subimal Mondal, executive director, IndianOil, and Anjali Pandey, vice president (engine business unit and component business), Cummins India, signed the agreement.

Ms. Pandey said, "In the new emission era of BS-VI, all diesel vehicles will require *IOC ClearBlue*, and the right quality will extensively help in controlling the NOx emitted. Its easy availability at fuel stations will ensure availability and consistent quality across the country."

India will shift to BS-VI auto fuel emission norms from 1st April 2020. Automobile companies are effecting several technical changes in diesel vehicles such as provisions for fitting diesel particulate filters, selective catalytic reduction (SCR) systems and exhaust gas recirculation (EGR). ■

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Syngas News

DENMARK

Haldor Topsoe and Sasol to offer joint GTL licenses

Haldor Topsoe and Sasol have announced that they have entered into a collaboration agreement to jointly license their GTL technologies. For many years, the two companies have worked together on numerous GTL projects and technologies, and Topsoe's *SynCOR*™ syngas generation technology and Sasol's Fischer-Tropsch technologies have been licensed for several world-scale GTL ventures. Under the new collaboration agreement, the companies will continue to offer these core technologies, but will now also provide Topsoe's hydroprocessing and hydrogen technologies. This gives potential customers access to a single-point licensing offering that covers the entire value chain from gas feed to liquid fuels. As single-point licensors, Sasol and Topsoe will offer customers all necessary technology licenses for a complete GTL solution and in addition provide basic engineering, catalysts, and hardware.

TechnipFMC has been pre-approved to provide licensor engineering support and carry out front-end engineering design, detailed design, procurement, and construction. TechnipFMC was the engineering, procurement and construction (EPC) contractor for the Oryx GTL facility in Qatar and has performed a number of front-end engineering designs for GTL facilities, including the Uzbekistan GTL.

Amy Hebert, Deputy CEO of Topsoe said: "It is a pleasure to announce this collaboration. Together, Sasol and Topsoe now offer customers complete and proven end-to-end GTL solutions. This is unique and extremely valuable for customers seeking bankable GTL solutions for monetizing abundant natural gas reserves. With this collaboration, we now offer customers a full range of solutions based on many of Topsoe's core technologies, and we are excited to expand our companies' global leadership for proven gas monetization solutions."

Marius Brand, Acting EVP Technology of Sasol, added: "Sasol and Haldor Topsoe's technology relationship spans more than 20 years, through which we have successfully commercialized several advanced technologies. We are delighted to enter into this collaboration arrangement, and with the support of TechnipFMC we're able to offer the best GTL technology to the market. Although Sasol announced in 2017 it would not pursue future equity participation in greenfield coal to liquids or GTL opportunities, we recognise that our Fischer-Tropsch technology has a role to play in monetising in-country natural gas resources otherwise not accessible. In addition, the technology could play a significant role, in conjunction with renewable energy resources, in the conversion of greenhouse gases to sustainable liquid fuels. The combination of the Sasol and Topsoe technologies offers a proven and robust solution for these applications." ■

Acting Executive Vice President of Sasol, Marius Brand, (left) and CEO and President of Topsoe, Bjerne S. Clausen, signing the partnership agreement, witnessed by (from left to right) Vice President of Sasol, Theo Pretorius, Deputy CEO of Haldor Topsoe, Amy Hebert, and Vice President of Topsoe, Fei Chen.

UNITED KINGDOM

WEC launches Hydrogen Global Charter

The World Energy Council (WEC) has launched the Hydrogen Global Charter. This initiative aims to be "a platform to recognise the momentum of hydrogen as a complement to electrification as well as the long-term storage option for renewables", according to the WEC, and will draw together disparate commitments to consume, enable, and invest in clean hydrogen around the world to create a common platform that recognises progress toward bringing scalable and cost-effective clean hydrogen to the market. Any company, government or organisation working to enable and create demand for clean hydrogen can sign the Charter. At its launch, two founding signatories included European energy infrastructure Snam, and SWEN Capital Partners.

Dr Angela Wilkinson, Secretary General of the World Energy Council said: "Global demand for energy is rising and there is no quick fix or silver bullet solution to challenges of energy security, equity and affordability and environmental sustainability. New hydrogen pathways can help achieve bolder ambitions for better lives and a healthy planet. Clean hydrogen can reach parts of the global energy system that cannot be electrified."

Haldor Topsoe wins IChemE award for its *TIGAS*™ technology

In November, members of the Topsoe *TIGAS*™ technology team received the 2019 Institute of Chemical Engineers (IChemE) Global Award in the Oil and Gas category at an event in Hull, UK. *TIGAS* is based on proven Topsoe technology platforms and catalysts, the key being the proprietary *SynCOR Methanol*™ and Gasoline Synthesis technologies. Topsoe offers all catalysts and technology for the process, and describes itself as the only single company in the world that offers an end-to-end gas-to-gasoline solution, including license, basic engineering, catalyst, and hardware. Recently, the world's only natural gas-to-gasoline plant in operation began production in Turkmenistan, based on *TIGAS* technology, with a capacity of 15,500 bbl/d. Topsoe says that TIGAS is suitable for regions with abundant gas resources, where it represents an attractive option to monetise natural gas by producing synthetic gasoline that complies with the highest environmental standards, contains no sulphur and very little unwanted by-products, which can be sold into a local or export market.

The new TIGAS-based methanol to gasoline plant, Turkmenistan.

Speaking at the awards, Kim Knudsen, executive vice president of Topsoe's Sustainables Business Unit said: "To us, the Oil and Gas award 2019 is the culmination of decades of complex catalyst development, pilot testing, reactor design, and process engineering. The triumph with TIGAS today has only been possible by sharing competences and experience across our entire company… We are extremely happy to receive this recognition from the renowned IChemE organisation and peers in the industry."

Waste-to-hydrogen plant secures funding

The UK's first waste-to-hydrogen plant has secured funding for the next stage of its development at its site in Ellesmere Port, Cheshire. Peel L&P Environmental has committed to funding the development of the distributed modular gasification (DMG) facility at its Protos Energy Park, using gasification technology developed by UK technology company Powerhouse Energy Group. The Protos facility will be managed by Waste2Tricity after the engineering company obtained the exclusive rights to use Powerhouse's technology in the UK and Southeast Asia. Projected to cost £7 million, it will have the capacity to process 35 t/d of waste plastics, aiming to produce 3.8 MW of electricity on site, to export 3.4 MW and to produce up to 2 t/d of hydrogen per day from the site.

David Ryan, CEO of PowerHouse Energy, commented: "This agreement represents the completion of the preliminary engineering stage and I am most encouraged that the PHE team have achieved a major uplift in the performance of the DMG process, including almost doubling the hydrogen output to two tonnes, significantly enhancing our partners commercial drivers. The commitment demonstrates significant commercial confidence from Peel L&P Environmental to the immediate and long-term deployment of the process in the UK."

Start-up for waste to energy plant

North Wales-based waste gasification plant Parc Adfer began full commercial operations in December, following a commissioning phase throughout 2019. The plant, located at Deeside and operated by Wheelabrator Technologies, will process up to 200,000 t/a of non-recyclable waste and is capable of generating 19 MW of electricity. Bill Roberts, chief operating officer of Wheelabrator UK, said: "Wheelabrator Parc Adfer will play an important role in securing future baseload electricity supply, reducing carbon emissions and improving sustainable waste management for the local area in North Wales."

SWITZERLAND

Clariant to sell Masterbatches business

Speciality chemicals company and catalyst supplier Clariant has agreed to sell its entire plastics additive Masterbatches business to PolyOne. The transaction values the Masterbatches business at $1.56 billion, on a cash and debt free basis. This amount is payable at closing, which is expected by Q3 2020. Clariant says that the proceeds from the divestments of the company's non-core businesses will be used to invest in innovations and technological applications within its core business areas, to strengthen its balance sheet and to return capital to shareholders. As a consequence of the divestment of the Masterbatches business and the anticipated divestment of the company's Pigments business by the end of 2020, Clariant's board is proposing an extraordinary cash distribution of CHF3.00 per share at the company's annual general meeting in March. Subject to a positive vote of Clariant's shareholders, the extraordinary distribution of approx. CHF 1 billion will be paid out post the closing of the divestment of the Masterbatches business.

Hariolf Kottmann, Executive Chairman of Clariant said: "This announcement is a significant milestone on our path to focussing on businesses with above-market growth, higher profitability and stronger cash generation. After the successful divestment of Healthcare Packaging in October 2019, the agreement to sell Masterbatches is an important step in delivering on our strategy defined in 2015 to concentrate on our three core business areas: Care Chemicals, Catalysis and Natural Resources. As announced, we are confident that we will execute the remaining divestment of our Pigments business in 2020 in order to build the new, more focused and stronger Clariant by 2021," he added.

NETHERLANDS

Koolen Industries invests in Proton Ventures

Dutch clean energy company Koolen Industries has invested €4 million in ammonia energy storage company Proton Ventures. Proteon designs and builds pressurised and cooled ammonia storage facilities, as well as small-scale ammonia production facilities called *NFUEL* units, and says that the investment will help it speed up its roll-out of the *NFUEL* technology around the world.

"Proton Ventures' unique and patented technologies enable the production of ammonia using clean energy sources," said Kees Koolen, CEO of Koolen Industries. "Ammonia is an ideal storage solution for solar power plants and wind farms as it is particularly well suited to store and transport large amounts of energy in efficient ways. This makes it perfect fit for

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Kees Koolen (L) and Haus Vrijenhot (R).

Koolen Industries as we continue to push the global transition to clean energy."

Hans Vrijenhoef, CEO of Proton Industries added: "It is as important to us that Koolen Industries is present and active across the entire energy chain; from clean energy generation and storage to the transportation and delivery of energy to the end customer. This creates great opportunities for ongoing cooperation and opens doors for us to bigger projects."

EQUATORIAL GUINEA

Study on methanol plant conversion to refinery

Equatorial Guinea's Ministry of Mines and Hydrocarbons (MMH) is set to order the dismantling of the Atlantic Methanol (AMPCO) methanol plant on Bioko Island, calling instead for its conversion into a modular crude oil refinery. The MMH has commissioned a feasibility study for the conversion of the Punta Europa methanol plant, part of the larger Punta Europa gas processing facility, which is owned by Marathon Oil and Noble Energy Inc. (each with a 45% share) and the remainder by the local Sociedad Nacional de Gas de GE SA. The ministry is unhappy about what it sees as lack of investment in the offshore Alba field, operated by Marathon, which feeds the plant, production from which is declining, and has suggested that Marathon's work programme and exploration and production budget have not been sufficient to keep the plant running.

Equatorial Guinea is now developing its new 'Gas Mega Hub' project, aiming to provide additional gas supply to processing facilities, both onshore and offshore. The first phase of this will be a new gas supply agreement signed between the MMH and Noble Energy, operator of the Aseng and Alen fields for gas supply to the Punta Europa gas complex, which includes the Malabo power station, AMPCO methanol plant and the Equatorial Guinea LNG plant.

IRAN

Apadana methanol plant to commission in 2021

Construction of the Apadana Petrochemical Plant is 47% complete and the project is on-course for commissioning in 2021, according to the company's CEO Jalil Ghasamni. Speaking to local press in December, he said that offtake of the output of the 1.65 million t/a methanol plant has been guaranteed by the Persian Gulf Petrochemical Industries Company (PGPIC). Previously known as the Veniran plant, after an abortive collaboration between Venezuela and Iran, Apadana uses methanol technology licensed from Casale. It has been built at a cost of $510 million. Iran's current methanol output stands at 8.3 million t/a, of which only 300,000 t/a are consumed domestically and the rest exported.

UNITED STATES

Kalama methanol permit saga rumbles on

The battle over an environmental permit for Northwest Innovation Works' (NWIW) proposed methanol plant at Kalama in Washington State continues, with the Port of Kalama now resorting to legal action to compel a "timely review" of the $2 billion methanol plant project by the Washington State Department of Ecology. After nearly five years of environmental review, the methanol project still has not had a final decision from the Department of Ecology for a key shorelines permit. Meanwhile, an environmental impact assessment by the company was initially rejected and re-submitted, but the Department of Ecology recently rejected a greenhouse gas emissions study on the proposed plant completed by Cowlitz County and the Port of Kalama, deciding to complete its own report, which will include GHG emissions incurred in extracting natural gas feedstock and transporting it to Kalama. NWIW has pledged to offset all its in-state greenhouse emissions, and the county/port climate change analysis concluded that the project would reduce global emissions by at least 10 million t/a, or the equivalent of about 2 million cars, by offsetting coal-based methanol production in China, where the methanol would be used for methanol to olefins (MTO) production.

FEED study on gas to gasoline plant

Primus Green Energy, together with joint venture partnerh IHI E&C International Corporation, has commissioned a front end engineering and design (FEED) study for a first of its kind natural gas-to-gasoline plant in Texas. The proposed plant will be a scaled-up version of Primus's demonstration plant in New Jersey, which has successfully produced methanol and gasoline using Primus's patented modular STG+ technology. The proposed plant would consume 28 MMcf/d of natural gas to produce 2,800 bbl/d of gasoline. The FEED study is expected to conclude in the middle of 2020.

STG+ combines steam reforming, syngas to gasoline production via a series of catalytic fixed-bed reactors via methanol and dimethyl ether intermediates, and liquid/gas separation, where the products are cooled and condensed. The gasoline product is sent to storage; the water is reused to make steam for the reformer; and the unconverted gas is recycled, with a portion being used to fuel the reformer.

TRINIDAD & TOBAGO

Methanex secures gas for January

Methanex says that it has entered into an interim agreement with National Gas Company of Trinidad and Tobago Limited (NGC) for the continued supply of natural gas to its Titan methanol facility. The supply runs for the calendar month of January, and extends a previous deal which expired on December 31st 2019. Methanex says that negotiations for a longer term natural gas supply deal will continue during the period of the interim arrangement to try and secure the future operations of the plant.

SWEDEN

Methanol from renewables project secures funding

European investment fund InnoEnergy will invest $1.89 million in Swiss eco methanol developer Liquid Wind so that the Gothenburg-based circular carbon energy company could develop a commercial scale renewable methanol facility in Sweden. Liquid Wind plans to convert waste carbon dioxide together with hydrogen from renewable power into renewable methanol. The company is working with a consortium of experts, including Haldor Topsoe, Carbon Clean Solutions, NEL, Axpo and COWI in the so-called FlagshipONE project. Liquid Wind says that it will now begin engineering for its first methanol facility in Sweden. Longer term, the company is aiming to build six initial facilities in Scandinavia and then replicate the operation internationally. Each plant will be designed to capture 70,000 t/a of CO_2 and generate 54,000 t/a of methanol. The FlagshipONE facility is expected to be operational on a commercial basis from 2023.

NIGERIA

NNPC to increase stake in GTL plant

Nigeria's state oil company the Nigerian National Petroleum Corporation (NNPC) says that it will increase its stake in a Chevron-operated gas-to-liquid plant to 60% as part of a cost dispute resolution with the US major. NNPC currently has a 20% stake in the plant, 100 km southeast of Lagos. The 33,000 bbl/d plant cost $10 billion to complete in 2014, four times the original cost estimate, and several years late. The plant produces synthetic diesel, liquefied petroleum gas and naphtha from natural gas using Sasol technology.

ROMANIA

Romgaz looking at new methanol plant

Romanian state gas company Romgaz is looking at a new 500,000 t/a methanol plant, with an investment of about €2-300 million, according to the company's general manager, Adrian Volintiru. The company is aiming to diversify its product portfolio and serve "a more complex palette of customers". The company has commissioned a market study by consulting firm Horvath & Partners, in order to highlight the opportunities in this segment.

RUSSIA

Tospoe wins license for Gaz Sintez methanol plant

Gaz Sintez has nominated Haldor Topsoe as licensor for the company's new 1.6 million t/a methanol plant, to be built at the port of Vysotsk near St Petersburg in Russia's Leningrad Region. Hyundai Engineering has been working on the FEED-package, and Russia's NIIK has been awarded the Russian general designer contract. The plant is expected to be completed in 2023.

The plant will feature Topsoe's SynCOR Methanol™ technology, featuring single-stage oxygen reforming, a methanol synthesis loop and rectification. Topsoe claims that as well as being the most cost-efficient large-scale methanol technology in industrial operation, it also offers environmental advantages and lower water consumption compared to traditional technologies. ■

CORRECTION

Further to our article in the September/October issue on The Future of Gasification (*Nitrogen+Syngas* 361, pp22-24), Linde Engineering would like to make clear that they do supply gasifiers for heavy residue and NG gasification, particularly for integrated complex plants and own investment.

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People

EuroChem Group has announced the appointment of Samir Brikho as chairman of the company's board of directors. Brikho has served on the board since 2018. He has also held senior management positions at Asea and ABB Power Generation between 1983 and 2000, before moving to Alstom, where he served as Chief International Operations Officer and Senior Vice-President, and CEO of Alstom Kraftwerke in Germany. In 2003, he became CEO of ABB Lummus Global and in 2005 he was appointed to the Group Executive Committee of ABB Ltd, and served as Head of the Power Systems Division at ABB Group. From 2006 to 2016 he was CEO of Amec Foster Wheeler. In 2009 and 2016 Brikho was chair of the World Economic Forum's Engineering and Construction Board.

He replaces **Alexander Landia**, who is leaving the board after more than six years' service but continues in other roles within AIM Capital SE group, the holding company of EuroChem Group AG.

Brikho commented: "I am proud to be taking over as Chairman at such an exciting point in EuroChem's history. I see enormous potential for the business and am looking forward to helping the company become the most successful player in the fertilizer sector."

The Agricultural Industries Confederation (AIC) has announced the election of **Angela Booth** as its new Vice Chairman. AIC says that Angela brings many years of broad experience in the industry, including several years as Chair of the AIC Feed Executive Committee, a member of the AIC Board, and several roles on industry executives and committees. She was previously the AB Agri Director of Feed Safety. In her career, Angela has had widespread involvement, including feed safety, operations, quality, nutrition, purchasing, legislation and sustainability.

"I'm delighted to assume the position of Vice Chairman at AIC, an organisation that continues to act as the leading voice for the UK farming industry," Angela Booth saod. "We operate in unpredictable times, making AIC's role as the leading voice for agri-supply trade members more vital than ever. AIC's members are key in supporting arable and livestock producers with their extensive knowledge and expert guidance. As it becomes more important than ever to both produce food efficiently and manage our natural resources, AIC will be a strong voice for its members in discussions with government departments, NGOs, and relevant bodies both in and outside of the UK."

Anglea Booth.

"I'm very pleased that Angela will be taking the role of Vice Chairman following her election," said Robert Sheasby, Chief Executive of AIC. "Angela has been a key figure at AIC in promoting members' interests across the UK agriculture industry. As the agri-supply element of agriculture faces a growing number of challenges and opportunities in the coming years, we need the insight and forward vision of leaders like Angela who will lead AIC members with a strong voice and intelligent outlook." ■

Calendar 2020

FEBRUARY

6-7

IMPCA Mini-Conference America,
MIAMI BEACH, Florida, USA
Contact: International Methanol Producers and Consumers Association,
Avenue de Tervueren 270 Tervurenlaan,
1150 Brussels, Belgium
Tel: +32 2 741 86 83
E-mail: info@impca.be

11-13

AFA Annual Forum & Exhibition,
SHARM EL SHEIKH, Egypt
Contact: Arab Fertilizer Association,
9 Ramo Buildings, Al Nasr Road,
Nasr City, Cairo, Egypt
Tel: +20 2 23054464
Fax: +20 2 23054466
Email: afa@arabfertilizer.org

17-19

Nitrogen+Syngas 2020,
THE HAGUE, Netherlands
Contact: CRU Events,
Chancery House, 53-64 Chancery Lane,
London WC2A 1QS, UK
Tel: +44 (0) 20 7903 2444
Fax: +44 (0) 20 7903 2172
Email: conferences@crugroup.com

19-21

Argus Africa Fertilizer 2020,
CAPE TOWN, South Africa
Contact: Argus Media, Ltd
Tel: +44 (0)20 7780 4340
Email: fertconferences@argusmedia.com

MARCH

3-5

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

9-11

Syngas 2020, MEMPHIS, Tennessee, USA
Contact: Betty Helm, Syngas Association,
Baton Rouge, Louisiana.
Tel: +1 225 706 8403
Web: www.syngasassociation.com

APRIL

20-22

IFA 88th Annual Conference,
NEW DELHI, India
Contact: IFA Conference Service,
49 Avenue d'Iena, Paris, F75116, France
Tel: +33 1 53 93 05 00
Email: ifa@fertilizer.org

MAY

20-22

IFS Technical Conference,
THE HAGUE, Netherlands
Contact: International Fertiliser Society,
PO Box 12220, Colchester, CO1 9PR, UK
Tel: +44 (0)1206 851 819
Fax: +44 (0)1206 851 819
Email: secretary@fertiliser-society.org

JUNE

2-4

Nitrogen+Syngas USA,
TULSA, Oklahoma, USA
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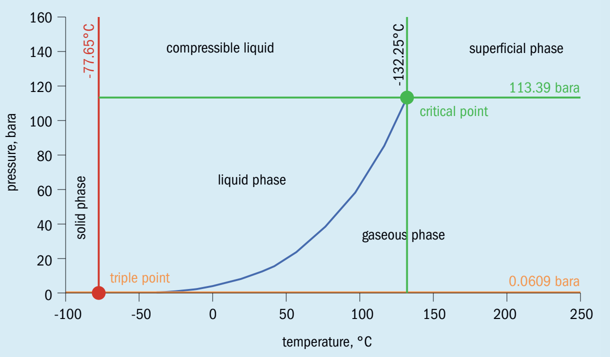
Plant Manager+

Problem No. 58 Should liquid ammonia be drained to the ammonia water tank or vent stack?

Liquid ammonia is one of the feeds to the urea plant. It typically comes from the ammonia plant at a pressure of about 20 bar. In the urea plant this liquid ammonia is further pumped up to synthesis pressure conditions, sometimes after passing through a buffer tank, a heater and/or a filter. According to the ammonia phase diagram, when liquid ammonia flashes to atmospheric pressure temperatures can drop to as low as -33°C under worst case conditions. In case one or more of the above mentioned items of equipment needs to be drained for maintenance, a decision needs to be made where to drain this liquid ammonia. In a urea plant the options are the ammonia water tank or the vent stack, but which is best option?

Ammonia phase diagram



Source: The Engineering ToolBox

Ebrahim Mohamad Kamal of Abu Qir Fertilizers Company in Egypt starts this interesting discussion: What are the potential hazards from draining liquid ammonia to the ammonia water tank as some people prefer to drain it to the vent stack, which in turn directs ammonia to the ammonia water tank? Is there a difference between draining liquid ammonia from the ammonia pump or ammonia filters to the ammonia water tank or the vent stack?

Ahmed Selim of AlexFert in Egypt replies: In our plant, the vent stack is not supposed to receive pure liquid ammonia such as that present in the liquid ammonia system.

Ebrahim replies: We suppose that draining liquid pure ammonia to the vent stack is less hazardous than to drain it to the ammonia water tank as there is no hammering and the ammonia ends up in the ammonia water tank after overflow from the vent stank but at a lower pressure.

Muhammad Umar Riaz of Fatima Fertilizer company Ltd in Pakistan joins the discussion: Normally the liquid ammonia circuit piping is designed to cater for the impact of cold embrittlement while filling the ammonia circuit and draining/venting ammonia (at lower pressure when ammonia evaporates it causes sudden cooling i.e. cold embrittlement). That is why the ammonia circuit filling is carried out by first pressurising the ammonia circuit with nitrogen gas in order to avoid exposure of ammonia piping at a very low pressure, similarly during depressurisation of the ammonia circuit when the ammonia pressure falls below that of the nitrogen (utility header) pressure, any further depressurisation of ammonia will be carried out under nitrogen pressure due to the effects mentioned earlier.

Ammonia circuit piping is also protected against these sudden cooling shocks by using a suitable material of construction such as killed carbon steel. First, if you drain liquid ammonia into the ammonia water tank it will cause sudden cooling and may lead to cracks in the pipeline downstream of the ammonia circuit. Secondly when liquid ammonia evaporates in the ammonia water tank it will ultimately increase the pressure and release into the atmosphere and pose a safety concern. That is why it is preferred not to drain liquid ammonia directly into the ammonia water tank but to evaporate it to the vent header, from where it can be absorbed in showering water/condensate and finally recovered in the ammonia water tank.

Ebrahim replies again: In our plant design all the drains of the piping system for liquid ammonia are directed to the ammonia water tank and not to the vent stack. This is also the case for the drains of the high pressure ammonia pumps and the candle filter on the suction of theses ammonia pumps. So if it more safe to drain liquid ammonia to the vent stack why are all drains are directed to the ammonia water tank?

Ahmed Selim replies: Draining liquid ammonia directly to the ammonia water tank has been applied for several years in many plants, including ours and we have not suffered from any damage to the ammonia drainage system. Don't you think that draining directly to the vent stack will actually increase the possibility of venting more ammonia vapour to the atmosphere compared to draining directly to the ammonia water tank? We know that drainage to the ammonia water tank from the ammonia system should be carried out slowly due to hammering and the impact of temperature and concentration on the tank after drainage. Also, can the material of construction used in the vent stack handle direct drainage of liquid pure ammonia and withstand the drop in temperature (cooling shocks).

