NEW TECHNOLOGIES FOR KEY INDUSTRIES

INNOVATING FOR TOMORROW

FEATURED TOPIC: INNOVATING FOR TOMORROW

BRINGING ORDER TO THE NANO COSMOS
Creating carbon nanotubes

SUN’S POWER ON DEMAND
Flexible storage options for solar energy

DRIVING MICRO-MECHANICS
Specialty gases advance the semiconductor industry

LOW-ENERGY OPTION FOR HOT AIR
More efficiency for blast furnaces

UNLOCKING SHALE’S TREASURES
To increase petrochemical feedstocks

FROM FARM TO FORK
Gas technology for the food industry

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Find out more at www.fascinating-gases.com.
Dear Reader,

Sustainable business success hinges on a company’s ability to innovate. Looking beyond success, innovations can also make a valuable contribution to improving future quality of life. However, they don’t just materialise on command. They are the result of painstaking, focused research and development work. Many of the key challenges facing society today – including the need to secure future energy supplies and put low-carbon mobility options in place – can only be mastered by bundling know-how across scientific disciplines. Which is why Linde has placed research and development at the very heart of its business. Framed by our clear strategic and technology focus, our experts are collaborating with world-renowned scientists and institutions in various projects around the world to bring high-tech applications to market maturity.

As one of industry’s key innovation drivers, we are already today working on solutions for tomorrow’s challenges. In nanotechnology, for instance, we recently teamed up with external scientists to develop a process capable of turning carbon nanotubes into a valuable material for the electronics industry. New technologies also play an enabling role in the drive to harness the power of nature. Our specialists are currently working flat out to develop efficient storage solutions based on molten salt with the power to deliver solar energy at night. Across a wide range of applications, our engineers are constantly exploring new and better ways to use gases – actively supporting the development of low-emission combustion engines and the fabrication of high-tech semiconductor materials, for example. You will also find that our proven application and engineering expertise is helping to increase efficiency in the recovery of unconventional raw materials such as natural gas from wet shale.

But you don’t even need to look that far. Our technologies are all around you. This edition’s special feature shows how our gas innovations are shaping the entire food and beverage value chain – from glasshouse cultivation through processing and transport right up to the final consumer.

I hope you enjoy reading this exciting, innovation-packed edition of Linde Technology.

Professor Dr Aldo Belloni
Member of the Executive Board of Linde AG
HIGH-TECH RESEARCH: Laying the foundation for tomorrow’s innovations.

MEDICAL TECHNOLOGY: Pain relief on tap.

STEEL INDUSTRY: Blast furnaces increase efficiency.

BROAD APPLICATION SPECTRUM: Gases in the food and beverage industry.
EDITORIAL

FRESH AIR FOR FARMED FISH
Aquaculture research centre develops oxygen systems

NEWS

BETTER ATMOSPHERE ALL ROUND
When pain relievers vanish into thin air

INNOVATING FOR TOMORROW
Tomorrow’s industries need new technologies and high-strength materials. Linde’s engineers are developing innovative solutions for many key manufacturing processes, thus laying the foundation for their future success.

BRINGING ORDER TO THE NANO COSMOS
Research: Engineering carbon nanotubes for electronics applications

ONE IN A MILLION
Mobility: Calibration gas mixtures detect pollutants – even in the lowest concentrations

SOLAR POWER ON DEMAND
Energy: Storage technologies based on salt are increasing the flexibility of solar power

DRIVING MICRO-MECHANICS
Electronics: Specialty gases and process technologies are advancing the semiconductor industry

INTERVIEW: “PUSHING THE BOUNDARIES OF INNOVATION”
Sven Gudor, Executive Manager Research and Technology, Sasol

LOW-ENERGY OPTION FOR COMBUSTION AIR
Blast furnaces – more efficient, less emissions

FULL STEAM AHEAD
Making natural gas fit for LNG carrier engines

INDISPENSABLE FOR FOOD AND DRINKS
Gas technology extending along the entire value chain

FROM FARM TO FORK
Broad variety of food-grade gases

COLD BLAST FOR BACTERIA
Cryogenic treatment for poultry

UNLOCKING THE TREASURE IN SHALE
Efficiently producing feedstocks for the petrochemical industry

