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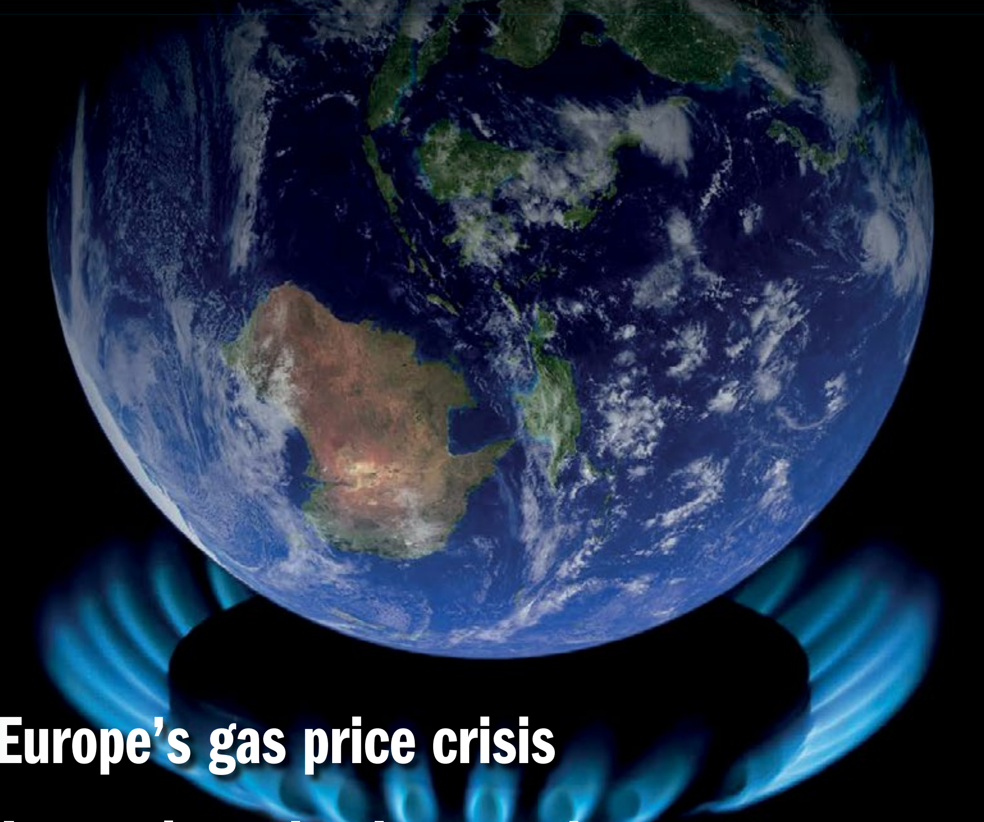

Europe's gas price crisis

Ammonia technology roadmap

Water gas shift performance

Advanced scrubbing technology

NITROGEN+SYNGAS
ISSUE 375
JANUARY-FEBRUARY 2022

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Hype and reality

> **"Only around 1.5% of the world's ammonia capacity is actually currently using low carbon technologies."**

As a quick glance through the Index of last year's articles and news items in this issue of the magazine will amply demonstrate, 2021 was a year full of project announcements for low carbon ammonia and methanol projects of all hues; blue, green, turquoise and many other shades besides. Market analysts CRU said in December that they calculated that there have been a total of 124 million t/a of low carbon ammonia projects announced, 80 million t/a of which came in 2021 alone, equivalent to 55% of current ammonia capacity. These range from tentative pilot plants that are fully costed and often with government grants already secured to blue sky visions of vast electrolysis hubs in the deserts of Arabia with timescales towards the end of the decade – it's often the case that the longer the proposed timescale, the less likely a project is to happen.

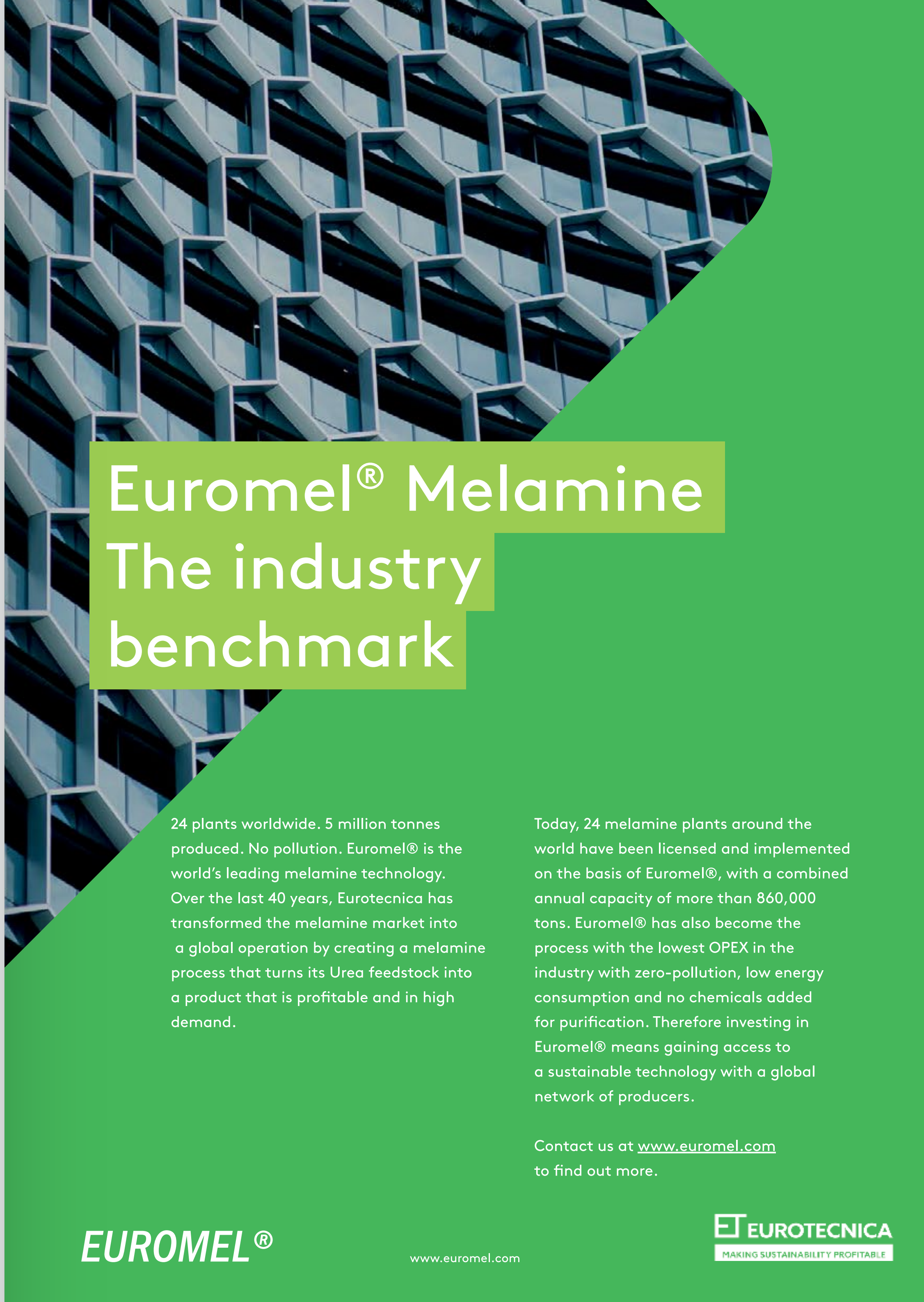
Indeed, it is fair to say that there has been an extraordinary amount of hype around green chemical production, and CRU's posting was perhaps a necessary splash of cold water, and a reminder that as things stand in early 2022, only around 1.5% of the world's ammonia capacity is actually currently using electrolysis (mainly from hydroelectric generation) or carbon capture as part of the production process, and most of that carbon capture is being used for enhanced oil recovery. Projects equivalent to perhaps another 3-4% of current ammonia capacity have had a positive final investment decision or reached a front-end engineering and design stage.

Yet as the IEA/IFA Ammonia Technology Roadmap that we discuss on pages 20-23 indicates, it is change on the kind of scale that is represented by the more speculative project announcements that will be required if the industry is to achieve the levels of carbon emission reduction that will be needed to meet targets of achieving net zero emissions by 2050. How to square that circle will be one of the key questions that the industry will have to grapple with over the next decade. As the roadmap indicates, some of this will no doubt come from increases in efficiency of use of nitrogen fertilizer, reducing the requirement for extra capacity, but most will have to come from electrolysis and carbon capture and storage, technologies that, as yet, have not been installed at world-scale (>1.0 million t/a) ammonia units.

Costs will be an important factor, although as we noted last year electrolysis costs continue to fall, and may increasingly end up below the cost of gas-based production in some regions, especially when deployed on a large scale. Carbon pricing may also end up playing a key role in early adoption of green technologies, but this in turn will require inter-government action to set a level playing field if capacity is not to drift to the lowest bidder. In the short term, green ammonia and methanol may also find that they are able to charge a premium price above conventional ammonia/methanol in some markets, such as marine fuels, where both compounds are increasingly being seen as a way of meeting IMO decarbonisation targets.

Yet even if much of the hype currently circulating falls victim to the second stage of the Gartner 'hype cycle' – the 'trough of disillusionment' - the overall direction of travel of the industry seems set now, and the pressure to decarbonise is only likely to increase as the years pass. ■

Richard Hands, Editor



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Price trends

Market Insight courtesy of Argus Media

NITROGEN

Mid-January was relatively calm as far as trading activity in the ammonia market went, but underlying sentiment remained very firm with several regions short of product. One of the main demand drivers was India, where buyers had been caught extremely short and were in the market for any delivery date on offer. However, cargoes in the Middle East and southeast Asia that might have been able to fill the Indian demand gap were instead being diverted to Morocco and northwest Europe to take advantage of the huge premium in delivered pricing.

In the western hemisphere, there was an absence of spot availability from the Black Sea and Trinidad, with the latter region looking increasingly tight amid reports of some production outages on the island. Price ranges were firmer in east Asia, as contract prices closed in on spot prices. West of Suez, markets were stable, but producers were offering product at prices above last done business.

Recent ammonia market drivers include supply shortages – suppliers are trying to find additional product to feed contractual shipments, particularly to Europe, Morocco and India. Limited cargoes are on offer but some availability is reported in Turkey, Egypt and the Baltic. Another key driver has been energy prices – the European gas feedstock prices driving the price rally remain volatile and traded in a range of $22-29/MMBtu in early January, before settling around $28.3/MMBtu on the 13th January. The average cost of European ammonia production earlier in January was down by around $90/t on the week, with the baseline estimate at $1,036/t.

Urea prices crashed in mid-January in many markets, particularly the US and Brazil, as widespread anticipation of a price correction forced its reality. In general, buyers remained on the sidelines at most levels of the market and sellers continued to lower prices trying to incite demand.

Brazilian buyers bid lower through early January and seller offers tracked lower with them, though trade itself was limited. Prices in early January were in the low-$700s/t c.fr, down by $100/t in a week. US prices pulled back as low as $575/st f.o.b. NOLA – equivalent to around $630/t c.fr US Gulf – the lowest since September 2021. Asian markets remained generally quiet, though prices fell there also.

Recent urea market drivers include producer length – many producers, from the Baltic through North Africa and the Middle East, still held uncommitted volumes for loading in January. Natural gas prices were also a key driver – while the rapid drops in urea prices have received most attention recently, natural gas prices remain elevated above historic norms, several nitrogen plants remain offline and Chinese exports remain severely restricted. ■

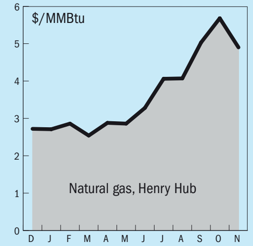
Table 1: **Price indications**

Cash equivalent	mid-Dec	mid-Oct	mid-Aug	mid-June
Ammonia ($/t)				
f.o.b. Black Sea	950-1,055	603-710	560-610	485-525
f.o.b. Caribbean	875-1,000	575-675	540-600	475-525
f.o.b. Arab Gulf	850-1,000	580-620	590-640	550-610
c.fr N.W. Europe	1,020-1,120	680-800	625-680	550-600
Urea ($/t)				
f.o.b. bulk Black Sea	800-905	685-765	390-435	370-435
f.o.b. bulk Arab Gulf*	810-910	730-845	439-470	435-470
f.o.b. NOLA barge (metric tonnes)	770-780	719-840	400-440	445-495
f.o.b. bagged China	830-920	520-630	415-450	400-460
DAP ($/t)				
f.o.b. bulk US Gulf	814-825	735-757	655-667	640-685
UAN (€/tonne)				
f.o.t. ex-tank Rouen, 30%N	680-740	n.m.	157	157

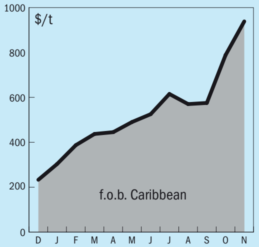
*Notes: n.a. price not available at time of going to press. n.m. no market. * high-end granular.*

END OF MONTH SPOT PRICES

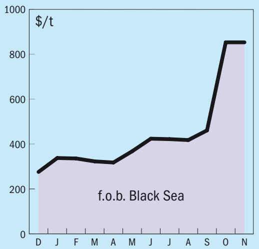
natural gas



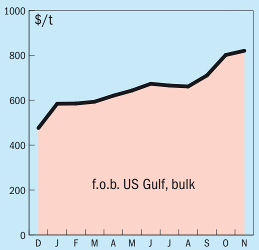
ammonia



urea

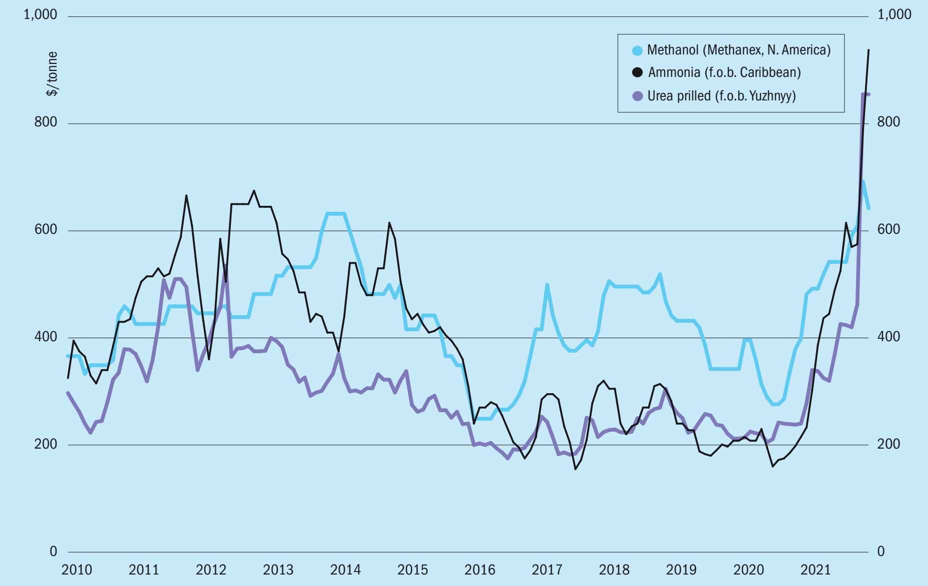


diammonium phosphate



Market Outlook

Historical price trends $/tonne



Source: BCInsight

AMMONIA

- The ammonia market has entered 2022 looking very different to last year, with early January Pivdenny prices $875/t higher on a mid-point basis than they were at the start of 2021, and the likelihood of further gains ahead.
- Continuing strong appetite for imports in Europe, the US, Morocco, Latin America and India is keeping the market in deficit, with supply options still limited.
- The sale of an Indonesian cargo earlier in January – understood to be for a European customer – highlighted just how tight the market is.
- European gas prices have come down from their peak but remain at very high values. Political uncertainty with Russia and cold weather is likely to keep them high for the next few weeks, supporting the current run of high ammonia prices.
- IHS Markit says that it looks likely that European gas prices will not fall significantly until the end of winter.

UREA

- In the near term, prices are expected to continue adjusting downwards. India is now out of the market until March or April and buyers seem to be waiting for the market to find a floor.
- Brazilian import buying has also slowed with high international prices and the restart of the PAU urea plant in Bolivia late last year.
- The US market remains volatile. Off-season NOLA prices fell by $125/st in a week, and prices seem likely to fall further as sellers try to tempt buyers back into the market.
- There are plenty of offers in Europe, but buyers are still attempting to wait for lower prices. However, high natural gas prices should remain supportive of higher urea prices while temperatures remain low in Europe.

METHANOL

- Methanol prices have been falling since November. Methanex's US non-discounted reference price (NDRP) dropped from $692/t in November to $642/t in December and $619 in January 2022. Spot prices were lower, at around $330/t in December compared to $530/t in October.
- US methanol production has been running at high rates, with new production from Koch and a restart for Natgasoline. At the same time, demand is in a seasonal lull, though it is expected to pick up later in the year. Increasing renewable fuel requirements may boost consumption for biodiesel production.
- In China, demand is also in the off-season. This has coupled with an easing in coal prices to take the edge of Chinese methanol prices, which fell to around $385/t by the end of December, down 12% on November, and the weakness is expected to persist in 1Q 2022. Prices in southeast Asia have fallen to just over $400/t c.fr.
- Overall the methanol market seems to be well supplied and demand is covered in the short term. ■

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FRANCE

IFA signs collaboration agreement with UN FAO

The International Fertilizer Association (IFA) has signed a memorandum of understanding with the United Nations Food and Agriculture Organisation (FAO) over collaboration to support the FAO's vision of transformative change and innovation in agriculture. Svein Tore Holsether, IFA Chair, signed the agreement at a live virtual signing in December together with FAO deputy director general Beth Bechdol. The agreement outlines collaboration to further shared goals and objectives with regard to the promotion of sustainable food and agriculture. Both parties will work together to raise awareness about the International Code of Conduct for the Sustainable Use and Management of Fertilizers (Fertilizer Code), promote education and knowledge transfer and continue their successful collaboration on fertilizer statistics.

Sustainable plant nutrition is a key focus for the fertilizer industry, which is dedicated to helping implement better management practices on a global level. The FAO's International Code of Conduct for the Sustainable Use and Management of Fertilizers is an important tool to achieve this.

IFA and FAO developed a workplan which includes education and knowledge transfer through joint seminars, webinars and scientific exchanges, among many other activities and to continue ongoing cooperation on global fertilizer statistics. ■

NORWAY

Work begins on green hydrogen feed for Porsgrunn

Norway's state environmental fund Enova SF has granted Yara $32.3 million for the latter's green ammonia initiative at its ammonia plant at Herøya near Porsgrunn. The finding will help instal a 24 MW electrolysis plant which will generate green hydrogen to be used in the ammonia plant, allowing 20,500 t/a of green ammonia to be produced, reducing the plant's CO_2 emissions by 41,000 t/a from around mid-2023. This initial installation will be a technology demonstrator and for quality assurance purposes, though longer term Yara aims to completely replace its gas-based feed at Porsgrunn with green hydrogen. Yara says that it has already cut its own emissions by about 45% since 2005 and will continue to reduce its own emissions and emissions from power production by an additional 30% by 2030.

Grant agreed for Barents Blue ammonia plant

Horisont Energi AS says that its Barents Blue clean ammonia plant has been awarded a $53.6 million grant by Enova SF, subject to approval by the EU Commission and European Free Trade Association Surveillance Authority. Should the grant be approved, Horisont Energi, with partners Equinor ASA and Var Energi AS, will proceed to the front end engineering design phase of the Barents Blue project in 2022. Construction work is planned to take place from 2023 to 2025, and the plant is expected to be in operation around the turn of the year 2025-2026.

Horisont Energi said that the European Union's Important Projects of Common European Interest (IPCEI) programme will provide it with "a unique opportunity to link the Barents Blue project to other projects and value chains in the 23 participating European countries, to create positive spillover effects and benefit from possible knowledge transfer, financing, market size and other economies of scale."

UNITED STATES

CF welcomes duty determination on UAN

CF Industries says that it welcomes the US Department of Commerce's preliminary determinations that urea ammonium nitrate (UAN) imports from Russia are unfairly subsidised at rates ranging from 9.66% to 9.84% and UAN imports from Trinidad and Tobago at a rate of 1.83%. The DoC made the determinations as part of countervailing duty investigations that are being conducted in response to petitions filed by CF Industries through certain of its production facilities, and as a result will impose preliminary cash deposit requirements on imports of UAN from Russia and Trinidad. It is conducting concurrent anti-dumping investigations into UAN from Russia and Trinidad. Preliminary determinations in these investigations are expected in late January.

GERMANY

Clariant working on ammonia cracking catalysts

Clariant Catalysts is participating in Germany's AmmoRef project, which is tasked to develop process technologies and catalysts for ammonia cracking to facilitate future hydrogen transport over for large distances. With €14 million in funding from the German Federal Ministry of Education and Research (BMBF), AmmoRef is part of the overarching €135 million TransHyDE project, which aims to revolutionise the nation's hydrogen transport infrastructure in preparation for a sweeping energy transition. TransHyDE is one of three hydrogen flagship projects aiming to prepare Germany's entry into a hydrogen economy.

Marvin Estenfelder, Head of R&D at Clariant Catalysts, commented, "Clariant has been involved in R&D and cross-industry collaborations in this field for many years, and we have already developed numerous catalysts for use in innovative hydrogen applications. We are confident that together we will make it possible to recover pure hydrogen from ammonia in the scales required for efficient and safe mass transportation of hydrogen."