Norozipour of Khorasan Petrochemical Company in Iran gives his opinion: I think the following arguments can be considered:

1. In our plant (Stamicarbon) the flow and quantity of liquid ammonia for draining to the ammonia water tank is usually very low.
2. From an environmental point of view it is important to collect any ammonia and hazardous material.
3. The production of ammonia requires energy consumption, therefore it is better to recycle it to the process instead of venting it to the atmosphere.

Mr Bhupen Mehta of IFFCO Kalol in India adds another consideration to the argument: A huge water volume will be required to collect the ammonia in the ammonia-water tank due to the ammonia-water saturation point at ambient conditions.

Prem Baboo of Dangote Fertilizers Projects in Nigeria shares his valuable experience: Good discussion and contribution by everyone. In addition, I think ammonia venting through the vent stack is very dangerous for the environment. Atmospheric ammonia has long been recognised as a key air pollutant contributing to the eutrophication and acidification of ecosystems. The advantages of draining through a closed drain into the ammonia water tank are:

1. Having a closed system for draining the ammonia into the water tank prevents ammonia escape to the atmosphere.
2. There will be some increased load in the waste water section (i.e. the steam requirement will be increased in the distillation tower/desorber), but the ammonia will be recovered (note ammonia is more costly than steam).
3. Most processes are typically total recycle processes so the ammonia must be recycled.
4. Nowadays advanced processes have some buffer tank to hold up the solution like ammonium carbonate and are also designed for shutdown solution hold up (e.g. carbonate solution tank (V-10 in Snamprogetti plants).
5. This is the routine practice to hand over HP ammonia pumps, filters, and ammonia booster pumps, all ammonia must be recovered through the ammonia water section. Some laws on pollution and for the environment to not allow ammonia to be vented. ■

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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Feedstock pricing and marginal producers

Floor prices in nitrogen markets are set by marginal producers high on the cost curve, usually using higher cost feedstocks. Recently, lower coal prices in China and the cost of imported LNG have begun to change the dynamic between producers on the margins.

In times of relative oversupply in the urea and other nitrogen markets, prices tend to be set by the production costs of producers at the margins. In the past decade, these have generally been either gas-based producers paying high imported gas prices, such as in Ukraine or India, or domestic, mainly coal-based producers in China, with the latter increasingly coming to set the floor price for urea.

Chinese coal prices

Globally, usage of coal dropped in 2019 compared to 2018, according to International Energy Agency figures. Coal-fired electricity generation capacity fell by 2.5% during the year, as concerns about greenhouse gas emissions and cheap natural gas (and falling renewables prices) drive a move away from coal-fired generation. In Europe coal-based power generation is on its way to being phased out, while in the US cheap shale gas has seen the proportion of electricity generated by coal fall from 57% at the turn of the century to 27% in 2018. US coal demand peaked in the late 2000s and has dropped by half since then. European coal demand peaked in the 1980s and has likewise halved since then. In spite of rapidly rising use in India and southeast Asia, global coal use seems to have plateaued and may be slowly falling.

This has led to coal prices falling globally, and China has been no exception. China remains the mainstay of coal demand, accounting for half of all coal consumption, and low international prices meant that the Chinese market sucked in imports from Australia and Indonesia in 2019 in spite of Chinese government attempts to protect domestic coal production. However, it appears that imports are likely to reduce in 2020 as the Chinese government continues to prioritise the development of large, efficient domestic mining operations.

On the demand side, Chinese coal-based electricity generation struggles with profitability, and at the start of 2020 the government introduced a new electricity pricing mechanism with a base price plus a variable 'float' range, up to10% above or 15% below the base price level, replacing a one size fits all benchmark tariff set by the National Development and Reform Commission (NDRC). Industry observers believe that the new price structure will result in lower prices in most of China outside of the large east coast cities, as there is already surplus generation capacity. Coal generation is also steadily losing ground to nuclear and renewable power, which the government guarantees purchase of their output to encourage 'clean' electricity generation. Aside from a blip in 2017, Chinese coal demand essentially peaked in 2013 and has been falling slowly since then.

The upshot is that – while coal prices in China peaked in late 2017 and early 2018, over the past two years there has been a growing glut of coal in China, leading to lower prices which have helped sustain Chinese urea producers and encourage Chinese exports of urea.

More efficient production

Another factor affecting Chinese coal-based ammonia-urea production has been a switch in terms of gasification technology. The use of more 'forgiving' gasification processes which can run on lower grade, bituminous coal rather than higher grade anthracite has led to a marked increase in productivity, coupled with the fact that the newer plants tend to be larger and gain efficiencies of scale in addition to smaller, older plants. Greater use of automation has also reduced staffing costs.

CRU calculates that there has already been a major swing away from anthracite-based production in China, with the proportion of Chinese urea capacity using anthracite falling from 50% in 2013 to 37% in 2019, at the same time that bituminous-based production has risen from 18% of the total to 33% in 2019, and projected to reach 39-44% in 2021. The ability to use cheaper coal has lowered the overall cost of Chinese urea production, although a number of anthracite based plants still exist at the margins.

LNG prices

Urea capacity based upon imported liquefied natural gas has often been at the highest end of the cost curve. Many Indian urea plants effectively operate on imported LNG as India runs a gas deficit.

The same has also become true of some of China's gas-based capacity. China is also running a gas deficit as it switches towards more gas-based electricity generation. Demand for gas is increasing by up to 10% year on year (a 14% increase has been estimated for 2019), and in spite of new pipelines from Russia, China is struggling to make up the deficit with imported LNG in spite of increased production from sour gas, tight gas and shale gas. In 2018 China imported 74 bcm of LNG, making it the second largest consumer of LNG in the world after Japan, which switched to LNG-based electricity generation after much of the country's extensive nuclear generation capacity was idled following the Fukishima accident. China overtook Japan last year to become the largest importer of LNG in the world, and the country's gas demand is expected to reach 510 bcm by 2030, more than double the figure for 2018.

China has been gradually liberalising gas prices but gas pricing in China can still be relatively opaque. Imported gas is typically pegged to global oil prices while domestic gas depends upon netbacks to production costs. A survey by the International Agency for Energy Economics in 2018 found gas prices ranging from $6-13/MMBtu throughout China, depending on location. However, what is clear is that these prices are high compared to gas prices in other major nitrogen producing countries like the US or Russia, and even India. This puts Chinese gas-based urea capacity towards the top of the cost curve, and as a result gas-based capacity in China has been squeezed, falling from 29% of urea availability in 2013 to 26% in 2019. Feedstock availability has also been an issue, with gas supply restrictions to Chinese gas-based urea producers during the peak winter electricity demand season.

Set against this, LNG prices have fallen as supply grows faster than demand. LNG exports from the US and Australia, amongst others, are set to increase LNG supply by 100 bcm between 2018 and 2023. In spite of rapidly growing Asian demand, particularly from China, and the US-Chinese trade dispute disrupting US deliveries to China, delivered LNG prices to northeast Asia had fallen from $9-10.00/MMBtu in 2018 to $5.10-5.20/MMBtu at the start of January 2020, lower than domestic Chinese gas prices. Delivered LNG prices to Europe were just $4.00/MMBtu.

India

India is developing new urea capacity to try and reduce its import dependency, as described in our article elsewhere in this issue. However, with the exception of the Talcher plant, which will use coal feedstock, all of the new urea capacity will depend on ammonia made from imported natural gas, as India does not have sufficient domestic gas capacity to operate these plants, and imports roughly half of its natural gas needs. Like China, India also often restricts gas availability during peak demand seasons, which coincide with periods of low rainfall when hydroelectricity is less available. The four new gas-based plants, together with the Talcher unit, should take India's urea capacity from 26.6 million t/a in 2019 to 33 million t/a in 2023.

Since 2014, Indian domestic gas prices have been linked to international gas hub prices such as Henry Hub in the US and the EU-UK International Balance Point. As a result, Indian domestic wholesale gas prices are held artificially low; at the start of January 2020 they averaged around $3.25/MMBtu. However, Indian urea producers do not pay this price, but rather a composite 'pooled' gas price which is also influenced by LNG prices, and the share of domestic gas consumed by the Indian fertilizer industry has shrunk, from around 60% in the 2014-15 financial year to just 30% in the 2019-20 financial year. Regasification costs are high in India, and this has pushed the pool price for fertilizer producers to over $10.00/MMBtu for most of the past two years. This comfortably puts Indian urea plants towards the top of the global cost curve. While LNG prices have fallen for the time being, India's fertilizer producers will be further exposed to global LNG prices, at the same time that low domestic wholesale prices do not encourage new exploration and production activity, meaning that the import gap will grow. However, as the Indian government has taken a strategic decision to operate urea capacity no matter what, it may pay the subsidy no matter what, and operating rates may not be closely linked to gas prices, at least until the new nutrient based subsidy scheme allows domestic fertilizer prices to float towards a market rate.

China still the floor setter

What does all of this mean for urea prices? Although Indian urea capacity is among the highest cost production worldwide, it is supplying a guaranteed domestic market and remains subsidised. As a result, it is China that continues to set the floor price for urea. The switch away from anthracite towards bituminous coal and the gradual sidelining of gas-based capacity in China means that increasingly it is the production costs of Chinese bituminous-based producers which will come to dominate. In November 2019, CRU put those costs at $275/tonne. One other factor to consider is the ongoing closure of Chinese urea capacity. Although new, larger and more efficient plants continue to be built, economic and environmental related closures have seen 19 million t/a of Chinese urea capacity close since 2013, and another 13 million t/a (net 5 million t/a) is likely to close by 2023. Chinese urea exports have already fallen from a peak of 13.7 million tonnes in 2015 to 2.4 million tonnes in 2018, although last year's lower coal prices and the falling remnimbi against the dollar encouraged more exports in 2019, and the 3Q 2019 figure had already reached 3.2 million t/a, with the full year figure is likely to be closer to 4.5 million tonnes. Continued capacity closures may reduce China to a seasonal exporter only, with producers elsewhere in the world setting urea prices outside those periods. ■

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Brazil's nitrogen industry

Brazil is the main centre for new nitrogen demand in Latin America, but in spite of major oil and gas discoveries in the 2000s, has failed to develop a downstream nitrogen fertilizer industry.

Brazil represents about half of South America's 420 million people, and 80% of the region's GDP. Although it is resource rich, the past decade has been a difficult time for Brazil. During the 1990s the Plan Real turned around what had been an economy plagued by inflation and debt, and it was tipped in 2001 as one of the nations to watch – the 'B' on in the 'BRIC' countries. By 2010 it was one of the fastest growing economies in the world, buoyed by a commodities boom and a consumer binge that lasted into 2012. By 2013, however, the economy was shrinking, with exports hit by a contraction in the commodity sector, and in 2014 the country entered the worst recession in its history, which lasted until 2017. The past two years have seen only relatively sluggish growth, and political turmoil as the Operation Car Wash corruption scandal led to the jailing of one former president, the impeachment and removal of a second, and the arrest of a third, and the election of controversial populist president Jair Bolsonaro in late 2018.

Oil and gas

Although its oil and gas reserves were relatively small compared to the size of the country, between 1995 and 2005, huge offshore discoveries tripled Brazil's proved oil reserves to 12 billion barrels, and another 3 billion barrels have been discovered since; the so-called pre-salt layer off the Brazilian coast has been the largest conventional oil discovery this century. Unfortunately, exploiting these reserves has proved problematic, not least because the sheer scale of them was a tempting target for corrupt government officials, and Brazil's state oil company Petrobras consequently found itself at the centre of the Operation Car Wash investigations.

Since the scale of the problems became clear, successive governments took steps to try and rein in the huge company. Upstream, Brazil has been inviting more foreign participation, ending the Petrobras monopoly on the offshore pre-salt deposits via a law in 2016. In 2018, there were also changes to Brazil's rules regarding minimum percentages of locally-sourced goods and services required in exploration and production contracts, known collectively as the 'Local Content' rules – reducing mandatory Brazilian participation by half, which also allowed greater use of floating production, storage and offloading (FPSO) units – some 36 are planned to help develop an estimated 21 billion barrels of oil equivalent in stranded oil and gas resources out to 2027.

Brazil's oil production was 2.7 million bbl/d by late 2018 (up from 2.0 million bbl/d in 2013), but the country hopes to lift this to 5.5 million bbl/d by 2028, most of this offshore, to counter falling onshore domestic oil production. On the gas side, Brazil produces 70% of its 35 bcm per year of natural gas requirements, with the rest coming either from pipeline via Bolivia (22%) and the remaining 8% from LNG imports from the US, Trinidad, Nigeria and elsewhere.

Brazil hopes to increase gas' share of electricity production, and aims to collect and use more offshore gas. Gas production has risen at 9% year on year over the past decade, but about two thirds of gas is associated gas from oil production, and a large proportion of this is reinjected into oil reservoirs because of lack of export infrastructure, especially from the major sub-salt fields. This lack of export infrastructure acts as an effective cap on oil output, with subsalt fields often containing gas-to-oil ratios of 40% or more. Around 1.3 bcm of gas is also still flared every year.

Petrobras controls 85% of gas production and infrastructure, and last year, Brazil announced plans to break up Petrobras' stranglehold on gas distribution infrastructure. It is hoped that a wave of privatisations among the 19 Petrobras owned state-controlled distribution companies (out of 27 total) will lure in international and domestic bidders. Petrobras has struck a deal with the government to sell off its gas transportation and distribution assets by 2021. There are also moves to diversify sources of gas by removing restrictions on unconventional gas production in Brazil and boosting pipeline imports from Argentina.

Nitrogen demand

Brazil is one of the world's largest agricultural producers, the largest exporter of coffee and sugar, and the second largest exporter of soybeans. Brazilian sugar cane ethanol also supplies a large proportion of Brazil's fuel needs. The country is also the world's fourth largest consumer of fertilizers. Brazil's relatively poor soils need extra application of fertilizers to achieve sufficient agricultural productivity. Overall Brazilian nitrogen demand represents about 60% of that for the whole of Latin America, and this is serviced particularly in the form of urea – Brazil's demand for urea reached 6.3 million t/a in 2018 (2.9 million tonnes N), according to IFA figures.

Agroconsult estimates that total fertilizer deliveries in Brazil reached 36.6 million t/a in 2019, 3.2% up on 2018. Poor weather in the US and the ongoing trade dispute with China affected US soybean and corn plantings, supporting a corresponding increase in Brazilian plantings, and lower dollar exchange rates encouraged overseas purchases. This year, however, the Convenio 100/97 agreement is due to expire; a series of tax breaks on sales of agricultural inputs such as pesticides, seeds and fertilizers, and as a new extension requires the unanimous approval of every state, it is currently unlikely that the existing agreement will be extended, leading to increases in fertilizer costs.

Nevertheless, as more area is brought into cultivation, plantings of soybeans and corn are expected to increase over the next few years, boosting Brazil's demand for fertilizers. Demand for nitrogen in Latin America is forecast to rise from 4.1 million tonnes N in 2018 to 4.5 million tonnes N in 2023, according to IFA, with Brazil responsible for most of that increase in demand.

Brazilian agriculture continues to expand.

Nitrogen production

Lack of gas availability has crimped Brazil's development of a domestic nitrogen industry in spite of its huge need for fertilizer and dependence on agricultural export commodities. By 2017, Brazil had four operating nitrogen complexes – two producing urea, owned by Petrobras, at Camacari and Laranjeiras, and two built by Fosfertil at Cubatao and Araucaria – the latter produced urea, but Cubatao was an ammonium nitrate plant, mainly producing industrial grade AN for the mining industry. The Fosfertil plants were bought first by mining company Vale, although Vale sold the Araucaria plant to Petrobras in 2012, and the Cubatao plant to Yara in 2017, before the remainder of Vale Fertilizantes was bought by North American producer Mosaic for its phosphate assets. Yara now operates the Cubatao plant to produce nitric acid, industrial grade ammonium nitrate and some technical grade urea.

During the 2010s, Petrobras had ambitious plans to develop three new fertilizer complexes, at Linhares, Uberaba and Tres Lagoas, at a total cost of $6.5 billion, with the strategic goal of reducing or ending Brazil's dependence on nitrogen fertilizer imports. However, the lack of additional natural gas availability, and the downturn in the economy first led to the Linhares project being cancelled, the Uberaba project postponed and work at Tres Lagoas, where a 720,000 t/a ammonia plant and 1.2 million t/a urea were reportedly 80% complete, being halted in 2014. In the wake of the Operation Car Wash scandal and its need to shed billions of dollars in debt and non-performing assets, Petrobras also announced the closure of the Camacari and Laranjeiras plants in 2019.

The closure of Camacari and Laranjeiras has removed another 1.02 million t/a of urea capacity from Brazil. Petrobras has been in negotiations with Russian fertilizer producer Acron to divest its nitrogen plants – Acron was reportedly considering buying and refurbishing the plants, using natural gas imported across the border from Bolivia, and inked a provisional gas supply agreement with Bolivian state gas producer YPFB in July 2019. However, Bolivia itself has been in political disarray following weeks of protests that led to the resignation of president Evo Morales in November, and work on exploration and development of new gas wells to replace ageing and declining production has been suspended. Cross-border talks with Brazil on gas trade have also been put on hold. As a result, Acron pulled out of talks on buying the idled plants in November 2019, and while Petrobras says that it "remains committed" to finding a buyer for the assets, there is noone in the frame at the moment.

The closure of Camacari and Laranjeiras leaves Araucaria, with a capacity of 660,000 t/a of urea, as the only nitrogen fertilizer plant currently operating in Brazil, and there are no new project developments on the horizon. On January 15th, as this article was going to press, Petrobras announced that it would also be closing the Araucaria plant by September 2020.

Nitrogen imports

The upshot of the closures of the urea plants and the continuing increase in demand for nitrogen projects in Brazil has been a surge in import demand – Brazil had already been one of the fastest growing markets for urea imports – imports rose during the 2010s from just under 3 million t/a in 2012 to 5.5 million t/a in 2017. In 2018 this figure rose to 5.9 million t/a, and the closures at Camacari and Laranjeiras during 2019 led to this rising 7% to 6.3 million t/a in 2019. The figure for 2020 is likely to be higher still, and with no new domestic capacity being built over the next few years, it is forecast to rise another 400-600,000 t/a to 2023. The closure of Araucaria will add another 600,000 t/a to this. In 2018 most of Brazil's imports came from Algeria (19%), Russia (19%), Egypt (10%) and the various Arab Gulf countries (35%), with the rest of the world making up the remaining 17%.

In the meantime, blending and distribution in Brazil has become big business, with around 80% of the fertilizer distribution market held by just four large, vertically integrated companies; Yara, Mosaic, Fertipar and Heringer. EuroChem opened a third blending plant in Brazil in 2019. ■

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Indian self-sufficiency in urea: miles to go?

Dr MP Sukumaran Nair, former Secretary to the Chief Minister and Chairman of the Public Sector Restructuring and Audit Board for the Government of Kerala, provides an update on India's plans to achieve self-sufficiency in urea production by 2022.

India's urea production declined marginally by 0.5% to 23.9 million t/a during 2018-19. Consumption during the year was 32.0 million t/a. Despite short inventories, the country imported 7.45 million tonnes of urea during the year. On average, India spends around Rs 160 billion ($2.26 billion) to import 7-8 million t/a of urea, mostly from Oman, China and Iran, making it the largest importer of urea globally. This figure is almost double that of the United States, the world's next biggest importer. But the Government is aiming to end urea imports completely by 2022. Considering an average 3.5% increase in consumption per year, a complete ban on imports is possible only if we are able to build additional urea capacity of 14-15 million t/a by 2022.

Plans to achieve this end

At present, there are 31 plants in the country manufacturing urea, 21 plants produce DAP and complex fertilizers and two plants manufacture ammonium sulphate as a by-product. Of the 31 urea manufacturing plants currently in operation in India, 28 plants use natural gas, while naphtha is used at only three plants. In 2017, 94% of India's urea production capacity was natural-gas based and only 6% was naphtha-based.

The Modi Government had announced its New Investment Policy (NIP) in January 2013 and its amendment in October 2014 to facilitate fresh investments in urea sector and to make India self-sufficient. It gave a new impetus to growth for the domestic industry which had been missing for the previous two decades.

Projects under way

- Chambal Fertilizers & Chemicals Limited (CFCL) has set up a brownfield project at Gadepan, Rajasthan with 1.27 million t/a capacity. Commercial production started in January 2019.
- Matix Fertilizers & Chemicals Limited has set up a greenfield coalbed methane (CBM) based ammonia-urea complex at Panagarh, West Bengal with 1.27 million t/a capacity at an investment of Rs 70 billion ($1 billion). After a wait for three years for gas, commercial production of Matrix started on 1st October, 2017 but could not be sustained for want of a steady supply of CBM. To run at full capacity, the plant needs 2.4 million m^3/d of natural gas but the, supplier Essar Oil and Gas Exploration and Production Ltd provided barely half the promised capacity. Matix is now exploring natural gas availability from the national gas grid from Phulpur to Durgapur and also a link to the upcoming Dhamra LNG terminal.
- The revival of five fertilizer plants built on coal/fuel oil as feedstock which closed down in 2002 following mounting losses, namely: Talcher (Odisha), Ramagundam (Andhra Pradesh), Gorakhpur (Uttar Pradesh) and Sindri (Jharkhand) – all plants of the Fertilizer Corporation of India Ltd. (FCIL), and the Barauni (Bihar) plant of the Hindustan Fertilizer Corporation Ltd, using modern technology under new leadership. These are intended to produce 6.35 million t/a of urea at a costing of Rs 380 billion ($5.4 billion) as brownfield investments. Hindustan Urvarak and Rasayan Limited (HURL), a joint venture of Coal India (CIL), NTPC and the Indian Oil Corporation (IOCL), in cooperation with Fertilizer Corporation of India (FCIL) and Hindustan Fertilizer Corporation (HFCL) will take up the revival of the Gorakhpur, Sindri and Barauni units. These plants will be connected to the GAIL's 2,650-km Jagdishpur in UP to Haldia in West Bengal pipeline to supply gas as feedstock, and are expected to start production by 2021.

The Gorakhpur plant is an important milestone towards self-sufficiency in urea production, being the first public sector investment since 2009. KBR has recently announced that it has been awarded an ammonia plant contract by Toyo Engineering Corporation for the HURL greenfield urea project. Construction of the Sindri unit began in October 2018. Mechanical completion and commissioning are scheduled for January 2021 and May 2021 respectively. By this time, the laying of gas pipeline to the plant will also be completed. The progress of the Barauni project, with a similar capacity, is reported to be on schedule. Mechanical completion and commissioning is also scheduled for January 2021 and May 2021 respectively.

- Ramagundam Fertilizers and Chemicals Ltd, a joint venture between FCIL, National Fertilizers Ltd (NFL) and Engineers India (EIL) was formed in 2015 to revive urea production at Ramagundam, Telangana. GAIL and the HTAS Consortium (consisting of HT Ramagundam A/S, IFU and the Danish Agribusiness Fund) are also equity partners in the project. Feedstock natural gas from the KG basin will be transported to Ramagundam via a spur of the Mallavaram-Bhilwara-Bhopal-Vijaipur pipeline. The project cost of the 1.27 million t/a plant has been revised to Rs. 61.2 billion ($860 million) and it is scheduled for commercial operation by March 2020, assuming the availability of gas by end of 2019.
- Talcher Fertilizers Ltd (TFL) a joint venture company of RCF, CIL, FCIL and GAIL, to revive the Talcher unit. The project was awarded on a lump sum term key basis to Wuhuan Engineering Co. Ltd of China. The Chinese company will implement coal gasification and ammonia/urea packages for the project. The project is expected to be commissioned by the third quarter of 2023. With an estimated investment of Rs 132.8 billion ($1.87 billion) the project will have a production capacity of 1.27 million t/a of neem-coated urea via gasification of a mixed feedstock comprising of high ash Indian coal and petcoke. TFL has been allotted northern part of North Arkhapal mine, Odisha as the captive mine for meeting its coal requirements and petcoke will be sourced from IOCL's Paradip refinery.
- During October 2015, the Indian government approved the revival of HFCL's Durgapur and Haldia units through a bidding route after settling land disputes with the Asansol Durgapur Development authority and Kolkata Port Trust respectively. Thereafter, revival of the units may be considered by the government depending on prevailing urea requirements and availability in the country. It was also decided that the revival of the Korba unit will be taken up later.
- In October 2018, the government approved the proposal in principle for setting up the Namrup IV project at the Brahmaputra Valley Fertilizer Corporation Ltd (BVFCL) on the basis of a proposed equity partnership of 52% to RCF, 26% to OIL, 11% to the government of Assam and 11% to BVFCL. The proposed new urea plant, at an investment of Rs 45 billion ($630 million), will have a capacity of 860,000 t/a, and will replace the existing vintage urea plants Namrup-II & III by 2023.
- The Indo-Oman joint venture OMIFCO announced in October 2018 that it has a plan to increase the company's total urea installed capacity from the current 1.65 million t/a to 3 million t/a. Earlier, the Oman government could not commit natural gas for the capacity expansion, but the recent commissioning of BP's Khazzan gas project, which will produce almost 1 billion scf/d of gas has brightened the prospects of the expansion plan. But here again priority allocation goes to domestic Omani supply and it is not likely to be producing ahead of 2023.

All the above will contribute to an installed capacity build-up of 10.16 million t/a of urea by 2023, which will yield around 9 million t/a of product at 90% plant availability.