GASES UNDER CONTROL
Greater safety and comfort in welding

THE PRESSURE IS ON
Boosting H₂ infrastructure efficiency

COLD PATH TO THE TOP
Cryochamber for elite athletes
Aquaculture research centre develops oxygen systems

FRESH AIR FOR FARMED FISH
Salmon are moving onshore – or at least the farmed variety are. Demand for fish is rising worldwide and natural stocks alone have long been insufficient to meet it. Consumption has doubled in the last 50 years – and will continue to grow along with the global population. Since open-water facilities have a number of disadvantages, including increased exposure to extreme weather conditions and higher food consumption, the trend is shifting towards onshore farms. Oxygen is by far the most important resource for these operations. At least 80 percent oxygen saturation in the water is a must. If the concentration falls below this, the fish cannot absorb enough nutrients from their food, they grow more slowly and become more susceptible to disease. To ensure cost- and energy-efficient oxygen supplies, even to large-scale facilities, experts at Linde’s innovation centre for aquaculture and water treatment in Ålesund, Norway, have developed the SOLVOX® OxyStream system. This releases a low-pressure stream of tiny bubbles into the water, enabling precise, energy-efficient adjustment of oxygen levels and its distribution throughout the tank.

LINK:
www.was.org
NEWS

AEROSPACE:
CALIBRATION GASES FOR ISS

The astronauts on board the International Space Station (ISS) spend much of their time conducting experiments under zero-gravity conditions. Not only does the ISS record physical and astronomical measurements, it also runs medical tests on the astronauts while they orbit the earth. Linde supports Danish Aerospace Company (DAC), a leader in the field of medical instrumentation for space applications, by supplying ECOCYL® specialty gas cylinders for DAC’s Portable Pulmonary Functional System. The medical instruments developed by DAC must be calibrated regularly to ensure accurate measurement of physiological parameters such as the astronauts’ respiratory function and fitness during flight. “We are delighted that ECOCYL® has not only been approved, but that it was selected from a strong list of contenders in the first place,” said Stephen Harrison, Global Head of Specialty Gases and Specialty Equipment at Linde. The aerospace industry sets extremely high standards not only for gas and mixture purities, but also for the actual gas cylinders. As space is at a premium on ISS, compact, lightweight design is also a must – and ECOCYL® excels on that front. The cylinders will soon get a chance to prove their value as they will be heading for ISS in an Ariane 5 rocket that will blast off from the European spaceport in Kourou, French Guiana, in summer 2014.

PETROCHEMICALS:
PARTNERSHIP FOR CONSTRUCTION OF ETHANE CRACKERS

Linde AG has signed an Enterprise Framework Agreement (EFA) with Shell Global Solutions International BV to build ethane cracking units on a global basis. The EFA is for ten years, with an option to be extended. The EFA covers licensing, engineering, procurement and construction services, as well as the supply of proprietary equipment for ethane cracking units. Under the agreement, Linde has already entered the Front End Engineering and Design (FEED) phase for a world-scale ethane cracker that Shell is currently evaluating.
LIQUEFIED NATURAL GAS:
NEW LNG REFUELLING STATION IN THE UK
Powered by LNG: Linde has delivered a new liquefied natural gas refuelling station to the British supermarket chain Asda. The new station has been installed at the chill distribution centre run by Asda Logistics Services (ALS) near Bristol. Thanks to the latest ‘zero loss’ technology that ‘temperature-conditions’ the gas prior to dispensing, no fuel is lost during refuelling at the ALS centre. The LNG station fuels 50 dual-fuel (LNG and diesel) Volvo delivery trucks for Asda. These vehicles typically run on LNG 60 percent of the time. “We are proud to be working with Asda on this environmentally friendly alternative to diesel,” said Mark Lowe, LNG Business Manager at BOC, a member of The Linde Group. With this partnership, Linde is making an active contribution to the transition to low-carbon transport. The switch to the dual LNG/diesel fuel technology was extremely smooth. “Alternative fuels are an important part of our green agenda,” commented Corinne Murphy, National Fleet Manager for ALS. “Working with BOC and Volvo will help us deliver our ten percent absolute carbon footprint reduction by 2015.”