Free NOx removal catalyst

Clariant has also launched a campaign to provide free nitrous oxide removal catalyst for nitric acid producers worldwide to reduce the climate change impact of nitrous oxide (N_2O). The company is offering a free fill of its *EnviCat N_2O-S* catalyst, which removes up to 95% of N_2O generated as a by-product of nitric acid production. to 10 nitric acid producers who do not have N_2O off-gas treatment in place. Through the campaign, the company intends to help avoid greenhouse gas emissions equivalent to several million tons of CO_2 every year. Of the approximately 500 nitric acid plants operating globally, more than half run without N_2O abatement, mostly in regions without applicable emission control regulations. Over 60 million tons of nitric acid are produced annually around the world, mainly for manufacturing fertilizers. Annually, N_2O emissions from the production of nitric acid and its derivative adipic acid are equivalent to about 100 million t/a of CO_2.

AUSTRALIA

Incitec moving forward on green ammonia plan

Incitec Pivot Ltd, Australia's largest supplier of fertilizers, says that it has completed initial feasibility studies on converting its Gibson Island ammonia plant to run on zero carbon green hydrogen, in conjunction with Fortescue Future Industries (FFI). The latter plans to construct an on-site electrolysis plant, which could produce up to 50,000 t/a of green hydrogen for conversion into ammonia, replacing the current fossil fuel gas feedstock. High natural gas prices had threatened Gibson Island with closure.

FFI is now moving forward with an engineering design study to refine cost, schedule, permitting and commercial agreements, and inform a potential final investment decision

FFI CEO Julie Shuttleworth said, "FFI's collaboration with Incitec Pivot is an exciting opportunity to harness existing infrastructure at Gibson Island, fast tracking the production of green ammonia at an industrial scale. Pending further approvals, this project could be Australia's first green ammonia production facility, demonstrating existing infrastructure can be retrofitted to utilise zero-emissions energy sources."

Australia facing AdBlue shortage

High international urea prices exacerbated by a Chinese export ban have left Australia facing a shortage of the AdBlue urea solution used in the catalytic converters of heavy diesel road vehicles for NOx abatement. Australia has only one urea producer, Incitec Pivot, with 290,000 t/a of capacity at Gibson Island, and usually imports 80% of its urea requirements from China.

'Project Haber' urea plant proposal

Gas exploration and development company Strike Energy, which is planning to build a 1.4 million t/a ammonia-urea plant near Geraldton in Western Australia, has been awarded a A$2 million grant to help fund project development. Strike is proposing to pipe natural gas 125 km from its own South Erregulla natural gas project near Eneabba to the urea plant site. The company says that it hopes to merge front-end engineering design (FEED) and subsequent engineering, procurement and construction (EPC) phases of development - it has started early FEED works, mainly to do with environmental approvals and has initiated a FEED/EPC tender process for Project Haber. The tender will be issued once drilling at South Erregulla – already well under way – proves the required gas supply is present. The company also initially intends to supply 2% of its hydrogen demand from its own dedicated 10 MW hydrogen electrolyser.

RUSSIA

Agreement for low-carbon ammonia supply

Russian gas producer Novatek and German energy company Uniper SE have announced the signing of a long-term supply agreement of up to 1.2 million t/a tons of low-carbon ammonia for the German market. Production will take place at Novatek's planned Obskiy Gas Chemical Complex in the Russian Arctic and be delivered to Uniper's planned ammonia import terminal in Wilhelmshaven, equipped with an ammonia cracker operating with renewable power.

The Obskiy plant will include carbon capture and storage facilities and the product price will be indexed to relevant European and global benchmarks. The imported low-carbon ammonia is set to be implemented as a hydrogen carrier, transformed into gaseous hydrogen and fed into the future German hydrogen pipeline system, as well as supplied directly as a clean feedstock and as a fuel.

"Our strategy pays significant attention to clean energy supplies, and we consider ammonia as the most efficient hydrogen carrier for seaborne transportation," said Leonid Mikhelson, Chairman of Novatek's Management Board. "We are now at the pre-FEED stage for a low-carbon ammonia and hydrogen plant with CCS facilities, and signing of term sheets for long-term supply demonstrates growing demand for low-carbon products, which is an essential precursor for the Final Investment Decision on this project," he added. "The plant will be located next to our LNG cluster in Yamal in order to minimise the infrastructure costs and provide the most competitive clean energy supplies to the global market."

SOUTH AFRICA

Green ammonia export plan

Linde is joining with UK-based Hive Hydrogen and local firm Built Africa to establish a green ammonia export plant in the Coega special economic zone near the port of Ngqura in Nelson Mandela Bay, in the Eastern Cape. The first phase of the 780,000 t/a, $4.6 billion project is planned to begin operation in 2025, with full operation by the end of 2026, using solar and wind energy to generate hydrogen. Hive Hydrogen is being supported by InvestSA, a branch of the South African Department of Trade, Industry and Competition.

CROATIA

Petrokemija shut down again

Croatian fertilizer producer Petrokemija said that it had stopped operations at its ammonia-urea plant at Kutina on December 3rd. The shutdown follows technical issues that have dogged the plant throughout 2021. The site was shut down from late December 2020 to February 2021 for a major maintenance overhaul including changeover of a new liquid sulphur tank at the site's sulphuric acid plant and the installation of a new combustion air preheater for the ammonia plant primary reformer. However, there was a further maintenance shutdown that began in May 2021 which was extended to June 30th due to what the company described as problems with "auxiliary processes". The ammonia-urea unit went down for three weeks again in September, and a full restart was not completed until October, but the plant was only on-stream for two months before being taken down by the latest technical issue. The company also reports issues with natural gas pricing in the current environment. Petrokemija's 3Q 2021 profits were 94% down on the same period of 2020, and last May the company announced a plan for 350 staff layoffs.

OMAN

Decarbonisation plan for Salalah ammonia plant

OQ, formerly the Oman Oil Company, has unveiled a $1 billion project called SalalaH2 to decarbonise the company's existing 1,000 t/d ammonia plant at Salalah and its integration into a complex including up to 1 GW of solar and wind based renewable energy capacity, and 400 MW of electrolyser capacity to produce green hydrogen and other green products. Other project partners include Linde, Japan's Marubeni trading house, and UAE-based Dutco. The Salalah site also currently includes LPG and methanol production. The project envisages a several year switch-over from gas-based to ultimately 100% renewable ammonia production and export.

Rudolphe Kotliar, Business Development Manager at Linde Clean Energy, told local media that the integration of the existing

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ammonia plant with new renewable energy capacity and green hydrogen production components will result in green products emerging from Salalah. "Renewable energy will also be supplied to the air separation units to produce green nitrogen that will be mixed with ammonia. Likewise, water production will be based on renewable energy, thus making green water. Oxygen output will be integrated into the process as well," he said.

SAUDI ARABIA

Thyssenkrupp signs deal for 2GW electrolysis plant

Thyssenkrupp Uhde Chlorine Engineers has won a contract from Air Products to supply and install a $ 5 billion, 2GW electrolysis plant for one of the world's largest green hydrogen projects at the ambitious Neom 'future city' development in Saudi Arabia. Thyssenkrupp will design and build the Neom plant based on its 20MW alkaline water electrolysis module, with commissioning expected in 2026. Neom, planned for the Red Sea coast, is a $500 billion development which is intended to be powered by up to 40GW of renewable energy.

"As a world market leader in electrolysis we bring in two decisive factors to realise such gigawatt projects: With our large-scale standard module size and gigawatt cell manufacturing capacity per year together with our joint venture partner De Nora we are able to deliver large capacity projects today," said Denis Krude, chief executive of Thyssenkrupp Uhde Chlorine Engineers. "With this gigawatt project, we are committed to invest into ramping up our manufacturing capacities further."

Neom, developer ACWA Power and Air Products will operate the 2GW facility upon commissioning. Air Products aims to convert the H_2 into carbon-free ammonia for export to global markets.

CHILE

Total Eren looking to mega-scale renewable ammonia plant

Total Eren, a partnership between French oil major Total and EREN renewable energies, says that it is engaged in a feasibility study for a 10 GW clean hydrogen development at Magallanes in southern Chile. The developer has already secured land in preparation for the project, and describes the region, in the southern tip of Chile, as having "the best onshore wind conditions in the world" as well as access to the sea for desalination, and ports to export green fuels. At the moment, up to 800,000 t/a of green hydrogen and 4.4 million t/a of ammonia production is being considered. Total Eren says that if the studies prove successful, it hopes to begin work on the H_2 Magallanes project in 2025, with first production by 2027.

Fabienne Demol, global head of business development of Total Eren, said: "We are delighted to present this large-scale green hydrogen project, a pioneering initiative that we are proud to officially launch today in Chile's Punta Arenas. I am eager to begin construction to contribute to Chile's ambition of becoming a top destination for green hydrogen investment in Latin America and meet the needs of our customers worldwide."

MEXICO

Local vote approves ammonia-urea plant

A referendum among 40,000 local citizens has approved the construction of a $5 billion ammonia-urea plant at Topolobambo by 76-24, albeit on a very low turnout (13%). The plant had generated controversy among the citizens of Sinaloa state. Construction had begun in August 2018 but a federal judge halted the project in March 2019 due to environmental concerns. In June that year Mexican president López Obrador called for a referendum on the project to be held, a proposal he renewed in August 2020. The project is a development by Gas y Petroquimica de Occidente (GPO), a subsidiary of Swiss engineering, procurement and construction group Proman AG, and envisages 800,000 t/a of ammonia and 1.0 million t/a of urea capacity being fed by local gas reserves, with a 1.4 million t/a methanol plant to follow in a later phase of development.

MAURITANIA

MoU signed on LNG and ammonia project proposal

Gas-to-power developer New Fortress Energy (NFE) has signed a memorandum of understanding with the government of Mauritania in west Africa for the proposed development of an energy hub, including natural gas, power, LNG, and blue ammonia, using existing offshore gas reserves. NFE says that it is aiming to use to use its "Fast LNG" technology, based around jack-up rigs or similar floating infrastructure, allowing lower cost and faster deployment schedules than conventional floating liquefaction vessels. Gas will be supplied to a new 120MW combined cycle power plant and the existing 180 MW Somolec power plant, as well as 'blue' ammonia capacity.

A separate proposal by CWP Energy signed an agreement with the Mauritanian government in November for a feasibility study on a 30GW of wind and solar energy development in the north of the country that could feed up to 10 million t/a of green ammonia production.

INDIA

Deepak Fertilisers begins work on TGAN plant

A foundation stone laying ceremony has been held to mark the beginning of construction of a new ammonia, nitric acid, ammonium nitrate solutions and technical grade ammonium nitrate (TGAN) plant at Gopalpur. The plant is being built by Smartchem Technologies, a wholly owned subsidiary of Deepak Fertilisers and Petrochemicals Corporation Ltd. Capacity will be 165,000 t/a of ammonia, 297,000 t/a of nitric acid, 377,000 t/a of AN solutions and 330,000 t/a of TGAN, with total investment budget put at $235 million.

Ammonium sulphate plant inaugurated

Steel producer BSL has inaugurated a new ammonium sulphate plant. The plant is fed by 180,000 m^3/h of coke oven off gas. BSL sells the ammonium sulphate as fertilizer in India. The inauguration was attended by R. Kushwaha, Executive Director (Projects), Atanu Bhowmik, Executive Director (Works), Sanjay Kumar, general manager (Services) Sanjay Kumar, and Rakesh Kumar, general manager (Coke Oven & BPP).

PAKISTAN

Ministry agrees more gas for fertilizer production

Pakistan's Ministry of Industries and Production has approved more gas supplies for the country's urea plants that supply the domestic sector – mainly Fatima Fertilizers and Agritech – for the period October 2021 – March 2022, placing them on a par with the export-oriented plants which have previously been favoured in terms of gas allocation, in order to ensure urea supplies to domestic consumers during the current period of high international urea prices. A gas price of \$4.77/MMBtu has been adopted.

NITROGEN INDUSTRY NEWS

TRINIDAD & TOBAGO

Study on green hydrogen

KBR says it has been awarded a study to help establish a green hydrogen market in Trinidad and Tobago as part of an ongoing technical cooperation financed by the Inter-American Development Bank (IDB). Under the terms of the contract, KBR will analyse strategies for maximising opportunities to establish a green hydrogen economy in Trinidad and Tobago, undertaking supply and demand dynamics for green hydrogen generation, transportation, and end use applications. The study will identify opportunities for the development of a low carbon economy, with a roadmap to Net Zero through technological innovation. It will assess the potential for green hydrogen production as well as the repurposing of the existing facilities for low carbon hydrogen. The assessment will include recommendations for a technical implementation plan.

"This study builds on KBR's proud history of supporting Trinidad and Tobago's advancing focus on clean energy solutions – establishing itself as a leader in the regional hydrogen economy," said Jay Ibrahim, President, Sustainable Technology Solutions, KBR. "The recent COP26 Summit brought into focus the threat of climate change on island nations. The opportunity to help the country meet its carbon reduction and sustainability targets firmly aligns with KBRs commitment of driving innovative solutions to support sustainability."

JAPAN

Sumitomo looking towards low carbon ammonia

Sumitomo Chemicals is reportedly in discussions with Yara over supplies of low carbon ammonia for fibre production at its Ehime site. The companies have agreed to jointly explore using clean ammonia produced by Yara, green ammonia produced using renewable hydrogen and blue ammonia produced from fossil fuels but with carbon emissions captured and stored or reused. Sumitomo has set itself a goal of cutting greenhouse gas emissions by 50% by 2030 compared to 2014 levels, and to reach net zero emissions by 2050.

CHINA

Stamicarbon to license urea technology

Stamicarbon has been awarded a licensing and equipment supply contract for two ultra-low energy grassroots urea plants Dongping, Shandong Province, for a local urea producer. Stamicarbon will deliver the process design package and the proprietary high-pressure equipment in *Safurex*® as well as associated services for the urea melt plants and prill towers. The two urea melt plants will each have a capacity of 2,334 t/d and will use Stamicarbon's proprietary *Pool Reactor* technology. The plants are expected to start up in the middle of 2023.

This contract represents Stamicarbon's fifth and sixth utlra low energy urea installations since its introduction. It builds on the success of the three earlier plants in China, of which Jinjiang Xinlianxin and Hubei Sanning are in operation and Henan Xinlianxin is under construction. The design allows for heat to be used three times (instead of two), bringing energy use to an unprecedentedly low level. It also substantially reduces plant operating costs by significantly reducing steam and cooling water consumption. The design can also be used as a revamp tool for both CO_2 stripping and conventional urea plants.

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UNITED STATES

Blue methanol project proposal

The Bia Energy Operating Company says that it is evaluating a $550 million blue methanol plant at the port of Caddo-Bossier in Shreveport, Louisiana. The unit would have a capacity of 530,000 t/a of methanol using natural gas feedstock with downstream carbon capture, reducing CO_2 emissions by more than 90% compared to other methanol plants. The company is expected to make a final decision in 1Q 2022, with construction expected to last approximately two years, and commercial operations to begin soon after.

State governor John Edwards said: "Louisiana welcomes and supports Bia Energy's plans for investment, job creation and increased economic activity in Northwest Louisiana. BEOC's proposed use of carbon capture technology is important, as we continue a trend of industrial growth in Louisiana that aligns with our commitment to achieve net-zero carbon emissions by 2050. We look forward to seeing this project progress and become operational in the near term."

US methanol capacity continues to increase, with Louisiana seeing the start-up of the 1.6 million t/a Koch plant last year, and Methanex deciding to proceed with a third plant at its Geismar, Louisiana site. The country already has 10 million t/a of capacity against 7 million t/a of demand, and exports to Europe and Asia are set to increase.

DoE provides loan guarantee for 'turquoise' hydrogen plant

The US Department of Energy has offered its first conditional loan guarantee to a non-nuclear project since 2016 to help finance a commercial-scale 'turquoise' hydrogen and carbon black plant in Hallam, Nebraska. The guarantee covers a loan of up to $1.04 billion to Monolith, a company which is pioneering a methane pyrolysis process, to expand its Olive Creek site from 14,000 t/a to 194,000 t/a. Monolith's process converts natural gas into hydrogen and high purity carbon black using renewable energy, converting the carbon dioxide to pure carbon and hence preventing its release to atmosphere. Kiewit has been awarded the engineering, construction, and procurement contract for the expansion, which is expected to be on-stream in 2024.

Monolith's technology was purchased from Kværner (now Aker Solutions) in 2013. Kværner built a commercial-scale methane pyrolysis facility using hot plasma in Norway in 1997, but decommissioned the plant in 2003. Monolith is now backed by Mitsubishi Heavy Industries (MHI), which bought into the project in December 2020, as well as a variety of venture capital investors and utility giant NextEra Energy Resources.

The Nebraska expansion is also expected to include an ammonia plant using the hydrogen to produce 275,000 t/a of carbon-free ammonia.

EGYPT

EBIC's green hydrogen plant to start-up in November

The Egypt Basic Industries Corporation (EBIC) says that it is looking to November 2022 for the start-up of the country's first green hydrogen plant. The plant is being developed by a consortium which includes Egypt's sovereign wealth fund, Norwegian renewables developer Scatec, ADNOC and Fertiglobe, the owning company of ENIC. Scatec will install 100 MW of solar powered electrolysis capacity, which will generate sufficient hydrogen to produce 90,000 t/a of ammonia at EBIC's existing Ain Sokhna ammonia facility. The consortium partners are targeting a start date of 2024 for operations

Methanol-ammonia plant for Ain Sokhna

Ain Sokhna is also the site for a new $2.6 billion methanol-ammonia development, backed by Egypt's Suez Canal Economic Zone. The project is intended to be executed in two phases, with completion of the first phase by 2025 at an investment cost of about $1.6 billion. The second phase, with an estimated cost of about $1 billion, would involve building downstream acetic acid, methanol to olefins, and nitric acid/calcium ammonium nitrate capacity over the period of a further three years. Targeted production capacity for the first phase is 1.0 million t/a of methanol and 400,000 t/a of ammonia. The partners in the International Methanol Company are Egypt's Abu Qir Fertilizers (25%) and Helwan Fertilizers Co (25%) and the Al-Ahly Capital Holding Co (50%).

GERMANY

FOERSTER buys Quest Integrity's syngas business

In December 2021 Germany's FOERSTER Group – formerly known as Magnetische Pruefanlagen GmbH – completed the acquisition of Quest Integrity's Syngas business unit. The acquisition includes both the business unit's technical staff and its LOTIS® and Mantis™ inspection technologies. As Magnetische Pruefanlagen, FOERSTER has been a leader in the field of reformer tube testing for ammonia, methanol, hydrogen and direct reduction iron (DRI) plants, with proprietary technology for checking tubes that are exposed to high pressure and temperature for damage. Test results are used to define preventive maintenance intervals to increase the service life and prevent failures that can lead to unscheduled system outages and production loss. Earlier in 2021 Magnetische Pruefanlagen merged with Institut Dr. Foerster GmbH & Co. KG to create FOERSTER, and also subsequently bought US Thermal Technology (USTT) in the Americas, creating synergies and expanding the company's sales network worldwide.

DENMARK

Maersk unveils new methanol-powered container ship design

Shipping giant Maersk has unveiled a new large 16,000 teu (20' equivalent unit) container ship design, powered by methanol. The company sees green methanol as the preferred future shipping fuel of choice. The design puts crew accommodation and the funnel at opposite ends of the vessel, to improve capacity and port and fuel efficiency. It will be able to operate on dual-fuel, incorporating conventional low-sulphur and green methanol. The design features a 16,000 m^3 methanol fuel tank, enabling the ship to travel long distances using the fuel – an important consideration, since it has less energy per kg than HFO or marine diesel. Maersk claims the vessel represents a further commitment to methanol as a fuel of the future, after it began construction of several 2,000 teu methanol-powered feeder vessels. Liquid at room temperature, methanol is more practical than hydrogen in terms of storage, with several times the energy density, as well as being less toxic than ammonia if spilled or inhaled. It is also clean burning, emitting no NOx or SOx, and only minimal particulate matter. Maersk says that it is evaluating both methanol made from renewable hydrogen and captured carbon, and biomethanol, as part of its life cycle emissions calculations. Maersk's move towards methanol fuelling is leading to the shipping industry taking green methanol much more seriously as a future fuel.

Haldor Topsoe to divest its shares in Faradion

Haldor Topsoe is to sell its 16% stake in rechargeable battery manufacturer Faradion, as part of a sale of the company to Reliance New Energy Solar Limited (RNESL), a wholly owned subsidiary of India's Reliance Industries. Reliance is paying £100 million ($134 million) for the company, and has also agreed to invest a further £25 million ($34 million) in Faradion. Topsoe says that it will continue its focus on battery technology based on its own lithium-nickel-manganese oxide (LNMO) materials.

UZBEKISTAN

Work complete on GTL project

EPC contractor Hyundai Engineering said in December that it had completed construction work on Uzbekistan's $3.6 billion gas to liquids (GTL) plant at Kashkadarya, 400 km southeast of Tashkent. The Oltin Yo'l GTL plant will process 3.6 bcm of natural gas per year to produce 1.5 million t/a of synthetic kerosene, diesel, aviation jet fuel and LPG, as well as naphtha, the latter being supplied to the Shurtan Gas Chemical Complex. The plant is owned and operated by state owned oil and gas company Uzbekneftegaz, and was designed using Sasol Fischer-Tropsch technology. It is the world's sixth large scale GTL plant, and will supply fuels to the local Uzbek market.