Gas availability

Making natural gas – the raw material for urea production – available to the upcoming plants will be a herculean task. Currently, India consumes approximately 175 million standard m^3/d, half of which is met through imports. The landed cost of spot LNG at Indian shores is hovering around $5.50/MMBtu, but long-term costs are closer to $9.50/MMBtu. Transmissions cost, marketing margins, and local taxes and levies are added to this price before it is delivered to the end consumers. During the recent visit of prime minister Modi to the US, Petronet LNG Ltd, India's gas major, signed a deal with Tellurian Inc, a US liquefied natural gas (LNG) developer in the proposed Driftwood project in Louisiana. By this agreement, Petronet LNG Ltd will spend $2.5 billion for an 18% equity stake in the $28 billion Driftwood LNG terminal, the largest outside holding so far in the project, and negotiate the purchase of 5 million t/a of gas over forty years at an affordable price to Indian consumers.

Import market

Reports say that the Chinese export of urea, especially during their non-cropping season under a very low export tariff is likely to dip in the coming years due to reduced production on account of environmental problems leading to shutdown of certain plants. With India gradually gaining self- sufficiency in urea production and with increasing US domestic production globally urea export is likely to undergo a sea change. The crisis is likely to deepen with the massive plants in the Arabian Gulf and Australia now under construction (like the gas based 2 million t/a Perdaman Fertilizers & Chemicals plant in Australia, likely to become operative by 2023). India is expected to gain from these developments.

Further policy refinement necessary

The New Urea Policy 2015 which became effective from 1st June 2015 had the objectives of maximising indigenous urea production, promoting energy efficiency in the urea units; and rationalising the subsidy burden on the Government of India. What has been achieved in three years is only an additional capacity of 1.5 million t/a. Only the public sector, with the support of cash rich CPSUs have come forward at the instance of the Government to revive closed plants. The policy was amended in 2015 incorporating new energy targets. Only two producers have so far responded to it; Chambal and Matix. It may also be noted that Tata got out of the fertilizer business last year. Therefore, more refinement is needed with regard to the investment policy to encourage the private sector.

The steps taken so far are proactive and will certainly reverse the increasing import dependency which prevailed over the last two decades. Considering an average growth in consumption of 3-3.5% annually, by 2023, the gap between domestic production and consumption will still be around 4 to 5 million t/a. Thus, elimination of imports by 2022 is not going to be achieved, and although it will be lower, it may be around five million t/a. ■

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ANNA 2019

Highlights of papers presented at the recent Ammonium Nitrate/Nitric Acid (ANNA) Conference, held in September in Vienna.

Borealis was the host for this year's Ammonium Nitrate/Nitric Acid conference, and so the venue was Austria's picturesque capital Vienna, with an excursion to Borealis' production site at Linz, 180 km to the west.

AN production from renewables

Production of ammonia and downstream products using renewable energy is a subject gaining increasing interest these days, and Stamicarbon looked at how this might be used to generate nitrates based on renewables. Joey Dobree of Stamicarbon took a 250-500 t/d calcium ammonium nitrate (CAN) plant as his baseline assumption, using ammonia produced from hydrogen generated by electrolysis and nitrogen from an air separation unit (ASU). The economic feasibility of such a project depends upon the cost of generating the hydrogen – and the costs of electrolysis continue to fall – and the availability of competitively priced alternatives. He showed that for a remote inland area, for example in Africa, the cost of transportation of fertilizers such as CAN from overseas can make local prices over $460/t, giving a plant based on renewables a 10-15% rate of return. It is also possible to produce 'hybrid' designs in regions where gas prices are high. Although these applications remain relatively niche for now, carbon taxes, falling electrolysis costs and economies of scale could start to make such plants economical outside niche cases.

AN safety

Safety remains very much at the forefront of AN production, and was the topic of several papers presented at the conference. Pieter Halliday introduced explosives safety body SAFEX International, which aims to spread best practice on the manufacture and use of explosives. SAFEX maintains an incident database updated by its members which now covers 20,000 entries dating back nearly a century.

Noel Hsu of Orica reviewed the science on ammonium nitrate detonation, and the effect of voids within the material, as well as the impact of chloride and other contamination – the latter with reference to a fortunately non-fatal explosion involving an AN tanker. Queenie Kwok of the Canadian Explosives Research Laboratory added some results from her own organisation's studies on the reaction between AN and sodium salts, frequently found in contaminants.

But these are not simply academic concerns – Jose Henrique Guimaraes of Yara reported on an incident in Brazil with a truck carrying technical AN from the Cubatao plant. Smoke was reported from the semi-trailer on the way to the customer. Water was used to stop the smoke but the transporter requested a safety check from the manufacturer before continuing. It was found that a missing cover above an unloading port coincided with a burnt patch on one of the 50kg bags of TAN. An exposed metal edge had torn the bag and allowed organic material from previous loads (grain) to mix with the TAN. Friction and microbiological heating from mould on the soya grains had then generated enough heat to begin decomposing the AN! The application of water had stopped the self-heating and decomposition of the AN. Based on the incident practices for carriage of AN bags was changed.

The use of water to tackle AN fires was the topic of Frank Wolf of Apache Nitrogen, and why it was a very good thing. Indeed, the more water the better was his message, although preventing a fire from starting, via non-combustible construction, segregated storage areas with continuous monitoring and good housekeeping to prevent contamination of course remained the best policy of all.

German sensor company Grandperspective highlighted their infra-red gas monitoring camera packages, which can alert plant and storage area operators to decomposition of AN in real time, as well as emissions of ammonia or other dangerous gases.

Of course, AN remains vulnerable to the possibility of deliberate misuse, and Michael Whitted of the Pentagon's Joint IED Defeat Organisation gave delegates an update on ongoing international efforts to combat the misuse of AN fertilizer – and urea – for improvised explosives.

Catalysis

On the nitric acid side of the conference, several of the papers looked at catalysis of the ammonia oxidation reaction. Sumit Rao of Hindustan Platinum described methods of catalyst deactivation, including blanketing with impurities or contaminants, poisoning with inhibitors that decrease reaction rates, mechanical embrittlement and chemical alteration of alloy constituents, all leading to a loss of active sites. Calcium, magnesium, iron, aluminium, carbon and silica are all known issues with precious metal nitric acid catalysts. It is therefore crucial to make sure none of these are present in the process feed. In some cases it is possible to restore reactivity of catalyst and Mr Rao gave some examples of these.

Christian Goerens of Umicore showcased work his company had performed on enhancing the efficiency of nitric acid catalysts and reducing N_2O production, in conjunction with thyssenkrupp and the Technical University of Darmstadt, as well as data analysis company Umesoft, which had progressed from computer reaction modelling to prototyping and lab and pilot scale experiments which fed back into the computer modelling studies. Lessons learned about the importance of gauze geometry have led to a new 'twisted' catalyst design which increases efficiency by up to 1% and reduces N_2O formation.

Emissions control

Because of nitrous oxide's large CO_2 equivalent value in terms of greenhouse gas production, reducing its production from the nitric acid industry remains a key concern. One paper described the work of the Nitric Acid Climate Action Group. The World Bank now operates a nitric acid climate auctions programme (NACAP), which supports price guarantees for eligible N_2O emission reductions from nitric acid plants with existing or new abatement projects.

John Pach of JM ran through abatement techniques – JM has so far completed 61 N_2O abatement projects worldwide in conjunction with Yara, with reductions equivalent to a total of 90 million t/a of CO_2 equivalent. Secondary abatement systems can reduce emissions by 95% but must have good gas mixing and distribution and sufficient mechanical integrity to ensure there is no shifting and by-pass of the catalyst bed.

Naveed Sukhera of Fatima Fertilizers in Pakistan gave some operator perspective, specifically with regard to an incident which led to an unexpectedly high pressure drop across his company's Uhde EnviNOx reactor. An ammonia gas sparger was found to be damaged during inspection having reached the end of its operating life, and a mixer plate had sheared and stuck inside the feed pipe partially blocking the flow, leading to the higher pressure drop. With assistance from thyssenkrupp, new parts were fabricated and replaced the damaged components.

Mathias Rode of Covestro (formerly Bayer Materials Science) likewise reported on issues with a demister upstream of the NOx compressor in a nitric acid plant in China. Corrosion had occurred in the compressor housing and impeller and this necessitated the installation of a new demister.

Another real world issue came from Bas Tilborghs of Yara, who described NOx emissions resulting from back flow through a secondary air line at Yara's Sluiskil plant in the Netherlands. A spurious trip in the steam turbine led to a turbo set shutdown, but a secondary air valve did not close quickly enough. Bas encouraged other plant operators to review their own check valves and safety logic circuits. ■

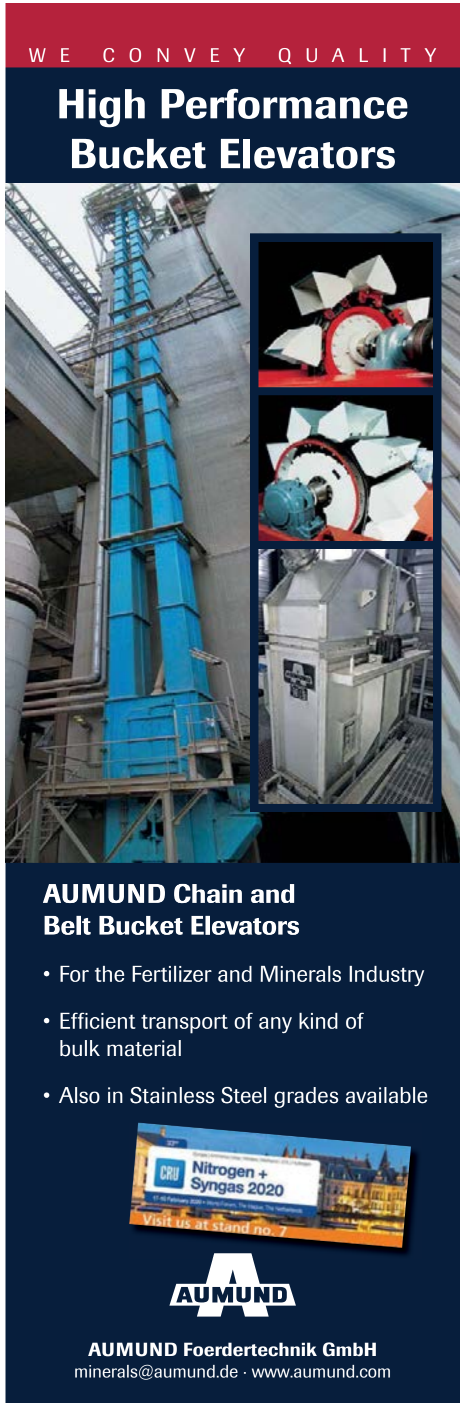

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PHOTO: UWC

Preventing ammonia leaks, Jul/Aug, p20.


PHOTO: CSB

High temperature hydrogen attack, Sep/Oct, p30.


PHOTO: METHANEX

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	Gas supply deal for new AN plant	Mar/Apr	10
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	Generators selected for H_2 to ammonia project	Mar/Apr	10
	Green ammonia proposal for Pilbara	Mar/Apr	10
	Perdaman granted major project status	May/Jun	12
	Pre-FEED agreement for ammonia/AN complex	Sep/Oct	12
	Topsoe to license world's largest ammonia plant	Nov/Dec	10
Azerbaijan	SOCAR to build new urea plant	Jul/Aug	12
Bangladesh	Tax on fertilizer imports withdrawn	Nov/Dec	10
Brazil	Gas sale contract signed	Sep/Oct	13
	New blending plant	Jul/Aug	13
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	Urea and methanol project finally declared dead	Nov/Dec	11
China	New melamine plant	Jul/Aug	13
	Second melamine unit commissioned	Jan/Feb	11
Denmark	Haldor Topsoe sells minority stake to Temasek	May/Jun	11
	Haldor Topsoe unveils green ammonia project	Mar/Apr	11
	Topsoe launches plant optimisation service	May/Jun	11
Egypt	El Nasr awards EPC contract	May/Jun	10
	EPC contract awarded for new ammonia plant	Nov/Dec	11
	Explosion at fertilizer factory kills ten	May/Jun	11
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	Fertilizers Europe criticises reduction of duty	Jan/Feb	12
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	New fertilizer plants still scheduled for 2021	Sep/Oct	12
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A flexible concept for ammonia production, Sep/Oct, p47.

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	Leigh Creek Energy advances UCG project	Sep/Oct	16
	Plans to build methanol plant in Darwin	Nov/Dec	14
	Waste to energy plant for Australia	May/Jun	14
Azerbaijan	Honeywell to modernise SOCAR hydrogen plant	Jan/Feb	14
Canada	Alberta government backs Nauticol methanol plant	Mar/Apr	12
	Loan secured for GTL plant	Nov/Dec	14
	Nauticol agrees to buy land for methanol plant	Jul/Aug	14
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Estonia	Feasibility study on new methanol plant	Sep/Oct	14
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	Wind-based hydrogen plant to seek permits	Mar/Apr	15
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Indonesia	Air Liquide to provide hydrogen plant for Pertamina	Jan/Feb	14
Iran	Kaveh methanol plant starts up	Jul/Aug	15
	Methanol tanker crippled by "mine"	Jul/Aug	15
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UAE	Work begins on solar hydrogen facility	Mar/Apr	15
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	Methanex makes investment decision	Sep/Oct	14
	New hydrogen plant for Las Vegas	Nov/Dec	12
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	West Virginia approves CTL plant	Nov/Dec	12
	Yuhuang plant to begin production next year	May/Jun	14
Uzbekistan	Finance in place for GTL plant	Jan/Feb	17
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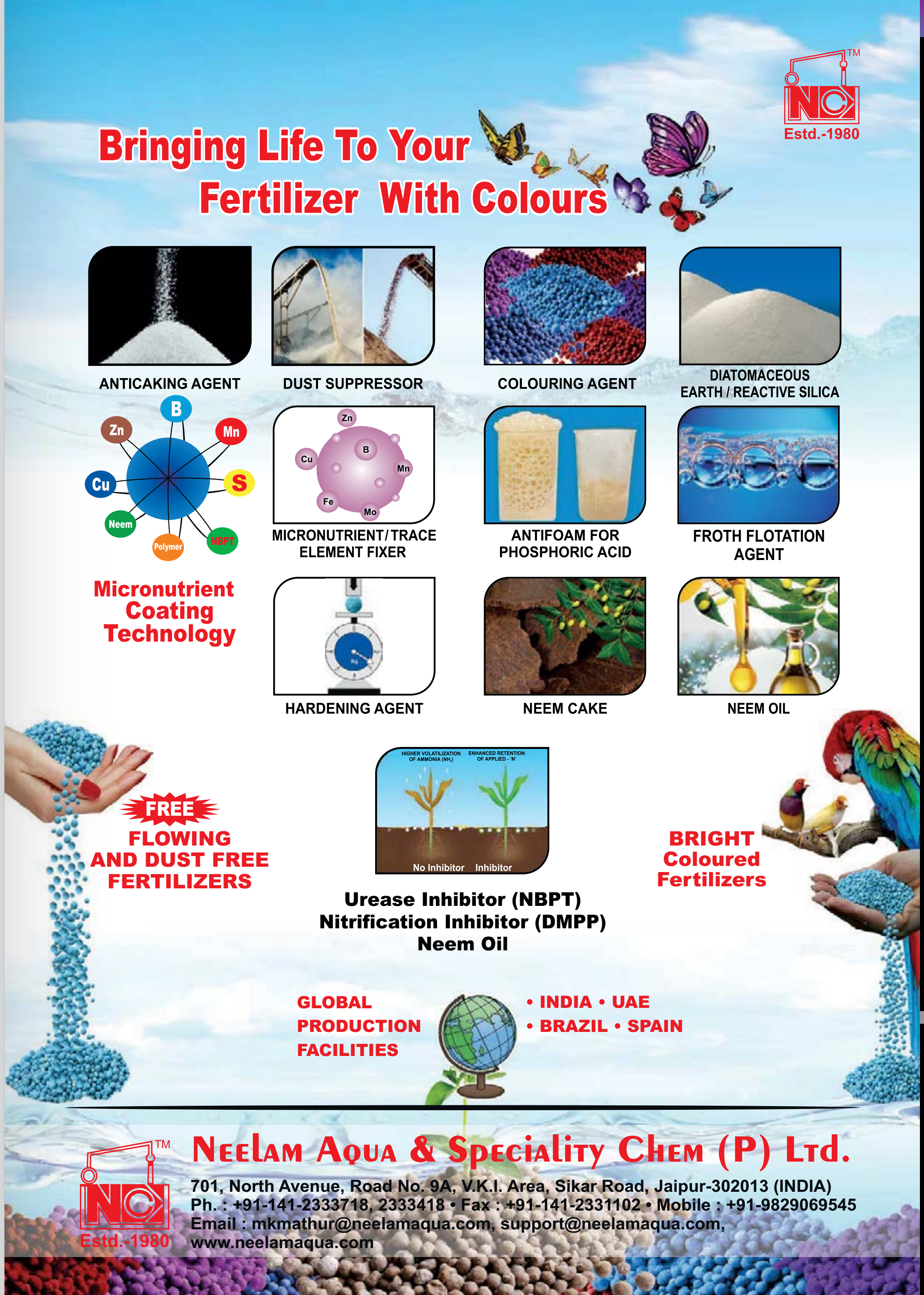

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Nitrogen + Syngas 2020

CRU's Nitrogen + Syngas conference and exhibition takes place this year at the World Forum, The Hague, in The Netherlands, from 17 to 19 February 2020.

Senior technical professionals from the nitrogen and syngas industries will be gathering 17-19 February in The Hague to attend CRU's annual Nitrogen + Syngas conference, which has become one of the largest gatherings for the global nitrogen and syngas industry – covering ammonia, urea, methanol, syngas, nitrates, GTL and industrial gases. This year the three-day agenda incorporates practical workshops, industry insights from CRU's nitrogen analysts and other industry experts, and a comprehensive dual-streamed agenda, featuring an extensive programme of technical papers focused on the latest technology, process and equipment innovations, and operational best practice. The content of the conference programme is guided by a technical steering committee of experts representing producers, licensors, and independent consultants, ensuring a high-quality platform for professional development and peer-to-peer learning.

Running alongside the conference is an exhibition of 90+ world-class process, materials, equipment and technology providers, offering a wide range of technical services. Networking and meeting time is also scheduled throughout the agenda to maximise interaction.

The first day of the conference will feature the Technical Showcase – 12 short presentations covering a wide range of topics – followed by the keynote plenary session in the afternoon which will explore the role of nitrogen and syngas producers in the circular economy.

The technical programme on the following two days will be run in parallel sessions and will feature sessions on: steam reforming, ammonia, urea, nitric acid, ammonium nitrate, melamine, plant safety and efficiency, equipment and materials of construction.

Technical programme selected highlights

New reforming technology lowers CO_2 emissions

Clariant and **TechnipFMC** will introduce Enhanced Annular Reforming Tube for Hydrogen (EARTH®) for hydrogen/syngas production. It is a drop-in insert for existing or new reformer tubes, comprising a unique geometric arrangement of a stable and mechanically robust structured reforming catalyst and concentric heat exchange tubes inside the main reformer tube to simultaneously achieve higher throughput and heat recovery in steam methane reformers. The EARTH® reactor technology can also be used to increase capacity by up to 20% and has carbon footprint benefits compared to conventional steam reforming technologies, allowing for up to 10% CO_2 emissions reduction per unit of hydrogen produced. Experience with EARTH® in an industrial HyCO/syngas unit in Europe will be shared. Significant fuel savings (>30%) were achieved and the furnace efficiency was increased by more than 20%.

CO_2 capture lessons learned

Engro Fertilizers will share operational experience of multiple units at its site that capture CO_2 including: a BASF process gas purification unit, BASF feed gas purification unit, MHI carbon dioxide recovery unit and Catacarb process gas purification unit. The presentation will cover in detail the operational problems that have been faced during start-up/shutdown and normal operation and will discuss the reactive and proactive measures taken to operate these facilities with full efficiency.

Europe's largest single train ammonia plant

In June 2019 **EuroChem Group AG** officially opened a new ammonia plant, EuroChem Northwest in Kingisepp, Russia, with the largest single train production capacity in Europe at 1 million tonnes per year. The plant is designed according to the KBR Purifier™ ammonia process. **KBR** will present various project milestones and design aspects of the project, including troubleshooting and lessons learned during commissioning of the project. Sensitive to local environmental concerns, the plant was built on a brownfield site and care was taken to avoid any negative impact on the surrounding areas. The facility features a closed water recycling system to prevent effluent discharges to the nearby Luga River, which flows into the Baltic Sea in the Gulf of Finland.

Optimising urea plant operation

Yara will discuss optimisation of a urea high pressure section with N/C soft-sensing. Yara's urea production plant in Ferrara, Italy, features an isobaric double recycle synthesis loop (IDR), including a urea reactor, both thermal and CO_2 stripping heat exchangers and a carbamate condenser. The strong influence of recycles and residence times on the process dynamics poses a great challenge to operate the plant stable at optimal conditions. The N/C ratio is one of the most relevant process parameters in the synthesis loop. The orthogonal least squares regression method has been applied to obtain a robust empirical online prediction of N/C ratio based on nine online measurements. After four years of successful open-loop utilisation, the N/C soft-sensor has recently been included in a model predictive control application.

CO_2 seal gas recovery

Fauji Fertilizer Company will share its experience with a novel CO_2 seal gas recovery system that has been implemented at a urea plant to reduce CO_2 losses to the atmosphere from the seals of a CO_2 centrifugal compressor, improve energy efficiency and decrease the overall carbon footprint. The modification was implemented without any change to the mechanical design of the compressor sealing system to ensure its reliable operation. Details of the various options considered for recovery of CO_2 seal gas and the basis for the selection of the ejector based system to recover the seal gas will be discussed.

Successful commissioning and start-up of an ACES21® urea plant

Toyo Engineering Corporation (TOYO) has recently successfully commissioned two urea plants utilising TOYO's ACES21® technology, a 2 x 2,000 t/d urea plant for Chambal Fertilisers and Chemicals Limited in India and a 1,725 t/d urea plant for PT Petrokimia Gresik (PKG) in Indonesia. Effective involvement of the owners with their broad experience of operating urea plants contributed to the successful commissioning of the plant. TOYO will describe the key factors and lessons learned during plant commissioning and start-up of the urea plants. PKG's efforts to ensure successful completion of the project from the owner's point of view and the performance during one year of operation will also be described.

Solving poor performance of the HP stripper in a urea plant

Poor performance of the HP stripper in a urea plant can have several causes, the most frequent cause being oil contamination, which clogs the holes of the liquid dividers in the HP stripper leading to reduced efficiency. **Abu Qir Fertilizers Company** will discuss a study carried out to investigate the poor performance of their HP stripper, which had occurred on more than one occasion. Solutions to the problem during operation of the plant and protective measures to prevent it from happening will also be discussed. The procedure to clean the internals of the HP stripper so that the plant can continue normal operations in case the plant has to be stopped as a result of bad stripping efficiency, will be described.

Root cause analysis of problems in a nitric acid plant

Johnson Matthey will present a recent case study from a MP nitric acid plant with a nitrogen loading of 12 t/d. The plant had performance issues early into a new campaign run, experiencing low conversion efficiency and high levels of N_2O emissions. The root cause analysis process and the fault tree analysis developed from an identification exercise of potential cause factors will be described. As part of the investigation Johnson Matthey used its proprietary kinetic model to simulate the performance of the gauzes and to determine the reaction profile within the catalytic packs. How the systemised design and modelling applies to the technology systems offered to the nitric acid industry will also be described.

New nitric acid plant in Uzbekistan

Navoiazot, the largest chemical company in Uzbekistan, has awarded Casale an EPC lump sum turnkey project for a new nitric acid plant with a nominal capacity of 1,500 t/d, based on dual pressure technology (former GPN/Borealis). **Casale** will present the process solutions adopted and provide an overview of the main project schedule and milestones. Key features of the design are the single ammonia oxidation burner that simplifies the plant layout and providing easier Pt gauze management, the combination of secondary and tertiary catalyst to achieve lower emission limits for NOx and N_2O with a simplified abatement arrangement and the extended absorption column design that integrates a closed loop chilling water circuit, which recovered a part of the ammonia evaporation latent heat to minimise the NOx slip. Start-up of the plant is expected mid-2020.

Enhanced efficiency fertilizer at a world scale urea production facility

Koch Fertilizer recently decided to incorporate an enhanced efficiency fertilizer (EEF) – SUPERU® premium fertilizer into its urea production facility located in Enid, Oklahoma. SUPERU is a 46% nitrogen urea granule that is stabilised by incorporating both a urease and nitrification inhibitor. SUPERU utilises Koch Agronomic Services proprietary N-TEGRATION™ technology that allows effective levels of NBPT and DCD to be uniformly incorporated throughout every urea granule. Koch Agronomic Services will discuss the intricacies of the installation and the success and value of utilising this technology at a fertilizer plant with the aim to help other producers understand how this works and how they can implement this system into their own plants.