HEALTHCARE:
FUND FOR RESPIRATORY MEDICINE
With its REAlfund initiative, Linde is supporting innovative developments in the therapeutic use of gases in medicine. The fund is aimed at anyone who specialises in the field of respiratory care, including doctors, technicians and caregivers. The fund will support researchers working on the advancement of respiratory medicine and thus help to improve the care and quality of life of patients. As part of its REAlfund commitment, Linde will provide funding of up to EUR 75,000 for individual projects extending along the entire care continuum.

HYDROGEN:
PROJECT WINS IN EUROPE
CONVERSION OF HEAVY OIL RESIDUE
Linde will deliver two hydrogen plants for Russian oil refiner PSC TAIF-NK by the end of 2015. The new plants at Nizhnekamsk, Republic of Tatarstan, Russian Federation, will each have a capacity of around 110,000 normal cubic metres per hour and will supply high purity hydrogen to the heavy oil residues conversion complex at the site. Linde will be responsible for basic and detail engineering, procurement and supply of equipment and materials. The contract is worth around EUR 120 million. “We are delighted to have this opportunity to cooperate with PSC TAIF-NK,” said Professor Dr Aldo Belloni, Member of the Executive Board of Linde AG. “We are confident that this agreement will lead to further key contracts for our gases and engineering business in this important Eastern European growth market.”

NEW STEAM REFORMER PLANT IN HAMBURG-HARBURG
Linde has signed a long-term contract to supply hydrogen to Nynas AB, one of the world leaders in naphthenic specialty oils (NSPs) and bitumen. This involves Linde building a new steam reformer plant in Hamburg-Harburg to the value of around EUR 30 million. The H₂ facility is scheduled to go on stream in the fourth quarter of 2015 and will have a capacity of 400,000 cubic metres of hydrogen per day. This will help Nynas increase its overall NSP production capacity by 40 percent.
Easing acute pain: Doctors advise inhaling a nitrous oxide/oxygen mixture for effective short-term pain relief.
When pain relievers vanish into thin air

BETTER ATMOSPHERE ALL ROUND

Whether in accident and emergency or the delivery room – just a few breaths of a nitrous oxide/oxygen medical gas mixture can calm patients and relieve pain. However, the use of nitrous oxide in everyday clinical settings is subject to workplace exposure limits designed to protect doctors, nursing staff and other healthcare professionals from excessive concentrations in the surrounding air. With this in mind, a team from Linde Healthcare and Linde’s Engineering Division has developed a new mobile device to dispose of this gas.

Sometimes, a mother has hardly been admitted before baby’s firstcries reverberate through the hospital corridors. More usually, though, childbirth takes several hours. The recurring contractions can take their toll on mothers-to-be, draining them of strength they could well do with later on in the process. That is why many maternity specialists favour the use of pain relief. Alongside narcotics and epidurals, there is another option: inhalable analgesics. “Over 70 percent of expectant mothers in the UK use the Linde medical gas mixture – consisting of nitrous oxide and oxygen – during labour,” reports Sybille Petersohn, Global Business Manager Analgesia at Linde Healthcare. And other European countries, too, are increasingly turning to Linde’s gas mixture in maternity care.

The gas mixture consists of 50 percent nitrous oxide (N₂O) and 50 percent oxygen. The pain-relieving properties of nitrous oxide were first identified in 1799 by the chemist Humphry Davy. In 1844 the American dentist Horace Wells used it to dull pain during tooth extractions. The gas mixture is also used successfully in emergency medicine and paediatrics, in procedures as diverse as colonoscopy, wound suturing and drawing blood (venipuncture). “Inhaling the nitrous oxide/oxygen mixture can effectively ease pain – and it wears off completely within thirty minutes,” states Petersohn. Although patients only usually inhale the nitrous oxide/oxygen mixture for short periods, doctors and hospital staff are exposed to the gas for longer. Since prolonged application of N₂O can result in side effects such as changes in blood values, guidelines are in place (as for all other anaesthetic gases) that specify the maximum gas concentration. Another factor is that nitrous oxide is a greenhouse gas. “However, the amount of nitrous oxide released during medical procedures is so negligible that it really cannot be associated with climate change,” cautions Dr Wolfgang Schmehl, Innovation and Development Manager at Linde Healthcare. Larger amounts of N₂O with a greater impact on the environment are emitted by agricultural operations, road traffic, and coal and gas-fired power plants.