CHINA

World's largest green hydrogen plant under construction

Chinese state oil company Sinopec says that it has started work on the world's largest solar-powered hydrogen electrolysis plant. The $470 million facility, which is being built in the western Xinjiang province, is expected to produce up to 20,000 t/a of green hydrogen using a 300 MW electrolysis unit. The facility also includes a spherical hydrogen storage tank with a capacity of 210,000 standard cubic meters, and hydrogen transmission pipelines with a capacity of 28,000 m^3/h per hour. The green hydrogen produced by the plant will be supplied to Sinopec Tahe Refining & Chemical to replace the existing natural gas and fossil energy used in hydrogen production. Ilt is estimated that the plant will reduce carbon dioxide emissions by 485,000 tons a year once it is put into operation in June 2023.

"Hydrogen energy is one of the sources of clean energy that has the most potential for development. This pilot project gives full play to Xinjiang's advantage in its wealth of resources and is a key project for Sinopec to build a No.1 hydrogen energy company. It's also a major strategic achievement for local-enterprise cooperation and is of great significance to promoting social and economic development in Xinjiang, advancing energy transformation, ensuring China's energy security and supporting the sustainable development of the global economy," said Ma Yongsheng, president of Sinopec.

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People

KP Engineering, LP specialising in the design and execution of customized EPC solutions for the refining, syngas, hydrogen and renewable fuels industries, has named **Bill Preston** as its new president and Chief Executive Officer. Based in Houston, Preston has served as KPE's president and Chief Operating Officer since 2015. During that time, he was responsible for leading significant growth and upholding KPE's core operational values of respect and integrity. As CEO, he will be responsible for the overall direction, execution and global expansion of the company. Preston has 34 years of experience leading and growing technology-based businesses in the engineering, oil and gas, energy and chemical production sectors. Prior to joining KP Engineering, he served in vice president roles for companies including a division of Texaco and ChevronTexaco, Linc Energy, Synthesis Energy Systems and GreatPoint Energy. He also served as CEO of The Energy Capital Group, developing syngas and chemical production facilities in the chemical and oil refining industries. He is currently the Executive Director of the Global Syngas Technologies Council, the hydrogen and syngas industry's premier trade association.

Preston commented, "I am proud to work alongside a talented group of industry professionals that are dedicated to engineering our customers' success, and I look forward to overseeing exciting developments and global growth within KPE through 2022 and beyond."

He will work alongside **Michael Roberts**, Senior Vice President of Operations; **Mahesh Thadhani**, Senior Vice President of Business Development, who was appointed in November 2021; **Doug Schnittker**, Vice President of Projects; and **Ken Fischer**, Vice President of Technology.

Nutrien Ltd has announced that **Mayo Schmidt** has left his position as president and CEO of Nutrien and has resigned from the Board. **Ken Seitz**, Executive Vice President and CEO of Potash, has been named the company's interim CEO. Seitz brings extensive global leadership experience in the agriculture and mining sectors and is well-positioned to progress the company's stated strategy and lead the integrated business during the transition.

Russ Girling, Chair of the Nutrien Board of Directors, said: "Nutrien has a talented and deep executive team, and we are confident that Ken Seitz and this team will continue to build on the organisation's record financial and operating performance. The Nutrien Board of Directors will work with an executive search firm to begin a global search to select a long-term leader that will take the company into its next phase, which will consider internal and external candidates."

Mr. Seitz said, "I look forward to working with the executive leadership team, delivering on our commitment to advance sustainable solutions to feed a growing world."

Seitz joined Nutrien as Executive Vice President and CEO of Potash in 2019. He

Ken Seitz.

has 25 years of global management experience working across more than 60 countries, and was a former president and CEO of Canpotex, one of the world's largest suppliers of Potash.

Johnson Matthey (JM) has appointed **Alberto Giovanzana** as managing director of Catalyst Technologies. Alberto joins JM from BASF where most recently he was Senior Vice President and Head of Global Technology for the €2 billion Nutrition and Health Division. Prior to this, Alberto ran BASF's Plastic Additives business in Europe, Middle East and Africa and has also held various marketing and operations roles. In his new role, Alberto will leverage the technical expertise at JM in the field of process catalysts and drive collaboration with customers to harness business opportunities in the energy transition and circular economy, according to the company.

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

Calendar 2022

MARCH

21-23

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

21-23

European Gas and Hydrogen Conference, VIENNA, Austria
Contact: Sandil Sanmugam, Energy Council
Tel: +44 20 7384 7744
Email: sandil.sanmugam@energycouncil.com

28-30

Nitrogen+Syngas Conference 2022,
BERLIN, Germany
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

31-2 APRIL

IFA 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

2-4

Nitrogen+Syngas USA Conference 2022,
Tulsa, Oklahoma, USA
Contact: CRU Events
Tel: +44 (0) 20 7903 2444
Fax: +44 (0) 20 7903 2172
Email: conferences@crugroup.com

31-2 JUNE

FHSOW 2022, SHANGHAI, China
Contact: CCPIT Sub-Council of Chemical Industry, Beijing
Tel: +86 10 84 255 960
Email: zhengyingying@ccpitchem.org.cn

JUNE

12-15

International Methanol Technology Operators Forum (IMTOF), LONDON, UK
Contact: Polly Murray, Johnson Matthey
Email: polly.murray@matthey.com

Plant Manager+

Problem No. 64 Reasons and solutions for leak detection system choking

A proper leak detection system for loose liners of high-pressure urea equipment is the number one safeguard for any urea plant, as has been proven by detailed safety studies and incidents investigations. However, leak detection systems easily choke especially when urea is present in the leaking solution. When no urea is present, the ammonium carbamate will dissociate above 60°C when flashing to atmospheric pressure in the leak detection system. But, when urea is present, it can solidify and at higher temperatures polymerise into biuret and triuret, which have even higher crystallisation temperatures. An early and reliable leak detection system is therefore very important. UreaKnowHow.com has developed such a system: the state-of-the-art AMMO LASER Leak Detection System.

Samee Ullah of FFCL in Pakistan starts this round table discussion with an important question: Is there any possibility that leak detection system tubing can get choked by anything other than carbamate leakage? Please share your experience.

Mark Brouwer of Ureaknowhow.com in The Netherlands replies and asks for further information: Other reasons can be: **1** urea leakage; **2** flushing with water and below zero ambient temperatures and **3** fouling. What kind of leak detection do you operate, passive or active. In case of active, is it a pressurised or vacuum system?

Muhammad Shoaib of Fatima Fertilizer Company in Pakistan replies for Samee: We are using a vacuum leak detection system. Please share your experience regarding unblocking choked tubes.

Mark responds: Choking can occur in the tubes of the leak detection system or behind the liner. When a tube is choked it can be simply replaced, but when there is clogging behind the liner it becomes complicated:

Option 1 is to flush with water to dissolve the crystals causing the clogging. However, we strongly advise NOT to do this as water introduces several kinds of stress corrosion phenomena to the carbon steel pressure bearing wall.

Option 2 is to remove the liner, clean it and then re-install it, but this is a big exercise.

Option 3 is to use a vacuum-based leak detection system and connect it to both leak detection holes. In this way one "bypasses" the clogged area.

Kashif Naseem in Saudi Arabia shares his experiences: Be proactive and conduct the leak detection system test after 2-3 years to check the tubes and liner segment clearance.

Prem Baboo of Dangote Fertilizers Projects in Nigeria shares joins the discussion: If we find choking, the first thing we do is find out the reason for the choking. The choking can sometimes be removed by pressurising the petal with instrument air up to 7.0 kg/cm². Only carry out this practice in running mode as with an empty reactor the maximum allowable pressure behind the liner is only 0.2 to 0.3 kg/cm²g subject to the condition of the liner thickness. Analyse in the lab for ammonia. The choking of weep hole tubing during operation of the plant is a serious problem and should not be taken lightly. The plant must be shut down if the lab analysis confirms ammonia.

Mark provides more information on unclogging leak detection circuits: A leak detection circuit can be clogged in the tubing part, this can be replaced or, after disconnecting it from the vessel, flushed.

It can also be clogged in the leak detection hole: these solids can be carefully removed mechanically.

Finally, if it is clogged behind the liner and cannot be reached, our advice would be to switch to an active vacuum-based system. A vacuum system is more flexible to connect to the available leak detection holes and ensures that the maximum liner area is under direct detection.

Majid Khan from Pakistan joins the discussion: In order to ensure that the leak detection system is clear with no choking, we flush the leak detection holes to ensure that all leak detection holes and grooves are clear. What is the best way to flush leak detection holes? Should steam be used?

Mark replies: We strongly advise against flushing with steam or condensate as it introduces the risk of (bi)carbonate stress corrosion cracking of the carbon steel pressure bearing wall. Cracks in the carbon steel behind the liner threaten the integrity of the vessel and will go undetected.

The only time the carbon steel can be inspected for these cracks is during a relining job.

Issa Norozipour from Khorasan Petrochemical in Iran joins the discussion: Can we use steam or steam condensate for removing any carbamate or urea behind the liner and immediately flush with purge gas like nitrogen?

Mark replies: How can you be sure you have removed all of the moisture?

Majid replies: In the past we have used steam to flush leak detection holes. Currently I am studying the alternatives for flushing. Can instrument air or nitrogen be used? What frequency would you recommend for flushing?

Mark replies again: Once clogged due to ammonium carbamate and/or urea, neither air nor nitrogen will dissolve it. Steam or condensate will dissolve it but will create the risks of cracks in the carbon steel. Our advice is to leave the solids (these are dry and not corrosive) and switch to an active vacuum-based leak detection system.

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LNG cargoes unloading at the Port of Rotterdam.

PHOTO: PORT OF ROTTERDAM

The current crisis in global gas markets

Recent spikes in natural gas prices, particularly in Europe, have highlighted the tightness of natural gas markets around the world going into the northern hemisphere winter. Are ammonia and methanol producers on for a run of high gas prices in 2022?

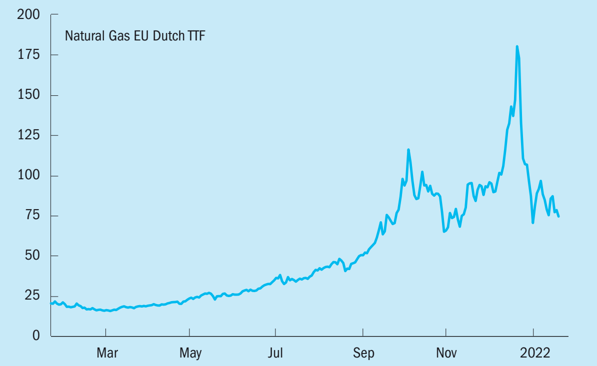
Ammonia and downstream markets have been dominated by a run-up in natural gas prices over the past few months. Notwithstanding all of the announcements of experiments or pilot plants using electrolysis to generate hydrogen feeds, natural gas remains the key raw material for ammonia production outside of China, where coal-based capacity still predominates. Each tonne of ammonia requires typically at least 36 MMBtu of natural gas, and so the price of gas is a key determinant of the cost of ammonia production.

Last year's gas price run began in Europe, escalating throughout September and October. The continent had seen record low gas prices in June 2020, as coronavirus lockdowns and mild summer weather reduced demand for natural gas. However, returning demand as lockdowns eased in mid-2021 combined with a variety of factors to push prices steadily higher, including a colder than average winter in 2020-21 which left storage depleted, followed by a hot summer that increased demand for power for air conditioning, and a prolonged period of still air which led to low output from Europe's large wind-powered electricity generation sector. This in turn led to more gas-fired power being used, at the same time that Russian supply remained relatively slack, in part due to pandemic-delayed maintenance on pipelines, something which also constricted supply from Norway. Problems were exacerbated in the UK by a fire at an electricity station handling a cross-Channel power cable which left the country unable to balance power generation with imports from France, where nuclear energy still predominates. The UK has low gas storage capacity and was forced to re-start its last coal fired power station in the autumn. Supplies from the key Dutch Groeningen gas field are also being wound down because earth tremors – see the article on that elsewhere in this issue.

The result has been something of a perfect storm for gas prices. The Dutch TTF gas benchmark, which stood at as low as \$1.50/MMBtu in summer 2020, stood at \$6.55/MMBtu in March 2021, but had climbed to \$35/MMBtu by October 2021, equivalent to a cash cost for ammonia producers of over \$1,000/t. Ammonia prices did not keep pace with soaring gas costs, at least to begin with, and this led to a wave of shutdowns across the continent. On September 15th, CF Industries announced that it was halting operations at both its Billingham and Ince fertilizer plans in the UK, although the government said it would provide financial support to keep the Billingham plant running, as these plants supply most of the UK's carbon dioxide for food and drink manufacture. BASF closed its Antwerp and Ludwigshafen plants in Belgium and Germany, Fertiberia ceased production at its Palos de la Frontera site in Spain, and Puertellano remained down for scheduled maintenance. Yara shut 40% of its European ammonia production in September, and OCI partially closed its Geleen plant in the Netherlands. Achema in Lithuania decided against restarting its ammonia plant following maintenance in August, and OPZ in Ukraine shut one ammonia line at Odessa, with Ostchem and DniproAzot likely to follow.

European gas prices actually dropped back from their highs during November due to milder weather and a number of LNG cargoes arriving. Prices dropped back to around \$25/MMBtu, at the same time that ammonia prices were reacting to the shutdowns and rising – to over \$1,100/t c.fr northwest Europe in December – allowing a number of plants to restart production. Yara said that by December 15th, most of its 4.9 million t/a of European ammonia capacity was back on-stream. However, with the Russian Yamal pipeline out of action, gas prices spiked again in December – Dutch TTF forward rates actually touched \$60/MMBtu before dropping back to \$45/MMBtu going into the New Year.

Fig. 1: **Dutch TTF gas price, 12 months, €/MWh**



Source: Trading Economics

European gas

Europe's gas woes are mainly down to structural issues with its market. Although the continent has gradually liberalised its gas market and reduced dependence on oil-indexed pricing, which had previously left prices dependant on the vagaries of the international oil market, Europe's dependence on imported natural gas continues to increase. In particular, in spite of attempts to diversify its supply, it remains highly dependent on imports of gas from Russia. Gas has become more important in Europe's overall energy mix due to stricter climate and energy policies. The EU Emissions Trading Scheme (ETS) sets a price for carbon emissions from power generation and large-scale industry which has eliminated most of the continent's coal-abased generation capacity. Most EU member nations are also winding down their nuclear power programmes. While there has been a considerable increase in power generation from renewable sources, these are often intermittent by nature, and base load generation therefore relies upon natural gas.

Europe's own gas production is also in long-term decline, both due to falling output from fields in the North Sea, Romania and elsewhere, but also due to that move away form fossil fuel generation, as well as the seismic issues with the Groeningen gas field as mentioned previously. To mitigate against this, Europe has increased its gas storage capacity, to hold gas in case of price shocks or supply disruptions. However, by June 2021 the previous cold winter and lack of supply from Russia meant that storage was less than half full; the lowest summer levels in a decade. Europe has also dramatically increased its capacity to import gas by sea as LNG, and takes large cargoes from the US, Qatar, Nigeria and Algeria. But in spite of this, Europe remains dependant on gas imports for about 2/3 of its gas requirements, much of that still comes from Russia. Europe imported 330 bcm of natural gas in 2020, according to BP figures, of which only about one third (115 bcm) was as LNG. Of the remainder, 167 bcm came via pipeline from Russia, or 50% of total imports.

Geopolitics

Geopolitics plays its role in the crisis as well. Because of tensions between Russia and Europe over issues such as Ukraine and NATO expansion, there is a suspicion that president Putin is using 'the gas weapon' again – restricting supplies of natural gas to put political pressure upon European governments. Russia has cut supplies of gas to Europe before, during gas payments disputes with Ukraine in 2005-6 and 2008-9, as well as during the Crimea crisis of 2014, with knock-on effects for European prices. Russian

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exports to Europe were running around 15% below capacity during 2021.

One bone of contention is the recently completed NordStream 2 pipeline. Ironically, this has been built to give Russia more of an option to maintain supplies to Europe at times when the gas supply to Ukraine may be interrupted. Previously around 40% of Russian gas reached Europe using pipelines through Ukraine. However, Germany has dragged its feet on signing off on NordStream 2, perhaps worried that it would presage further Russian pressure on Ukraine.

There are also pricing disputes with Europe. European consumers have gradually forced Russia's state gas supplier (and monopoly exporter) Gazprom to give up oil indexation of gas pricing and long term fixed price contracts for sales to Europe and accept a spot price model instead. Europe also wants other private Russian gas companies, such as Novatek, to be able to use NordStream 2, something Gazprom is resisting.

But most of all, it is the ongoing standoff between Russia and the US and its allies over Ukraine which is playing into the current gas price crisis. With 100,000 Russian troops on or near the Ukrainian border, and inconclusive talks with the US in early January, European gas prices have risen by 30% on concerns that supplies could be interrupted were the conflict to turn hot.

Elsewhere

While this winter's gas price crisis has been a largely European affair, it has not been exclusively so. Northeast Asian demand for LNG has also been running at high levels, helping LNG prices to peak in December at $48/MMBtu, before falling back to $33/MMBtu at the end of the year. With Australia exporting a record amount of LNG in 2021, this has also had a knock-on effect on gas prices in some parts of Australia. However, in North America, gas production continues to be unaffected, and Henry Hub prices remain below $4.00/MMBtu.

As far as ammonia prices go, soaring European prices have dragged up prices all around the world, beginning with Black Sea prices, where supplies are mainly destined for Europe, reaching record prices of above $1,000/t f.o.b. This in turn has led to US Gulf Coast c.fr ammonia prices reaching $1,000/t in December, and likewise Middle Eastern f.o.b. prices. With European prices so high, Middle Eastern producers have supplied only contract volumes to Asian consumers and sent cargoes west through Suez instead.

For producers with fixed or relatively low gas costs, this has been a bonanza. In the US and Middle East, producers are able to take advantage of high product prices at the same time that gas prices remain low. Not everyone has been able to take advantage of this, however; Trinidadian producers have been committed to long-term supply contracts and have only been able to sell small ammonia volumes on the spot market. But for markets which rely upon imported ammonia, such as India, or industrial consumers in e.g. Taiwan and South Korea, it is unwelcome price pressure on operations.

Where do we go from here?

This will be a difficult season for European ammonia producers. If gas prices remain high, it may be possible for ammonia prices to fall to a point where nitrate plants can be run on imported ammonia. Platts has suggested that there may be a tipping point around $680/t ammonia (equivalent to around $18/MMBtu gas). But there is likely to be demand destruction among natural gas consumers, and indeed on nitrogen consumers. The main impact of high nitrogen prices is likely to be felt in lower applications of fertilizer for the coming year, and/or higher costs to farmers which will be passed on to consumers as higher food prices. Nitrogen application has a particular impact upon wheat, rice and corn production – most nitrogen fertilizer goes to produce these staples. European applications of nitrate for winter wheat are already down, and a prolonged run of high prices for urea will start to impact Asia in a couple of months.

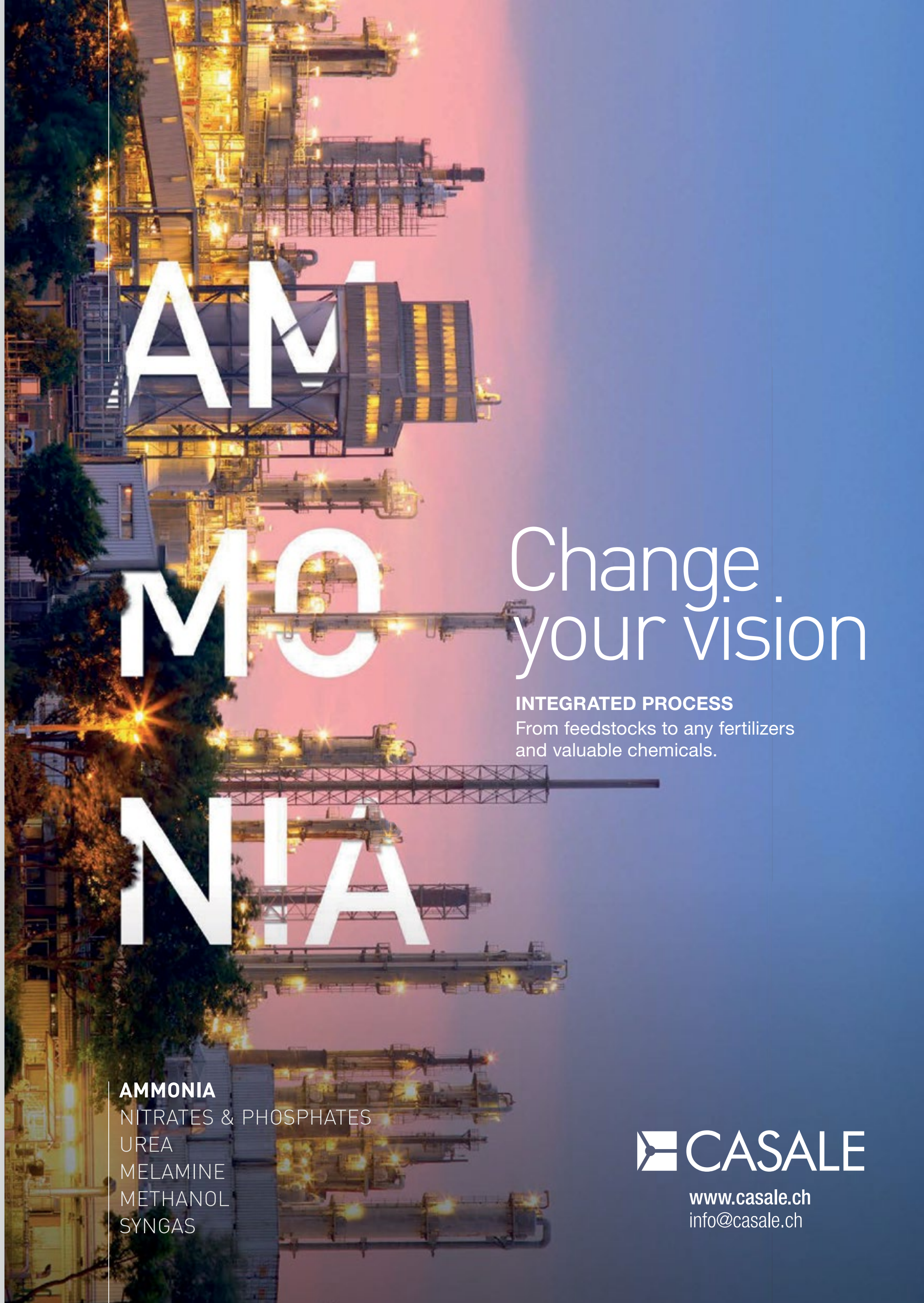
Governments worldwide are starting to intervene to mitigate this as much as possible; India is looking to subsidise urea costs to farmers, for example. Higher food prices are already being felt worldwide as a result of covid-related supply chain disruptions and increased demand for biofuels. Lower yields due to lower nitrogen applications and high input fertilizer prices are likely to exacerbate this and may cause domestic issues for governments. The last time that food and fertilizer prices spiked this high, in 2008-9, it led within a year to the 'Arab Spring'. Kazakhstan has already faced riots in the past few weeks due to high energy prices.