Low carbon hydrogen technology

Today, industrial hydrogen with the majority of users in refineries, ammonia and methanol production, is predominantly made by steam methane reforming of natural gas which produces carbon dioxide as a byproduct. Global production of hydrogen is forecast to grow and a low carbon gas solution for hydrogen production will be important to achieve the aims of the Paris Protocol and impact on climate change. To address this challenge, Johnson Matthey has developed the Low Carbon Hydrogen (LCH) technology which is capable of producing high purity hydrogen with a CO_2 capture rate in excess of 97% for use in carbon capture and storage (CCS). **Johnson Matthey** will describe the new technology and its key features. Compared to conventional steam methane reforming LCH technology offers several benefits:

- recovery of high grade heat at the maximum energy;
- uses high reformer temperatures to minimise methane in the syngas and hence CO_2 emissions;
- increases energy efficiency and capex benefits by recovering all the carbon dioxide at process pressure;
- minimises the amount of difficult to capture CO_2 in combustion products.

Advanced urea spray nozzles reduce dust formation

thyssenkrupp Fertilizer Technology will present its new advanced urea spray nozzles which have been developed to improve the spray pattern of urea solution droplets in such a way that the amount of dust generated as well as the build-up rate of scaling on the walls of the UFT® fluid bed granulator walls is reduced, while maintaining excellent product quality and a longer running cycle. The results of tests carried out in tkFT's pilot plant and the demonstration at industrial scale at GPIC's urea plant in Bahrain, which produces urea at rates more than 20% above nameplate capacity, showed a significant reduction in dust (-30%), while keeping the process parameters in such a range that a retrofit of an existing urea plant is possible without major mechanical modifications to any of the related equipment. In 2018 the new type tkFT spray nozzles have been implemented in a new 3,500 t/d urea plant in central Asia with outstanding results in terms of product quality, production flexibility and operational reliability. ■

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Influence of flame velocity on secondary reformer design

The different flame velocities of reactants in the combustion space of a secondary reformer have a significant impact on the gas inlet temperature of the catalyst and the methane conversion in front of the catalyst. Based on this fact, Hanno Tautz Engineering introduces an alternative secondary reformer design. Compared with the state-of-the-art-technology, the alternative design shows advantages for hydrogen production efficiency and product capacity.

Steam reforming and optional secondary reforming or auto thermal reforming in the second stage after the steam reformer is a well-established technology for syngas production for ammonia plants. The mass balance of these catalytic processes is normally close to equilibrium conditions.

The consideration of reaction kinetic effects in the combustion space of the secondary reformer shows that a significant amount of hydrogen from the steam reformer syngas is consumed by oxidation in the first reaction step. In the second step, hydrogen is produced again from the methane reforming reaction mainly in the catalyst space.

The principle influence of this fact on operation conditions, process design options and revamp conditions will be discussed in this article.

Flame velocity

The flame velocity is a characteristic value for the combination of reaction kinetics, diffusivity and heat conduction under experimental conditions. The values for laminar flame velocities of hydrogen, methane and carbon monoxide are shown in Table 1[1].

The flame velocity of hydrogen in air is at least five times higher than for methane and carbon monoxide. The flame velocity is dependent on pressure, local temperature, gas mixture, air or oxygen atmosphere, turbulence degree and several other factors.

That means, if the distribution from an injection point and the reaction of hydrogen in a reaction space is much faster than for methane and carbon monoxide, the available oxygen will be consumed by hydrogen combustion as long as hydrogen or oxygen is available.

The principle influence of hydrogen combustion in the secondary reformer on gas inlet temperature in the catalyst and the methane conversion in front of the catalyst is shown in Fig. 1.

Fig. 1: **Hydrogen combustion and methane conversion in the secondary reformer**

Hydrogen combustion and reforming:

$$2H_2 + O_2 \rightarrow 2H_2O \qquad 2 \times -242 = -484 \text{ kJ/mol} \qquad (1)$$

$$2H_2O + 2CH_4 \rightarrow 2CO + 6H_2 \qquad 2 \times 206 = 412 \text{ kJ/mol} \qquad (2)$$

Sum:

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2 \qquad -72 \text{ kJ/mol} \qquad (3)$$

Methane partial oxidation:

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2 \qquad 2 \times -36 = -72 \text{ kJ/mol} \qquad (4)$$

Methane combustion:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad -802/2 = -401 \text{ kJ/mol} \qquad (5)$$

Table 1: **Laminar flame velocity in air (m/s)**

	Flame velocity in air, m/s
Hydrogen	2.1–2.6
Methane/ethane/propane	0.38–0.53
Carbon monoxide	0.2–0.4

Heat formation

Reactions 1-4 in Fig. 1 show the main reactions for syngas production and reaction 5 shows the reaction for total combustion of methane.

The product stoichiometry of the main reactions (1)-(3) with hydrogen combustion and subsequent methane reforming is the same as for partial oxidation of methane (4), independent of the reaction pathway.

In reality the overall balance is determined by the reaction kinetics of all components for oxidation like methane, hydrogen and carbon monoxide.

The important observation is that the heat generation per mole oxygen consumed is about seven times higher with the oxidation of hydrogen (1) than with the partial oxidation of methane (4). And it is 20% higher than the total combustion of methane (5). That means with the higher flame velocity of hydrogen we can expect much higher local temperatures under current secondary reformer reaction conditions with hydrogen combustion than with the assumption of partial oxidation of methane for the whole amount of oxygen.

Fig. 2: **Summary of conventional processes with secondary reforming**

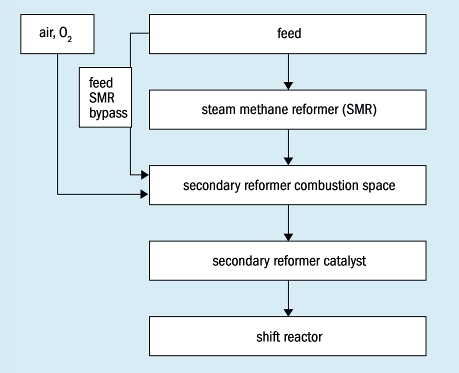
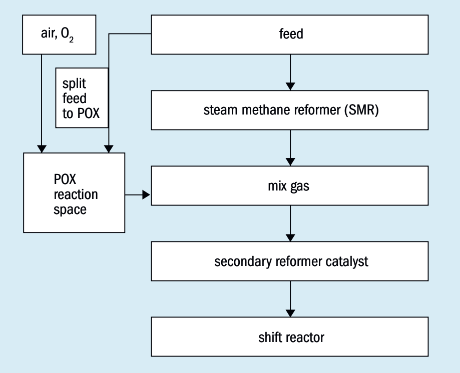


Fig. 3: **Alternative process for secondary reforming**



Process configurations

Typical process configurations for secondary reforming are summarised in Fig. 2, where in one case the whole feed gas is converted in the steam reformer[2,3] and in the other case the feed gas is split where one part is directed to the steam reformer and the other part bypasses the steam reformer and is routed directly to the secondary reformer[4]. In both cases the steam reformer syngas and optionally the mixture of steam reformer syngas and feed gas can be oxidised with air or pure oxygen in the combustion space of the secondary reformer or ATR to produce the heat for the reforming step in the catalyst. According to the higher flame velocity of hydrogen, a significant amount of hydrogen produced in the steam reformer is consumed for heat production in the secondary reformer.

The combustion of hydrogen from the steam reformer syngas gas in front of the catalyst and the related higher heat production can be avoided by an alternative process, shown in Fig. 3.

A part of the feed gas stream is directly contacted with oxygen or air before mixing with the steam reformer syngas gas, e.g. in a partial oxidation reaction (POX). Under these conditions no hydrogen from the steam reformer syngas can be oxidised and the heat from the product gas of the partial oxidation can be used for reforming of the methane in the secondary reformer catalyst after mixing with the steam reformer syngas.

Gas temperature and methane conversion

The principle effect of hydrogen oxidation in the combustion space in front of the secondary reformer catalyst is demonstrated for the following cases:

- Secondary reforming (SR): All feed gas is converted in a steam reformer and passed into a subsequent secondary reformer.
- Alternative secondary reforming (SR_A): Partial oxidation of feed gas from the split stream before mixing with syngas from the steam reformer.
- Bypass secondary reforming (SR_B): Oxidation of gas mixture from bypass flow together with syngas from the steam reformer in the secondary reformer combustion space.

These cases will be applied to a basic design of a new secondary reformer plant and a revamp design of an existing secondary reformer plant with a fixed steam reformer capacity.

There are at least two important parameters for the design:

- **Catalyst inlet gas temperature** – With rising temperature, problems with ruby formation, nickel evaporation and catalyst sintering and aging will increase.
- **Methane conversion capacity of the catalyst** – This determines the methane slip after the catalyst and is related to the catalyst inlet temperature.

In the basic design, 35% of the feed gas flow is routed as a split stream of the steam reformer to the POX reaction space or directly to the combustion space of the secondary reformer to react together with the steam reformer syngas and oxygen. With this configuration the size and capacity of the steam reformer can be reduced and the hydrogen efficiency can be increased for a certain product capacity.

In the revamp design, the feed gas flow is increased by 40% and the oxygen supply by 73% related to an existing steam reformer capacity. The parameters for standard secondary (SR) reforming are kept constant. The additional gas is routed directly to the POX reaction space (SR_A) or to the combustion space of the secondary reformer (SR_B).

To show the principle effect of hydrogen combustion in the secondary reformer space the proportion of oxygen consumption by hydrogen combustion is assumed for 40%, 70% and 100%. The remaining oxygen is assumed to be equally consumed by partial oxidation of methane and carbon monoxide oxidation.

The influence on the gas temperature with pure oxygen in front of the catalyst is shown in Figs. 4a and 4b.

For both design cases the alternative process shows significant lower gas inlet temperatures in front of the catalyst. For the revamp design, the bypass process

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Fig. 4a: **Gas temperature in front of catalyst, basic design**

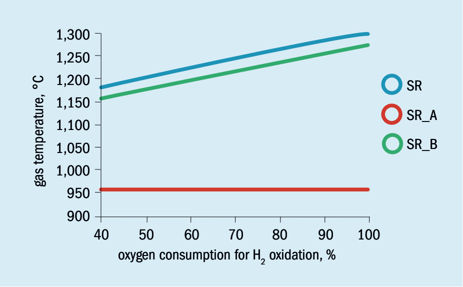


Fig. 4b: **Gas temperature in front of catalyst, revamp**

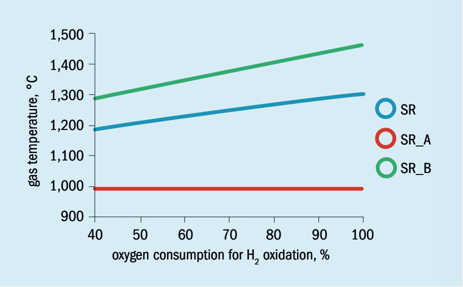


Fig. 5a: **Methane conversion in front of catalyst, basic design**

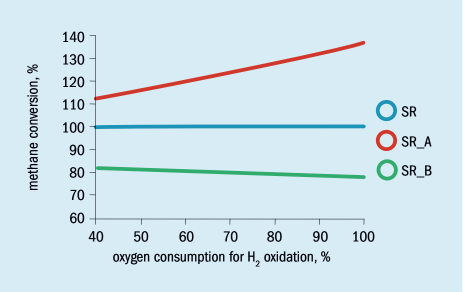
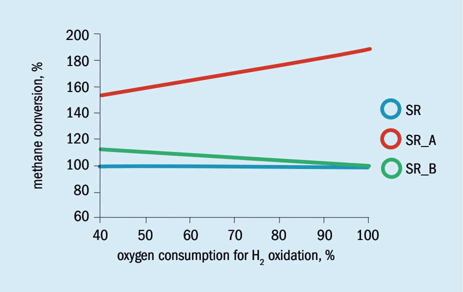


Fig. 5b: **Methane conversion in front of catalyst, revamp**



(SR_B) shows gas temperatures with more than 1,400°C which are already critical. For the operation of the secondary reformer with air the maximum gas temperatures are about 100°C lower.

The methane conversion in front of the catalyst is related to methane conversion in the standard secondary reformer process (SR) with steam reformer and subsequent secondary reformer without bypass of a feed flow (Figs. 5a and 5b).

It can be seen, that the methane conversion is significantly higher for the alternative process than for the standard process SR and bypass process SR_B, because the oxygen for the heat formation is consumed by partial oxidation of methane and not for combustion of hydrogen from the steam reformer syngas.

Discussion

With a split feed gas stream with one part going to the steam reformer and the other part to the POX reaction or in the secondary reformer combustion space the hydrogen product capacity and the hydrogen production efficiency for a given steam reformer capacity can be increased.

For new plants, the steam reformer can be built smaller and for the revamp of existing plants the product capacity can be increased significantly. This means, that each secondary reformer (SR) is a source for additional hydrogen or ammonia feed gas.

The alternative process (SR_A) shows the following advantages related to the existing bypass process (SR_B):

- higher methane conversion in front of catalyst;
- lower gas inlet temperature in the catalyst and related lower ruby formation and aging of the catalyst;
- higher hydrogen efficiency than bypass process;
- no risk of burner damage and flame impingement on the catalyst;
- especially attractive for revamp activities because lower gas temperature in front of the catalyst and methane conversion capacity of the catalyst is kept within tolerable limits.

In the simplest case the alternative process can be operated with conventional proven technology with a standard reactor for partial oxidation, a gas mixing space for reformer syngas and POX syngas and a catalyst section for secondary reforming of the mixed syngas.

The design of a special POX burner which separates the POX reaction from the steam reformer syngas, which can be introduced in an existing secondary reformer can bring significant additional cost opportunities[6]. The application will need to be checked from case to case.

To evaluate the possible product increase and the related investments for existing secondary reformer plants an individual analysis related to the actual boundary conditions in respect of combustion conditions and tolerable capacity increase in downstream process units is necessary. ■

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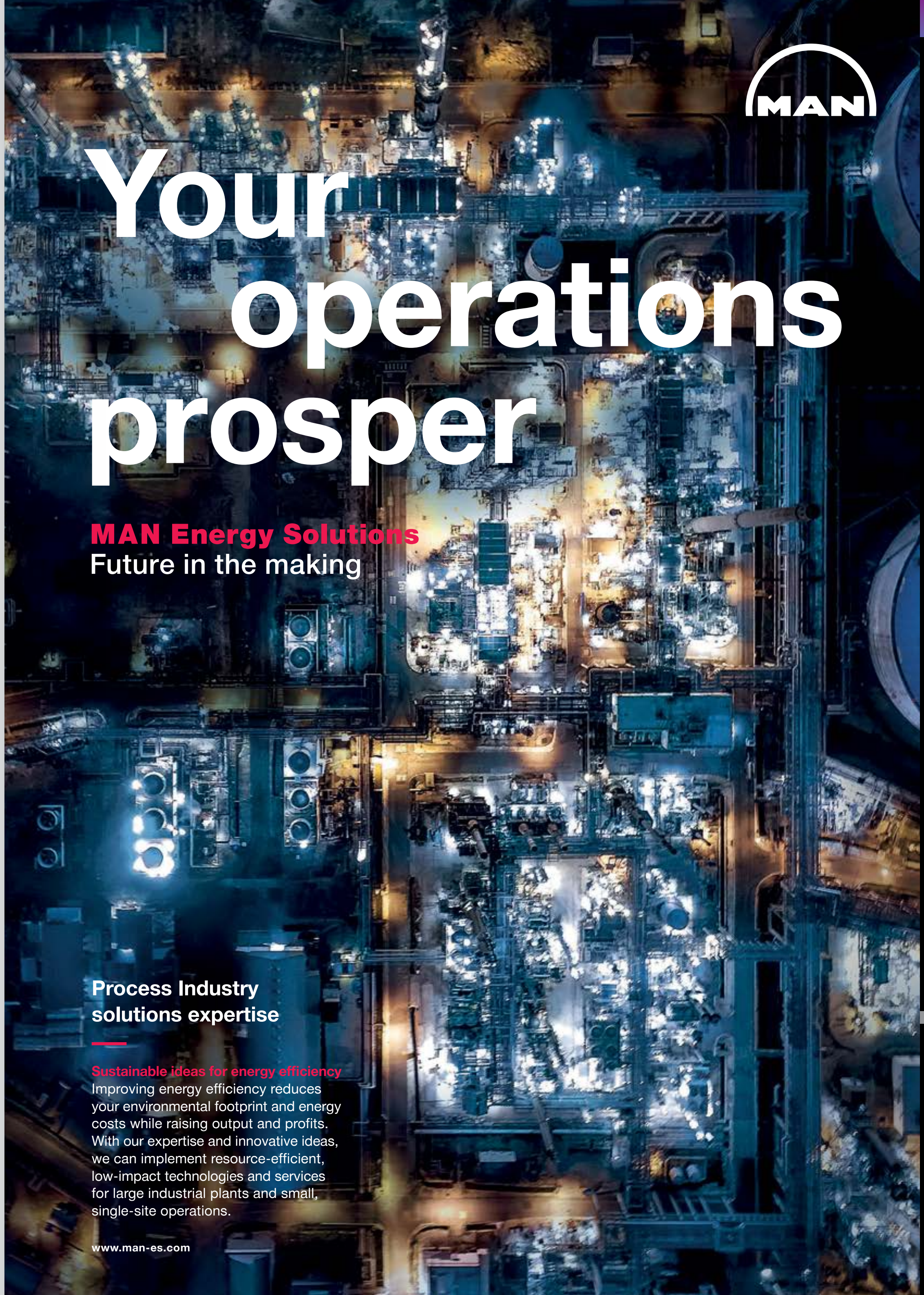

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Ammonia plant upgrade and purge gas recovery

Cryogenic purge gas recovery units are very tolerant to increased flow from ammonia plant debottlenecking, especially the cryogenic cold box section. However, overload of the dehydration system upstream of the cold box can lead to fouling, loss of hydrogen recovery performance and the need for costly shutdown and thaw. Awareness of key plant parameters and some simple precautions can avoid such problems. **A. J. Finn** and **T. R. Tomlinson** of Costain provide some guidance.

Fig. 1: **Ammonia plant showing purge gas**

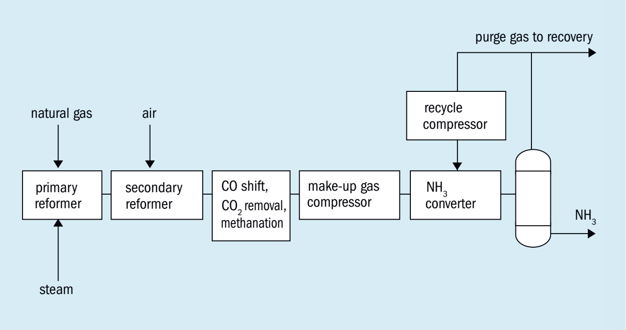
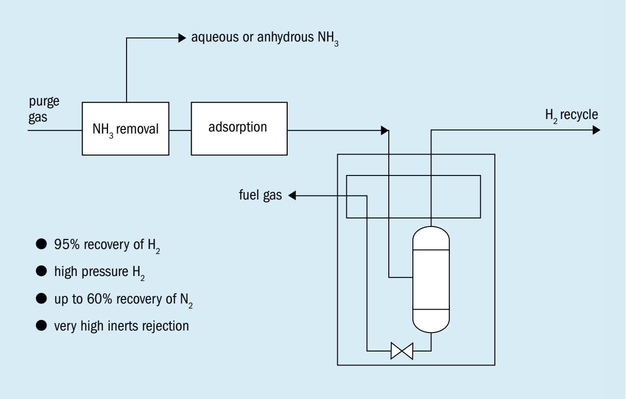


Fig. 2: **Ammonia recovery and cryogenic hydrogen recovery**



Ammonia plant purge gas recovery units (Figs 1 and 2) recover both ammonia and hydrogen, leading to increased energy efficiency (by about 0.7 GJ/tonne ammonia). Typically, this reduced specific energy has enabled as much as 4-5% more ammonia production. Overall ammonia plant optimisation might increase this even more.

Cryogenic hydrogen recovery is common on larger ammonia plants (1,500 t/d and above) due to higher hydrogen recovery at high inerts (argon and methane) rejection than with semi-permeable membranes and because all hydrogen is recovered at high pressure, thus saving on the cost of compression to synthesis gas pressure. Cryogenic units have great flexibility for variable purge gas flow, as shown by the fact they can recover up to 60% nitrogen if required. Many smaller hydrogen recovery units also use cryogenic technology. Costain has installed about 40 such cryogenic units on ammonia plants to help clients reduce their energy use.

A cryogenic unit's ability to cater for high purge gas flow enables the ammonia synthesis loop to be operated at low inerts levels, to increase hydrogen and nitrogen conversion to ammonia. Normally, if the purge gas inerts level is maintained at about 10% or more (ammonia-free basis), the cold box can operate at a low enough temperature to achieve both high hydrogen recovery (95%) and high inerts rejection, even at up to 50% of nominal design capacity.

A cryogenic unit helps ammonia plant performance substantially if either the primary reformer or the process air compressor are bottlenecks. Increased methane slip from the primary reformer, as gas flow increases, is easily accommodated. By increasing cold box separator temperature, nitrogen recovery can be increased from less than 30% to about 60%, so as to work around process air compressor limitations and increase secondary reforming.

Fig. 3: **Purge gas recovery unit**

The ability of cryogenic units to maintain high hydrogen recovery, have operational flexibility, be energy efficient, simple to operate and have very high reliability is all well known by plant operators[1]. It may thus be considered from operational experience that a purge gas recovery unit needs little attention, even for a major ammonia production upgrade. However, in planning such a capacity increase, a process engineering assessment of each section of the purge gas recovery unit is needed – ammonia recovery and regeneration, feed gas pre-treatment and the cold box. Any limitations can often be dealt with by relatively small plant modifications. The effect of increased purge gas on these three sections will be considered in turn.

Cold box

The cryogenic separation relies on there being sufficient inerts in the purge gas to provide Joule-Thomson refrigeration and maintain energy-efficient auto-thermal operation. The cold box contains one or more multistream aluminium plate-fin heat exchangers and normally just one phase separator, though there may be a second separator to give medium pressure hydrogen and very high hydrogen recovery[2]. High purge gas flow leads to high separator vapour velocities. Separators are normally designed with a suitable margin. Ultimately, at flows of over 30% above those used for vessel sizing, they would incur liquid entrainment, but any effect from this on hydrogen purity and overall cold box performance would be small.

Plate-fin heat exchangers are very accommodating to increased flows as overall heat transfer coefficient increases with flow to the power of about 0.7. Therefore a heat exchanger with 20% thermal margin can cope with a 50% increase in feed gas flow and maintain design performance, as long as the pressure drops are tolerable. This can be verified by rigorous exchanger rating. Therefore cold box performance is not normally a big consideration, especially if the temperature of the feed gas to the cold box can be reduced.

Pipework pressure drops have to be reviewed and the trim of the cold box level control valve to fuel gas may might need changing to minimise pressure drop. However, any physical changes should be minimal. Thus the cold box would not typically be a bottleneck to increased purge gas flow.

Ammonia recovery and regeneration

Ammonia recovery uses ammonia absorption in a lean solution (of water of very low ammonia content) obtained from the downstream rich solution regeneration. The ammonia absorber is typically designed at a relatively low approach to flood to minimise it being a bottleneck. How much the purge gas flow could be increased would need assessment of the installed packing performance. A modern packing could better provide sufficient surface area for vapour-liquid contact whilst reducing pressure drop with lower approach to jet flood. Potentially much more purge gas could then be processed without reaching hydraulic limits and without needing to change the absorber vessel. In some circumstances no change would be needed to the column packing even for much increased purge gas flow.

The ammonia regeneration system is mostly influenced by the ammonia-water solution flow. Lean solution flow to the ammonia absorber might need increasing in direct proportion to the purge gas flow (assuming the same purge gas ammonia content) to avoid excessive absorber operating temperatures. However, the lean solution flow specified for design would be based on sufficiently wetting the absorber packing, so increased purge gas flow may not actually need an increase in lean solution flow. This could be easily checked and reviewed.

If lean solution flow did need to be increased the ammonia regeneration system could be a bottleneck. The individual equipment items of the regeneration system would need checking, especially pumps and the regeneration column capacity. Higher lean solution flow would need to be checked against pump capacity. Changes to pump motors might be avoided. As with the absorber, modern packings may provide more regeneration column capacity with no loss of separation performance.

The main duty of the regeneration system is to provide lean solution of sufficiently low ammonia content (typically 1%) to the ammonia absorber at low temperature. Therefore if the lean solution were water-cooled (to achieve low treated gas temperature from the absorber), the performance of the relevant cooler would need checking to ensure the required lean solution temperature could be met for higher flow.

It would be beneficial to reduce the ammonia content of the purge gas feed to the ammonia absorber, typically by increased chilling of the purge gas upstream. A lower lean solution flow would then suffice. A reduction of say 25% from e.g. 2 mol-% to 1.5 mol-% ammonia would mean the lean solution flow could be decreased by at least 25%. This could be easily assessed by process simulation,

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properly taking into account the heat release as ammonia dissolves into solution, the effect on absorber operating temperatures and on ammonia volatility. A plant model could be aligned with known performance and benchmarked to help identify equipment margins e.g. on regeneration column packed height.

The ammonia recovery and regeneration systems could thus be assessed and any changes identified from site operating data, process simulation and review of equipment limits, including column hydraulics and whether new packing would be of benefit. As with all upgrade projects, pipeline fittings and instruments would need checking, including flowmeter rangeability and thermowell vibration. Two phase lines in particular would need checking for vibration.