Stepping up actively to health and environmental responsibilities, Schmehl and his team from Linde Healthcare worked with colleagues from Linde’s Engineering Division to devise a solution that would remove as much nitrous oxide as possible following exhalation by a patient. The resulting medical technology has been deployed in hospitals since the start of 2012 in countries including Sweden, the Netherlands and Germany. Called EXCIDIO®, the Linde development enables safe and climate-friendly scavenging of N₂O. In simplified terms, it consists of equipment located downstream of the ready-to-use nitrous oxide/oxygen mixture preparation
DIGITAL AGE DAWNS FOR MOBILE GAS CYLINDERS

An emergency calls for absolute concentration by doctors and paramedics – there is no margin for error. “To improve operation of mobile oxygen cylinders, we have now replaced the mechanical pressure gauge (manometer) with a digital display and added other helpful functions,” reports Helmut Franz, Global Business Manager Medical Gas Packaging at Linde Healthcare. LIV® IQ tells the operator at a glance how much gas is left in the cylinder and how much longer the oxygen will last. It also constantly compares the oxygen flow actually reaching the patient with the set flow rate. If the flow is blocked, a visual and acoustic alert warns emergency staff, who can take immediate action. And if the oxygen level in the cylinder falls below a certain threshold, LIV® IQ also emits visual and acoustic warning signals. “These innovations all help to improve the quality of patient care while bringing the benefits of safe, mobile oxygen delivery to daily clinical workflows,” concludes Franz.

that directly disposes of the exhaled nitrous oxide. As before, the patient inhales the pain-relieving gas mixture through a tube connected to a respiratory mask over their nose and mouth. “But now, a special device attached to the tube diverts the air they breathe out into a collection tank, thus preventing the gas from escaping into the surrounding air,” Schmehl explains. From this tank, the N₂O is then sucked into the newly developed system and catalytically converted. “Following this nitrous oxide conversion, our EXCIDIO® equipment only releases the harmless reaction products nitrogen and oxygen,” outlines Schmehl. In other words, the nitrous oxide evaporates into thin air.

The requirements for the new disposal system were clearly defined, if ambitious: “We needed a mobile device for use in day-to-day clinical settings that would break down the nitrous oxide as completely as possible without undesirable by-products. We also wanted a device that could be deployed in direct proximity to patients,” specifies Schmehl. The team knew from the outset that N₂O could be converted into nitrogen and oxygen by means of special catalysts. “What we had to find out was which materials would be most suitable and how we could manage the high temperatures required,” Schmehl explains. The catalytic reaction only reaches optimum efficiency above 350 degrees Celsius, and peak temperatures inside the EXCIDIO® system actually exceed 500 degrees during normal operation. “Breaking down nitrous oxide involves an exothermic reaction, which releases a lot of energy in the form of heat,” describes Dr Ulrike Wenning, a chemist in Research and Development at Linde Engineering. Along with her colleagues, Wenning systematically tried out suitable catalysts and ran a series of tests on potential candidates to investigate their reaction behaviour.

Ideally suited to daily clinical workflows

“We also tested, varied and optimised other components such as heat exchangers, gas preheaters and suction systems,” adds Dr Karl-Heinz Hofmann from Linde Engineering. The Linde experts are not allowed to share more detailed information about aspects such as insulation, however, as patents have already been filed for the newly developed materials. As a chemical engineer, Hofmann was also responsible for process simulation. A pilot facility constructed and operated on the Linde Engineering site in Pullach, near Munich, provided the basis for his various computational models. “We deliberately decided to use larger dimensions when building the prototype – making it roughly the size of a cupboard,” reveals Hofmann, the intention being to ensure all components were flex-
Experts at Linde have developed the mobile EXCIDIO® device to convert the inhalable analgesic nitrous oxide/oxygen mixture as completely as possible into nitrogen and oxygen following exhalation by the patient. Tailored to everyday clinical requirements, EXCIDIO® can be used in direct proximity to patients.

**LATEST MEDICAL TECHNOLOGY FOR BEDSIDE CARE**

Hot innovation: EXCIDIO® converts a gas volume of seven cubic metres per hour, with temperatures inside exceeding 500 degrees Celsius.