Impact on renewables

One of the so far mostly overlooked consequences of the current price environment could be a fresh look at renewable energy and how it might impact upon both the power and chemicals sectors. Europe has already tightened its climate goals for 2030 and 2050, leading to the EU's carbon price under the Emissions Trading Scheme rising from about €30/t at the start of 2021 to over €60/t. While this is a substantial increase, the European Commission estimates that, since early 2021, the impact of wholesale gas price increases on electricity prices is nine times greater. It seems by no means certain that natural gas will continue to be the cheapest feedstock for ammonia production, certainly in Europe. Longer term, there are measures that Europe can take to try and mitigate high gas prices; joint gas storage facilities, coordinated buying, greater hedging against price fluctuations, more storage capacity etc. But that dependence on Russia is unlikely to be broken in the medium term. Continued economic growth in Asia is likely to keep LNG prices high and continue to leave Europe at the mercy of Russian gas imports.

Meanwhile, even with less wind than usual in northern Europe, renewables reached 42% of the EU energy mix from April-June 2021, compared to 32% for fossil fuels. Increasing this further would require substantial investments in electricity storage or ways of converting that power during periods of excess, perhaps stored as hydrogen or ammonia, perhaps feeding into a wider European distribution system for ammonia. It has certainly been suggested that increasing renewable generation could help break Europe's cycle of dependence on imported natural gas. Overall, this winter's price crisis seems likely to accelerate European moves towards greater use of renewables.

Nor is it solely Europe where such considerations are being made. Incitec Pivot had made a determination to close its Gibson Island ammonia plant at Brisbane in Queensland because of high natural gas prices. Now however it is conducting a study with Fortescue Future Industries on a potential conversion to wind and solar based hydrogen from electrolysis. ■



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The IFA/IEA Ammonia Technology Roadmap

Yara's Heroya ammonia facility, Porsgrunn, Norway. The company is in the process of converting it to renewable feedstock.

PHOTO: ERNST VIKNE/WIKIMEDIA COMMONS

Last year the International Energy Agency (IEA), in conjunction with IFA, published the Ammonia Technology Roadmap, which looks at ways of achieving decarbonisation of the nitrogen fertilizer industry by 2050. In this article we look at the scenarios and technology options that will define the industry over the next three decades.

The ammonia industry is one of the most crucial parts of the chemical sector. Ammonia is the second largest chemical produced by tonnage in the world, after sulphuric acid, with 185 million tonnes manufactured in 2020, according to IFA. As the key way of fixing nitrogen, the Haber-Bosch process is responsible for virtually all nitrogen fertilizer produced, with the ammonia being converted into urea, ammonium nitrate, ammonium phosphate and other compounds. Around 70% of all ammonia produced is destined for use as a soil nutrient, with the other 30% providing feedstock for a range of industrial applications, from nitric acid and caprolactam to, hydrazine, polyurethane, metallurgy, water treatment and, via urea solutions, for nitrogen oxide scrubbing in diesel engines.

Production of ammonia is very energy intensive, however. Depending on the feedstock used for its production, ammonia averages around 2.4 tonnes of carbon dioxide emitted per tonne of ammonia produced; twice as much as steel per tonne, and four times as much as cement. This means that direct emissions from ammonia production currently amount to 450 million t/a of carbon dioxide equivalent (CO_2e) globally – comparable to the total energy emissions of South Africa. Indirect CO_2 emissions are around a further 170 million t/a CO_2e per year, and stem from two main sources – electricity generation and urea hydrolysis in soils, with further contribution from N_2O emission from downstream nitric acid production. This makes ammonia responsible for over 1.75% of all CO_2 emissions.

Reducing emissions

Ammonia consumption is likely to grow, to help feed an increasing and increasingly more affluent global population. At the same time, the threat posed by climate change means that governments around the world are trying to reduce carbon equivalent emissions of human activity towards net zero by 2050. This will mean significant changes for the ammonia industry over the coming three decades.

Table 1 shows the relative carbon intensities of a variety of production processes for ammonia. Most ammonia today comes from the first two routes; processing natural gas using either steam methane reforming (SMR) or autothermal reforming (ATR). However, China, which is responsible for around 30% of ammonia production, is heavily biased towards coal gasification, as are a number of smaller producers such as Vietnam and South Africa. Production from oil fractions or water electrolysis together amount to only 4% of ammonia production at present (Figure 1).

As part of its look at current ammonia production technology and how emissions might be reduced, the study recently published by IFA and the IEA also considers methane pyrolysis, though it admits that no commercial-scale installations currently exist, and the technology is still under development. The process involves using very high-temperature heat provided by electrical plasma to split methane into its constituent hydrogen and carbon atoms, without burning it. Instead of CO_2, the carbon output is in the form of solid carbon, which can be sold for use in certain carbon black applications, or otherwise stored/sequestered. The first commercial facility producing ammonia from methane pyrolysis-derived hydrogen is expected to come on-stream in 2025, producing what developer Monolith Materials call 'turquoise' ammonia.

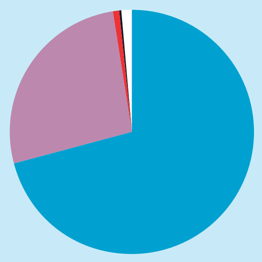
While use of carbon capture and storage (CCS) – so-called 'blue' ammonia production – could dramatically reduce emissions from fossil fuel-based production, at present only small volumes of CO_2 are captured and sequestered from ammonia production; around 1.5 million t/a of total production. Projects that have already been announced could convert another 2.5 million t/a of fossil fuel-based production to carbon capture and storage by 2030, and around 3 million t/a of production to 'green' water electrolysis based on renewable feedstocks, but this would still only represent around 4% of total ammonia production.

Table 1: **Energy required to produce a tonne of ammonia (best available technique)**

		Energy intensity (GJ/t)					CO_2 intensity (t CO_2/t)
Production route	**Feedstock**	**Fuel**	**Electricity**	**Steam**	**Gross**	**Net**	
Natural gas SMR	21.0	11.1	0.3	-4.8	32.4	27.6	1.8
Natural gas ATR	25.8	2.1	1.0	0.0	28.9	28.9	1.6
Coal gasification	18.6	15.1	3.7	-1.3	37.4	36.1	3.2
SMR with CCS	21.0	11.1	1.0	-3.1	33.1	30.0	0.1
ATR with CCS	25.8	2.1	1.5	0.0	29.4	29.4	0.1
Coal with CCS	18.6	15.1	4.9	2.6	38.6	41.2	0.2
Electrolysis	0.0	0.0	36.0	-1.6	36.0	34.4	0.0
Biomass gasification	18.6	16.5	1.4	0.0	36.5	36.5	0.0
Methane pyrolysis	40.5	0.0	8.4	-1.6	48.9	47.3	0.0

Source: Technology Roadmap

Fig. 1: **Ammonia capacity by feedstock, 2021**



Source: IFA

Production cost

Of course, ammonia production is very sensitive to production cost; one reason why it has gravitated towards natural gas-based production. Feedstock cost is the main cost in ammonia production, although capital expenditure and pay-down can also be substantial for a new plant. Where higher capital cost routes like gasification are used, it is usually because the feedstock is available at comparably lower cost.

Among the emerging routes to low carbon ammonia there are two main categories; those using carbon capture and storage and those using electrolysis-based routes. CCS routes are similar in cost to their unabated counterparts because they are in regions with the lowest capex and energy costs. The slightly higher cost for the CCS-equipped route (10-25% for the natural gas-based routes and 15% for coal gasification) is attributable to slightly higher energy consumption, CO_2 transport and storage costs, and the increased cost of capex and opex for the capture equipment. The cost of the electrolysis path, conversely, is mainly dependent on the cost of the electricity used, over 90% of which is consumed by the electrolyser. Where a dedicated variable renewable energy (VRE) source is used, capex is higher as a proportion of cost than if the plant is able to hook up to a local grid, in part due to the lower capacity factor for a solely local renewable energy source.

For methane pyrolysis and biomass gasification, the cost is more uncertain due to the lack of a commercial-scale plant in operation today. Cost premiums for biomass appear to be very large, owing to the very high energy intensity (37 GJ/t including feedstock) and the relatively high cost of bioenergy. Costs for methane pyrolysis depend upon revenue obtained from sale of the carbon black co-product. This can be around \$360/t, but the market is not large enough to absorb large numbers of pyrolysis based ammonia plants.

Scenarios

The IEA/IFA Technology Roadmap uses scenario analysis to explore three possible futures for ammonia production; Stated Policies; Sustainable Development; and Net Zero Emissions by 2050.

The Stated Policies scenario is relatively self-explanatory; it assumes that progress over the next 30 years occurs via currently stated government policies, in line with commitments made at the COP-26 meeting in Glasgow, and it projects forward current trends in consumption and production. This would see ammonia production increasing by 37% by 2050, driven primarily by economic imperatives and population growth. Emissions from ammonia production fall by about 10% under this scenario. This puts cumulative direct emissions from ammonia production under current trends amount to around 28 Gt between now and 2100, equivalent to 6% of the remaining emissions budget associated with limiting global warming to 1.5°C. The report assumes that this is an unsustainable outcome.

Sustainable Development assumes that governments fully align with the goal of the Paris Climate Agreement for an eventual rise in global temperatures of "well below 2°C". Here, the implementation of strategies for improving end use efficiency of ammonia, especially in nitrogen fertilizer application, lead to slower growth in total production, amounting to an increase in consumption of 23%. In this scenario, direct CO_2 emissions from ammonia production fall by over 70% by 2050 relative to today, with nutrient use efficiency measures contributing 20% of that fall. Energy efficiency measures contribute about 25% of emissions reductions in this scenario, including adoption of best available techniques (BATs), operational improvements, and switching from coal-based production to less energy intensive gas-based production (fuel switching contributes 10% of emissions reduction in this scenario). However, the largest share of emissions reduction comes from deployment of near-zero-emissions technologies,

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including electrolytic hydrogen generation (30% of emissions reduction) and CCS (15%). This requires more than 110 GW of electrolyser capacity and 90 million t/a of CO_2 storage by 2050.

Finally, the Net Zero Emissions by 2050 Scenario describes a trajectory for the ammonia industry that is compatible with reaching net zero emissions globally for the energy system by 2050, where emissions fall by 95% by 2050. In this scenario, the additional emission reductions compared to the Sustainable Development scenario are driven by even more rapid deployment of electrolysis and CCS technologies. The difference between the components of these scenarios is one of degree, not of direction.

Near-zero-emission technologies are not yet available at commercial scale in the marketplace. CO_2 separation is an inherent part of ammonia production today, but permanent storage of the CO_2 is not yet widely adopted. Electrolysis-based ammonia production has already been conducted at scale using high load factor electricity, but challenges remain to use hydrogen produced from VRE. The Sustainable Development Scenario requires $14 billion in annual capital investment for ammonia production to 2050. Of this, 80% is in near-zero-emission production routes. The Net Zero Emissions by 2050 Scenario in fact requires only slightly higher annual investment: $15 billion per year to 2050.

Reducing nitrogen demand

In 2020 annual global nitrogen demand reached 152 million t/a. The IEA/IFA Stated Policies Scenario assumes that demand for nitrogen grows by another 40% by 2050, reaching 208 million t/a, equivalent to an average annual growth rate of about 1.0%. This is slower than the 1.7% average for 2010-2020, but assumes that China's rapid industrial development in the first two decades of the 21st century is not repeated, as its economy shifts towards higher-value manufacturing and a larger share of consumption-led growth. This slows industrial ammonia demand from around 4% per year to 1.3%. Demand for fertilizer is assumed under that scenario to continue to grow at its current rate; around 0.9% year on year.

At a global level, nitrogen demand for fertilizers was 14 kg per capita in 2018, varying from 35 kg in the United States, 22 kg in Brazil, 20 kg in China and 13 kg in India. In general, mature economies see declining demand per capita due to mature markets and pursuit of nutrient use efficiency (NUE) measures. In the report's Sustainable Development Scenario, a more assertive pursuit of measures to improve NUE leads to slower total nitrogen demand growth of 0.7% per year, and hence a total nitrogen demand increase of 25% by 2050 instead of 40%. This also assumes that the use of urea-based fertilizers declines by 28% by 2050 compared to today, replaced by ammonium nitrate and calcium ammonium nitrate. Urea is dominant today due to its high nitrogen content (46%) and greater convenience for storage, transport and application relative to the other derived fertilizer products. However, in the context of a sustainable future for energy and agricultural systems, urea has the disadvantage that its production requires CO_2 that is later released during hydrolysis after its application to the soil. This CO_2 from urea use – around 130 million t/a CO_2e in 2020 – is equivalent to about 30% of the total emissions from ammonia production, and hence the Sustainable Development Scenario sees greater uptake of AN and CAN, which do not release CO_2 during their use.

Further demand contractions are assumed to come from increased NUE. In the Sustainable Development Scenario NUE improves such that global demand for ammonia for conventional uses is 5% lower in 2030 and 10% lower in 2050 compared to the Stated Policies Scenario. The greatest potential for demand reduction comes from the largest end use, fertilizers, accounting for 65% of the reduction in 2050. Plastics recycling accounts for about 10% of the reduction, driven by an increase in the average plastics collection rate to 50% by 2050, relative to 16% today. Other measures in industry and other end uses account for the remaining demand reduction.

Aside from conventional applications, the Sustainable Development Scenario and Net Zero Emissions by 2050 Scenarios also see growth in ammonia demand for use as an energy carrier, primarily as a maritime fuel and in the power sector. In addition to the 230 million t/a of ammonia demand from conventional uses in 2050, 125 million t/a of ammonia is assumed to be used as an energy carrier – this brings total ammonia demand to 355 million t/a; about twice the 185 million t/a produced in 2020.

Reducing emissions from production

This is a difficult task to achieve in only 30 years, because existing assets, especially written-down assets, have a momentum of their own. Ammonia production facilities have long lifespans, often of up to 50 years. The current average age of installed ammonia capacity is around 25 years since start-up, but this figure varies widely from region to region. In Europe it is more like 40 years, compared to just 12 years in China, where a lot of new capacity has been built in the past 20 years.

While encouraging progress on near-zero-emission technologies is being made, these emerging routes are typically 10-100% more expensive per tonne of ammonia produced than conventional routes, depending on energy prices and other regionally varying factors, and technologies which modify or are otherwise able to use existing capacity are likely to make more headway.

Nevertheless, in both the Sustainable Development and Net Zero Emissions scenarios, most of the emissions reductions from the industry come from deployment of near-zero-emission technologies. Under sustainable development, 70% of the industry would be using such technologies by 2050, comprising 20% natural gas with CCS and 25% electrolysis (see Figure 2). This total figure rises to 95% for Net Zero Emissions, comprising 20% gas+CCS and 40% for electrolysis. This means rapid deployment of new infrastructure. The Sustainable Development Scenario requires more than 110 GW of electrolyser capacity and 90 million t/a of CO_2 transport and storage infrastructure by 2050. This means installing on average ten 30 MW electrolysers (the largest facility in operation today) per month and 1 large capture project (annual capture, transport and storage capacity of 1 million t/a CO_2) every four months between now and 2050.

How to get there

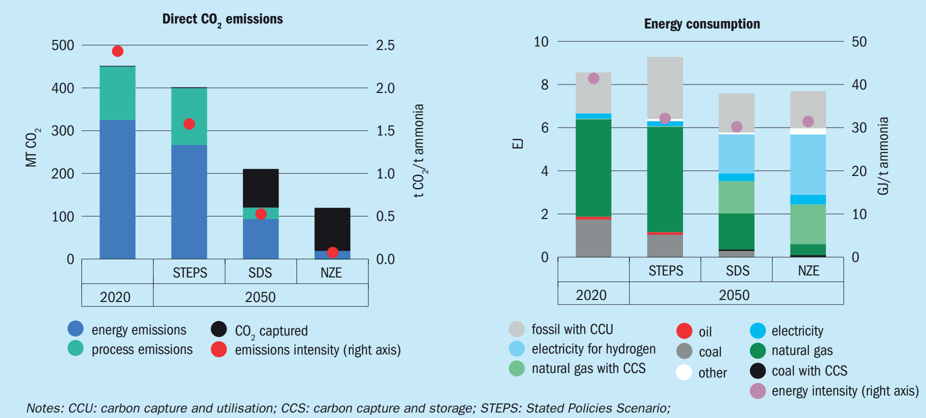
The report acknowledges that governments will need to play a central role in achieving change on such scale. It advises that governments will need to establish a policy environment supportive of ambitious emission cuts by creating transition plans underpinned by mandatory emission reduction policies, together with mechanisms to mobilise investment. Targeted policy is also required to address existing emissions-intensive assets, create markets for near-zero-emission products, accelerate research and development and incentivise end-use efficiency for ammonia-based products. Governments should ensure that enabling conditions are in place, including a level playing field in the global market for low-emission products, infrastructure for hydrogen and CCS, and robust data on emissions performance.

But other stakeholders will also have a crucial part to play. Ammonia producers will need to establish transition plans, accelerate R&D activity, and engage in initiatives to develop supporting infrastructure. Farmers and agronomists will have to prioritise best management practices for more efficient fertilizer use. Financial institutions and investors will need to use sustainable investment schemes to guide finance towards emission reduction opportunities. Researchers and non-governmental organisations can help develop labelling schemes, continue research on early stage technologies and galvanise support for key technologies.

And the timescale is relatively short for such radical change. The current decade – from now to 2030 – will be critical as a period in which to lay the foundation for long-term success, with around 10% of cumulative emission reductions to 2050 taking place by then in both the Sustainable Development Scenario and Net Zero Emissions by 2050 Scenario. Vital near-term actions include establishing strong supportive policy mechanisms, taking early action on energy and use efficiency, developing supporting infrastructure, and accelerating R&D.

The ammonia industry may be on the cusp of perhaps the most dramatic period of change in its history, equivalent to the switch from coal to natural gas based production in the 1950s, 60s and 70s. It may see widespread closures in areas where it has been long-established, such as China, and a move to areas where there is abundant solar power, such as the Middle East, North Africa and Australia. It will be a challenge for producers and consumers alike. But the rewards could be considerable for those who are able to master the technologies, and of course for the planet as a whole. ■

Fig. 2: **Direct CO_2 emissions and energy consumption for ammonia production by scenario**



Notes: CCU: carbon capture and utilisation; CCS: carbon capture and storage; STEPS: Stated Policies Scenario; SDS: Sustainable Development Scenario; NZE: Net Zero Emissions by 2050 Scenario.

Source: IEA, 2021

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PHOTO: PETER HEELING/WIKIMEDIA COMMONS

A drilling rig in the Groeningen gas field.

Closing down the Groningen gas field

Gordon Feller looks at Gasunie's plans to build a new nitrogen plant at Zuidbroek to allow for the progressive shutdown of the Groningen gas field, one of the largest in Europe.

What's next for gas in Europe? One answer to this question comes from the world's largest provider of finance for economic development; the Luxembourg-based European Investment Bank, owned by the member states of the European Union. The EIB is lending a large sum to Dutch gas companie Gasunie to finance the construction of a nitrogen facility in Zuidbroek, near Groningen.

From their global headquarters in the Dutch city of Groningen, NV Nederlandse Gasunie invests in and operates natural gas infrastructure and transportation systems and storage facilities. They are especially active in the Netherlands and Germany. Gasunie owns the Netherlands gas transmission network, which has a total length of over 12,000 kilometres. It also owns a 3,100 kilometres long network in Germany. The relationship between Gasunie and the EIB goes back a long way; the second project the European Investment Bank financed in the Netherlands was with Gasunie in 1969. This is the 7th collaboration between the EIB and Gasunie since then.

Nitrogen plant

The investment in question entails the construction of a nitrogen plant in Zuidbroek, the Netherlands. The EIB will provide financing of €240 million out of the project's total cost of €502 million.

The project is focused on constructing a 180,000 m³/hr nitrogen production plant and its associated facilities (gas and electricity connections as well as gas blending stations). Excess nitrogen will be sent to an existing salt cavern when needed, which was converted into an underground nitrogen storage at the time of the construction of a nearby nitrogen plant (at the existing Zuidbroek 1 capacity is 16,000 m³/hr nitrogen) operated by Gasunie Transport Services BV since 2012.