Cold box pre-treatment

The water and ammonia in the treated gas from the ammonia absorber must be removed prior to the cold box. This is achieved by the molecular sieve adsorber system. Two molecular sieve containing vessels are employed with one always in operation removing water and ammonia. After a specific on-line time this vessel is thermally regenerated, by heating it to about 200°C, whilst the other freshly regenerated adsorber vessel is in operation. The permitted level of water and ammonia in the cold box feed is negligible and good adsorber operation is essential.

Increased purge gas flow may also lead to increased treated gas temperature and therefore increased purge gas water and ammonia content, so that the adsorption duty is much increased. The adsorber system could be overloaded, with ammonia passing to the cold box. It would not be obvious this is happening.

Some operators believe that freezing can be detected by increased cold box pressure drop. This is unlikely. Freezing would occur on the feed gas passages of the aluminium plate-fin exchanger, reducing heat transfer performance and thus making it difficult to achieve the desired cold box separator temperature (typically about −180°C). Therefore unexplained increase in cold box separator temperature is a good indicator of freezing.

Less feed gas condensation from reduced exchanger capacity means less liquid being formed, and as liquid let-down in pressure provides critical process refrigeration (by the Joule-Thomson effect) so freezing ultimately means insufficient refrigeration for the cold box to operate satisfactorily. Insufficient removal of ammonia (and possibly water) in the adsorber system would therefore be potentially very significant – leading to poor inerts rejection, increased purge gas flow to counteract this effect, further cold box contamination due to high purge gas flow, and so on.

> **“A properly assessed capacity upgrade of a cryogenic purge gas recovery unit can ensure excellent performance is maintained.**

Unforeseen cold box contamination would ultimately necessitate cold box shutdown, thaw-out and cool down. This procedure may take several days. The plate-fin heat exchanger would need to be warmed, properly thawed, all contaminants removed and then cooled down in line with ALPEMA[3] limitations. Doing this too quickly may lead to thermal stressing of the heat exchanger, loss of mechanical integrity and leaks. Whilst simple exchanger leaks can be repaired, this would require complete emptying and refilling of the cold box insulant and up to two weeks off-line. Excessive thermal stressing may require a new plate-fin exchanger assembly and indeed even a new cold box. Such problems can be avoided by a relatively simple assessment of the adsorber system and mitigation measures if the adsorption duty is excessive to ensure the cold box cannot be fouled.

Molecular sieve dehydration systems are well-understood[4]. Ammonia adsorption is a little more specialist in two aspects: (a) how much ammonia is removed in parallel with water adsorption (b) the bed mass transfer zone (MTZ) length for ammonia. Costain has proven design and assessment methods for these. The MTZ is calculated via a well-proven correlation, derived from operating plant experiments and used successfully by Costain for adsorber design and evaluation for many years.

As noted, high purge gas flow will likely lead to higher levels of water and ammonia in the treated gas from the absorber and thus more water and ammonia to be removed by the molecular sieve adsorbers. This can be assessed and solutions identified; whether by more regular replacement of molecular sieve, different molecular sieve, shorter adsorber cycle times (taking care of ensuring sufficient bed heating and cooling), and other means. The effect of increased gas velocity and consequent molecular sieve attrition and dusting would also need addressing. Necessary changes, either to the molecular sieve adsorber system or upstream, could be made to reduce the processing duty on the adsorber system. Any changes would likely be relatively simple. Otherwise, measures such as feed gas chilling (and water and ammonia knock-out) could be evaluated and defined.

Conclusion

Cryogenic purge gas recovery units are energy-efficient and can accommodate increased purge gas flow from ammonia plant debottlenecking and performance optimisation. Equipment capacity checks, to ensure good performance, are relatively simple, reliable and well-understood. Any debottlenecking of the ammonia recovery and regeneration systems should be limited, with little or no new equipment being needed. The cold box will not normally require any modification other than possibly to the level control valve trim. The limiting equipment will likely be the molecular sieve adsorber system, something easily overlooked but that can cause significant cold box problems. Assessment by proven techniques and resulting modifications can work around adsorber system limitations.

A properly assessed capacity upgrade of a cryogenic purge gas recovery unit, including equipment, piping, fittings and instruments, can ensure excellent performance is maintained for both low capital and low operating costs, even for substantially increased purge gas flow. ■

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Methanol routes to a lower carbon footprint

'Green' methanol means many things to different people. It encompasses low carbon emissions methanol manufacture at scale, recovery of material through waste gasification and conversion to methanol and power to liquid (e-fuel) methanol via electrochemistry and sometimes a combination of all of the above. Each route has a place in reducing the overall carbon footprint of production and subsequent use of methanol, driven by both governmental incentives or societal demand. In this article **Andrew Fenwick** of Johnson Matthey reviews the various routes to manufacture.

Drivers for green chemicals

In common with the rest of the syngas community, the producers of methanol are being encouraged by society to reduce their emissions at point of manufacture and if used as a fuel or fuel component, in use.

Global energy demands are increasing and so too is the need for more renewable and sustainable sources of energy to help transition us to a post-fossil fuel powered world. Increased energy efficiency is one of the simplest means of reducing our primary energy usage but increased renewable or zero carbon energy vectors will also be required if we are to maintain similar (or aspired) standards of living.

Governments are responding to this challenge by mandate. For example, in 2018 the EU increased its renewable energy target to 32% by 2030, with many countries planning to ban fossil fuel powered cars by 2040. It is also increasingly likely that we will need to significantly decrease our net equivalent carbon dioxide (CO_2) emissions by increasing our use of carbon capture and storage (CCS) of CO_2 and where storage of CO_2 is not possible, then carbon capture and (re)-use (CCU).

Government mandates for fuel blending quotas and incentives for renewable fuels as well as carbon taxes should have an impact on the willingness of the market to pay a premium for renewable methanol. In Europe the policy driver is the EU's Renewable Energy Directive (RED), which was revised (RED II) in December 2018. The EU RED II and Fuel Quality Directive (FQD) classify renewable methanol from non-biological sources as a renewable fuel. The UK, since 2008, has introduced its Renewable Transport Fuel Obligation (RTFO) scheme. Fuels that are categorised as Renewable Fuels of Non-Biological Origin (RFNBO) are incentivised by awarding double credits per litre or kilogram supplied. These credits are known as Renewable Transport Fuel Certificates (RTFCs) and can be traded between suppliers of fossil transport fuels or eligible biofuels. In terms of CO_2 tax, in the EU a cap-and-trade system was introduced in 2005, the European Trading Scheme (ETS), for the trading of carbon emission credits. The Republic of Korea, the Chinese province of Guandong and the US state of California have also implemented cap-and-trade programs.

Additionally the IMO has announced aspirational targets "to reduce CO_2 emissions per transport work, as an average across international shipping, by at least 40% by 2030, pursuing efforts towards 70% by 2050, compared to 2008". The use of methanol in these large marine engines has been ably demonstrated recently and the use of green methanol will accelerate this sector's push for lower emissions. Methanol will have an advantage over LNG in that it is bunkered in more ports and is easier to convert existing ships to than LNG.

One of the largest users of energy is as fuel in the transportation sector. There are a few main routes to a sustainable source of energy for this sector:

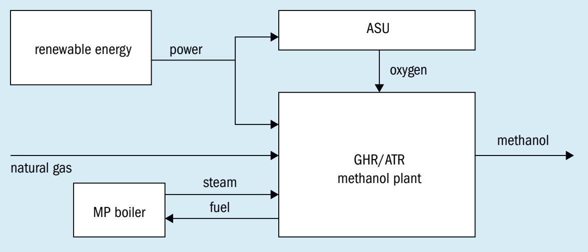
Route 1: Renewable or non-carbon emitting electricity can be harnessed to power vehicles, with energy stored in batteries on board. However, certain transportation modes such as aircraft, heavy-duty trucks and marine vehicles demand a high power and energy capacity that are currently unmet by battery storage alone.

Route 2: Alternatively, renewable electricity can be utilised to electrochemically convert one chemical to another with a higher energy potential. The most well-known of these is the conversion of water to hydrogen (H_2). Low carbon hydrogen can also be produced from natural gas using a combination of steam reforming and water gas shift, followed by capture and storage of the CO_2. As the energy density of the final fuel (H_2) is low, this significantly reduces the range of aeroplanes and ships, without significant storage volume. This is where the next two options can be useful.

Route 3: Waste or biomass can be converted into chemicals or fuel, typically through a syngas intermediate or pyrolysis step. Pyrolysis can convert hydrocarbon sources but has the disadvantage of creating a wide range of final products which need separation and/or blending before final use.

On the other hand, gasification is a flexible process to convert a wide range of waste hydrocarbons/biomasses to synthesis gas (syngas), a mixture of gaseous hydrogen and carbon oxides, from which useful chemicals or fuels can be efficiently produced.

Fig. 1: **Johnson Matthey GHR/ATR methanol plant utilising renewable electricity**



Source: Johnson Matthey

Route 4: Lastly, the combination of carbon monoxide and/or carbon dioxide with hydrogen derived from electrolysis, can be utilised to produce the same chemicals or fuels. Other variants of electrolysis include co-electrolysis of carbon dioxide and water to syngas and even further, to final products e.g. methanol, methyl formate and ethylene.

Forming part of a suggested future of zero net emissions, the "methanol economy" would look to utilise both renewable electricity and also waste CO_2 that would otherwise be emitted to the atmosphere or captured for sequestration. It is envisaged that methanol, utilised as a fuel, or fuel building block, can bridge society's need to reduce its net carbon dioxide emissions.

The choice of product is a consequence of process economics and market demand. As GHG emission reduction often plays an integral part, a full life cycle assessment (LCA) is required to confirm CO_2 mitigation benefits, taking into account the whole value chain from CO_2 origins to the final use of the product. The production of methanol is an attractive choice, since it has many uses. 'Green' methanol can be used as a fuel, for example in the M15 blends common in China, or as an energy carrier for hydrogen. Both these applications benefit from the high energy density of methanol (16 MJLHV/litre, about half that of diesel). Methanol can be converted into higher performance fuels, e.g. by the ExxonMobil methanol-to-gasoline process (or equivalent), or via molecules such as dimethyl ether. In addition, methanol is well established as a chemical intermediate for important molecules such as formaldehyde. Fuel applications are perhaps best placed currently to benefit from incentives, and the larger fuel pool gives the potential for greater impact on CO_2 levels than chemicals production.

Low carbon methanol

Operators of large scale methanol plants are constantly looking to improve the economics of production. Licensors of methanol technology, including Johnson Matthey (JM), have risen to the challenge by improving the feedstock efficiency of their designs. This has the natural consequence of decreasing carbon emissions, as the typical non product use of feedstock is as fuel to provide heat and power for the overall process. In order to largely eliminate the carbon emission at point of manufacture, the operator has three choices:

- capture the emitted CO_2 and sequester it;
- use a fuel which does not produce (net) CO_2 as a combustion product e.g. H_2 or bio-derived fuel or;
- utilise a process that imports power and heat from an external renewable source.

Capturing of CO_2 from the flue gas of conventional natural gas based plants is already undertaken at QAFAC, Qatar and GPIC, Bahrain but these plants primarily have been designed to increase the throughput of the plant, not to totally eliminate the CO_2 emissions. The parasitic load of the CCU unit is slightly outweighed by the efficiency gains of balancing the stoichiometry of the syngas but the overall efficiency gain is modest and net CO_2 emissions are not significantly better. In principle, all the CO_2 could be captured from the flue gas of the methanol plant and any CO_2 not utilised within the process, exported for sequestration.

CO_2 capture is also practiced on all gasified coal methanol plants but in this instance the CO_2 is captured in order to correct the stoichiometry of the produced syngas. The captured CO_2 is then vented to atmosphere and the CO_2 emissions per tonne of product methanol is significantly higher than that from a natural gas based plant.

A second option of utilising H_2 as the fuel source is likely to be the most economic for existing methanol plants, in order to eliminate CO_2 emissions. Most natural gas based plants have suitable fuel and burner systems to utilise pure H_2 as fuel without significant modification, as they already burn significant quantities of methanol loop purge gas, rich in H_2. The simplest route for an existing plant would be to capture CO_2 from the existing syngas in the syngas section, resulting in an excess of H_2 and that excess H_2 utilised as the fuel source. This would however reduce the output of the methanol plant.

Another option would be to build a new dedicated H_2 plant, where the CO_2 is captured at pressure, reducing the parasitic load of the CCS unit. In JM's opinion, this would best be practiced by utilising a GHR/ATR H_2 plant. Alternatively, the H_2 could come from electrolysis (see later sections) which would have the advantage that the existing plant could be uprated, should it currently be feedstock limited.

The BioMCN™ methanol plant in the Netherlands already utilises feedstock/fuel derived in part from biogas. Biogas is typically a 60:40 mixture of CH_4:CO_2, derived from the fermentation of biomass. Most existing biogas is utilised as fuel for electricity generation, as the sources are dispersed geographically. Governments such as the Netherlands and the UK are looking to significantly increase their biogas production, and as the feedstock becomes more widely available, the syngas industry is likely to increase its consumption and hence reduce its net carbon emissions significantly.

For new plants that don't have access to bio-derived feedstocks or are sited where the geology is not suitable for sequestration of CO_2, they can be futureproofed by having a plant design such as the Johnson Matthey GHR/ATR methanol plant (Fig. 1), as utilised at Coogee Chemicals plant in

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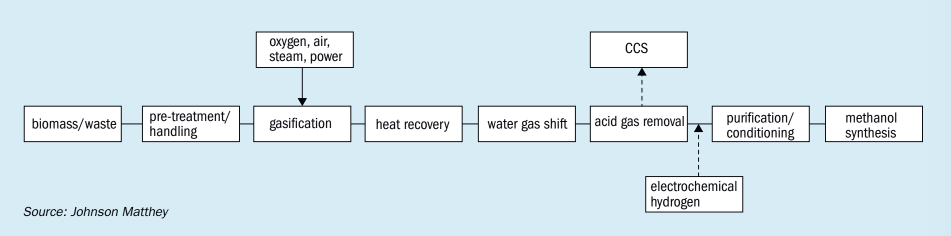
Fig. 2: **Typical gasification route to methanol**



Source: Johnson Matthey

Australia. This plant largely eliminates the CO_2 emissions at point of manufacture, as the energy required from compression and heat is supplied from external electricity sources. The Johnson Matthey GHR/ATR methanol plant also significantly saves on water utilisation, as the cooling load is also greatly reduced compared to ATR only or SMR/ATR designs.

Gasification of waste (or biomass)

Gasification of municipal solid waste (MSW) can reduce net equivalent CO_2 emissions by reducing the potential of methane emissions from the landfill, as biomaterial can biodegrade to methane when in the ground. Gasification or incineration of the MSW will eliminate this potential vent.

Gasification of waste (or biomass) and conversion to methanol will compete for feedstock with energy recovery by incineration or conversion to other more valuable end products e.g. Fischer Tropsch conversion to naphtha/kerosene/diesel. Key to the success of gasification technology will be the performance of the gasification unit versus the varying calorific values of the constituents to be gasified. To produce a syngas that is suitable for conversion to methanol, higher temperature gasification is generally required, in order to minimise the formation of methane in the gasifier.

Most gasification plants produce a syngas that is sub stoichiometric in hydrogen, and hence excess carbon is usually removed as CO_2 downstream of a water gas shift unit. This acid gas removal unit also removes the majority of the H_2S/HCl formed in the gasifier but other key poisons such as HCN will also need to be dealt with. The CO_2 emissions from a gasification plant can be considerably higher than for a natural gas based plant, on a per tonne of methanol basis, unless the captured CO_2 is also sequestered.

Addition of an external H_2 stream can adjust the stoichiometry of the syngas, considerably reducing the CO_2 emissions and in principle, remove them completely. This can be advantageous if the gasified material is limited in supply. Reducing or eliminating the emission of CO_2 will consequently increase the production of the product methanol. Methanol as a final product in this instance has an advantage in that both the CO and CO_2 can be converted to final product, utilising all the carbon in the feedstock, maximising the value of the limited feedstock.

The addition of this extra H_2 will mean the adjustment of the operation and design of the acid gas removal unit and the elimination of the shift unit. Dealing with the residual catalyst poisons may become more difficult, without the operation of the acid gas removal unit.

Fig. 2 shows a typical gasification route to methanol.

A number of new projects have been announced recently e.g. ENI Livorno and this process is already commercially in operation since 2016 at the Enerkem Inc. facility in Edmonton, Alberta, Canada.

The economics of gasification of municipal solid waste can be considerably improved by the avoidance of waste tipping fees. These 'gate fees' can compensate for the lower renewable fuel incentive if the material to be gasified is low in biomass.

Power to methanol

In seeking to reduce the world's dependence on fossil fuels and associated greenhouse gas (GHG) emissions, methanol production using electrochemistry has certainly provoked much research interest in recent years and is an already demonstrated concept. Forming part of a suggested future "methanol economy" this would look to utilise both renewable electricity and waste CO_2 that would otherwise be emitted to atmosphere or captured for sequestration.

The alternative production of fuels and chemicals such as methanol, which are traditionally made from fossil fuel feedstocks, by employing wind, solar photovoltaic, hydro or geothermal electricity can also help to address the problem of storing this often variable energy whilst balancing the grid and utilising cheap electricity when generation exceeds demand.

Schemes such as this are known as power-to-fuels, solar-to-fuels or power-to-gas. Many of them rely on a two-step process involving water electrolysis to produce hydrogen, which is used for thermocatalytic reduction. In the case of CO_2, various product options are available including syngas, formic acid, methanol, methane or higher hydrocarbons. Electrolytic hydrogen can also be used to reduce nitrogen to ammonia. An alternative scheme would be to use the renewable electricity for the direct electrochemical reduction of CO_2 and water (co-electrolysis) to the aforementioned fuels and chemicals. One question that arises is which fuels or chemicals industry should target for production: beyond methanol, a range of other molecules have been produced from electrochemical reduction of CO_2 at the research scale. These include ethylene, methane, formic acid, ethylene glycol, propanol and ethanol. This has the attraction of using a single reactor but is more technically challenging and less well-developed.

One further aspect to consider is the inherent intermittency of some renewable power sources such as wind and solar photovoltaic. Without direct connection to the electricity grid or a form of energy storage the plant economics suffer, often requiring a high annual plant utilisation (high on-stream factor).

The energy requirements of these systems can be illustrated by the case of

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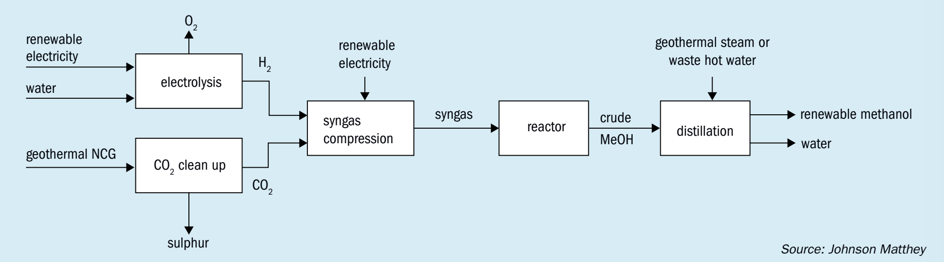
Fig. 3: **A simplified flowsheet of the CRI process**



Source: Johnson Matthey

electrolytic hydrogen production followed by thermocatalytic CO_2 reduction. The electricity required for a water electrolyser operating at 2 volts and with 100% faradaic efficiency is 191 $\text{GJ}_{(\text{electric})}/\text{tonne}_{(\text{hydrogen})}$ (53 kWh/kg). The direct CO_2 hydrogenation reaction for methanol synthesis can be represented overall by equation (1), assuming that the CO_2 is ultimately converted to methanol, with any carbon monoxide formed via the reverse water-gas shift reaction also being hydrogenated to methanol.

$$CO_2 + 3H_2 = CH_3OH + H_2O \qquad (1)$$

For an ideal stoichiometric conversion of hydrogen then the equivalent electricity consumption rate is 36 $\text{GJ}_{(\text{electric})}/\text{tonne}_{(\text{methanol})}$ (10 kWh/kg). This energy demand for the electrolyser is similar whether the methanol is produced by CO_2 hydrogenation using electrolytic hydrogen or directly through the co-electrolysis of CO_2 and water. Variations in electricity consumptions between the two routes will be due to different operating voltages and faradaic (or current) efficiencies for the electrochemical unit operations, slip of oxygen into the hydrogen stream, compression duties and any inefficiencies for the downstream operations for deriving pure methanol (e.g. synthesis loop carbon efficiency, product separation and purification). Including those losses, a more realistic value for early adopter plants might be 13 kWh/kg.

The electricity consumption for the electrolysis step contributes a significant fraction of the overall methanol production cost. Referencing electricity prices derived from fossil fuels for G20 countries in 2017 of between \$0.05/kWh – 0.17/kWh, then taking an average cost in the United States in 2017 of \$0.07/kWh, the minimum electrolyser energy costs (operating at 2 volts) are \$700/$\text{tonne}_{(\text{methanol})}$. Taking a low value in 2017 for on-shore wind of \$0.03/kWh this then reduces to \$300/$\text{tonne}_{(\text{methanol})}$. However, solar and solar/wind combination farms are now guaranteeing electricity at \$0.02/kWh which reduces the cost to \$200/$\text{tonne}_{(\text{methanol})}$.

This value increases to \$260/$\text{tonne}_{(\text{methanol})}$, including losses mentioned above, equivalent to a natural gas cost of \$8.3/million Btu (HHV) for a conventional plant (~31.3 million Btu/tonne including fuel). Additional variable and fixed plant expenses including capital charges will also need to be accounted for in the overall production cost, thus renewable methanol will generally be costlier to produce and need to command a premium value, compared to conventional fossil fuel derived methanol (dependant on natural gas price). For such schemes, plausible economics could exist but would need to be evaluated on a case-by-case basis with the local availability of inexpensive renewable electricity and a source of clean CO_2 being fundamental requirements. From the stoichiometric mass balance using equation (1), the CO_2 specific consumption rate is approximately 1.4 $\text{tonne}_{(CO2)}/\text{tonne}_{(\text{methanol})}$, which would be an input for the life cycle assessment to establish the carbon footprint and climate change mitigation to compare with conventional methanol for fuels and chemicals.

This power requirement and the fact that the largest water electrolyser modules are currently available at 2-3 MWe per stack, already supports a view that localised small-scale electrochemical plants would initially be the focus, rather than compete directly with world-scale conventional methanol facilities (typically 5,400 t/d). Additionally, electrochemical processes tend to scale linearly when compared with large thermal-catalytic processes akin to fossil-fuel methanol, which can exploit the reduced production costs from the economies of scale, so the economics of a project may be dominated by external incentives until the technology matures and average generation costs come down for the electricity.

For the previous example with a \$260/$\text{tonne}_{(\text{methanol})}$ electricity cost, it will only achieve parity vs a typical natural gas based plant with a 3\$/million Btu (HHV) natural gas price, with a CO_2e credit of ~120\$/te CO_2e, given that the specific consumption rate of CO_2 is 1.4 $\text{tonne}_{(CO2)}/\text{tonne}_{(\text{methanol})}$. Other incentives such as renewable fuel use requirements may mean that the methanol produced can realise a premium vs methanol produced via a non-renewable route. It may also be recognised that a large proportion of a final gasoline or diesel price is often government levies that could be waived.

An example of an already operating commercial facility producing renewable methanol is that owned and operated by Carbon Recycling International (CRI). The George Olah (GO) plant is located in Iceland's Svartsengi geothermal field near Grindavík on the Reykjanes peninsula. The plant was first commissioned in 2012 with a capacity of 1,300 t/a of renewable methanol and was expanded in 2015 delivering 4,000 t/a. It utilises captured CO_2 from the nearby Svartsengi geothermal power station and renewable electricity from the Icelandic grid to produce electrolytic hydrogen for use in methanol synthesis (Fig. 3). The methanol is used in gasoline blends with the GO plant utilising 5,500 tonnes of CO_2 per year. The renewable methanol product from this facility is sold under the brand name of Vulcanol™ and is displacing a small amount of fossil fuels in the transport sector. The renewable methanol fuel blends are for sale in Iceland and other countries including Denmark, Sweden and The Netherlands. The renewable methanol produced was the first renewable fuel from non-biological origin to be certified according to the International Sustainability & Carbon Certification (ISCC) Plus, with GHG savings of up to 90% when compared to gasoline.

Table 1: **Properties of electrolysers**

	Alkaline	**PEM**	**Solid oxide**
Conducted species (ion)	OH^-	H^+	O^{2-}
Electrolyte	KOH or NaOH solution	Nafion	ceramic oxides
Typical conductivity, S cm^{-1}	0.05-0.25	0.1-0.2	0.05-0.15 at 800°C
Catalysts	nickel gauze	platinum (cathode) iridium oxide (anode)	nickel
Products from CO_2	water electrolysis only	many	mainly CO or syngas

Source: Johnson Matthey

Electrolyser types

There are three main types of electrolysers, all of which can play a role in the synthesis of renewable methanol. The first of these is alkaline electrolysers, which have been commercially available for a number of years. These use nickel electrodes at temperatures below 100°C to split water from a strongly alkaline electrolyte, typically over 20% potassium hydroxide, with a porous separator between the electrodes to stop electrical shorting across the electrodes. Modern alkaline electrolysers are typically available in cells of 1-3MW, which are coupled together into stacks of up to 100MW. The lifetime of these systems can be over 80,000h.