Treatment: The patient inhales the nitrous oxide/oxygen mixture through a respiratory mask over their nose and mouth – and exhales it into a collection tank.

Conversion: The nitrous oxide is catalytically converted into nitrogen (blue) and oxygen (red).

EXCIDIO® can process a gas volume of seven cubic metres per hour.

Thermal efficiency was a particular priority for the Linde experts when developing EXCIDIO®. Outlining the particular requirements for practical deployment of the N₂O conversion equipment, Hofmann says: “While we usually have more time to start up larger systems, daily clinical routines mean it all needs to be up and running in less than an hour.” The EXCIDIO® project has already demonstrated how effectively medical know-how and engineering expertise can enrich each other at The Linde Group. In clinical practice the use of the pain-relieving nitrous oxide/oxygen mixture has become even easier and safer.

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Tomorrow’s industry will face a number of challenges – including the need to increase energy efficiency, conserve natural resources, network a digital world and engineer new materials. Innovative solutions from Linde will help provide the answers.

**RESEARCH**
Nanotubes are taking off in the world of high-tech electronics. Linde experts have developed a new process to disentangle the nanotubes and maximise their performance.

**MOBILITY**
Combustion engines have to get cleaner. Calibration gas mixtures from Linde help test institutes detect even the lowest concentrations of exhaust gas impurities.
Energy
Demand for solar power doesn’t stop when the sun goes down. Working with partners, Linde has developed a new salt-based system to store the sun’s energy efficiently.

Electronics
Intelligent microsystems are networking real and virtual worlds. Specialty gases from Linde are helping to fabricate the ultra-fine semiconductor structures needed for this.

Around the world, engineers in research and key industries such as energy, automotive and electronics face huge challenges. But these challenges also represent opportunities for companies that can provide the right answers. Success factors include the ability to recognise trends early and develop a focused strategy. But the true key to success lies in a company’s power to innovate. In most cases, innovations are the result of focused teamwork in the R&D departments of larger enterprises. Alliances with universities and scientific institutes can also help inspire ideas and create fresh momentum for new technologies or materials. Cross-disciplinary teamwork is essential to bring new product and application ideas to market maturity. Linde specialists have been working with external experts, for instance, to develop a process that turns carbon nanotubes into a valuable material for the electronics industry. Ultra-pure specialty gases from Linde are indispensable in certain semiconductor fabrication steps. Our gas and process know-how is just as valued in the automotive industry, where it helps to measure exhaust gas emissions. Our engineers are also helping to advance the energy sector, creating innovative solutions for the industry of tomorrow.
Innovative process to enable carbon nanotube electronics

BRINGING ORDER TO THE NANO COSMOS

Carbon nanotubes (CNTs) are heralded as a next-generation wonder material – especially for electronic components. Yet CNTs are rarely used in electronics because even the best commercially available bulk CNT materials fall far short of achieving this ideal performance. Linde materials experts in California, however, have now made a technological breakthrough that could enable carbon nanotubes to achieve their potential in a wide range of applications.

The high-tech world is shrinking. Electronic components and complex circuits are moving closer together in devices such as mobile phones, cameras and tablets. Flatpanel displays are also becoming thinner, and less expensive despite incorporating additional functionality such as touch sensing. The trend toward smaller, faster, smarter yet cheaper electronics relies on the development of a new generation of low-cost, high-performance electronic materials. The material currently used to make transparent electro-conductive films in displays, indium tin oxide (ITO), is expensive and incompatible with some of the newer display manufacturing processes. Carbon nanotubes (CNTs) offer the ideal alternative. The measured electrical and mechanical properties of individual carbon nanotube molecules are indeed truly extraordinary. The walls of these tubes consist of carbon atoms arranged in a hexagonal, honeycomb-like lattice, a structure that makes the microscopic material extremely strong. CNTs are thought to be the strongest material in the world and are already being used to strengthen plastic components for wind turbine rotors and extreme sports equipment. These “miracle” tubes also conduct electricity and heat better than any other material, giving them the potential to revolutionise the electronics industry. “CNTs could significantly improve the properties of transparent conductive films (TCFs) used in displays and solar cells,” explains Kevin McKeigue, Head of Nanotechnology in Linde’s Clean Energy and Innovation Management department. He and his colleagues are therefore keen to make the tiny carbon heavyweights fit for electronic components.