The air separation plant will produce high purity nitrogen gas, which will be compressed and then blended with imported high calorific value gas (H-gas). The mixed gas, a 'pseudo-Groningen' gas, will then be injected as low calorific value gas (L-gas) into the Dutch gas network, thus replicating the gas technical specifications used in the Netherlands and surrounding regions/countries and allowing for the reduction of supplies from the Groningen gas field. The project's main components are several key elements of the facility: air separation units to extract the nitrogen; compressing and cooling units; and mixing stations.

As with all such projects, an extensive and in-depth Environmental Impact Assessment was required by the EIB, in order for the project funds to be approved. The primary environment impacts during construction concern the disturbance to communities, in particular the expected increase in traffic volume, as construction will take place concomitantly with the installation of a solar park and wind farms nearby. The technology which is being used for the air separation units is considered by Gasunie to be "the best technology available to produce nitrogen at high degree of purity level and in large quantities". It is a cryogenic nitrogen production plant. This type of installation operates at very low temperatures and requires a large amount of energy/electricity.

Groningen

Adding nitrogen to imported gas is needed for its use inside Gasunie's Dutch network. It will allow Gasunie to progressively close down the Groningen gas fields. In view of earthquakes caused by the extraction of natural gas from the Groningen gas field, the Dutch Ministry of Economic Affairs and Climate Policy mandated that Groningen gas production is to reduce as quickly as possible to achieve a complete shut-down of the field in 2030. However, because gas from the Groningen field is of a lower calorific content than other gas supplies, their high calorific content risks damaging the network and would entail the replacement of all end-users' appliances. Hence the addition of the new nitrogen plant, which will provide nitrogen to be compressed and blended with imported gas before it goes into the Dutch gas network.

The project is categorized as one of "strategic importance" to the Netherlands, since it supports the official request from the

Ministry of Economic Affairs and Climate Policy (EZK) to urgently decrease Groningen gas production to 12 bcm by 2020 and thereafter to proceed to a complete shutdown of this field by 2030, in order to reduce the induced-seismicity risk in the region. According to national legislation, the project (new nitrogen plant, gas blending station and, among other things, the associated construction of approximately 4 km of natural gas transmission pipelines) falls under the National Coordination Scheme (RCR). This means among other things, that the project must fit within a Spatial Integration Plan (RIP) that is determined jointly by the Ministry of Economic Affairs and Climate and the Ministry of the Interior and Kingdom Relations. This procedure also includes the decisions required for the project (permits, approvals etc.) and is coordinated by the Ministry of Economic Affairs and Climate.

> "the Dutch Ministry of Economic Affairs and Climate Policy mandated that Groningen gas production is to reduce as quickly as possible.

Site selection

The precise location of this project was chosen based on a study which considers the environment as one of the main criteria. Out of five locations studied, the most appropriate is Tussenklappen, in Zuidbroek, considering spatial integration and distance to existing facilities. A separate procedure has also been launched by Gasunie to apply for a modification of the nitrogen storage plan regarding the change in the utilisation of the existing salt cavern at Heiligerlee. This is already used as a buffer nitrogen storage to the existing nitrogen plant in Zuidbroek. The underground nitrogen storage is not part of this project's scope. However, taking a risk-based approach, the EIB did review and assess the environmental and safety elements of this facility

The project is being implemented within agricultural lands, in a location where natural gas installations and nitrogen production infrastructure are already in place. As such, existing infrastructure will be used wherever possible. The gas and electricity connections will be buried. Emissions from the production process mainly consist of oxygen with a few impurities and are in line with emissions standards defined in Dutch national legislation. Cryogenic processes typically occupy large ground surfaces. The nitrogen plant is being designed such as to minimise landscape impacts through a specific landscape integration plan. The project is located in an industrial gas estate, at some distance from residential areas. For this reason Gasunie says that the impacts on population and human health are considered to be "low".

Given the low temperatures and the high volumes involved, cryogenic nitrogen production processes are energy-intensive; the selection procedure was partly based on Total Cost of Ownership (energy consumption, operations and maintenance), with emphasis placed on overall energy consumption levels, such as using more efficient electromotors, installing centrifugal compressors and integrating heat exchangers in the ASU. The plant will be electrically-driven with green electricity supplied by TenneT from solar and wind sources, supplemented by a back-up power generation (diesel) that can operate continuously for a period of three days and would potentially run on an occasional basis. The national electricity grid factor has been used to account for the energy supply emissions.

Given its proximity to the Groningen area, the project is designed to be seismic-proof, in line with the Eurocode 8 Directive and national legislation. The project is also located on a low-lying polder which potentially constitutes a flood-prone environment. The flooding risk is exacerbated by climate change in the area, such as rising sea levels, wetter winters and drier summers. This has been taken into consideration in the Draft Spatial Integration Plan. The flooding risk and associated safety standards are controlled regionally by the Groningen Province in consultation with the agencies that set the safety policy objectives on these matters. An adjacent dyke is planned to be completed in 2021, which will reduce the flooding probability in the project area to 1:1,000 years from the present 1:300 years. The project's infrastructure will also be raised on higher grounds to further mitigate flooding risk on its components. Additional flood-proofing elements might be incorporated into the project's design, which are to be captured in the "Final Spatial Integration Plan".

Public consultation

Public consultations, with a serious effort at stakeholder engagement, have been a high priority for the EIB's own team – and for Gasunie. They consulted with regional authorities (municipality, province, water, conservancy, etc.) for a period of months at the outset of the project development. Relevant opinions and comments were incorporated into the RIP. A public hearing near Heiligerlee also took place. Most of the comments raised by the public refer to the salt cavern in Heiligerlee, which is not part of the RIP but is connected with the nitrogen production plant.

The outcomes from the public consultations have been integrated in the final RIP documentation and the design of the project was slightly modified to further mitigate flooding risks and noise pollution. The comments concerning the salt cavern in Heiligerlee were addressed in the form of clarifications in the final RIP documentation and will be further incorporated as much as applicable and feasible in a separate permitting procedure submitted by the Gasunie for the modification of the nitrogen storage plan. ■

Computer rendering of the new nitrogen plant at Zuidbroek.

IMAGE: GASUNIE

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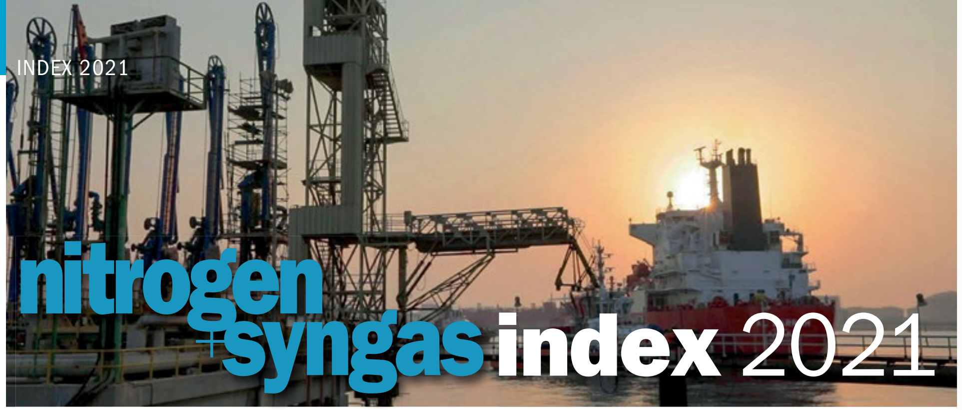

PHOTO: SAUDI ARAMCO

An ammonia tanker being loaded at Dharan, Saudi Arabia.

A complete listing of all articles and news items that appeared in *Nitrogen+Syngas* magazine during 2021.

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Better water gas shift performance

The production of syngas from hydrocarbon feedstock uses a number of catalytic steps to increase efficiency and maximise conversion while minimising energy consumption. In this article we report on the latest developments in water gas shift catalysis from Johnson Matthey, Clariant and Topsoe, and shift converter design from Casale.

JOHNSON MATTHEY

Catalyst solutions delivering value in water gas shift

The water gas shift conversion is an important aspect to the economic operation of an ammonia plant. The reaction has a key role in the generation of hydrogen (15-20% of the hydrogen is generated via water gas shift) and also converts carbon monoxide to carbon dioxide which is more readily removed from the process:

$$CO + H_2 \rightleftharpoons CO_2 + H_2$$
$$\Delta H = -131.2 \text{ kJ.mol}^{-1}$$

The minimisation of the carbon monoxide slip means that there is less hydrogen consumed in the methanation of carbon oxides, and lower methane flows to the synthesis loop reducing the required purge flow. The exothermic nature of the reaction also generates heat which can be recovered into boiler feed water or steam systems.

The water gas shift process is divided between two unit operations: a high temperature shift (HTS) and a low temperature shift (LTS). Since greater equilibrium conversion of carbon monoxide is favoured at lower temperatures, a compromise is required between achievable conversion and kinetic rate. The HTS is used to do the bulk of the carbon monoxide conversion at a faster rate at higher temperatures. The LTS is then used for the final 5% of the hydrogen generation at conditions more favourable to the equilibrium.

A by-product of the water gas shift process is methanol. Methanol is undesirable since its formation consumes hydrogen that could otherwise be used for ammonia synthesis, and methanol emissions from the process can be a serious environmental concern.

High temperature shift

The first stage of the water gas process in an ammonia plant is the high temperature shift (HTS). The HTS operates at an inlet temperature of around 350°C and reduces the mole fraction of CO in the syngas to 2-4%.

High temperature shift catalysts

HTS catalysts consist of iron and chromium, promoted with copper. This formulation is selected for its thermal stability at HTS conditions. The incorporation of chromium oxide creates an intimate mix in the iron structure, which limits deactivation. This allows iron-chrome HTS catalysts, such as KATALCO™ 71-series, to operate at high temperatures without deactivation compromising the performance at lower temperatures. The KATALCO 71-series contains a very low proportion of hexavalent chrome. This is particularly important in reducing the hazards of catalyst handling. In service, the trace amounts of hexavalent chrome are converted to trivalent chrome, and formation of hexavalent chrome at shutdown can be minimised by carefully following plant shutdown procedures.

Diffusion limitations are an important factor in the catalysis of the HTS reaction. Therefore, the pore structure of the catalyst pellet is key in its performance. The structure of the KATALCO 71-series catalysts incorporate patented structural promoters that broaden the pore-size distribution which increases the activity. The benefits of the pore structure and better diffusion characteristics mean that KATALCO 71-series catalysts can be operated at lower temperatures without performance being limited by pore diffusion.

Pressure drop

Minimising the pressure drop is an important consideration in the overall process economics. The pressure drop characteristics of a catalyst is dictated by the pellet design. The design of the KATALCO 71-series pellets optimise the aspect ratio to achieve high voidage in a packed bed to deliver the best combination of pressure drop, strength and activity. Utilising patented developments in pellet design that have shown the benefits of shaped pellets, such as KATALCO 71-5F, JM can offer improved pressure drop and conversion over unshaped pellets.

The catalyst should also be able to tolerate plant upsets and retain its low pressure drop characteristics. Unplanned events that impact the HTS are likely to be wetting incidents related to boiler leaks, which can lead to increased pressure drop from the build-up of boiler solids. Robust catalysts, like the KATALCO 71-series, have good strength and open pore structure to withstand rapid cycles of wetting and drying.

Case study

A hydrogen plant in North America experienced a boiler leak of an estimated 45,000 kg/hr of water onto the catalyst for a three-month period. However, the KATALCO 71-series catalyst did not fail catastrophically as might be expected under such conditions. It continued to operate, allowing the customer to produce hydrogen until an appropriate shutdown could be planned and taken. This not only saved the plant the costs of an unplanned shutdown, but also ensured that other operations were not unduly affected. This reliability and managing of other hydrogen consumer production was valued in the millions of US dollars.

Poisoning

JM's latest development in technology combines strong purification expertise with the design of low pressure drop systems for shift reactors to develop PURASPEC™ 2272 – a new purification tool for use in the HTS to help protect and extend downstream LTS catalyst life.

PURASPEC 2272 support media is a patented technology solution of JM to improve the water gas shift process. It utilises a low pressure drop active adsorbent support media that replaces the inert support media at the bottom of the HTS reactor. PURASPEC 2272 actively captures chloride which would otherwise poison the low temperature shift (LTS) catalyst downstream.

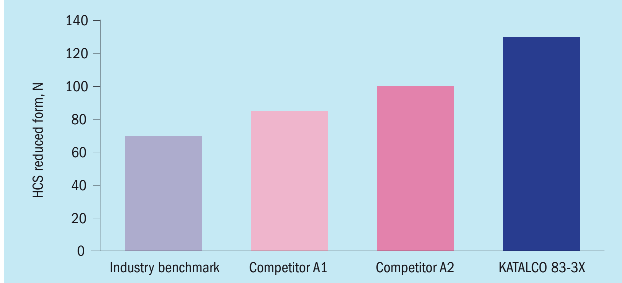
JM has used its expertise in purification science along with its proven STREAMLINE engineering skills to develop PURASPEC 2272 – an innovative new product which combines the functions of a low pressure drop support with that of a chloride trap.

Start-up exotherms

In some cases of high temperature shift operation exotherms can be observed when introducing steam to fresh catalyst charges. The cause of this was first identified by Johnson Matthey as the rehydration of catalyst, not, as was believed by some, the formation of hexavalent chrome. If the catalyst is held under a nitrogen purge at relatively high temperature, the surface can become dehydrated.

Then, on introduction of steam, the surface rehydrates resulting in an exotherm. Johnson Matthey can identify the conditions under which this is most likely to occur and advise a start-up procedure to avoid high temperatures. If high temperatures are seen, it again highlights the need for thermal stability in HTS catalyst, and practical experience shows that KATALCO 71-series catalysts can survive these incidents without any detrimental effects.

Fig. 1: **Horizontal crush strength (HCS) of LTS catalysts in-service reduced form**



Source: Johnson Matthey

Initial desulphurisation

All HTS catalysts contain some residual sulphate. This is converted to H_2S during the reduction of the catalyst and has the potential to poison downstream catalysts. KATALCO 71-series catalysts are manufactured via a nitrate route whereas other catalysts may be made via sulphate routes. For catalysts manufactured via the nitrate routes, any sulphur present is not intimately bound in the pore structure of the catalyst but tends to be present at the surface. This means that the sulphur is easily reduced and removed in the fastest start-up time. For catalysts formed by a sulphate route, the sulphur in the finished catalyst is concentrated in the bulk of the structure, and the desulphurisation of these materials is slower.

Low temperature shift

Following the high temperature shift, the remaining carbon dioxide conversion is carried out in the low temperature shift (LTS). The LTS operates at an inlet temperature of around 200°C and reduces the mole fraction of CO in the syngas to 0.2-0.4%.

Low temperature shift catalysts

LTS catalysts consist of copper with zinc oxide and alumina, and other components, such as alkali metals, that can be used to alter selectivity reducing the by-product methanol make. This formulation is selected for its activity. Though it has good activity, it is not thermally stable enough to be suitable for high temperature shift conversion and is therefore only used in the LTS duty.

Catalytic activity at low temperature is an important catalyst parameter. Since the equilibrium of the water gas shift reaction dictates that higher CO conversion is achieved at lower temperatures, activity at low temperatures is key. For example, the KATALCO 83-series catalysts show activity such that the equilibrium can be achieved below 200°C and an approach to equilibrium close to zero can be achieved through the catalyst life. KATALCO 83-series catalysts have been operated at inlet temperatures as low as 190°C, and the operating temperature is often dictated by the dew point of the inlet gas rather than the catalytic activity.

Pressure drop

Pressure drop is an important parameter relating to the economics of the syngas generation train. Catalyst pellet design can improve the pressure drop of an LTS reactor, and catalyst strength throughout its lifetime is as important as the strength of the fresh pellet. The high strength of KATALCO 83-series catalysts minimises the rate of increase of pressure drop during operation, and its formulation gives high strength after reduction, steaming and any unplanned wetting events.

The relevant strength of any LTS catalyst is that in the reduced state since that is the state of the catalyst in service.

The horizontal (or side) crush strength of KATALCO LTS catalyst is compared to both the industry benchmark and recent competitive advances above in Fig. 1. This clearly shows why JM LTS is the most reliable option if an increase in pressure drop, and the losses that arise from lower rates are something that an operator wants to avoid.

Condensation on the catalyst or wetting from an upstream water quench system are the most common operational upsets in the running of an LTS. An LTS catalyst

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should therefore be resistant to these conditions and retain its activity and strength.

Reduced catalyst strength is important. Some low temperature shift catalysts can be too weak. KATALCO 83-3X is the optimum choice for maximum level of mechanical strength after reduction.

The outstanding mechanical stability of KATALCO 83-3 series catalysts deliver a benefit of lower pressure drop increase with time on-line and consequently a longer lifetime. There is also a much lower exposure to risk of production losses caused by pressure drop where deformation of weaker pellets can lead a resistance to flow. There are many incidents in industry where weaker LTS catalysts have caused incidents causing pressure drop losses that can be measured in one to tens of millions of dollars.

Methanol formation

Low temperature shift conditions and catalysts can result in the formation of methanol as a by-product. Methanol emissions can cause plants to exceed the consent limits under environmental legislation and can cause problems in the treatment of process condensate. In addition, the formation of methanol removes hydrogen from the process, which would reduce the capacity for ammonia synthesis. The formation of 1 tonne of methanol equates to the loss of production of 1.05 tonnes of ammonia.

To avoid the formation of methanol, LTS catalysts can incorporate alkali promoters which inhibit the methanol synthesis reaction, such as KATALCO 83-3X which includes carefully optimised levels of alkali, which retains the shift activity of the catalyst while minimising the methanol production.

Poisoning

The lifetime of the LTS catalyst is most often determined by the capacity of the catalyst to absorb sulphur and chloride poisons that are present in the process gas. The temperature of the LTS is low enough that thermal deactivation does not show as significant an effect as the poisoning. It is unavoidable that low levels of sulphur and chloride are present at the LTS, and therefore the catalyst must be designed to tolerate and accommodate them.

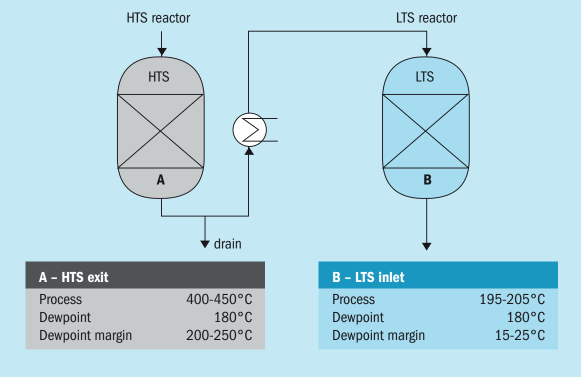
It is important that the LTS catalyst shows good poison retention. In this way, catalysts such as KATALCO 83-3 and KATALCO 83-3X show good self-guarding properties, retaining the poisons at the front of the bed. This means that over the lifetime the poisons accumulate in a defined poisoned section at the top of the bed, meaning that the catalyst below still demonstrates excellent activity. Throughout the life of the catalyst, the front of the poisoned section moves through the bed until there is insufficient active catalyst remaining and the bed must be changed.

It is also possible to operate with an LTS guard reactor. This is a relatively small vessel that contains a sacrificial bed of catalyst designed to collect the poisons and allow the main catalyst to operate downstream. The guard reactor can then be replaced more frequently to extend the life of the main bed. It is even more important that a guard catalyst should have a sharp front of the poisoned section to maximise the poisons capacity and avoid poisons slipping to the main bed.

Although KATALCO 83-3 series catalysts are self-guarding and have a high capacity for chloride poisons, the fact is that chloride poisons are highly mobile in an LTS if the bed is wetted. LTS beds operate with a low margin of 15-25°C against dewpoint meaning wetting can occur and result in chloride washing into the bed (Fig. 2).

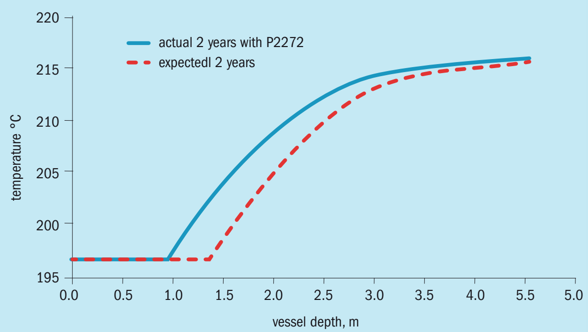
The use of PURASPEC 2272 at a location below the HTS gives several benefits including keeping chlorides from the LTS reactor, and in the event of wetting allowing chlorides to leave via a drain rather than entering the LTS.

Fig. 2: **Shift process conditions and dewpoint margins**



Source: Johnson Matthey

Fig. 3: **Low temperature shift temperature profiles for expected operation and actual operation when PURASPEC 2272 is installed**



Source: Johnson Matthey

Table 1: **The energy saving benefits gained for a 1,500 t/d plant for various gas costs**

LTS bed life	Base case	Guarded case	CO reduction	Energy saved	Annual value	Annual value
Year	LTS_{exit} CO%	LTS_{exit} CO%	Delta CO%	million Btu	$ @ $4/million Btu gas	$ @ $20/million Btu gas
0	0.21	0.21	0	0	-	-
1	0.22	0.215	0.005	0.0055	12,045	60,225
3	0.25	0.24	0.01	0.011	24,090	120,450
4	0.33	0.29	0.04	0.044	96,360	481,800
5	0.52	0.425	0.095	0.1045	228,855	1,144,275
6	0.95	0.735	0.215	0.2365	517,935	2,589,675

Assumptions: *1,500 t/d plant predicted LTS performance; 0.1% CO increase, reduces efficiency by 0.11 million Btu/t with H_2 recovery.*

Typical results from an ammonia plant utilising PURASPEC 2272 upstream of an LTS charge are shown in Fig. 3. The reaction profile clearly shows that when using the PURASPEC 2272 solution the deactivation rate is lower than is typical.