PEM electrolysers (Proton Exchange or Polymer Electrolyte Membranes) work in a similar temperature range to alkaline systems. The key difference is the use of a solid state polymeric electrolyte such as Nafion which conducts protons well when hydrated with water. The electrode catalysts are coated onto each side of the electrolyte, and gas diffusion layers added to ensure good dispersion of the gas across the two electrodes. Unlike the alkaline electrolyser, the PEM system has two different catalysts: typically Pt-based catalysts for the reduction of protons to hydrogen at the cathode, and iridium oxide-based materials for the oxidation of water at the anode. The use of precious metals is generally required due to the harsh operating conditions in the electrolyser, with low pH and strongly oxidising electrochemical environment. Research is ongoing into non-precious metal catalysts, but stability over the desired long lifetime is an issue. The main advantage of PEM electrolysers over alkaline is that they can run at higher current density (reaction rate) and hence can produce more hydrogen per square metre of footprint. PEM electrolyser devices tend to be 1-2 MW in size and have been coupled to 100 MW systems.

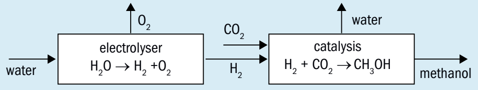
An alternative low temperature approach is to use PEM-like systems but at high pH. In this case, the conducted species is not the proton but the hydroxide ion. Much progress has been made on the conductivity and stability of AEMs but none has emerged with the ubiquity of the Nafion ionomer for protic environments. One advantage of using an alkaline environment is that a greater range of materials can be used as catalysts and for other roles in the cell.

The final class of electrolysers which can be used in the synthesis of renewable methanol are solid oxide electrolysers. These are based on thin ceramic electrolytes, which have good conductivity for oxygen ions at high temperatures such as 800°C. The catalysts tend to contain base metals such as nickel, whilst electrolytes are often yttria-stabilised zirconia (YSZ) or doped cerias such as gadolinium-doped cerias (GDC). One key advantage of the solid oxide system is that it can be very energy efficient if heat integration can be used advantageously in other parts of the system. Solid oxide systems are less well-developed than alkaline or PEM electrolysers, and system sizes tend to be smaller.

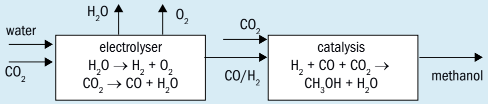
Electrochemical systems

There are various methods for incorporating electrolysis into processes for the synthesis of renewable methanol (Fig. 4). Perhaps the simplest and closest to market is to use electrolysis to produce hydrogen from water, followed by catalytic reaction with CO_2 to make methanol. A range of electrolysers for the production of hydrogen are commercially available, and

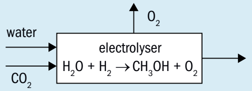
Fig. 4: **Different approaches for the use of electrolysis in methanol synthesis**



a) electrolysis of water to make hydrogen followed by catalytic methanol synthesis



b) electrolysis of water and carbon dioxide to make syngas followed by catalytic methanol synthesis



c) direct electrocatalytic synthesis of methanol from water and carbon dioxide

Source: Johnson Matthey

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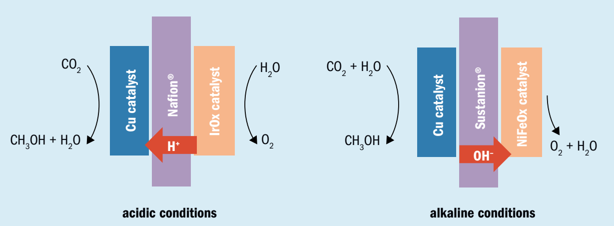
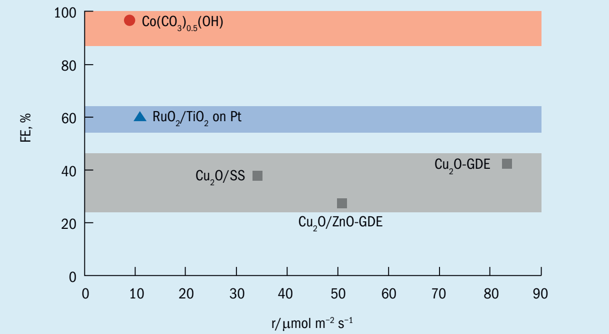
Fig. 5: **An overview of cell configuration of for acidic (left) and alkaline (right) conditions**



Source: Johnson Matthey

Fig. 6: **Comparison of literature CO_2 electroreduction catalysts in terms of their faradaic efficiency (FE) and their production rate (r). GDE is a gas diffusion electrode, and SS is stainless steel.**



Source: Johnson Matthey

as well as the CRI renewable methanol facility in Iceland a range of pilot schemes are in place aiming to make renewable methanol and other basic chemicals such as ammonia.

A second approach to the synthesis of renewable methanol is to make both components of syngas, CO and hydrogen, by electrolysis, and then convert the syngas to methanol using the conventional catalytic approach. Electrolysers for the reduction of CO_2 are less well-developed than those for water electrolysis, although a number of companies are working in the area. CO production by electrolysis has been demonstrated at lab scale using both solid oxide and PEM technologies.

The direct production of methanol by co-electrolysis has also been demonstrated at lab scale using PEM electrolysis systems. In principle this presents an advantage by using the smallest number of reactors. However, getting good efficiency at high enough reaction rates has proven to be challenging and there is a significant amount of scientific endeavour dedicated to better understanding and utilising electrolysis for the conversion of CO_2 to useful products such as ethylene, methanol and methane. In general, solid oxide cells are not preferred in this application because methanol tends to decompose at high cell temperatures.

One factor worth noting is that the amount of electricity (number of electrons) is the same in each case: six electrons per molecule of methanol. The various methods differ in whether they use hydrogen as a carrier for the electrons, or whether and to what extent they are transferred directly to the CO_2. The efficiency of the different electrolysers and the temperature range of operation will also be a factor.

Catalysts for the direct synthesis of methanol

Systems are being developed which allow CO_2 to be reduced to methanol, in situ. These can be run in acidic or alkaline conditions, with slight differences depending on the conditions chosen. In acidic conditions, the conducted species is H+ whilst in alkaline it is OH-. This has consequences for the reaction mechanism and the configuration of the cell, as shown in Fig. 5. There is a small body of literature surrounding the electrochemical reduction of CO_2 to methanol, and comparisons between catalyst performances is difficult due to variations in reaction medium, operating conditions, stability of catalyst during operation and cell/electrode setup. Two important factors for comparison of CO_2 reduction catalysts are the faradaic efficiency (the efficiency with which electrons are transferred to useful products) and the rate of formation of the target molecule.

Fig. 6 shows several catalysts from the literature used to produce methanol electrochemically. The maximum faradaic efficiency achieved with copper-based catalysts is currently 40%. This efficiency limit is likely related to the suppression of hydrogen evolution and the CO adsorption strength of copper-based materials.

One of the key challenges in low temperature conversion of CO_2 to methanol is avoiding the production of hydrogen. The thermodynamic reduction potential of carbon dioxide to methanol (0.02 V vs the relative hydrogen electrode, RHE) is only marginally different from that of the facile hydrogen evolution reaction (HER) at 0.00 V vs RHE. Therefore, good CO_2 reduction catalysts will be less active to the HER by having an increased HER overpotential before onset. This in turn allows for a more efficient charge transfer of CO_2 to form useful products. In addition to HER, there are also many competing CO_2 reduction products which makes finding a selective catalyst essential. Cu-based catalysts have been highly researched due to their relatively high faradaic efficiencies towards hydrocarbons and oxygenates.

Several mechanisms for the CO_2 reaction pathway to methanol have been suggested using a six-electron reduction reaction, either going via a formate or a carbon monoxide intermediate, depending on the metal used. A mechanism of direct dissociation of CO_2 to CO and an adsorbed oxygen atom has also been proposed.

Oxygen evolution reaction

The electrocatalytic production of methanol from CO_2 is a reduction reaction which requires a counter oxidation reaction to donate electrons to CO_2 and complete the electrochemical cell. The oxidation of water to form O_2 (oxygen evolution reaction, "OER") is attractive with respect to the ready availability of water as a feedstock and the production of oxygen as a benign and sometimes useful by-product.

However, the slow kinetics and low efficiency of the OER is one of the major barriers for this reaction. To overcome this problem, it is necessary to create a highly active catalyst which is also extremely stable in order to withstand the high electrode potentials involved in the OER. Iridium oxide has been shown to be both a reasonably active and stable OER catalyst in acidic conditions. Under alkaline conditions, more catalysts are stable and base metal catalysts have shown promising catalytic performance, as well as being low cost and readily available. Nickel catalysts, such as those in conventional alkaline electrolysers, can be used. Bifunctional catalysts, for example NiFeOx, have been shown to have very high activity in alkaline conditions. Iron doping increases the activity in nickel-based catalysts. The Fe-induced partial charge transfer mechanism activates the nickel centre in the catalyst, in a similar way to that observed for PGM electrodes.

Conclusions

Methanol is an attractive target molecule for CO_2 reduction, given its potential for zero net carbon emissions and its wide range of downstream applications. Of particular interest are fuel applications, where renewable energy can be used to generate 'green' methanol which can qualify for financial incentives. Of the various approaches possible, reacting hydrogen produced by electrolysis of water with CO_2 is the closest to market. Lower TRL methods include co-electrolysis to either syngas or directly to methanol. The materials science needed to give robust, high performing catalysts for direct methanol synthesis is an area of current scientific focus. Copper catalysts are amongst the most attractive options for methanol synthesis, whilst improved materials for the water oxidation counter-reaction are also being developed.

One of the biggest barriers to investment in this area are the evolving governmental incentives for production and or disincentives for CO_2 emission, which vary from country to country. Additionally, it is not clear what premium may be achieved on the sale of green methanol, as existing companies are understandably reticent to announce what premium they are able to command for their product which at the moment is in short supply.

JM is positive that each of the routes outlined will contribute to the growth of a robust green methanol market. As a leading methanol catalyst and technology provider and through close collaboration with its customers, JM is already solving the complex problems in each of these areas. JM looks forward to announcing its success in each of these areas in the coming months and years. ■

Reference

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Renewable methanol

thyssenkrupp Industrial Solutions (tkIS) offers and builds Power-to-X plants and can provide all processes of the value chain, from water electrolysis and CO_2 recovery to green ammonia, green methanol and green SNG. Renewable methanol production, which combines the application of carbon capture and utilisation with chemical energy storage, is a particularly promising sustainable solution.

tkIS has been active in the methanol process industry for many decades and owns world-class synthesis gas generation and synthesis technologies. tkIS recently reinvented its methanol business by adding the AdWinMethanol® technology to its portfolio, which is capable of producing methanol in quantities exceeding that of any available conventional technology. In addition, tkIS offers renewable methanol production technologies utilising tkIS' proprietary water electrolysis technology with the power from renewable sources such as wind, solar, or hydroelectric energy. The hydrogen required for the process is generated by means of tkIS's water electrolysis technology and CO_2 is obtained from biogas plants, flue gas, or waste gas. tkIS' UHDE green methanol technology is suitable for capacities from 10 to 1,000 t/d methanol and more. For small capacities tkIS co-operates with the Swiss company Swiss Liquid Future (SLF).

Smart solutions for climate protection

tkIS has developed various environmentally friendly processes based on hydrogen supply via alkaline-water-electrolysis (AWE) for applications in energy, mobility, the chemical industry and agriculture. Energy generated through renewable sources can now be converted with tkIS's AWE and downstream Power-to-X processes to "green" SNG, methanol and ammonia. Methanol can also be further used in the chemical industry and mobility sector.

Water electrolysis

At the centre of thyssenkrupp's electrolysis technologies are its patented large electrochemical cells which allow very high efficiency in industrial scale hydrogen production. The principal design is well-proven in more than 600 electrolyser plants with more than 200,000 electric cell elements, making thyssenkrupp the world's No. 1 supplier for electrolytic production equipment.

Based on the experience from its established chlor-alkali electrolysis technologies, thyssenkrupp Uhde Chlorine Engineers (a joint venture of tkIS and Industrie De Nora) introduced zero-gap technology with a high efficiency cathode and anode design and coating for alkaline-water-electrolysis (AWE) technology. Optimised high-performance separators, based on a proven design, were also applied. As a result, tkIS' AWE can provide availability of 98% for more than 30 years lifetime and a stack efficiency of more than 82%.

Raw materials for AWE-based H_2 are basically power and fresh water. Power can be directly sent via a transformer rectifier to electrolysis, whereas water has to be treated in a demineralisation unit to satisfy the required purity specification. During hydrogen production in AWE, oxygen is produced as a by-product. Hydrogen and oxygen are both cleaned, oxygen is not further required for this process but could be used for any other downstream process. Hydrogen, which is produced with a purity of 99.95%, is cooled and thereby also dried, possibly deoxygenated and compressed to methanol synthesis pressure.

Renewable energy is not typically available constantly, resulting in fluctuation of power supply. The AWE technology copes perfectly well with these preconditions. The start-up of AWE can be realised within minutes and loading conditions can be changed within seconds. Hence, the AWE offers the flexibility, which is required from renewable energy sources to adapt to power fluctuation, but also to react quickly to power markets to improve process economics.

To provide not only the best available technology, but also the best EPC execution concept, tkIS decided to design highly modular, prefabricated skids with a size of 10 MW and 20 MW each. The main driver for a skid-mounted design was the cost efficient installation on site. The individual electrolyser units can be combined to any desired plant size.

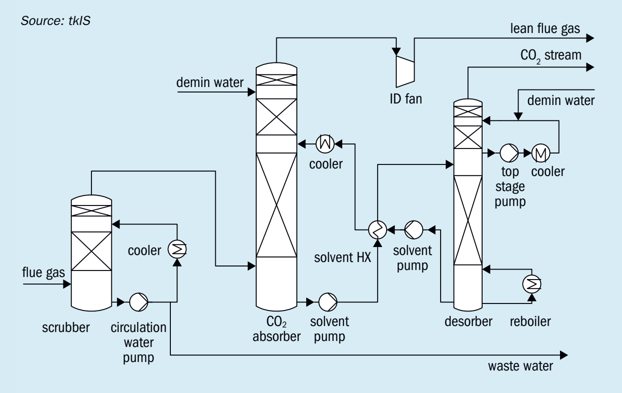
CO_2 recovery from flue gas

For green methanol production, hydrogen from AWE is used as a raw material, but carbon dioxide, recovered e.g. from flue gas, is also required. CO_2-rich flue gases are emitted from almost every industry sector, e.g. cement production, power plants, and steel production. For all kinds of industry, it becomes more and more important to improve process efficiency and decrease emissions of greenhouse gases. Some countries have already raised carbon taxes which can have a negative impact on the economics of conventional industrial processes.

tkIS, a sustainable, technology-oriented company, is part of thyssenkrupp AG (tk), one of the leading steel-producers in the world. To decrease CO_2 emissions at the tk steel plant in Duisburg, tkIS established a pilot plant for CO_2 recovery from flue gas by means of amine gas treating (see Fig. 1).

Flue gas is sent to a pre-scrubber where water soluble components (sulphurous) are removed by washing with small amounts of water. Subsequently desulphurised flue gas is sent to a CO_2 absorber where CO_2 is absorbed by solvent. Lean flue gas is then sent to battery limits and loaded solvent is sent to the desorber, where CO_2 is separated and aqueous amine solution is regenerated. The solvent is returned to the absorber column, and the purified CO_2 stream can be sent to downstream processes such as methanol synthesis. With this amine-based CO_2 removal technology 90% of CO_2 can be recovered from flue gas.

Fig. 1: **Pilot plant concept for CO_2 recovery unit**



Source: tkIS

Methanol as energy storage and carrier

As already mentioned, one of the main challenges of using renewable energy is the fluctuation of supply, another is the often large distances between the locations of production and use of renewable energy, which causes considerable transmission losses.

Energy storage and carrier solutions can be useful to overcome these challenges. SNG, ammonia, redox flow batteries and methanol have been considered for potential energy storage and carrier solutions in the energy sector. Methanol in particular is highly suitable as a high-density energy carrier, as it provides the opportunity to store green energy in terms of green fuel. The basic requirement for green methanol production is renewably-produced hydrogen, but CO_2 is also required (see Fig. 2). Carbon capture and utilisation may be a promising solution for a significant reduction of greenhouse gas emissions. Furthermore, the economics of renewable methanol production can be improved via carbon emission trading. As a result, sector coupling should be taken into account for sustainable plant concepts.

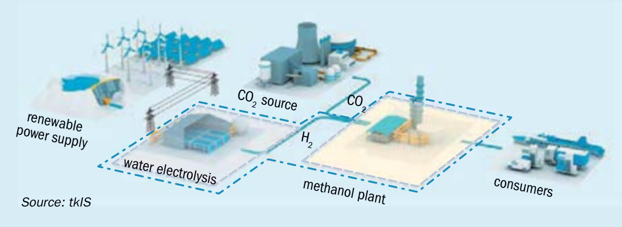
Decentralised production of e-methanol in direct proximity to power plants or CO_2 sources is an interesting and promising example of sector coupling. By blending green methanol to the gasoline pool, available infrastructure and logistics can be used. E-methanol, which can be produced self-sufficiently, independent from oil or fuel imports, can be used to substitute fossil gasoline.

As the cement industry is one of the largest CO_2 emitters, sector coupling of the cement industry with renewable energy production and the mobile/chemical sector is another promising option (see Fig. 3). Oxygen from electrolysis can be used in the cement plant for oxy-fuel combustion. By using oxy-fuel combustion, a high CO_2 content in the flue gas can be reached. As a result, efficient capture and use of CO_2 for production of renewable methanol can be realised.

Renewable methanol production technology

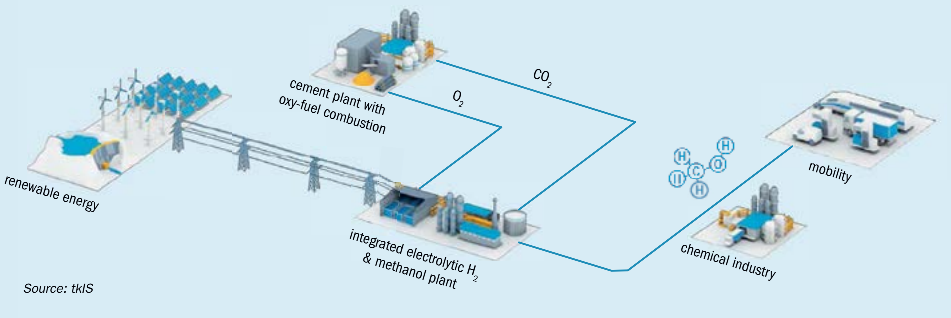
Renewable methanol plants are very similar to conventional world-scale methanol plants. Both processes can be divided into three steps; syngas production, methanol synthesis and methanol distillation. They differ in the way they produce syngas. In conventional methanol plants, syngas for methanol synthesis is produced via steam reforming, partial oxidation or autothermal

Fig. 2: **Renewable methanol plants: sector coupling with transport sector**



Source: tkIS

Fig. 3: **Renewable methanol plants: sector coupling with cement plants**



Source: tkIS

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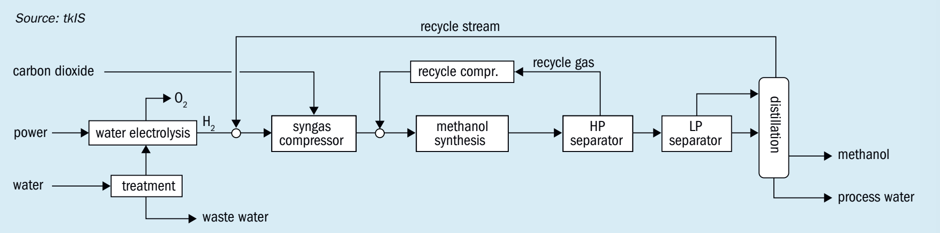
Fig. 4: **Advanced plant configuration optimised for renewable methanol**



Source: tkIS

reforming of natural gas, or by gasification of solid or liquid fossil fuels.

In renewable methanol plants, hydrogen is produced via water electrolysis. The carbon dioxide required for the methanol synthesis can come from a flue gas recovery unit or a renewable source such as a biogas or bioethanol plant. Both gases are mixed and sent to the methanol synthesis section. Crude methanol is purified in the methanol distillation section to achieve the desired methanol specification.

The concept for methanol synthesis is quite standard. For methanol synthesis from CO_2 commercially available Cu-based catalysts can be used. Reactor temperatures of between 210°C and 270°C have to be realised with this catalyst type. A minimum temperature is necessary to start the reaction and a maximum temperature should not be exceeded to prevent catalyst deactivation and reduce by-product formation. As CO_2-based methanol synthesis is less exothermic compared to CO-based methanol synthesis, a comparatively high cooling temperature is chosen. Formation of methanol from CO_2 is also favoured by high pressure, so a reaction pressure in the range of 60 to 80 bar is used.

In the methanol reactor the following main reactions take place:

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

Less catalyst is required for conventional CO-based methanol synthesis compared to methanol synthesis from CO_2, but a higher number of hot spots in the reactor can lead to higher by-product formation during methanol synthesis from CO.

To achieve near isothermal conditions during methanol synthesis, a water-cooled tube bundle reactor is used where process gas on the tube side is cooled by evaporating water on the shell side of the reactor. After partial evaporation, a steam water mixture leaves the shell side at the top. This type of reactor is already in operation in conventional methanol plants. The process concept for renewable methanol syntheses is shown in Fig. 4.

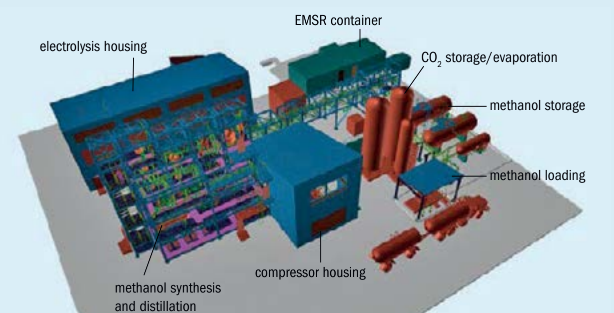
Fresh water is sent to the water treatment unit to meet the specification for AWE. Subsequently, demineralised water is electrolysed to hydrogen and oxygen.

Depending on the battery limit conditions of CO_2, gas supply of hydrogen and CO_2 can be coupled to improve process efficiency. If CO_2 is supplied in liquid state, the cooling energy of CO_2 evaporation will be used for hydrogen cooling. Normally CO_2 is supplied at lower than synthesis pressure, so a common compression of carbon dioxide and hydrogen is realised. Carbon dioxide, recovered from a CO_2-emitting process is added in stoichiometric composition to hydrogen.

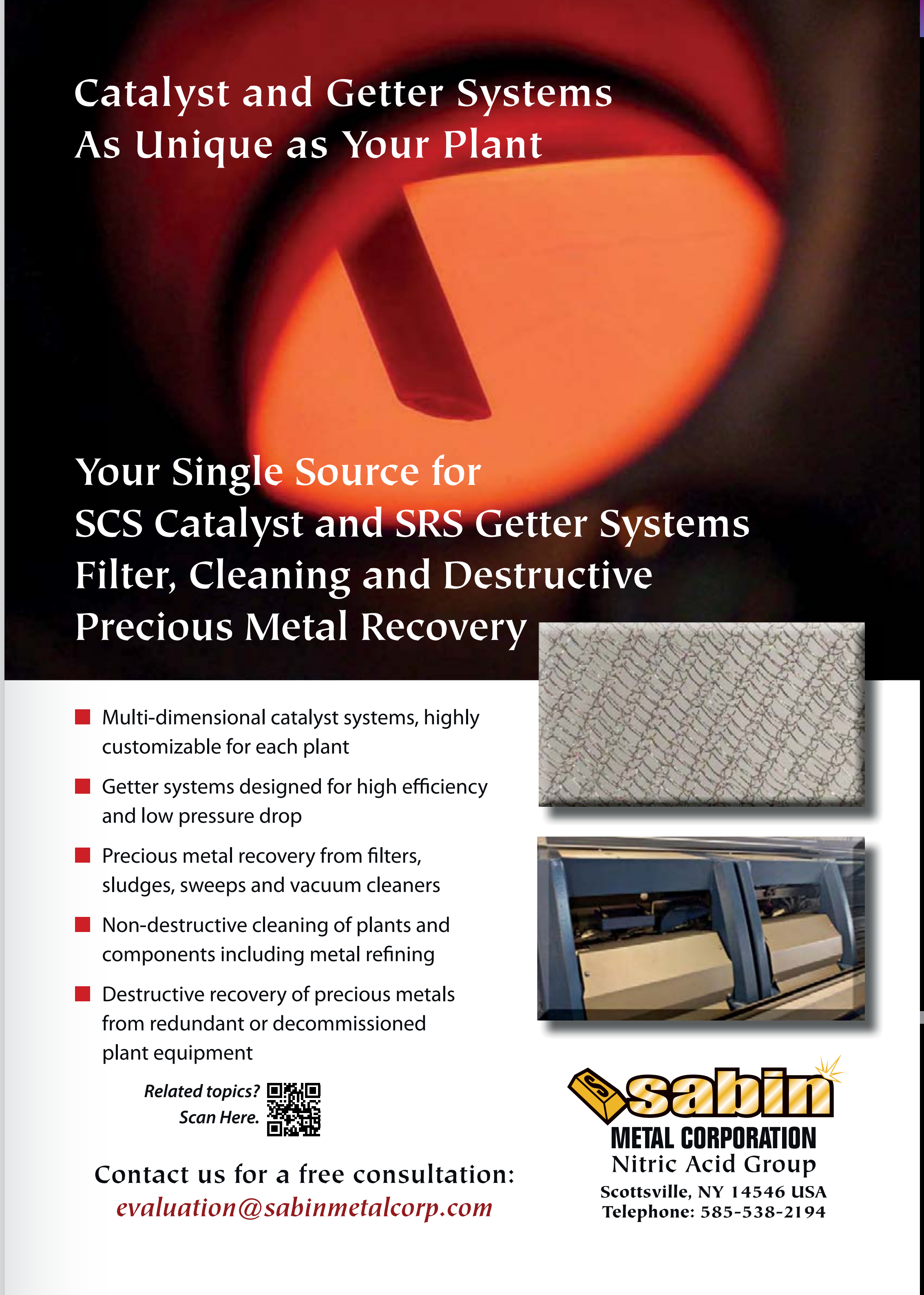
Hydrogen is mixed with the recycle stream from the column overhead and sent to the first compressor stage. Depending on the battery limit conditions, carbon dioxide is added to one of the following compressor stages. Compressed feed gas is mixed with recompressed recycle gas from the high pressure separator and is fed into the methanol synthesis reactor. In the high pressure separator unreacted gas is separated from crude methanol. Crude methanol is sent to the low pressure separator and subsequently to the methanol distillation column. In the distillation column dissolved carbon dioxide and light by-products are separated at the column head, heavy by-products and water accumulate at the column bottom, and pure methanol is withdrawn as a sidestream. Process water is routed to battery limits; fuel methanol can be further used for gasoline blending.