CNTs are rarely used in the electronics industry because commercially available CNT materials are not in a form that allows their extraordinary properties to be fully exploited. Scientists and engineers at Linde’s facility in San Marcos, California, are therefore concentrating their efforts on transforming these commercial CNTs into a useful form. “Nanotubes can be produced by several methods including by vapourising carbon using an electric arc. This in itself is a relatively simple process,” explains McKeigue. It’s the next step that presents a challenge. “Once they have been created, the nanotubes have to be disentangled to achieve their maximum performance in most applications.” For some applications, the CNTs also need to be sorted strictly according to type. Both of these processes are difficult to achieve in practice. A quick look through a scanning electron microscope reveals that the fine
Magical tiny tubes: Nanotubes consist of carbon atoms arranged in a hexagonal lattice. Their special properties hold huge potential for many high-tech sectors.
strands of single-walled nanotubes are bundled together like the fibres of a rope and those ropes are tangled together in an unruly mass that looks somewhat like a plate of spaghetti.

CNTs in this form do not yield the high-performance TCFs required by TVs, laptops and smartphones. To achieve good TCF performance, the CNTs need to be unbundled, dispersed in a solution and then deposited as a uniform thin film on the display panel. The conventional approach to CNT dispersion involves placing the nanotubes in a surfactant solution and using ultrasonic energy to essentially rip the CNT bundles apart. The drawback to this process is that high-power sonication can severely damage single-wall nanotube structures and also break them apart, reducing their length. “This has a negative impact on the electrical properties of TCFs produced using this process,” details Siân Fogden, Manager for Market and Technology Development at Linde Nanomaterials. “The shorter the tubes, the lower the overall conductivity of the film, and this compromises the quality of the resulting product,” she continues.

Sorting the CNTs according to their different properties is an even greater challenge. “Some of the nanotubes have metallic properties and some have semiconducting properties,” continues McKeigue.

Each type is suited to different applications. The semiconducting CNTs could, for example, be used to make thin-film photovoltaic cells for solar power. Although different methods for separating carbon nanotubes exist, none of them are suitable for industrial-scale production. An enrichment process involves first dispersing the CNTs, again typically using high-energy ultrasound. The different types of CNTs can then be separated using an ultracentrifuge. Unfortunately, the yield from such processes is very low – less than one percent of the CNTs make it into the final product – and even those that survive can be damaged from the sonication process.

New electrostatic method
And so Linde technologists faced a number of hurdles in their search for a way to transform commercially available CNTs into high-performance electronic materials that could be ramped up to industrial scale. Now, in collaboration with University College London (UCL), Imperial College (IC) and the Centre national de la recherche scientifique (CNRS) Bordeaux, the nano experts have come up with a reliable method for disentangling, separating and dissolving the carbon tubes. McKeigue, who acts as a “talent scout” for new technologies at...
Linde, first started working with UCL/IC researchers on this problem back in 2009. This collaboration between academic researchers and industry experts is starting to pay off. The new method is known as salt-enhanced electrostatic repulsion (SEER) and can be used to both disentangle bundles of single-walled carbon nanotubes and sort them according to their electronic properties. Liquid ammonia plays an enabling role in this innovative process – a chemical with which Linde engineers have many years of experience. Placed in an ammonia-based solution, the nanotubes are reduced and become negatively charged. Electrostatic repulsions between the charged tubes cause them to disentangle and spontaneously dissolve into the liquid ammonia as individual nanotubes. Following the removal of the liquid ammonia and the addition of an organic solvent to the nanotube salt, a solution of individual CNTs is formed which is an ideal ink to use to print high-performance TCFs.

Uniform nanotube length

Scalability is one of the major benefits of this process. “Unlike other dispersion and separation technologies, SEER can be scaled up to any size without any drawbacks,” elaborates Graham McFarlane, Head of Linde Nanomaterials. The new method is streets ahead of other approaches. “With our process, the average length of carbon nanotubes in the solutions is 20 micrometres – and this figure doesn’t change,” clarifies Fogden. “The sonication used in other methods breaks the tubes, significantly shortening them, in some cases down to one or two micrometres,” she continues. And this has a negative impact on their properties. The scientists now want to go a step further and improve the “individualisation” of tubes in the resulting TCFs. In other words, they intend to make the tube bundles even thinner. “Ideally, only individual CNTs would remain at the end of the deposition process. This would maximise the transparency of the film while retaining the required conductivity,” adds McFarlane.