In addition, providing chloride protection and extending the life of the catalyst, PURASPEC 2272 can provide significant protection against potentially damaging events such as unexpected transient events causing condensation. The value from this protection can be seen in the following energy saving benefits gained for a 1,500 t/d plan t for various gas costs (Table 1).

Case study

A large North American hydrogen plant experienced short catalyst lives due to chloride poisoning. During a 5-year period, it replaced a competitive LTS catalyst and its associated guard material five times. Catalyst lives averaged just one year. The plant then changed to a full bed of KATALCO 83-3X, which gave excellent performance for more than three years.

This saved the operator both replacement catalyst and unscheduled shut-down costs, estimated to be worth at least $600,000. In addition to the cost savings achieved by the plant operator, this case study also demonstrates the excellent inherent poisons resistance of KATALCO 83-3X products.

These benefits could be further enhanced by use of PURASPEC 2272, further increasing the life of the LTS and allowing flexibility on extending turnaround intervals while delivering increasing value through the lifetime through lower CO slip, and significantly lowering the risk of chloride migration in any wetting incidents. ■

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CLARIANT

Further enhancing the benefits of LTS catalysts

The copper/zinc-based low temperature shift (LTS) catalyst is one of the highest total cost catalysts used in a typical ammonia or hydrogen plant and has a significant impact on the economics of the plant. Therefore, selecting a highly active and stable catalyst for the low temperature shift (LTS) converter is extremely important when considering the potentially harsh operating conditions under which it may have to work. With the risk of condensation (wetting), sulphur poisoning, and high temperatures (due to poor temperature control), a high-quality LTS catalyst is essential to ensure proper catalyst operation without any production loss. In addition, the catalyst needs to withstand more severe operating conditions during catalyst activation and start-up.

In an ammonia plant, a more active LTS catalyst decreases the inert concentration in the ammonia synthesis loop, reducing purge gas losses and increasing ammonia production's energy efficiency. As a rule of thumb, 0.1% more CO converted in the LTS means approximately 1% additional ammonia, especially in plants without purge gas recovery units. Clariant's second generation, copper-zinc based, high activity, low methanol catalyst, ShiftMax® 217, was developed to provide enhanced activity to allow higher conversion at low temperatures in addition to excellent crush strength in both the oxide and reduced state for increased robustness to enable longer catalyst life and to reduce risks of failure under upset conditions. Since its introduction in 2010, ShiftMax® 217 has been used by over 60 customers worldwide.

The following case study demonstrates the outstanding stability and robustness of ShiftMax® 217 that helped OCI Geleen overcome a water exposure incident without prematurely changing the catalyst.

Case study: OCI Geleen

Safe operations of LTS reactors under harsh conditions

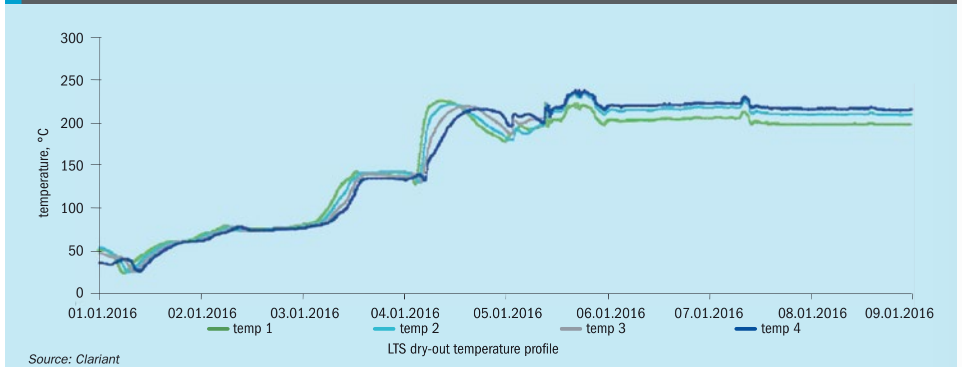
OCI is a major ammonia producer operating multiple ammonia production sites around the world. OCI Geleen originates from the former DSM divisions DSM Agro and DSM Melamine. In Geleen, the Netherlands, OCI operates two ammonia plants (AFA2 and AFA3), each with a capacity of 1,550 t/d ammonia. The AFA2 plant was designed and constructed by Bechtel, commissioned in 1971, and was revamped in 1997 and 2001. The AFA3 plant was designed and built by Kellogg and is based on Kellogg's reduced energy ammonia technology. The plant was commissioned in 1984.

Ammonia plant 3 (AFA-3) had been operating ShiftMax® 217 since 2012. In November 2015, an incident occurred that required the immediate shutdown of the plant. The focus of operations was stopping the plant as quickly and safely as possible. Therefore, the normal shutdown procedure could not be used, and the high temperature shift (HTS) and LTS reactors were taken out of operation in a non-standard manner (no circulation with nitrogen and direct depressurisation of the gas make-up section). Operations were able to minimise the ingress of oxygen, but the condensation of steam could not be prevented, resulting in severe wetting of the HTS and LTS catalysts.

During the shutdown period, condensate was drained from the inlet and outlet lines of the HTS and LTS. However, it was impossible to drain all the water because of the piping layout. This meant that any remaining water in the lines would end up going into the reactors upon restart, thereby wetting the catalysts. Wetting of the catalyst can lead to a thermal shock on the catalyst surface and condensation inside the pores, which can mechanically damage the catalyst and lead to an increased pressure drop. OCI was afraid that the Copper-Zinc-based LTS catalyst would be damaged because this catalyst type is weaker than other catalysts (e.g., HTS, Reforming) in an ammonia plant.

To recover the wetted HTS and LTS catalysts, Clariant advised OCI to use a slow and well-controlled dry-out procedure for both shift reactors to minimise the water vaporisation within the pores of the catalyst pellets, which can cause additional physical damage if it is too fast. The following dry-out procedure was used (Fig. 1):

Fig. 1: LTS temperature profile during the dry-out procedure

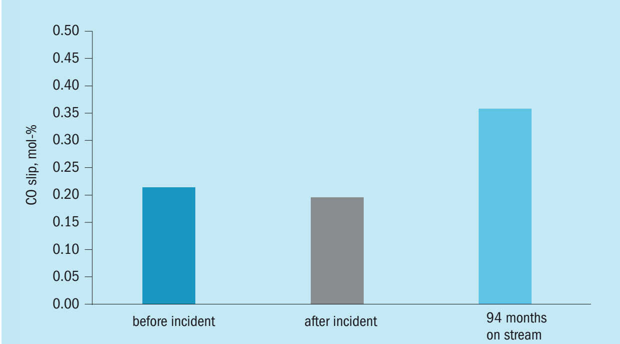


Source: Clariant

Fig. 2: LTS temperature profiles AFA3

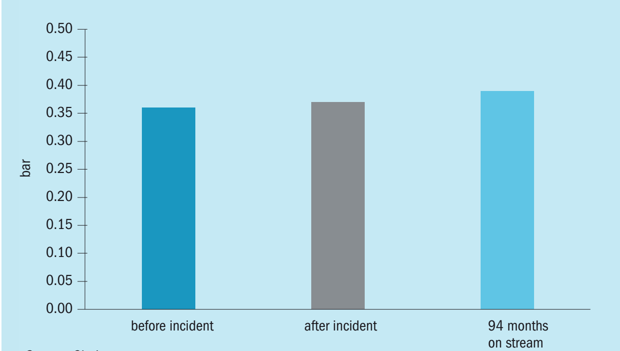
Source: Clariant

Fig. 3: CO slip outlet LTS AFA3



Source: Clariant

Fig. 4: Pressure drop over LTS reactor AFA3



Source: Clariant

- Before start-up, the inlet and outlet lines of the HTS and LTS were drained.
- Nitrogen circulation was started at low pressure to slowly remove moisture from the catalyst pores.
- The drain ports were left partially open during the nitrogen circulation until the water was no longer present.
- The catalyst beds were heated up in nitrogen circulation at a rate no greater than 30°C/hour. The inlet temperature was held when the catalyst bed temperatures no longer followed the inlet temperature. This was an indication that the dew point was reached. The inlet temperature was maintained at 10-15°C above the estimated steam dew point for approximately 12 hours to ensure slow vaporisation of the liquid from the catalyst pores.
- After this period, the heat up continued at a rate of 30°C/hour up to 225°C, at which point the reactor was ready for the normal start-up procedure. When the recommended temperature was reached, the LTS reactor was bypassed until process gas was introduced.

After the start-up, a catalyst performance evaluation was conducted to assess whether the wetting incident had permanently damaged the catalyst. As shown in Fig. 2, there is a slight decrease in the conversion of the LTS catalyst after the incident. Note, however, that the inlet temperature is 3°C lower after the incident. If the inlet temperature had been the same, only a minor difference would be visible.

Fig. 3. shows that the CO slip was stable after the incident and still at a low level after 94 months of operation. Fig. 4 proves that the dry-out procedure was successful since there was no appreciable change in pressure drop. The comparable pressure drop demonstrated the robustness of the catalyst before and after the incident.

The lessons learned at the OCI Geleen plant show that damage to wetted LTS catalyst can be minimised by using a proper dry-out procedure before restarting production. Clariant's LTS catalyst ShiftMax® 217 has proven to be robust, even in a severe wetting incident. Hence no early changeout was necessary.

This incident demonstrates that combining a robust and highly active catalyst, such as ShiftMax® 217, and close cooperation between operating plant and catalyst vendor leads to safe plant operation and significant savings due to avoided downtime and avoided catalyst replacement costs.

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New ShiftMax® 217 Plus LTS catalyst

Clariant has not stopped at the highly active and robust ShiftMax® 217 but developed ShiftMax® 217 Plus, the next generation of LTS catalyst for ultra-low methanol formation and outstanding physical strength. It utilises the proven chemical composition of ShiftMax® 217 and exhibits the same high activity but with further improved selectivity and mechanical strength.

Due to the introduction of an optimised production process, ShiftMax® 217 Plus exhibits a more homogenous distribution of the active metals and promoters within the catalyst matrix. The catalyst selectivity is enhanced by the optimised promoter concentration and distribution.

Lower by-product methanol formation

By-product methanol formation consumes hydrogen leading to H_2 yield losses and/or lower energy efficiency and technological and environmental problems (VOC/COD emissions).

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

Excessive methanol make will not only contaminate CO_2 and process condensate, but it also causes loss of ammonia production. As a rule of thumb, every tonne of methanol produced in the LTS results in 1.1 tonnes of ammonia loss. Methanol formation is driven by gas composition, operating conditions (similar to methanol synthesis), and catalyst type. Therefore, the methanol formation rate may be reduced by increasing the steam to gas ratio, using low-methanol catalysts, and improving the aging behaviour of the catalyst.

In laboratory tests, ShiftMax® 217 Plus demonstrated ultra-low methanol formation without compromise on activity. Compared to the commercially proven version ShiftMax® 217, the new catalyst provided the same high level of CO conversion but formed 40% less methanol (Figs. 5, 7).

The ultra-low methanol make provides several benefits:

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

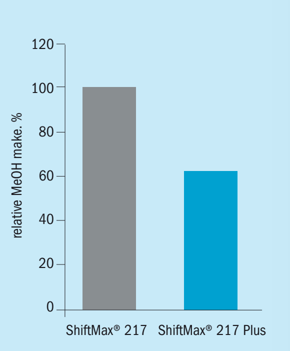
Mechanical stability

Apart from the strongly reduced MeOH formation, ShiftMax® 217 Plus has higher mechanical strength, as shown in the significantly improved side crush strength (SCS) after reduction (Fig 6). This will result in a lower pressure drop increase with time on stream and consequently to a longer catalyst lifetime.

Conclusion

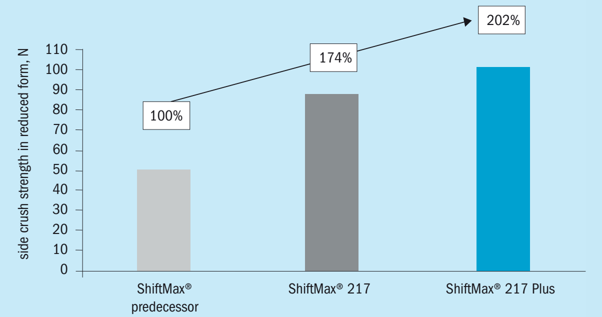
The convincing case study at OCI Geleen and the successful launch of ShiftMax® 217 Plus impressively point out that Clariant continuously evaluates product performance from customer feedback and combines it with intensive R&D efforts. In this manner, Clariant continues to innovate and further enhance the benefits of its catalysts to bring additional value to customers.

Fig. 5: **By-product methanol formation**



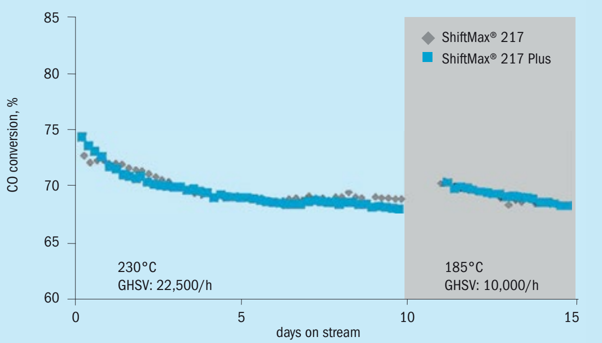
Source: Clariant

Fig. 6: **Side crush strength after reduction**



Source: Clariant

Fig. 7: **High activity**



Source: Clariant

TOPSOE

New formulation for HTS catalysts is industrially proven

The fundamental iron-chromium composition of today's conventional HTS catalyst was first discovered in 1914 by Bosch and Wild and has been in commercial use since that time. The iron oxide in the catalyst is commonly produced as hematite (α-Fe_2O_3) and reduced in situ to generate the catalytically active phase of magnetite (Fe_3O_4). Chromium oxide is added to the catalyst as a textural promoter because unpromoted magnetite easily sinters under HTS conditions, leading to reduced surface area and significant loss of activity. In moderate amounts, chromium oxide also functions as a chemical promoter, enhancing the intrinsic catalytic activity of iron oxide. Another valuable promoter, copper, was discovered in the 1980s, as demand began increasing for more energy-efficient plants. The addition of copper was found to increase catalyst activity and selectivity, which reduced by-product formation from Fischer-Tropsch reactions at lower S/C (steam to carbon) ratios.

Challenges of conventional Fe-based HTS catalysts

In the last few decades, a large number of research efforts in HTS catalysis has been motivated by the drawbacks of modern iron-based catalysts, for example, the presence of toxic hexavalent chromium and over-reduction of iron oxides at low S/DG (steam to dry gas) ratios.

Chromium promoters in fresh Fe-Cr-Cu catalysts are often present as surface Cr(VI) species (i.e. in CrO_3) that reduce to Cr(III) (i.e. Cr_2O_3) under HTS conditions. Cr(VI) is a Category 1 carcinogen and is water soluble, meaning that it can be washed out of the catalyst into the condensate stream during start-ups, resulting in an environmental clean-up issue and resulting in lower chromium content in the catalyst and consequently less stability. As Cr(VI) is also very exothermic during reduction, this can lead to very high catalyst temperatures that, in worst case scenarios, may exceed the design temperature of the reactor. To avoid potential damage to the catalyst and the reactor, extra procedures must be performed during start-up, adding to plant downtime. Accidental leaks of the volatile Cr(VI) are a risk to personnel safety and to

Fig. 1: **SK-501 Flex™ catalyst**

Source: Topsoe

the environment, and such incidents can be very costly for a plant due to unplanned downtimes and long-term liability issues. Catalysts containing Cr(VI) must be compliant with the European REACH regulations, and spent catalysts must be disposed of in accordance with toxic waste regulations.

The risk of over-reduction of iron oxides in conventional HTS catalysts is also a major issue because of the limitation it puts on S/DG and therefore S/C ratios. At S/C ratios lower than approximately 2.8 the iron in conventional HTS catalysts will be reduced to lower oxides, metallic iron species or iron carbides:

$$5Fe_3O_4 + 32CO \rightleftharpoons 3Fe_5C_2 + 26CO_2$$

Iron carbides in turn are very effective catalysts for the highly exothermic methanation reaction and Fischer-Tropsch reactions:

$$n\,CO + (n+m/2)\,H_2 \rightleftharpoons C_nH_m + n\,H_2O$$

This production of higher hydrocarbon by-products consumes hydrogen that would otherwise be used for valuable hydrogen or ammonia production and results in physical damage to catalyst pellets. Loss of catalyst mechanical strength in turn leads to increases in pressure drop as well as premature catalyst unloading and replacement. The addition of copper promoters is effective in inhibiting the Fischer Tropsch reaction at low S/C ratios, but it does not eliminate it.

To avoid the negative consequences of by-product formation, it is important to maintain a minimum S/C ratio not only during normal operation but also during reduction and activation. Fe-Cr-Cu catalysts require special considerations during start-up to ensure that they are properly reduced not only to avoid iron over-reduction but also to avoid damaging consequences of the exothermic reduction of Cr(VI) to Cr(III).

A new formulation for HTS catalysts

Although much work has been done in developing improved Fe-Cr-Cu catalysts that address the above challenges, the basic formulation of commercially viable high temperature shift catalyst remained unchanged until 2016 when Topsoe introduced SK-501 Flex™, a new HTS catalyst based on zinc oxide and zinc aluminium spinel and containing no iron or chromium (Fig. 1). This fundamental composition has long been known to have some degree of activity for the WGS reaction. Topsoe's contribution is the addition of certain promoters and an effective preparation method that give the new catalyst a high level of activity, even after extended periods of operation. Furthermore, the notable absence of chromium makes this new formulation safer to handle and more environmentally friendly.

The performance of SK-501 Flex™ has been optimised as a result of meticulous, systematic studies of the catalyst parameters by the company's R&D division. The zinc aluminium spinel, coupled with the right amount of promoters, manages stability while maintaining a high level of poison resistance.

Benefits of SK-501 Flex™

The most significant benefits of SK-501 Flex™ compared to conventional Fe-Cr-Cu catalysts are:

- extended operational flexibility;
- higher production rates;
- improved energy efficiency;
- exceptional activity and stability;
- minimum by-product formation;
- no risk to personnel health and safety;
- low environmental impact;
- hassle-free start-up.

The innovative composition of SK-501 Flex™ offers ammonia and syngas producers the possibility to operate the plant at S/C ratios previously unattainable with commercial catalysts, to achieve greater improvements in capacity increase.

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Additionally, low S/C ratios make it possible to significantly reduce energy costs. At a modern ammonia plant, operation with SK-501 Flex™ could bring energy consumption 1.6% closer to the theoretical minimum (see Fig. 2). Such energy savings would be achieved from reduced steam input and from an overall reduction in natural gas consumption.

The exceptional activity of SK-501 Flex™ also contributes to better energy efficiency. The activity allows for lower inlet temperatures, keeping conversion high even at lower plant S/C ratios (Fig. 3). This translates into lower pressure drop over the reactor and less energy consumption by the compressors.

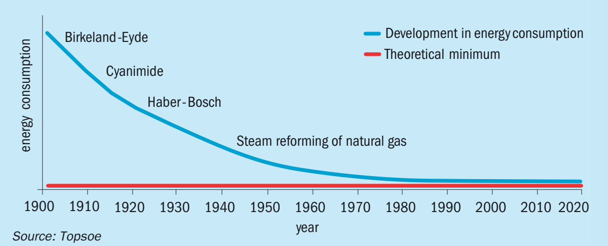
With SK-501 Flex™, there is no longer a risk of over-reduction at low S/DG ratios. There is no formation of the higher hydrocarbons, acids or esters catalysed by over-reduced iron oxide, even at extremely low S/C ratios). This eliminates the consumption of valuable hydrogen and the contamination of process condensate due to these byproducts.

A small amount of methanol is formed over any type of HTS catalyst due to the equilibrium reaction for methanol from the reaction of CO_2 and H_2.

Like Topsoe's ultra-low Cr(VI) SK-201-2 catalyst, start-up is easy and hassle-free with the chromium-free SK-501 Flex™. There is no need for extra start-up procedures that are normally needed when hexavalent chromium is present in the catalyst. With SK-501 Flex™, activation is fast and takes place in connection with the start-up of the reforming section, saving producers costly downtime.

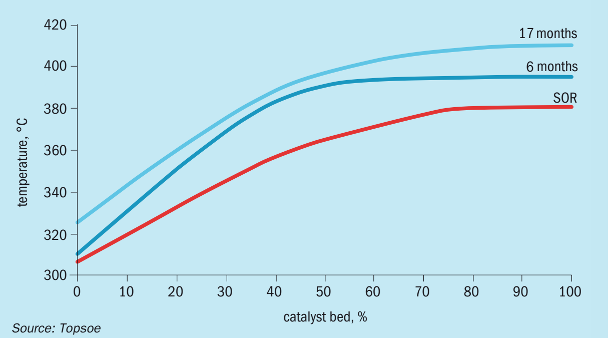
The complete absence of chromium also allows plants to avoid the potential risk that chromium poses to personnel health and safety and to the environment during product handling and operation. By avoiding this risk, plants reduce the possibility of unplanned and costly downtimes as well as long-term liability issues.