The UHDE green methanol process can be easily adjusted to local and specific project requirements. The plant can either be provided as a so-called stick build lay out, taking advantage of regions with low construction prices, or in modules, prefabricated and precommissioned in workshops for quicker installation. Due to tkIS' modularisation expertise, a wide range of plant capacities can be realised in modularised design. A 3D model of tkIS' advanced modularised renewable methanol plant including water electrolysis is shown in Fig. 5. ■

Fig. 5: **Advanced modularised concept for renewable methanol**



Source: tkIS



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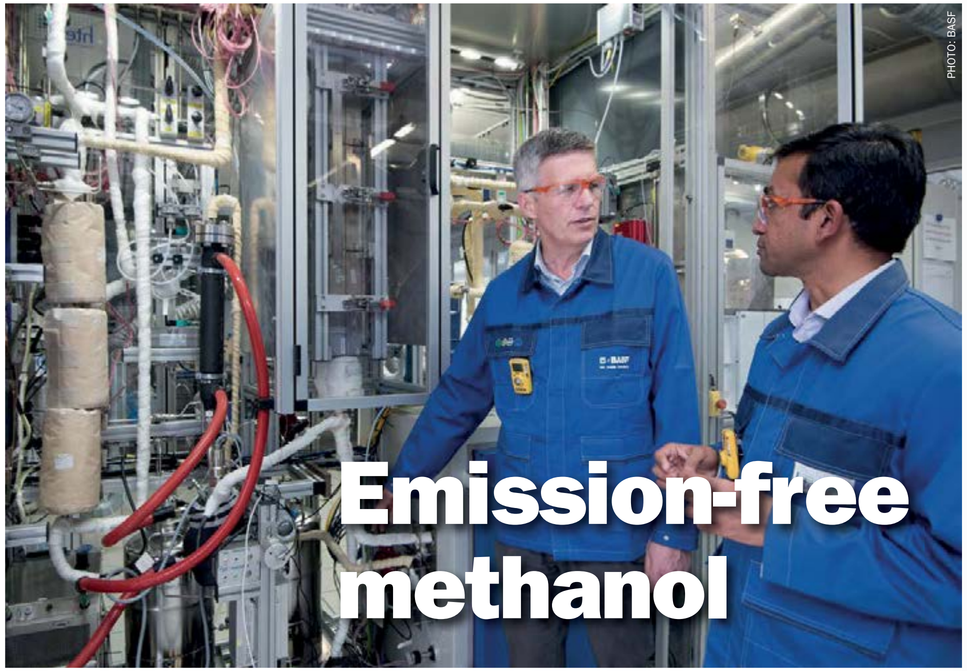


PHOTO: BASF

Emission-free methanol

BASF has filed a patent application for a greenhouse gas-free method for producing methanol. If successful on a large-scale, the process could eliminate carbon dioxide emissions throughout the entire production process from synthesis gas generation to pure methanol.

Above: Aspects of the new CO_2 emission-free methanol synthesis process were tested in a pilot plant at BASF's subsidiary hte GmbH, the high throughput experimentation company, in Heidelberg, Germany. Project manager Dr Maximilian Vicari and hte expert Dr Nakul Thakar are pleased to have solved challenges that arose during catalyst activation and operation of the plant.

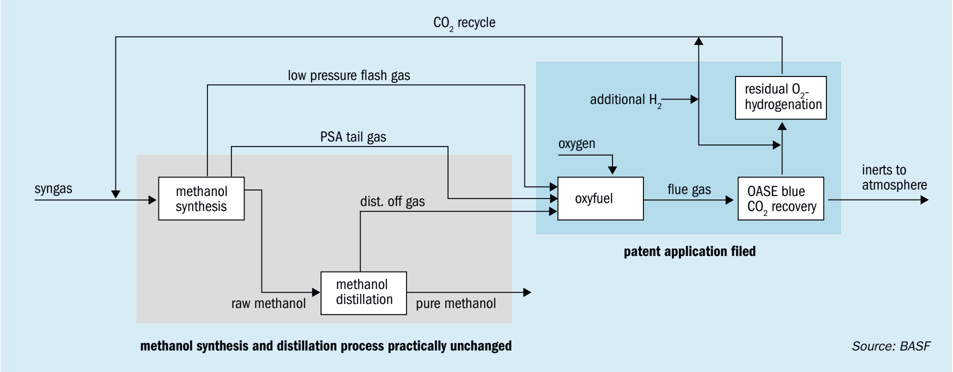
BASF has set itself the target of carbon-neutral growth by 2030. Since 1990, the company has already halved its emissions from 40 million to 22 million tonnes despite doubling its production volume during the same period. The amount of CO_2 per tonne of product has fallen from 2.2 to 0.6 tonnes. "Completely new technologies are needed in order to further substantially decrease CO_2 emissions. That's why we have initiated an ambitious research program," explained Dr. Martin Brudermüller, Chairman of the Board of Executive Directors at BASF.

The aim is to identify technologies and processes that significantly reduce CO_2 emissions and that can be implemented on an industrial scale. A research and development team led by Dr Maximilian Vicari, Director Global Technology Operating Division Intermediates at BASF, recently made great progress in this respect: The "Emission-free Methanol" project within the Carbon Management program has been developed and refined to the extent that a patent application has been filed for the process. "The objective of our project is not just to reduce CO_2 emissions, but to prevent any CO_2 emissions in the entire production process, from natural gas to pure methanol. By doing this, we hope to achieve a 100% carbon yield from synthesis gas generation to the end product methanol," said Vicari.

New emission-free methanol process

The new process begins by producing the synthesis gas through partial oxidation of natural gas, with no carbon dioxide emissions at all. The methanol synthesis and distillation steps of the process can be applied with almost no changes. The partial oxidation process was tested in a joint study with Linde Engineering and proved to be beneficial. "It is the only process we are currently aware of that generates a synthesis gas without any CO_2 emissions and that does not exhibit any serious technical problems. The study we compiled together with Linde clearly confirmed that this procedure harbors the fewest technical risks," Vicari explained.

Fig. 1: **BASF's CO_2-free methanol process**



Source: BASF

A waste gas stream is ejected from the methanol synthesis cycle in order to prevent the accumulation of components that cannot be converted to methanol, e.g. methane or nitrogen. Hydrogen is recovered from this waste gas stream by means of pressure swing absorption. The raw methanol product is also produced as a liquid stream. The pressure of this stream is reduced to 6 bar (absolute), during the course of which a CO_2 and methane component is produced in what is known as the low-pressure flash gas. Low-boiling components such as CO_2 and dimethyl ether are then separated from the raw methanol stream in a distillation column. Methanol, water and several higher-boiling substances remain in the sump. The pure methanol distillation then takes place. The methanol synthesis and distillation process thus produces three waste gas streams, which are unavoidable even when the process is run in an optimal manner. The waste gases from distillation and pressure swing absorption and the low-pressure flash gas are collected and subsequently combusted in an oxy-fuel process with pure oxygen. "As a result, there is a minimal amount of flue gas with a maximum CO_2 content, which has a very advantageous effect on the next stage – OASE gas scrubbing," commented Vicari.

This flue gas is then subjected to gas scrubbing in the tried-and-tested BASF OASE® process, in order to completely wash out the CO_2. OASE blue is an optimised post-combustion capture technology (PCC) for use after combustion. With low energy consumption, low solvent losses and an exceptionally flexible operating range, OASE blue is an important technology for use in the separation of carbon dioxide in waste gases or other gases containing oxygen from sources including fossil fuel power plants or combustion turbines. The technology is based on the separation of carbon dioxide using aqueous amine solutions. OASE blue plays a special role due to the ease of retrofitting this system compared to other separation procedures and the ability to adapt it to the gas streams to be treated. The corresponding CO_2 scrubbing is characterised by a low energy requirement, low washing agent consumption, low emissions, low investment and maintenance costs and a high level of plant availability.

The goal – no carbon loss

Thanks to the recovery of CO_2, the contained carbon is not lost, but is again available for methanol synthesis and is fed into the synthesis gas or into the process for producing synthesis gas. Hydrogen from renewable sources is also added following the gas scrubbing in order to ensure the correct stoichiometry during the methanol synthesis. Small quantities of residual oxygen from the oxy-fuel combustion can then be catalytically hydrogenated. Fixed-bed catalysts containing copper and precious metals can be considered as suitable catalysts. As such, it is possible to reduce the oxygen content to values below one ppm by volume. Inert gases in the process, such as nitrogen and argon, are discharged following the gas scrubbing to avoid accumulation of these components.

The new process from BASF enables methanol to be generated from synthesis gas with a high yield and with the required purity. As no significant procedural changes are necessary in the actual methanol synthesis and distillation, the concept also allows existing plants to be retrofitted. The key feature is the virtually complete material use of components containing carbon for methanol synthesis and the avoidance of any CO_2 emissions. The CO_2 is not only fed back into the system, but also increases the yield of methanol. BASF expects the new process to be implemented on an industrial scale in a first plant within the next ten years.

Methanol from renewable sources

Another approach for reducing greenhouse gases is the generation of methanol based on renewable raw materials. Since November 2018, BASF has been producing methanol based on renewable raw materials in accordance with the principle of biomass balance under the name "EU-REDcert Methanol." Instead of fossil sources such as natural gas, second-generation renewable raw materials are used as well as waste and residual materials. In doing so, BASF is reducing the emissions of greenhouse gases by at least 50% compared to conventionally produced methanol. The biomass-certified methanol is identical to the conventionally produced compound in terms of its chemical and physical properties. BASF is marketing EU-REDcert methanol to customers and also uses it itself as an intermediate for other biomass-balanced products. Both of these new approaches – the innovative CO_2-free production process and the increasing use of renewable raw materials – are significantly reducing greenhouse gas emissions. ■

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Reforming catalyst under continuous development

M. Wilson, **J. Brightling** and **M. Carlsson** of Johnson Matthey detail the development of steam reforming catalyst, with a focus on an operating case study, where Johnson Matthey has combined pelleted and structured reforming catalysts to deliver additional value from an existing asset.

Although the fundamentals of steam reforming chemistry remain the same, the operating conditions within a reformer are becoming more intense. The expected performance and life of a catalyst are increasing, resulting in demand for robust catalyst supports and formulations, capable of performance through the harsh reality of operating plants, with minimal loading variation and stresses, ability to cope with feedstock variation, shutdowns and steaming.

Building on knowledge and success of the KATALCO™ ranges of ceramic supported catalyst, such as KATALCO 25- and 57- series, Johnson Matthey has invested in CATACEL SSR™ technology, a metal foil based structured catalyst that delivers a dramatic improvement in the catalyst performance. CATACEL SSR technology allows previously unachievable combinations of heat transfer properties, reactive surface area and pressure drop characteristics within tubular steam reformers. These enhanced catalyst performance parameters can be tailored and targeted for each steam reforming plant such that maximum operational benefit is realised for existing plant operators or for those designing new steam reforming units.

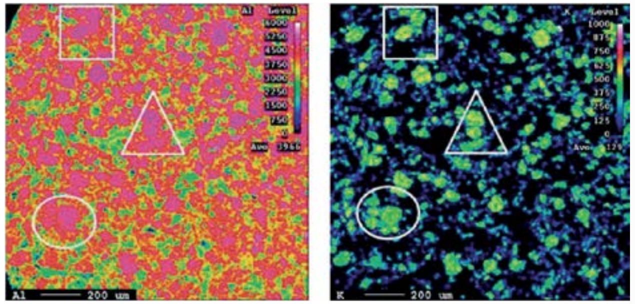


Fig. 1: EMPA images showing aluminium (L) and potassium (R) distribution in a catalyst support highlighting areas of K-Al reservoirs.

Steam reforming catalyst developments

Steam reforming catalysts are for the most part made from shaped ceramic supports onto which the active nickel (Ni) species is impregnated and treated to give stable dispersed nickel oxide (NiO). There are a range of forming techniques and support formulations which all dictate both the chemical and mechanical properties of the final catalyst.

The chemical properties of the support and catalyst that need to be considered include stability in operation as well as transient conditions which include loading, start-up, shutdown and trip conditions. Looking closer at the role of the support, one important consideration in steam reforming is the propensity to form carbon. Carbon formation on the surface of a catalyst is affected by the surface acidity, as positively charged sites catalyse the cracking reaction and therefore increase the rate of carbon formation. Alpha alumina, a commonly used support, contains acidic sites. One way to make the surface less acidic is to add a compound of a group 2 metal such as Calcium (Ca), as seen in KATALCO 57-series. This modification of the support not only changes the surface acidity but also the mechanical properties, as well as the interaction between the surface and the Ni/NiO. This is important when considering that NiO has to be reduced in-situ to generate the Ni-metal sites which are active towards the steam reforming reaction. The support structure can be further modified to include dopants such as potassium (K), in KATALCO 25-series, which further enhances the carbon formation resistance of the catalyst by enabling faster gasification of carbon than its formation. Both for an unpromoted catalyst such as KATALCO 57-series and for a promoted catalyst such as KATALCO 25-series, it is important that the ceramic phases are stable in the extreme conditions which the steam reforming catalyst is exposed to. Under consideration are ensuring hydrothermal stability, minimising the sintering and phase change effect of steam on the support and also prevention of formation of inactive Ni-spinel phases. Looking closer at the KATALCO 25-series in the electron probe micro analysis (EPMA) image in Fig. 1, areas which are rich in Al (left image) and K (right image) are present, indicating potassium-aluminates which are there as potassium reservoirs for the catalyst. The use of a range of phases allows for the release of potassium at an appropriate rate under a range of process conditions and maintains high activity in terms of carbon removal.

Fig. 2: **KATALCO QUADRALOBE™ stress map**

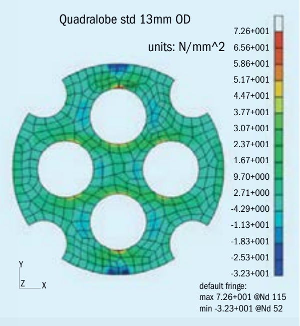


Fig. 3: **Crack propagation through dense material (a) and porous material (b) showing how the crack has become blunt due to material porosity.**

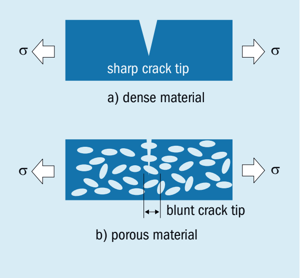
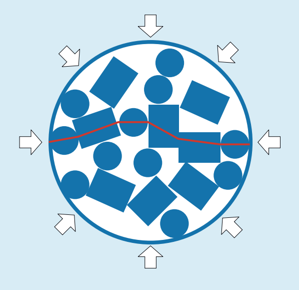


Fig. 4: **Stress chain (red line) caused during tube contraction due to insufficient rearrangement**



The mechanical properties of the catalyst are a combination of the inherent material properties of the support together with its porosity, which are important to optimise for overall catalyst performance. Both the mechanical properties and the porosity are a function of formulation and manufacturing/forming technique and post-forming processing. With regard to the porosity, nitrogen gas sorption and mercury porosimetry are routinely used at Johnson Matthey to gain information on the pore structure/void space of both catalysts and adsorbents, measuring surface area, porosity, pore size distribution and inter-pore connectivity.

Each technique in isolation cannot give insight into the spatial distribution of the pore network. By integrating the two techniques however, scientists at Johnson Matthey have increased their understanding of the role of pore structure in reforming catalysts. Examining and analysing existing catalysts allows for the development of new catalysts with a pore structure that is designed for a particular application with optimum selectivity and activity. Designing a catalyst with small pores at a certain porosity will have the end result of a higher total surface area than an equivalent porosity with larger pores. Focusing on the diffusion limited reforming reaction, the optimised combination of pore volume and pore size and therefore surface area results in minimised diffusion limitations and maximised metal dispersion.

The mechanical strength of a catalyst pellet has been shown to be related to porosity and pore structure. The tensile strength decreases exponentially with the porosity, as shown by the Ryshkewitch-Duckworth equation:

$$\ln\left(\frac{\sigma t}{\sigma 0}\right) = c_1\,(D\text{-}1)$$

Where σt is the tensile strength, $\sigma 0$ is the tensile strength of the material at full density i.e. zero porosity ($D = 1$) and c_1 is a constant related to the bonding capacity. Hence there is a direct tradeoff between overall porosity and physical strength. Generally ceramic catalysts will fail in tensile mode, where tensile stresses may be developed within the catalyst structure (as shown in Fig. 2). Whether or not crack propagation occurs through the porous substrate will be dependent on the porosity both with regards to size and connectivity.

It is well understood in the field of material science and in particular crack mechanics that, 'blunt crack' tips have a higher threshold fracture toughness, as pictorially shown in Fig. 3, when a crack meets a pore the crack will become blunt which will decrease the stress concentration, potentially stopping it from propagating further, preventing breakage. Cracks with sharp tips propagate easier than cracks with blunt tips.

The strength of the catalyst must be high enough to allow loading through conventional means without breakage but still have sufficient porosity to maximise activity as detailed above.

The final consideration with regards to mechanical properties of the catalyst is how it will break, as in some circumstances the catalyst will need to fail in such a way as to minimise pressure drop build-up. In a conventional steam reformer, this would be during a trip/shutdown when the tubes are allowed to cool down. As the tubes initially heat up, the associated thermal expansion leads to some settling of the catalyst. On subsequent cooling, there is insufficient rearrangement when the tubes contract to avoid stress chains to build up, as illustrated in Fig. 4.

These stress chains are a function of the packing structure of the catalyst, which is influenced by the catalyst's external shape. The size of the fragments created during breakage to release this stress chain are a function of the catalyst shape as well as material properties.

The KATALCO 57-series catalyst, a calcium aluminate supported catalyst, has been optimised taking all of these aspects into consideration. The calcium content increases the basicity of the surface to minimise carbon formation without introducing interactions that detrimentally affect the ease of reduction of the NiO. The porosity of the support has been optimised to have a bi-modal distribution of pores between 100 and 20,000 Ångtröms, ensuring a high surface area for dispersion on the active Ni, minimising diffusion resistance and giving a high mechanical strength. The KATALCO 57-Q series catalysts has been designed to break into large pieces, as shown in Fig. 5, which has as little detrimental effect on pressure drop as possible.

Alternative formulations with high strength and non-optimised porosity can

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Fig. 5: Q-shape broken showing resultant large pieces having small impact on pressure drop.

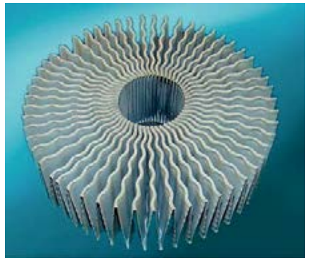


Fig. 6: Coated CATACEL SSR fan.

lead to formation of many small fragments which would have a greater negative impact on the pressure drop over the lifetime of the catalyst. Similar detrimental effects would be present if the shape design was poor, for example having many external features which could interlock, facilitating build-up of stress chains. Alternatively, an intricate internal design can lead to many fragments being created when the pellets break.

Feedback from multiple users confirms that the robustness of the ceramic support in JM's catalyst leads to less breakage of catalyst when loading. Additionally, the robustness of JM's ceramic support is evident by the fact that JM catalysts are much more likely to display a lower rate of pressure rise over time. Many JM customers have experienced a change to a more favourable rate of pressure drop development, when they have switched to JM steam reforming catalyst from a competitive steam reforming pellet.

Metal foils and catalyst coatings

An alternative catalyst design to traditional randomly packed pellets is the use of coated metal foil technology, which has been shown to have several benefits, both with regards to catalyst design but also operation, one of which is the elimination of any breakage due to the stress chain phenomenon described above. Several high-quality metal alloys possess the combination of mechanical properties that allow them to be formed as thin metal foils and used as carriers for catalysts. These metal foils are light, extremely durable and can operate efficiently and robustly in very high temperature environments. CATACEL SSR technology uses a special high temperature alloy as a substrate material. Alloy strip is formed into engineered foil structures called fans (see Fig. 6).

A key factor in their success as a catalyst is the proprietary coating process that ensures that the catalytic coating is tough and long-lasting. The coating contains promoters that allow reduction and start-up on either natural gas or pre-reformed naphtha feeds with no special reduction procedure. The fans are coated with a nickel based steam reforming catalyst using a proprietary process that ensures the catalyst remains attached to the surface of the foil during the catalyst lifetime. The fans are stacked one upon another in the reforming tube, separated by thin metal washers.

There are a number of constituents of catalyst coating that are required to ensure that the binding of the coating to the metal foil is robust and durable. The preparation of catalysts by use of coating technology opens up the possibility of using a range of active catalyst components, stabilisation additives and other promoters that are not always feasible in more traditional catalyst systems.

Structured catalysts

A structured catalyst is a system in which the fundamental characteristics of a catalyst coated metal foil are used to design a precision engineered reaction media. The inherent and repeating structure that can be produced in such an engineered system ensures that the reacting gases within a tubular steam reformer are guided in a highly controlled flow path through the steam reforming reactor. This provides reproducibility of behaviour from tube to tube and allows the designers of these structures to engineer unique features with the structure that deliver high voidage, high geometric surface area and desirable patterns of gas flow.

The stacked fans deliver superior heat transfer by impinging gas on the internal surface of the reforming tube rather than relying on convective heat transfer mechanisms. During operation, gas flows down the tube and encounters the first fan structure. It cannot move through the fan and therefore it is forced out of the triangular ducts. The process gas thus jets directly onto the internal surface of the reformer tube, where it gathers heat. Having nowhere else to go, the gas flows around the edges of the fan and back into the triangular duct on the underside of the fan (see Fig. 7). The washers that separate the fans from one another facilitate this flow back into the fan. Once inside the fan, the gas is free to move to the next fan in the stack and repeat the process.

Key features of CATACEL SSR technology

CATACEL SSR technology is designed to leverage the high voidage, high geometric surface area and controlled gas flow that is available in a structured catalyst system to gain the maximum possible process benefits within the unique environment of a tubular steam reformer. Hence, the low voidage of the CATACEL SSR structure provides the operator with an intrinsically low pressure drop reaction media and the high geometric surface area delivers a high activity steam reforming catalyst.

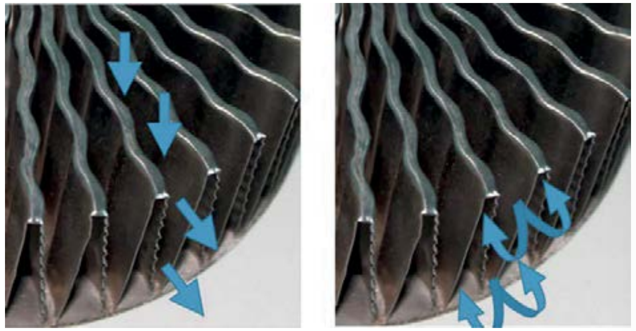


Fig. 7: Gas forced out of duct and back into the underside vents.

The outstanding design feature of CATACEL SSR technology is however the distinctive "fan" structure that is created by the precise manipulation of the underpinning metal foil. This feature carefully directs the gas flow in and through the CATACEL SSR structure and, most importantly, causes radial impingement of the gas onto the internal wall of the reformer tube. The "jetting" mechanism, as shown by CFD (Fig. 8) acts to destroy the stagnant, and heat transfer limiting, gas film that exists on the internal wall structure of the tubular reactors that are used in the steam reforming process. This "jetting" process repeats itself radially around the reformer tube and axially down the tube and it is this innovative behaviour that lifts the heat transfer characteristics of the CATACEL SSR technology to unsurpassed levels.

CATACEL SSR technology operational benefits

Heat transfer coefficients (HTCs) with CATACEL SSR technology can be 20-30% higher than those obtained with conventional ceramic pellets and with a lower pressure drop (PD). Furthermore, the fans offer a high geometric surface area, 1.5 to 2 times that of simple conventional pellets, and this is highly beneficial in areas where reaction is strongly pore-diffusion limited as activity is then proportional to surface area. The design of the fans can be tailored to achieve high heat transfer, high activity or low PD depending upon the requirements of individual plants and so can deliver maximum benefit in each case.