Fig. 2: **Impact of ammonia technology development on energy consumption**



Source: Topsoe

Fig. 3: **Temperature profiles from industrial reference of SK-501 Flex™**



Source: Topsoe

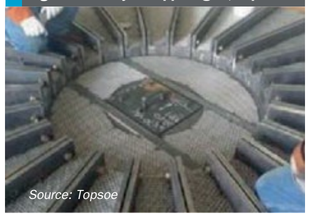
Reactor loading schemes with SK-501 Flex™

There are multiple loading scheme possibilities for SK-501 Flex™. It can be loaded alone in the HTS vessel or as part of a split loading, where SK-501 Flex™ is loaded on top of a conventional iron-based HTS catalyst such as Topsoe's SK-201-2. Split loadings can be recommended in the case of moderate decreases in S/C ratio, for which the gas has the highest potential for causing overreduction of the Fe-Cr-Cu catalyst in the top of the vessel.

A top layer of the TK-20 guard catalyst above SK-501 Flex™ is an additional loading option and is recommended for plants that typically experience impurities in the process gas or in the quench water/steam. These impurities, such as silica, potassium and sodium compounds, can also enter as a result of boiler leakages upstream of the HTS reactor. The HTS catalyst is particularly vulnerable because it is often the first in the train of catalysts operating at temperatures at which condensation of volatile contaminants can occur. The consequences include serious pressure drop issues and uneven flow distribution. Composed of inert magnesium aluminate spinel, TK-20 provides high porosity and high bed void fraction, which effectively trap and distribute foreign material over a relatively large volume.

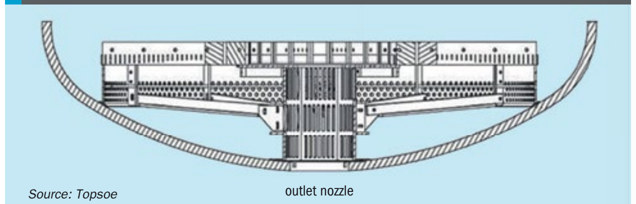
Further pressure drop reduction is possible by replacing most of the aluminum support balls with a catalyst support grid in the bottom of the HTS reactor. The support grid consists of a modified outlet collector, outlet brackets, outlet connector rods, skirt section and a mesh grid section, all of which float in the bottom of the vessel. Fig. 4 shows side and top views of the support grid.

Fig. 4a: **Catalyst support grid, top view**



Source: Topsoe

Fig. 4b: **Catalyst support grid in vessel, side view**



Source: Topsoe

Operating data from industry

Operating data for the new catalyst in a European hydrogen plant are shown in Fig. 5. It was installed to help the plant achieve higher efficiency by decreasing the S/C ratio to 2.5. With the previous catalyst, the minimum S/C ratio was 2.8. During more than 60 months the catalyst demonstrated its performance with low and stable pressure drops and activity levels that exceed the expected activity of many standard HTS catalysts.

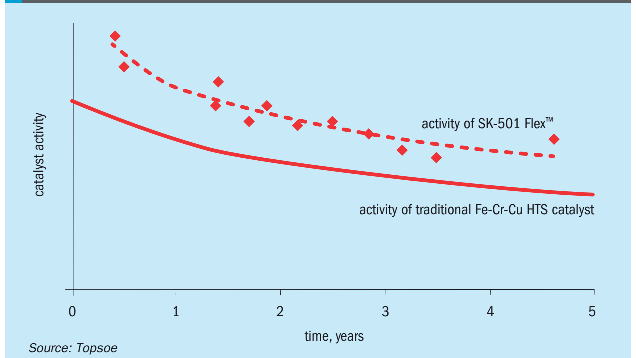
Increased production rates

The higher activity will give a higher conversion in the HTS reactor throughout the catalyst lifetime. In a standard 100,000 Nm³/hr hydrogen plant, the extra production is in the order of 0.3-0.5% just by changing catalyst. Even higher production gains can be achieved by lowering the S/C ratio. With the possibility of operating the plant at S/C ratios previously unattainable with commercial catalysts, producers can achieve improvements in capacity increase. For example, a decrease in S/C from 2.75 to 2.25 can result in 3-5% more hydrogen produced, using the above plant as a basis and simply reducing the steam flow to the plant and increasing the flow of hydrocarbon feedstock. Table 1 shows the comparison.

On top of the production increase, other benefits such as reduced natural gas fuel consumption in the steam reformer, energy requirement in the cooling train between the HTS and PSA unit, and an increased steam export can be achieved.

The use of Topsoe's catalyst can be an inexpensive revamp option for a plant looking to increase its production rate; only requiring a catalyst replacement as opposed to extensive capital expenditures.

Fig. 5: **Industrial performance**



Source: Topsoe

Table 1: **Comparison between conventional and new catalysts**

	Fe-Cr-Cu based catalyst		SK-501 Flex™	
Age	Start of run	End of run	Start of run	End of run
Natural gas flow, Nm³/hr	40,760	40,760	46,590	46,590
Steam carbon ratio, mol/mol	2.75	2.75	2.25	2.25
HTS inlet temperature, °C	330	348	306	335
H_2 amount, Nm³/hr)	100,000	99,350	104,350	103,200

Applications of SK-501 Flex™

The SK-501 Flex™ catalyst can be used in the HTS reactor at any modern ammonia, syngas or hydrogen plant. The catalyst can be installed as a direct replacement of a conventional HTS catalyst and can play a vital role in the case of revamps as well as new plants. When reducing the plant S/C ratio, the effects of reduced steam input and increased feed gas flow must be considered carefully, and a detailed assessment of the plant must be made.

With the removal of the S/DG limitation, other factors that may determine the operating S/C ratio include feed gas composition and its possible fluctuations, steam requirements in the CO_2 removal section, distribution of duty between primary and secondary reformers, operating pressure, reformer firing rates, and the possibility of metal dusting in the waste heat boiler.

The advantage of SK-501 Flex™ is the opportunity to reduce steam addition and therefore benefit from significant energy savings. One example of another application is the gasification of carbon-based fuel to syngas, a process that is made more efficient by utilising the WGS reaction. The catalyst can also be used in a reverse WGS process. In such cases, it is not only the catalyst's ability to operate at low S/DG ratios that make it a good candidate but also its impressive thermal stability.

Summary

Topsoe's latest development in HTS catalysis is industrially proven. With this new catalyst, producers are able to operate at S/C ratios that until now were unattainable, giving the producers more plant flexibility and the subsequent benefits of reduced energy consumption and increased production rates. Additional benefits are a result of its iron and chromium-free formulation and include improved personnel safety, reduced environmental impact, hassle-free start-up, and minimum by-product formation. The possible applications in which the catalyst can be used are numerous, ranging from hydrogen plants, ammonia, and syngas plants to cutting-edge projects such as biogas production, CO_2 capture and storage, and modern fuel cell power generation. ■

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CASALE

Optimising CO conversion with the Casale isothermal shift converter

Casale's axial-radial catalyst bed technology is a well proven and established technology used in both HT and LT adiabatic shift converters. Since 1995, with the first reference in China, the axial-radial design has been adopted by Casale in more than 50 shift converters. In addition to the adiabatic shift converter, Casale also offers an isothermal shift converter design, representing the latest development in Casale reactor technology for new grass roots ammonia or hydrogen plants.

Casale axial-radial converter design

Fig. 1 is a schematic view of the gas flow path in an axial-radial converter. As shown, most of the process gas passes through the catalyst bed in a radial direction, resulting in a lower pressure drop than in the case of pure axial flow since the gas velocity is smaller. A typical value for the pressure drop through the catalyst bed is 0.3 bar.

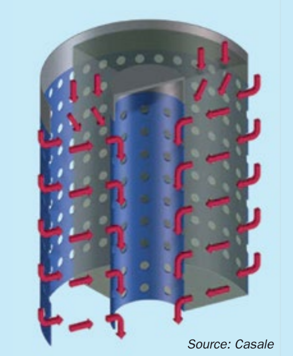
The balance of the reacting gas flows downwards through the top layer of catalyst in an axial direction, thus eliminating the need for a top cover of the catalyst bed. This feature allows both simple construction of the converter internals and complete catalyst volume utilisation (even in the top part).

Furthermore, most of the pressure drop is concentrated at the inlet and outlet of the catalyst bed, where perforated walls control the gas flow through the bed. This configuration allows an optimal gas distribution, independent of possible non-uniform catalyst packing inside the bed due to poor loading or other reasons.

Fig. 2 is a schematic of the Casale axial-radial adiabatic shift converter. The success of the axial-radial design can be attributed to its numerous advantages:

No possibility of channelling: The gas distribution in the catalyst bed is independent of the catalyst loading, age and condition, since it is controlled by the perforated walls and not by the catalyst itself. This ensures perfect distribution and full utilisation of the bed in all operating conditions and loads, and independent of catalyst poor distribution, ensuring a longer life for the same catalyst volume.

Fig. 1: Casale axial-radial concept



Source: Casale

Fig. 2: Casale axial-radial adiabatic shift converter

Source: Casale

Low pressure drop: The lower gas velocity of the axial-radial flow in the catalyst, compared with the axial bed, ensures a low pressure drop even in case of unexpected events, such as carryover of powder or water droplets.

Use of small-size catalyst: The axial-radial converter allows using smaller size catalyst with no detrimental effects on pressure drop. It is well known that in any pore-diffusion limited reaction such as the CO-shift conversion, the apparent catalyst activity is inversely proportional to the pellet dimensions since only the outer portion of the pellet tends to be used. Smaller size catalyst is more active than larger size catalyst thanks to its higher surface area per unit of volume, and this higher activity facilitates a longer catalyst life for the same loaded volume.

Protection of catalyst from water droplets: In many plants, the pressure drop of industrial axial shift converters builds up during the operating life, because of water droplets carried over by the incoming gas, which tend to form a caked layer at the top of the bed.

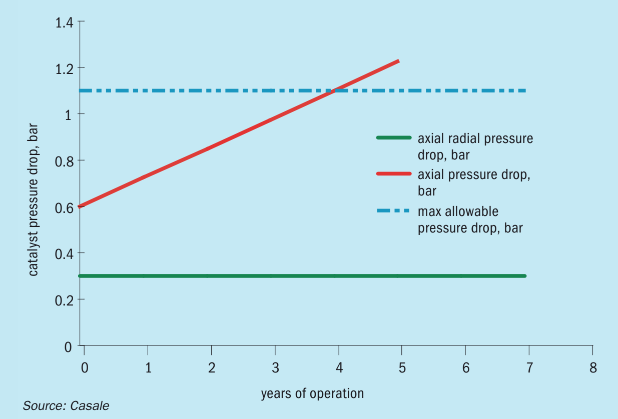
When the pressure drop exceeds the maximum admissible value the top layer of catalyst is skimmed off or, in the worst case, the whole catalyst charge has to be replaced.

The axial-radial bed design, for fluid dynamic reasons, concentrates the water droplets contained in the gas feed on the top layer of catalyst (axial part of the axial-radial bed). The caked layer, which may eventually form, will simply shift the incoming gas toward the radial inlet distributor, thus minimising the effect on the total pressure drop. Therefore, even in the event of a severe leakage of water from an upstream boiler, the shift catalyst and internals will be protected from any damage.

With axial-radial internals, the total bed pressure drop therefore remains constant with time because the catalyst pressure drop is negligible during the whole catalyst lifetime and all the pressure drop is concentrated in the nozzles and in the perforated walls, that do not change their characteristics with the time.

Fig. 3 shows a typical pressure drop trend for shift converters. It is apparent that a low and constant pressure drop, as achieved with axial-radial internals, can increase the operating life of the catalyst, compared with the axial internals if affected by water impingement.

Fig. 3: **Typical shift converter pressure drop trend**



Source: Casale

Fig. 4: **3D rendering of isothermal shift converter**

Source: Casale

Casale isothermal converter design

Casale's latest shift converter design, the isothermal shift converter, allows isothermal operation of the reactor by heat exchange with a coolant flowing in a panel type heat exchanger dipped vertically into the catalyst mass. Fig. 4 shows a 3D rendering of the isothermal shift converter.

Compared to an adiabatic converter, a lower temperature is reached at the bed outlet of the isothermal converter with the same catalyst volume and process gas inlet temperature, thus performing a higher conversion.

The high efficiency of the isothermal design enables lower synthesis gas consumption (to attain the same production), or higher production (with the same synthesis gas). Moreover, the heat removed by the exchange plates can be recovered (by heating boiler feed water or generating steam) thus reducing the amount of equipment to be installed.

Principles of isothermal design

The isothermal reactor mainly consists of a catalytic bed with a plate-exchanger dipped into the catalytic mass for direct heat removal. The continuous catalytic layer is cooled by means of the exchange plates vertically immersed inside the catalytic mass. The catalytic bed is supported on a layer of alumina balls of different size. The reaction heat of the isothermal stage is removed by heat exchange with boiler feed water inside the plates.

The heat exchange rate is carefully evaluated to obtain the best possible reaction path inside the catalyst. In view of this target, the design of the reactor internals requires particular care and knowledge.

Moreover, the control of the reactor is designed to allow stable and efficient operation under all possible operating conditions. In particular, the parameters to be controlled are the inlet temperature to the catalytic bed and the BFW temperature within the plates. The latter can be controlled through partial or complete bypass of the plates or by steam generation pressure (in case of a steam rising arrangement).

High performance

The performance of the isothermal axial-radial design, based on the innovative concepts explained in the previous paragraphs, are superior to the adiabatic design and can be summarised as follows:

Efficiency: The CO conversion performed in the isothermal converter is higher, thus making it possible to reduce the make-up gas consumption for a given hydrogen production.

Pressure drop: The heat exchanger plates installed in the converter allow a more compact plant flowsheet, resulting, in particular, in a more compact heat recovery train in the same plant section. As a result, the pressure drop on the gas side is lower.

Mechanical features

Conscious of the important role that reliability plays in the operation of converters, Casale has developed the isothermal design up to successful industrial implementation with the most careful attention to every mechanical detail.

A summary of the most significant features in the isothermal design are:

- the vessel is filled with one continuous layer of catalyst;
- the heat removal inside the catalyst is performed by the heat exchange plates;
- the heat exchange elements are suitably designed for this specific service, considering the critical environment where they will operate (catalyst actions, thermal expansion, mechanical stress, material resistance…);
- the cooling elements are grouped in packs;
- all of the internal parts are designed to allow easy replacement, without touching the pressure vessel;

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- easy access is granted to the catalytic bed and to all critical points;
- the loading and unloading of the catalyst is conveniently performed by easy and normal operations.

The fabrication of the plates, apart from the collectors, is completely automated, thus ensuring constant quality in the construction of each single element. After fabrication, the plates are hydraulically tested and controlled in order to guarantee their perfect realisation. All parts are then assembled in the manufacturer's workshop to ensure that they correctly fit together before being inserted into the pressure vessel. Casale encourages its clients' inspection engineers or other technical personnel to inspect the fabrication work while it is in progress, and this is especially important during the fitting trial.

Catalyst loading and unloading

The catalytic bed is continuous and rests on a layer of inert material loaded on the bottom of the converter; there is no separation between the catalyst and the inert material. This allows simple and fast catalyst loading and unloading from the top and catalyst discharge from the drop-out nozzles in the bottom.

The loading is performed by means of the Casale dense loading tool.

The internals

The converter includes only an isothermal stage, which forms one continuous bed resting on a layer of inert balls.

The heat exchange is performed with the BFW flowing in the exchange plates. All of the process gas enters the reactor through the top inlet nozzle.

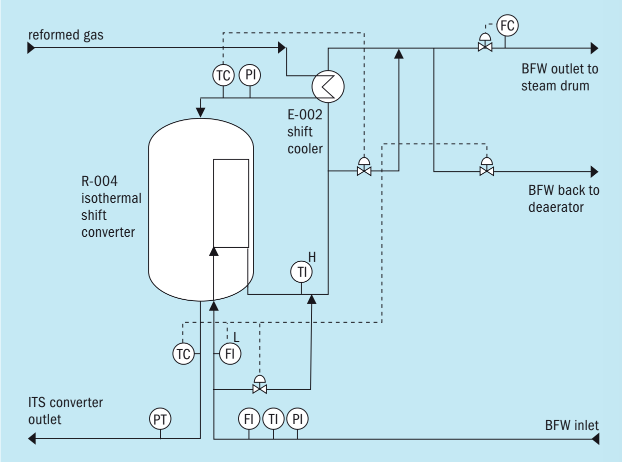
The gas flow path in the converter is axial-radial (inward or outward).

The gas inlet and outlet collectors have stainless steel perforated walls (AISI 304 or 304L), which control the gas pressure drop across the converter to ensure an even gas distribution in the catalyst.

The exchange plates are arranged in the converter in concentric rounds. They are supported, in order to avoid problems due to differential thermal expansion.

The construction material for the exchange plates is duplex SS (preferred material). The exchange plates are manufactured in modules, which can pass through the top opening of the vessel.

Fig. 5: **Typical process flow diagram – BFW heating scheme**



Source: Casale

The boiler feed water is distributed to the plates by means of pipe-ring collectors, wherefrom individual pipes feed the coolant to the plates. The heated water or BFW/steam is collected from the plates in an outlet pipe-ring collector.

All converter internals (exchange plates, inner gas collector, water collectors) are designed and constructed to pass through the vessel top opening.

Process flow path

Fig. 5 shows a typical process flow diagram for a BFW heating scheme.

The make-up gas, available at battery limits, enters heat exchanger E-002, where it is cooled down to the appropriate catalyst inlet temperature (230°/260°C, depending on the catalyst age).

The gas then enters the shift converter (R-004) and flows in an axial-radial path, through the catalyst bed, where the reaction takes place. Boiler feed water flows in the plates, acting as boiler feed water heater, and removes the reaction heat.

The temperature of the reacting gas in the catalyst mass is monitored by means of three thermocouple bundles, located inside of the catalytic bed.

Additional thermocouples, located in the inlet and outlet pipelines, monitor the temperature of the inlet and outlet gas.

The converter outlet temperature is controlled by the water flow rate through the plates, and by means of bypass of the plates. Such control enables the converter to cope with variations in load and catalyst aging as well as with small changes of the plant feed type.

The temperature of the water outlet from the plates is monitored by a thermocouple. The saturation temperature should not be approached, in order to avoid water vaporisation in the exchange plates.

Advantages of the isothermal shift technology

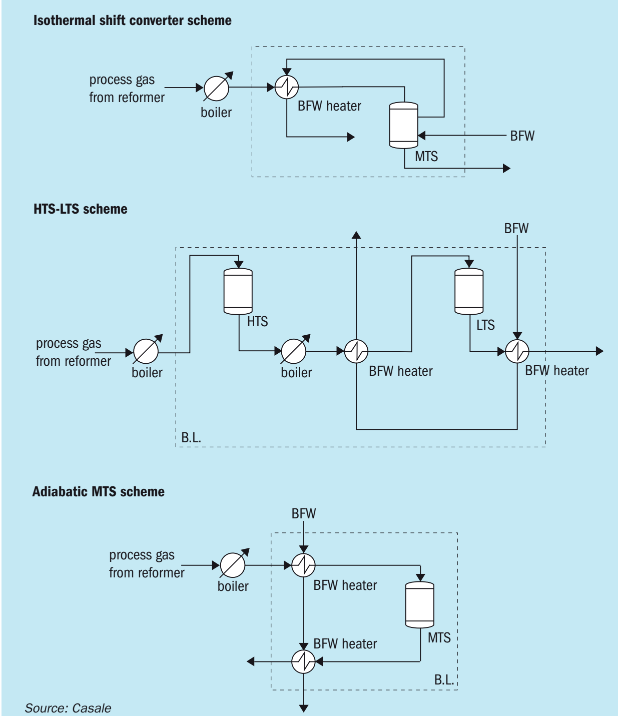
Fig. 6 shows three different possible configurations.

The main benefits of Casale isothermal technology can be summarised as follows:

- fewer items of installed equipment (higher operability and less maintenance);
- significant reduction in operating and installation costs;
- higher CO conversion with same catalyst volume;
- lower catalyst volume at fixed CO conversion;
- better catalyst utilisation;
- only one type of catalyst is required;
- Casale axial-radial flow minimises pressure drop across the converter.

The Casale isothermal design follows the best reaction path to optimise the converter performance. In fact, it maximises the CO conversion at a fixed catalyst volume or, at fixed CO conversion, it requires the less catalyst volume.

Fig. 6: **Technologies considered in the proposal**



Source: Casale

Considering the end-of-run conditions, Table 1 summarises the performance of the technologies analysed for a particular example:

As can be seen in Table 1, with the isothermal design, thanks to the better reaction path through the catalytic bed, at the same CO conversion of standard configuration (HTS + LTS) a significant saving in catalyst volume is achieved.

The CO conversion for the adiabatic MTS configuration is less than in isothermal design, with the same catalyst volume. In addition, since the adiabatic MTS works close to equilibrium conditions, in order to have a CO slip of less than 1% on dry basis, the installation of a cooling stage is necessary, like in the HTS + LTS configuration. So, only with the isothermal technology is it possible to perform the CO conversion in a single stage, minimising the number of installed equipment items, simplifying the process configuration and reducing the investment costs.

References

In addition to the adiabatic shift converters in operation, Casale has one isothermal MTS converter in a hydrogen plant in Russia, in operation since 2013.

Casale also has significant experience with the design and operation of isothermal methanol converters, which operate under very similar conditions, with 18 converters in operation. ■

Table 1: **Performance of the technologies analysed for a particular example**

	Adiabatic HTS + LTS	Adiabatic MTS	Isothermal MTS
EOR conditions			
Inlet temperature, °C	345 (inlet HTS) 220 (inlet LTS)	250	250
ΔT across converter, °C	83 (HTS) 37 (LTS)	106	-15
Final CO slip (dry basis), mol-%	< 1%	< 2%	< 1%
Hydrogen production, Nm³/h	~ 178,000	~ 174,000	~ 178,000
Converter volume, m³	140 (60 + 80) 2 vessels	80 1 vessel	80 1 vessel
Heat exchangers			
Boilers	1	0	0
BFW heaters Installed area for BFW heaters	2 +90%	2 +80%	1 reference

Source: Casale

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Scrubbing systems prove their value

Stamicarbon offers advanced scrubbing technologies for fertilizer granulation plants and prilling towers. This article describes the technology and experience with the second operational MMV scrubber, which is installed at the Dakota Gasification Company's (DGC) urea granulation plant, and highlights the successful pilot test with its JV scrubbing technology.

As countries are moving towards a carbon-free, sustainable future, the fertilizer industry has to contribute to reducing emissions and accelerating the transition to a green economy. Worldwide, emissions regulations and specifically fine particulate emission regulations are becoming increasingly strict. While older scrubbing technology easily collects larger particles, a high degree of sub-micron dust capture required a new approach.

Stamicarbon, the innovation and license company of Maire Tecnimont Group, and EnviroCare International have, in response to this, co-developed the high-efficiency Micro-Mist™ Venturi (MMV) scrubbing technology for granulation plants and the Jet Venturi (JV) scrubber for prilling towers. It removes sub-micron filterable particulate, condensable particulate, and soluble gases at very high efficiencies with low energy input, while reducing liquid effluent waste streams.

Stamicarbon currently has two advanced technology wet scrubbers in operation on the outlet of urea granulation plants and three more MMV scrubbers in the construction and start-up phase. These MMV scrubbers are multi-staged and have a modular box concept design for easy transportation and assembly.

The DGC granulation plant

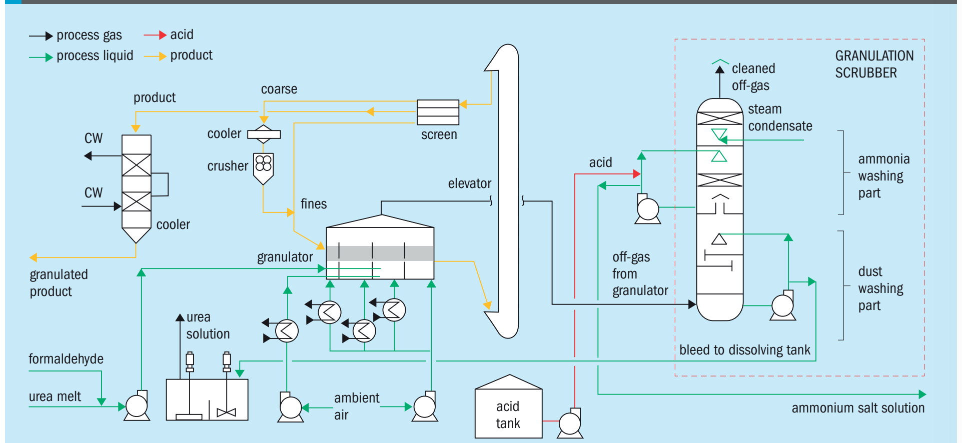
Stamicarbon and Dakota Gasification Company signed a license agreement for the construction of a brownfield urea melt, granulation, and DEF plant in Beulah, North Dakota, in the United States. This urea plant utilises Stamicarbon's state-of-the-art LAUNCH MELT™ Pool Reactor technology and the latest optimised LAUNCH FINISH™ Fluid Bed Granulation technology. Both plants have a capacity of 1,000 t/d, each.

The installed granulation plant (see Fig. 1) is characterised by minimising the number of equipment items, while keeping its original high performance.

Granulation plant output

- The complete solid product flows via gravity through the main screens.
- The coarse product is fed to the crusher after cooling to a temperature of 70°C.

Fig. 1: **Process flow diagram of the 1,000 t/d urea granulation plant for Dakota Gasification Company, North Dakota, USA**



Source: Stamicarbon

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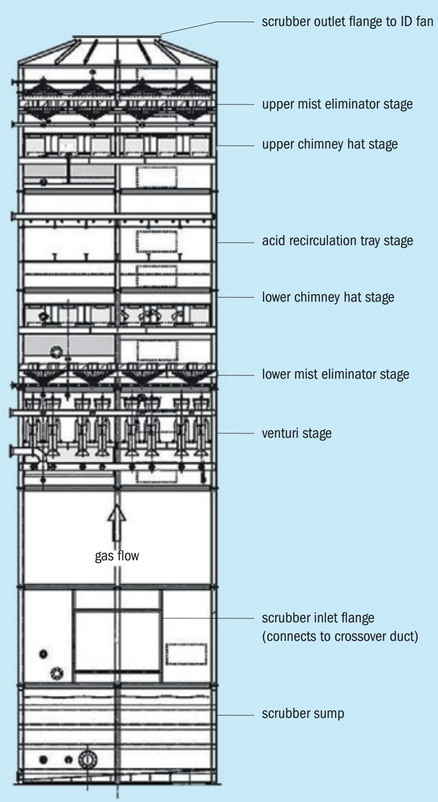
Fig. 2: **Side view of the EnviroCare MMV scrubber installed at DGC**



Source: Stamicarbon

- The crushed product and the fine recycle flow are combined and recycled back into the granulator as so-called seeds.
- The on-spec product in the outlet of the main screen is cooled to a storage temperature in a Solex product cooler, which makes use of cooling water instead of cooling air. After the product is cooled down, the final product is directed to the storage.
- The dust-loaded fluidisation and cooling air from the granulator and all the dedusting points are collected and fed to a single MMV scrubber.
- The clean air is thereafter exhausted through the off-gas fan into the atmosphere.

To reduce the required amount of fluidisation and cooling air, a water injection system can be provided into the discharge of the fluidisation air fan. This is only operated on exceptionally hot days, to increase the relative humidity and to reduce the total air consumption.

The modular MMV scrubber box concept

The DGC MMV scrubber is designed to produce two separate concentrated blowdown streams: one with concentrated urea solution and the other one with concentrated ammonium sulphate (AS) solution.

The scrubber is fabricated from 316L Stainless Steel plate, and its size is 12 ft x 20 ft x 75 ft (3.7 m x 6.3 m x 22.9 m). It is fabricated in a shop in eight sections that are delivered and assembled onsite. Because each box is 12 ft wide and approximately 9 ft tall, the boxes can be easily shipped on a common carrier to site and be offloaded and stacked. This MMV scrubber system consists of the following equipment: a quench scrubber vessel, a cross over duct, a MMV scrubber vessel, several pump stations, an acid recycle tank, and associated field instrumentation.

MMV process description

A side view of the DGC box scrubber can be seen in Fig. 2. Exhaust gases exit the urea granulator and flow downwardly into the quench vessel. The quench cools, saturates and removes large particulate from the exhaust gases prior to entering the MMV scrubber vessel. The main components of the MMV scrubber vessel include the venturi stage, lower mist eliminator stage, lower chimney hat stage, acid recirculation impingement tray stage, upper chimney hat stage and upper mist eliminator stage. The venturi stage utilises finely atomised water droplets combined with high differential velocity to scrub gas-entrained aerosols and fine particulate from the gas stream not captured in the preceding stages. Two mist eliminator stages remove remaining water droplets from the gas stream. Two chimney hat stages inhibit scrubber water injected in upper stages from draining into lower stages. The acid recirculation impingement tray stage captures water-soluble volatile compounds. The treated gas stream then proceeds through the ID fan to the stack. Due to the placement of the ID fan, the pressure inside the scrubber is below atmospheric pressure.

During the crystallisation process of urea melt in a granulator, urea dust is generated and some ammonia present in the urea melt is released and both components are emitted into the air. At the DGC plant both components (urea dust and NH_3) were collected simultaneously in a single MMV vessel.

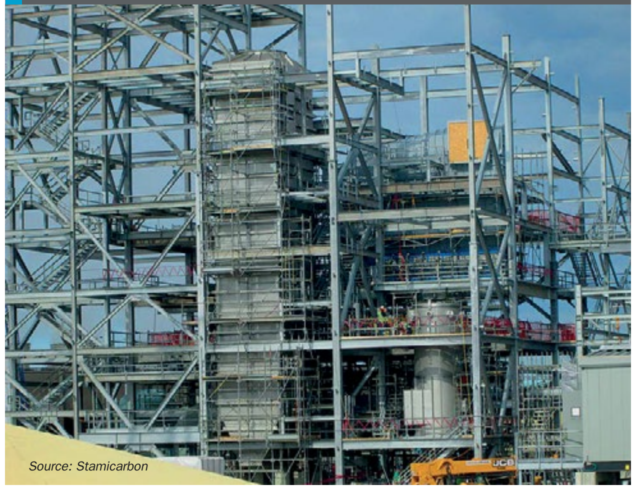
The majority of the urea dust is collected and separated from the air flow in the quench. The urea scrubbing solution is partly re-circulated as scrubbing solution to the quench and partly pumped to urea dissolving vessel. The remaining sub-micron urea dust is additionally collected at the multi venturi stage section and this dilute urea solution is also send to the quench (make up) and the dissolving vessel, and finally recycled back into the melt plant.

Downstream of the MMV stage, ammonia abatement takes place. To efficiently capture ammonia, it is required to apply acidic scrubbing with sulphuric acid. The ammonium sulphate (AS) solution generated after the reaction between the ammonia present in the off gas and the sulphuric acid scrubbing is concentrated by circulation, stored in the AS tank, and finally sent to OSBL. Because of this single MMV scrubber set-up it is important to keep both liquid streams (urea- and AS solution) separated.

The MMV operation

The quench vessel, installed downstream of the urea granulator (see Fig. 3), is designed to remove large particulate while saturating the incoming process gases.

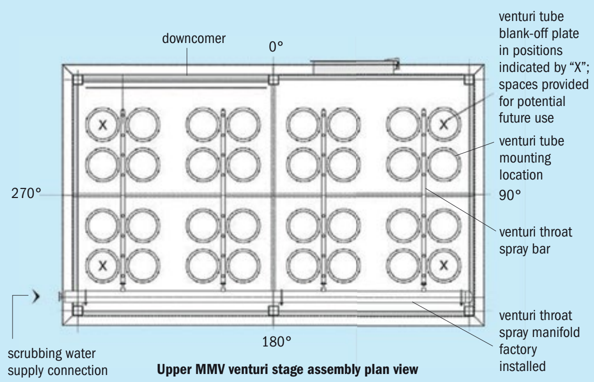
Fig. 3: **The granulator, quench and MMV scrubber installed at DGC**



Source: Stamicarbon

The first stage that the granulator exhaust gasses encounter as they exit the cross over duct and enter the MMV scrubber vessel is the venturi stage section. The primary function of the venturi stage is to capture any residual fine, sub-micron particulate including condensable constituents and aerosols that have carried over from the quench stage. The venturi stage consists of a solid diaphragm with mounting locations for 32 venturi tube assemblies (28 venturi tubes initially installed at DGC, see Fig. 4), eight factory installed venturi inlet spray bars, and four venturi throat spray bars. Venturi tubes, mounted in parallel, produce extremely high particulate collection efficiencies by creating of an elevated relative velocity differential between the water (being injected by sprays) and particulate laden gas stream. The exit of the venturi tube is designed to recover the velocity pressure, minimising the fan energy requirement for the system.

Fig. 4: **DGC venturi diaphragm**



Source: Stamicarbon

Each venturi tube assembly consists of a mounting plate, inlet cone, throat, low energy loss outlet diffusion cone assembly, throat spray nozzle connection, and outlet deflector plate. Factory installed venturi throat spray bars distribute water via flex hoses to the throat spray water feed connections on each of the venturi tubes. Throat spray supply water is modulated via the throat spray pump, which is variable frequency driven (VFD), to control pressure drop across the venturi stage for differing operating conditions. As gas flow decreases, the corresponding pressure drop across the venturi stage falls unless more water is added. To maintain the venturi stage differential pressure when gas flow decreases, the VFD increases the throat spray water flow, which also maintains the high scrubbing efficiency. Each throat spray is centred in the venturi tube throat to spray counter to the gas flow.

A chevron mist eliminator (ME) array is installed above the venturi stage. The equipment installed in this stage functions to keep the water in the venturi stage and minimise carryover to the downstream stages. The ME irrigator sprays continually rinse the bottom (upstream) side of the chevrons to reduce the possibility of urea build-up on the ME.

The lower chimney hat stage is installed above the lower ME stage. The chimney hat stage prevents recirculated acidic solution in the upper stages from draining into the recirculated venturi dilute urea solution in the lower stages.

The acidic recirculation tray stage is installed above the lower chimney hat stage. This stage consists of two levels of

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dual orifice impingement trays. Scrubbing water dosed with sulphuric acid is continually recirculated over the top of the trays via the ammonium sulphate (AS) solution vessel. Process gasses are forced to pass through recirculated AS solution via small perforations in the trays. Gas phase ammonia, not captured in the previous stages is scrubbed in this stage and converted to AS using the sulphuric acid solution. The AS solution is concentrated and bled off to storage where it is collected for resale value by an AS crystallisation unit.

The upper chimney hat stage is installed above the acid recirculation tray stage. The equipment installed on this stage prevents AS droplets to enter the next stage and a small portion of the recirculated demister water (ME spray water) in the upper stages from draining into the recirculated AS solution in the lower stage.

An upper chevron mist eliminator (ME) array is installed above the upper chimney hat stage. The equipment installed in this stage functions to keep water from the acid recycle scrubbing stage entrained in the gas stream from carrying over to the ID fan and stack. The ME irrigator sprays rinse the bottom (upstream) side of the chevrons to reduce the possibility of build-up. An on/off block valve, mounted in the field piping upstream of the sprays allows for them to be sprayed as required. The chevrons are intermittently backwashed from above via the ME backwash spray bars. Washing of the mist eliminator prevents particle build up by ensuring proper drainage of captured particulate laden droplets under all operating conditions. The backwash nozzles provide intermittent cleaning using large droplets that do not carry over to the stack.

The MicroMist scrubber system utilises six pump stations to circulate the various scrubber water sources, providing the corresponding design nozzle injection pressures. All six of the pump stations are similar in design. Each station consists of two water pumps although only one pump is required to operate to provide design pressure and flow to the corresponding spray nozzles.

The remaining pump is a standby pump. The pumps are installed in parallel with common inlet and discharge piping. Each pump train consists of an inlet simplex strainer, discharge check valve and pressure gauge, and inlet/outlet isolation valves to facilitate equipment maintenance.

Test results

After the plant was successfully commissioned and the scrubber had been running stable for several weeks, the official stack test was performed. DGC hired an independent company to conduct particulate matter emission compliance test program on the urea granulation stack. This test programme was completed in accordance with the North Dakota Department of Health, Air Quality Division. Emission testing was conducted following the methods specified in 40 CFR, Part 60, Appendix A; and 40CFR51, Appendix M.

The performed stack test measurements were: filterable particulate matter (FPM), condensable particulate matter (CPM), total particulate matter (TPM), and opacity. FPM was measured using EPA Method 5. CPM was measured using EPA Method 202. TPM is simply the addition of CPM and FPM. The opacity was measured using EPA Method 9.

The purpose of the emission testing programme was to demonstrate the particulate matter emission rates during the normal operating condition. The achieved results of the test program, without any additional fine tuning of the scrubber showed that the total particulate matter was <10 mg/Nm^3 and visible emissions were determined in accordance with EPA Method 9. The opacity measured by using EPA Method 9 was zero (0%).

In-operation observations

Throughout the first year of operation, the DGC plant employees steadily improved and optimised the equipment tuning, resulting in smoother operating conditions with no upsets. At times, the unit produced above the original capacity factor, reaching 115% production capacity factor briefly, and 105% for a sustained period.

Although from routine lab tests, DGC noticed more than expected AS values measured in the quench urea water. The ammonium sulphate solution data is the sulphuric acid and ammonium sulphate solution circulating in the middle/top part of the MMV scrubber (ammonia abatement) and the quench urea water data is the solution in the quench scrubber upstream of the MMV. Quench loop sulphates values have remained minimal but constant and did not lead to any product quality issues.

The most logical explanation why AS can appear in the quench loop is that some AS solution was leaking through the chimney hat and flowing upstream to the lower MMV stages. Stamicarbon and EnviroCare were comfortable with the designed chimney hat stage, but there were some flow dynamics that caused splashing to allow AS solution to migrate downward through the chimney hat openings and into the upstream stages.

After some tests, it was decided to modify the lower chimney hat diaphragm during the first scheduled maintenance for the DGC plant between 5 October 2019 and 10 November 2019. During this shutdown the lower chimney hats in the MMV scrubber were modified to prohibit splashing, and 4 additional venturi tubes were installed to lower the venturi stage pressure drop.

During this scheduled shutdown, DGC thoroughly inspected the quench and MMV scrubber internals for anything out of the ordinary, like shifted or displaced equipment (mist eliminator sections, DOI trays, venturi tubes). The spray nozzle plumes were confirmed to be uniform and all spray nozzles each specific area or stage operated similarly. The nozzle bodies were visually checked for excessive wear that could compromise function. All flex hoses, gaskets and nozzles appeared to be in good condition, and none needed to be replaced.

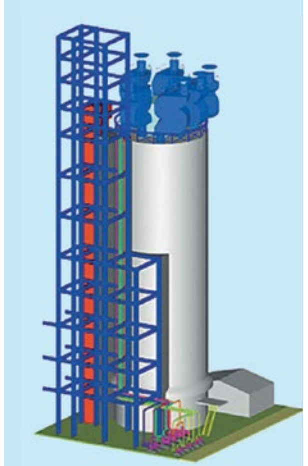
As mentioned earlier, four additional venturi tubes were added (to 32 in total) to provide a larger operating range for the venturi throat spray pumps. With the addition of four additional venturi tubes, the plant has much better control since the throat pump is operating mid-range instead of at the bottom of its range and still meeting their earlier achieved emission guarantees (same pressure drop setting).

After the shutdown, there was a significant decrease in AS concentration (from 0.28% to 0.002%) in the quench urea solution after the chimney hat was modified.

Jet Venturi scrubber for prilling towers

The exhaust gas from a prilling tower has a very fine dust, with an extremely large surface area and with the share of sub-micron particles ranging up to 70 wt-% of the total dust load. Such a fine dust creates a highly visible, persistent plume that doesn't dissipates easily. Because of this, environmental regulations for prilling tower emissions are becoming stricter. Allowed emission levels are currently maximum 50 mg/Nm^3 for dust within Europe. The limits are even

Fig. 5: **JV scrubber installation on top of a prilling tower**



Source: Stamicarbon

Fig. 6: **Pilot testing Jet Venturi scrubber**

Source: Stamicarbon

more stringent in some other regions. In that regard, Stamicarbon and EnviroCare International have been working on developing a Jet Venturi (JV) Scrubber for prilling towers with a significant high content of sub-micron particles. This scrubbing technology makes it possible to reach very low emission levels.

JV scrubber design

The technology is suitable for both natural and forced draft prilling towers. The scrubbing unit can be placed on the ground (at grade level) or on top of the prilling tower. The latter is preferred since less ducting is required, which has benefits in terms of capex and leads to no additional pressure drop.

Moreover, by utilising their jet effect, the applied venturis move the off gas through the dust scrubber themselves. The result is that operation of a Jet Venturi scrubber itself does not require any additional fan capacity.

For a forced draft prilling tower, the JV scrubbing units are preferably mounted directly on the air exhaust stacks, with each stack having a dedicated scrubbing unit (Fig. 5). The scrubbing units comprise a few compact stages that progressively treat and clean the off gas from dust and ammonia contamination:

> **"Jet Venturi scrubber plant owners can rest assured that the most stringent environmental regulations are being met.**

- quench scrubbing stage in which coarse urea particulate is removed from the gas stream by spraying recirculating urea solution;
- primary JV stage with multiple venturi elements installed in parallel for removing fine particulate by recirculating concentrated urea solution;
- secondary JV scrubbing stage with multiple venturi elements installed in parallel for removing remaining fine particulate by recirculating diluted urea solution;
- optional acidic scrubbing stage to reduce the ammonia emission.

Pilot

A pilot unit was set up in cooperation with a Stamicarbon client. The idea was to prove the concept by using a single Jet Venturi lay-out, thus to have two Jet Venturi elements in series representing primary and secondary scrubbing stages.

The treated gas was extracted from one of the prilling tower stacks (highlighted in yellow in Fig. 6) and via connecting pipe (highlighted in green) fed to the pilot unit (highlighted in blue).

Conducted tests demonstrated that the expected dust emission from the prilling tower with implemented Jet Venturi scrubber is less than 15 mg/Nm^3, way below the current European emission limit of 50 mg/Nm^3. This technology is also suitable in combination with debottlenecking of existing prilling towers.

Conclusions

The operational results and the small modifications to the DGC scrubber installation have been included into the latest MMV scrubber design. The final emission performance of the MMV scrubber for dust of less than 10 mg/Nm^3 (dry basis) and an opacity of zero percent prove that this technology is very efficient and valuable for a granulation plant meeting the given air permit or environmental regulations.

Based on the real-plant experience with the MicroMist™ Venturi scrubber and the on-site tests conducted with the Jet Venturi scrubber plant owners can rest assured that the most stringent environmental regulations are being met, while decreasing its investment cost. ■

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