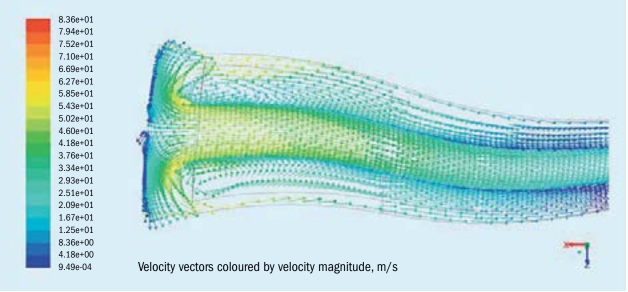
CATACEL SSR technology breaks the usual relationship that requires higher PD for improved thermal and catalytic performance, achieving far higher HTC and activity than is possible from ceramic based pellets while offering significantly lower PD.

CATACEL SSR technology produces a combination of high heat transfer, low pressure drop and high reactive surface area that cannot be achieved with any other catalyst system that is available in the industry. The technology is, within its field, highly disruptive and provides unique value and a basis for innovation for all operators and designers of steam reforming process technology.

Design flexibility

Every operating steam reformer is unique in respect of, for example, feed properties, reformer tube length, reformer tube metallurgy, reformer tube internal and external diameters, burner design, fuel composition, furnace size and furnace geometry. In order to optimise the economics of operation in such a system a great deal of design information and process data are required as inputs to complex programmes such as Johnson Matthey's PRIMARY model. To date, suppliers have been able to deliver a limited range of catalysts that provide no more than binary changes in the factors that a process operator or designer can vary within these models when seeking to optimise performance. For example, small pellets such as KATALCO MQ have aided enhanced heat transfer but penalties may be encountered in respect of pressure drop. The patent protected fan structure can be designed and manufactured with a range of fan heights, with different densities of folds and with a variety of fine design features. These variables produce a vast combination of heat transfer, pressure drop and reactive surface area combinations that, when integrated with an understanding of the characteristics of each reformer unit, can be altered to maximise value for every reformer and every customer.

Fig. 8: **CFD simulation showing jetting of gas from fan onto tube wall**



Impact on plant operation

Value creation comes from the enhanced heat transfer, larger reactive surface area and lower pressure drop characteristics of CATACEL SSR technology, which can deliver the most value to the operator of a hydrogen or syngas plant where a design or an operating process limit is constraining the efficiency or capacity. It is commonly found that CATACEL SSR technology can deliver:

Currently operating units

- 1%-2% throughput increases (direct replacement for standard pellets)
- 2%-10% trim fuel savings (direct replacement for standard pellets)
- 20% decrease in pressure drop compared to standard pellets
- Steam to Carbon decrease of 0.5 units (mol/mol) when replacing standard non-alkalised pellets

Revamps

- 10%-20% throughput increase with no change in tube wall temperature margin
- Tubes can be changed to lower cost, thinner wall, systems

New plants

- Decrease in tube count by 10% - 20%
- Decrease in tube wall thickness and or longer tubes
- 5%-20% lower capital cost of the radiant box

Case study: US Methanol plant

G2X Energy Pampa Fuels, a wholly owned subsidiary of Consolidated Energy Ltd. which is part of the Proman Group, owns and operates a nominal 185 t/d (22 million US gallons per year) methanol plant located in Pampa, Texas.

During a revamp of the plant, further development opportunities targeted the existing SMR unit, which included replacing the tubes in the reformer. JM worked with Pampa Fuels to review the potential to introduce new products that could be utilised to increase the capacity of the methanol plant. One such product was JM's innovative reforming technology, CATACEL SSR.

CATACEL SSR technology breaks the usual relationship that requires higher pressure drop for improved thermal and catalytic performance, achieving far higher heat transfer coefficient (HTC) and activity than is possible from ceramic based pellets while offering significantly lower PD.

This combination of features presented Pampa Fuels with real opportunities for

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major improvements in the operation of the SMR, summarised below in Table 1:

High HTC would reduce the tube wall temperature (TWT) and extract more heat from the combustion gases, leading to improved thermal efficiency of the reformer. The lower TWT would also increase the tube life.

High activity would reduce the methane slip while further lowering the TWT. Further, the higher activity combined with the lower TWT would reduce the risk of carbon formation, with beneficial effects on the life of the catalyst.

Low PD could yield benefits either through reduced load on the plant compressors or higher reformer (and therefore plant) throughput, the latter being the one of most interest.

Operating data

Since the plant uprate and restart in 2018, the newly installed catalysts in the reformer have delivered on the expected performance. Front end rate reached a peak of over 123%. The reformer methane slip as shown in Fig. 9, is trending lower, along with TWTs, as per expectations.

Fig. 10 shows the PD of the SMR (normalised to 100% rate) loaded with CATACEL SSR catalyst and KATALCO 57-Q series plotted against plant rate. Across a wide range of rates, the PD has displayed very steady performance. For comparison, results from the previous, full pellet charge of KATALCO Q-series are shown from various points throughout the catalyst life. The new catalytic combination has delivered improved reforming performance and a lower normalised PD.

Table 1: **Reformer performance projections**

Johnson Matthey catalyst performance projection	**100% natural gas KATALCO pellets**	**120% natural gas SSR over KATALCO pellets**
Inlet conditions		
Relative throughput, %	100	120
Steam to carbon ratio	3.13	3.00
Inlet temperature, °F	896	950
Inlet pressure, psig	301.3	310.0
Exit conditions		
Exit syngas dry flow rate, %	100	122
Exit temperature, °F	1,564	1,624
Exit pressure, psig	274	284
Catalyst pressure drop, psi	27.5	25.9
Flue gas temperature, °F	1,768	1,854
Exit composition (dry)		
Hydrogen (H_2), %	73.79	74.20
Nitrogen (N_2), %	0.32	0.26
Carbon monoxide (CO), %	13.91	15.44
Carbon dioxide (CO_2), %	8.28	7.52
Methane (CH_4), %	3.70	2.58
Extreme values and KPIs		
Max tube wall temperature, °F	1,613	1,671
Minimum TWT margin, F	145	123
Approach to equilibrium, °F	3.7	3.4
Carbon margin		
Minimum carbon margin	unlikely	unlikely

Source: Johnson Matthey

Conclusion

Johnson Matthey has been pushing the boundaries of conventional pellet technology for many years, while also defining new and innovative structured catalyst solutions with CATACEL SSR technology. The combination of the very latest JM catalyst developments and plant equipment upgrades has led the G2X Energy Pampa Fuels facility to achieve a substantial increase in methanol production. Early performance has matched expectations and allowed the plant to operate at over 121% of the previous feed rate and deliver a proportional increase in methanol product. This is due to the low pressure drop of CATACEL SSR catalyst, used for the first time in conjunction with KATALCO Q-series pelleted catalyst, resulting in lower methane slip and greater process gas throughput. ■

Fig. 9: **Methane slip of SMR comparing new charge of CATACEL SSR/KATALCO Q with previous load of all KATALCO Q**

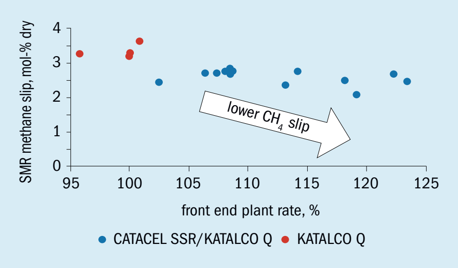
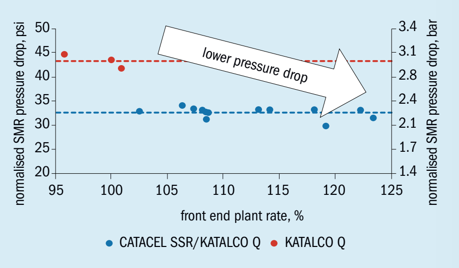


Fig. 10: **Normalised PD of SMR comparing new charge of CATACEL SSR/ KATALCO Q-series catalyst with previous load of all KATALCO Q**



Novel carrier improves performance

The increased severity of operating conditions in modern steam methane reformers requires catalysts with high catalyst activity and good mechanical stability to avoid premature replacements or unplanned shutdowns. **F. Morales Cano**, **M. Stenseng** and **M. Feddersen** of Haldor Topsoe describe a new catalyst formulation with a very homogenous and stable carrier material delivering the high activity and high mechanical strength required for long time operation.

Even mature areas like steam reforming catalysts have room for improvements. By investing in R&D and performing fundamental studies of the different carrier systems and their properties during fabrication and industrial use, Topsoe has developed a new and more robust carrier system. This system forms the basis for a new range of Topsoe steam reforming catalysts – the TITAN™ series.

What defines a good steam reforming catalyst?

In order to have a well-functioning steam reforming catalyst, the following objectives should be met:

- high and stable activity which ensures conversion very close to equilibrium at the outlet of the tubes;
- ability to avoid carbon formation in the upper part of the tubes;
- good resistance to the small amounts of sulphur which enters with the feed streams;
- a catalyst shape which results in a low pressure drop across the reformer;
- high mechanical strength to withstand the thermal cycles taking place throughout its lifetime.

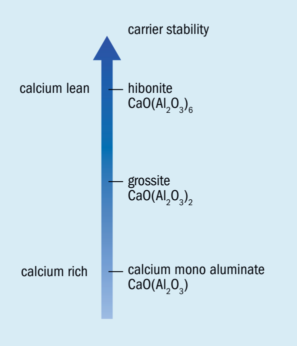
All of the above points are very much dependent on the design and formulation of the carrier material, as this is the main platform for making the finished active catalyst and fulfilling the above objectives.

Hibonite-rich carrier system

The new series of TITAN™ catalysts comprises a hibonite ($CaAl_{12}O_{19}$)-rich carrier with excellent mechanical and thermal stability under the harsh operation conditions in reformers. The manufacturing process involves solid-state synthesis methods in the presence of titanium (Ti) promoters, which enhance the hibonite formation and minimise the formation of calcium (Ca)-rich aluminate phases such as grossite ($CaAl_4O_7$) and calcium mono-aluminate ($CaAl_2O_4$). As revealed from Topsoe's detailed fundamental studies, Ca-rich aluminate phases may have a negative impact on the catalyst performance and therefore a carrier with a high fraction of hibonite phase is most desirable, as depicted in Fig. 1.

The addition of Ti promoters decreases the free energy of formation of hibonite during the synthesis process, leading to higher hibonite content in the new carrier system. The hibonite phase features hexagonal plate-like grains arranged in a three-dimensional structure providing a highly porous structure whilst ensuring excellent mechanical strength and stability (see Fig. 2).

Fig. 1: **Schematic of different calcium aluminate phases and their relative stability in the carrier system**



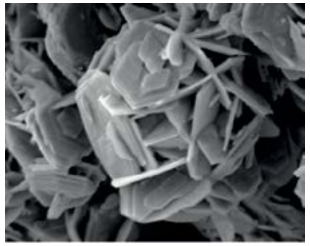


Fig. 2: Scanning Electron Microscopy (SEM) image showing the hibonite plate-like structure consisting of hexagonal grains arranged in a three-dimensional framework.

Nickel is loaded onto the carrier by means of novel impregnation methods that enable the deposition of small and well dispersed nickel nanoparticles over the hibonite platelets, as seen in Fig. 3. The result is an innovative catalyst with very high and stable reforming activity throughout the catalyst lifetime and with an improved end-of-run activity.

During reforming operation, any reforming catalyst will unavoidably age and lose some active surface area due to sintering of the active nickel nanoparticles on the catalyst surface and consequently, it will lose some catalytic activity. The sintering phenomena occur gradually over time, and the degree of sintering depends on the operating conditions as well as the composition and microstructure of the catalyst. An advantage of the new TITAN™ catalyst series is the unique hibonite-rich microstructure with outstanding thermal stability, resulting in a low and contained sintering of the Ni particles

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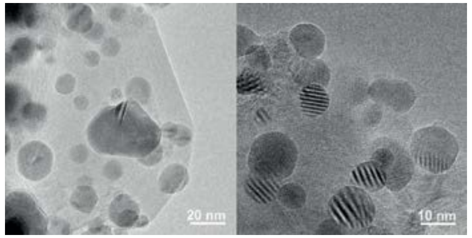
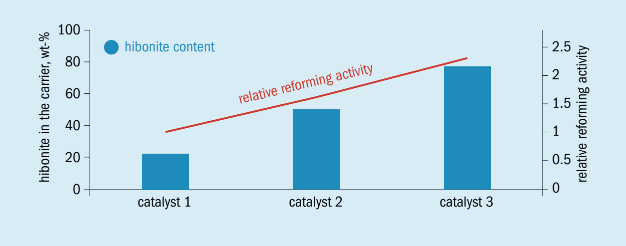


Fig. 3: In-situ TEM images of TITAN™ under conditions of 550°C and 1mbar H_2, revealing small nickel metal particles deposited on the hibonite surface.

Fig. 4: **Relative methane reforming activity of aged catalysts as a function of hibonite content in the carrier**



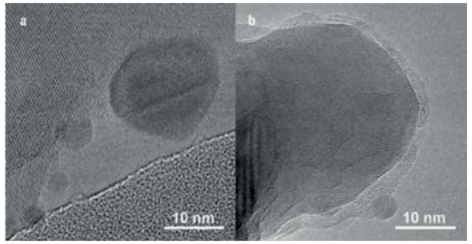


Fig. 5: In-situ TEM images of hibonite-rich catalyst (a) and grossite-rich catalyst (b) acquired at 550°C and 1 mbar H_2, after 20 and 120 min., respectively. Both catalysts were previously aged in the lab under controlled atmosphere.

during the catalyst lifetime; in other words, the catalytic activity will remain more stable towards end-of-run, relative to other conventional industrial catalysts.

Fundamental studies

The hibonite-rich composition of the new carrier system provides a remarkable boost of the catalytic performance of the new TITAN™ series, which becomes evident after long operation times in the reformer. In order to simulate several years of operation in a reformer, Topsoe has carried out aging treatments of different catalysts in the lab under controlled atmospheres by applying high temperature and high steam pressure conditions. The purpose is to induce sintering of the nickel particles as it occurs during aging in industry. The synthesis and evaluation of catalysts containing variable hibonite contents, as determined by X-ray powder diffraction (XRPD), has led to new insights on the optimal calcium aluminate composition for reforming applications.

As seen in Fig. 4, the carrier composition has indeed a strong influence on the activity per mass of catalyst. As the hibonite content increases in the aged catalysts, the reforming activity follows the same trend; the highest methane reforming activity was achieved with the most Ca-lean aluminate carrier containing over 80 wt-% hibonite.

The results from fundamental studies reveal that the superior activity of the hibonite-rich catalyst is attributed to:

- the ability of the hibonite structure to stabilise small Ni particles;
- the higher number of nickel active sites on the hibonite carrier due to absence of free CaO species potentially binding to the nickel surface.

Topsoe has observed the latter phenomenon for grossite-rich catalysts using combined in-situ transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) studies. The results reveal that the new TITAN™ catalyst contains smaller nickel particles, relative to the more calcium-rich (grossite) catalysts, thus providing a larger active nickel surface area for the reforming reactions.

In-situ TEM studies show that grossite-rich catalysts are more difficult to reduce due to the presence of CaO species forming an overlayer on the nickel particles that blocks some of the active nickel sites. Fig. 5 displays an example of an aged TITAN™ catalyst (a) and an aged grossite-rich catalyst (b), inspected by in-situ TEM under reductive atmosphere. The nickel particles on the TITAN™ catalyst reduced easily to metallic nickel after short reduction times and exhibited a very clean nickel surface. On the other hand, the nickel particles supported on the grossite-rich carrier did not fully reduce under the same conditions even after longer reduction times, since a NiO overlayer was still present around the nickel particles. This is evident in Fig. 6b by the oxygen signal around the particle. Fig. 6 shows elemental chemical maps produced by scanning transmission electron microscopy (STEM-EELS). The reason for the hampered nickel reduction is ascribed to the presence of CaO species on the nickel surface, as indicated by the EELS calcium chemical map from Fig. 6c. The EELS maps acquired on the same sample area from Fig. 5b confirm the presence of a CaO layer encapsulating the nickel particle. The results are therefore consistent with the much lower reforming activity of the grossite-rich catalyst.

Benchmarking of industrial catalysts

The reforming activity of the RC-67 TITAN™ catalyst was benchmarked against two other industrial catalysts well established in the market. The catalyst samples were firstly aged in the lab and subsequently tested for methane reforming activity as well as measured for sulphur capacity. As seen in Fig. 7, the activity of the RC-67 TITAN™ catalyst is much higher than the other two industrial catalysts, which exhibit relative activities below 30%. The sulphur capacities obtained for the two conventional catalysts were also significantly lower than for the TITAN™ catalyst.

The phase quantification in the three aged catalysts reveals that the hibonite content is also substantially higher in RC-67 TITAN™. It is therefore demonstrated that a high fraction of hibonite in the catalyst is crucial for ensuring superior high reforming activity and stability.

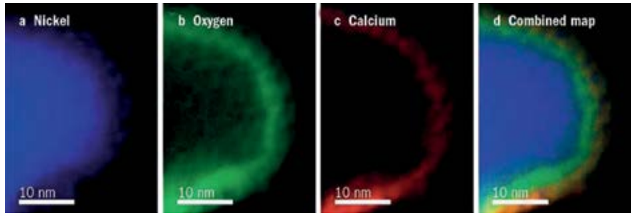
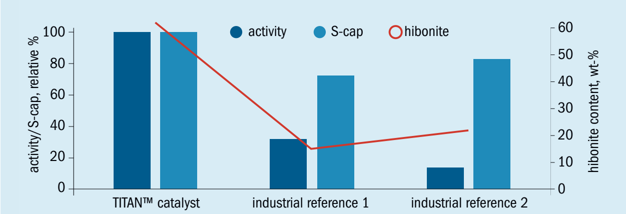


Fig. 6: Scanning Transmission Electron Microscopy (STEM-EELS) mapping in the same area as Fig. 5(b). The elemental chemical maps reveal the concentration gradient of Ni (a), O (b) and Ca (c) elements. Combined map (d).

Fig. 7: **End-of-run reforming activity and S-capacity of the TITAN™ catalyst compared to two industrial Ca-aluminate based catalysts***



Alkali-promoted TITAN™ catalyst to reduce carbon formation

Potassium-promoted catalysts have long been used to reduce carbon formation in top-fired reformers and/or when operating with heavy natural gas as feedstock in the plant. While the previous generations of alkali-promoted reforming catalysts have been successfully applied for many decades, the use of these catalysts may, due to low potassium stability, result in alkali fouling downstream. This was mitigated by the introduction of the RK-400 catalyst series. Building on this know-how, the TITAN™ series includes a new generation alkali-promoted calcium aluminate-supported catalyst, promising more reliable and efficient protection against carbon formation and higher catalytic activity than older conventional catalysts. The new catalyst is based on a hibonite-rich carrier where potassium is bound into the carrier as a K-beta-alumina phase, forming an integral part of the carrier structure. The K-beta-alumina phase is designed to be a potassium reservoir that ensures slow, gradual and stable release of potassium to the nickel particles. Fig. 8 illustrates how the potassium partially adsorbs on the nickel step sites, thus preventing nucleation of graphene islands and formation of pyrolytic carbon.

Fig. 8: **The design of RK-500 TITAN™ with the K-beta-alumina reservoir that prevents carbon formation under reforming operation**

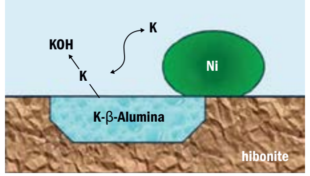
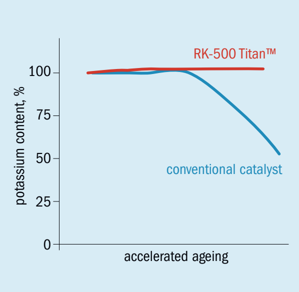


Fig. 9: **Potassium content in spent catalysts after exposure to gas mixtures of $H_2O/H_2/CO_2$ at different aging temperatures**



This design of the new TITAN™ alkali-promoted catalyst also minimises the leaching of potassium during operation, which is known to be a problem for downstream exchangers when operating with some non-Topsoe catalysts. Fig. 9 illustrates the superiority of the RK-500 TITAN™ with respect to potassium stability compared to conventional catalysts.

Industrial experience

A well-performing tubular reforming catalyst has a huge impact on the overall economics of the industrial unit. This impact is due to various improvements in process parameters that are monitored during daily operation. The following two examples illustrate improvements that have materialised after the installation of TITAN™ catalysts.

Example 1: 1,620 t/d ammonia plant

The first example is an ammonia plant with a top-fired reformer operating with a competitor catalyst. The plant was operating very far from equilibrium, resulting in much higher methane leakage than necessary. After installing TITAN™ catalysts in their reformer, a large performance improvement was observed. The methane slip was lower and the approach to reforming equilibrium was reduced by 15°C compared to the previous catalyst after approximately six months of operation. The decreased methane leakage results in a better utilisation of the natural gas feedstock and a lower inert level in the ammonia synthesis loop, resulting in lower opex.

Example 2: 825 t/d ammonia plant

The second example is an ammonia plant that used to run competitor catalyst. When the TITAN™ catalyst was installed, the pressure drop was lower than for the previous catalyst at start-of-run even though the plant load was more than 25% higher. The decreased pressure drop enables the plant to increase its throughput even further.

Due to its excellent properties and high performance, Topsoe's TITAN™ tubular reforming catalyst has quickly taken off in the reforming market, obtaining 18 references in 14 months. ■

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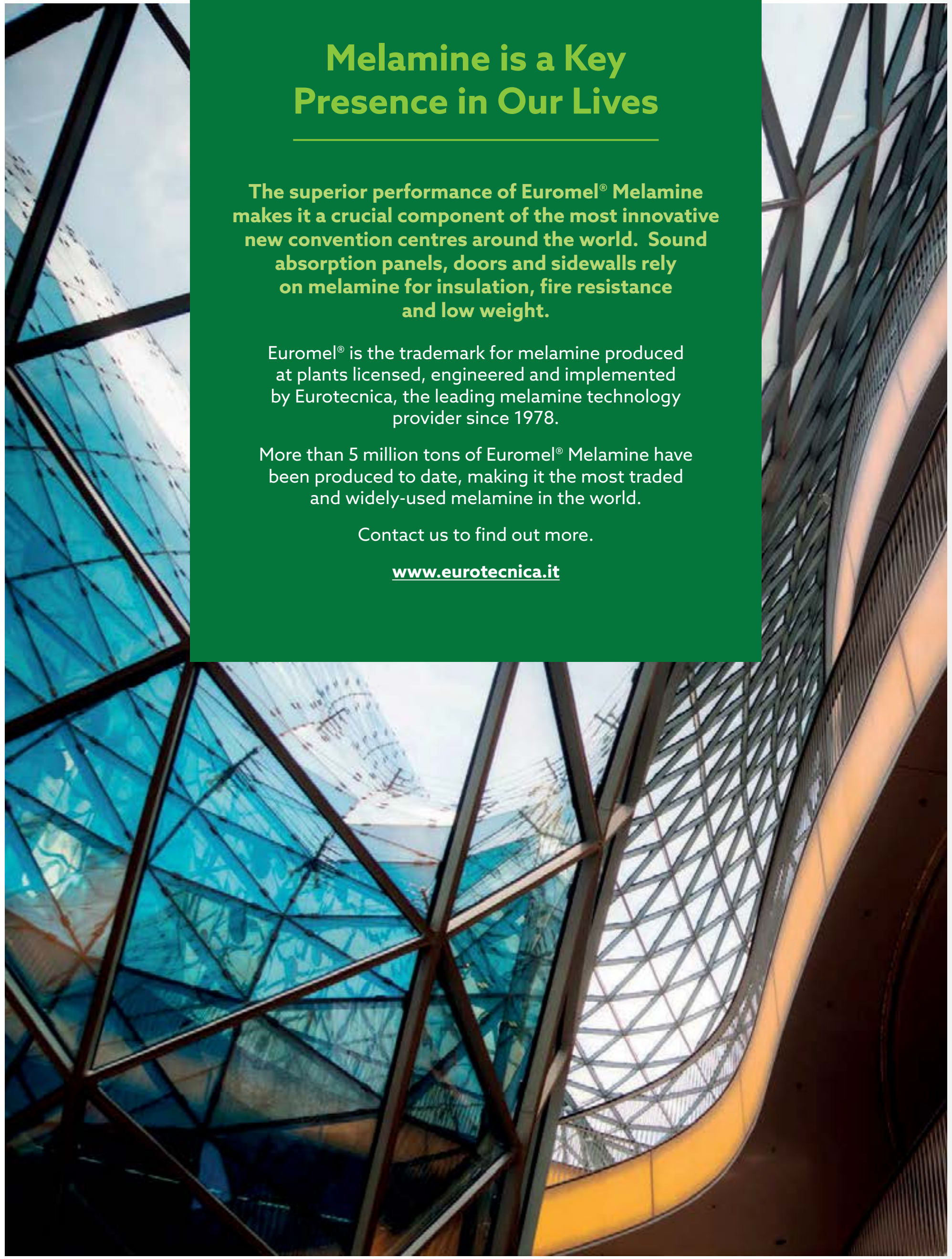

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