Yet the nanotubes still have to meet the extremely strict standards required by screen manufacturers. “The conductive films must have a minimum transparency of 90 percent and a maximum sheet resistance of 100 Ohms,” details McFarlane. Linde’s nano experts have already achieved this threshold and hope to better it.

This would open up the interesting option of replacing indium tin oxide, an expensive semiconductive mixed oxide. Nanochemist Prof. Karl S. Coleman of Durham University also sees potential applications in electronic sensors and batteries. “If we can achieve our purity targets for separated semiconducting and metallic CNTs, we would be looking at a raft of further applications,” says McKeigue.

**LINKS:**

www.london-nano.com  
www.cnrs.fr
Accurate exhaust measurements for cleaner mobility

ONE IN A MILLION

Strict emissions thresholds are prompting the automotive industry to develop cleaner engines. Automotive lab tests use highly sensitive instruments to measure even the slightest traces of pollutants. To ensure that these instruments deliver accurate results, however, they have to be calibrated using extremely precise gas mixtures. Linde offers a vast selection of calibration mixtures for a wide range of pollutants. One of these has even made its way into the Guinness Book of Records.

There are around one billion cars in the world today. And each one needs fuel. Vehicle engines guzzle billions of tonnes of petrol and diesel, releasing a range of combustion residues. Many of these pollutants can cause respiratory problems. Some are even carcinogenic. Modern catalysts and soot filters have enabled car manufacturers to make vehicles cleaner. However, global emissions thresholds are set to fall further. In the European Union, for example, the new Euro 6 standard will bring the ceiling for emissions even lower in 2014. The nitrogen oxide threshold for petrol engines will be capped at 60 milligrams per kilometre, down significantly on the 150 milligrams permitted at the start of 2000.

This makes it increasingly difficult for car manufacturers and emissions testing bodies to accurately measure the dwindling concentrations of pollutants in exhaust gases. “We are talking about detecting just a few pollutant particles in one million parts of air,” explains Michael Hayes, Head of Environmental & Calibration Gases at Linde US. “Measuring a few parts per million or parts per billion is like looking for a needle in a haystack,” adds the Linde expert. An analytical instrument has to be extremely precise and – even more importantly – perfectly calibrated to accurately measure whether an engine is clean enough to comply with the requisite thresholds. Test institutes, carmakers and even manufacturers of sensor chips also calibrate their equipment using standardised gas mixtures dosed to exact specifications. Linde has been delivering these kinds of mixtures under the brand SPECTRA® for many years now in specialty gas cylinders ranging in size from portable solutions to six-foot cylinders. The company Bosch, for example, uses Linde gases to test its exhaust sensors before they are installed in cars. “We need highly precise mixtures for our sensor tests so that we can simulate the exact exhaust emissions produced by petrol and diesel vehicles,” says Vaclav Pixa, Technical Plant Manager at Bosch in the Czech Republic. “Business continuity for our labs hinges on a continuous, reliable supply of these specialty gases,” adds Pixa.

The stricter emissions standards presented Linde with new challenges. Instruments that measure concentrations in parts per million (ppm) require precisely prepared calibration gases. “Our gas mixtures must be suitable for analysing samples with ppm accuracy, but also for detecting several different substances,” explains Hayes. These include emissions such as nitrogen oxides and highly volatile hydrocarbons known as volatile organic compounds (VOCs). “So we need to mix a range of gases with ppm detection capabilities. We have been refining our mixing procedure for several years now,” continues the Linde expert. Hayes and his colleagues had to focus in particular on the effects of water and oxygen molecules as they immediately chemically react with some calibration gases and would quickly render a mixture unusable. In their new process, water molecules are expelled by heating the cylinders in a multi-step process. Any remaining oxygen molecules are...

“MOBILITY

“We need highly precise specialty gas mixtures for the sensor tests to simulate vehicle emissions.”

Vaclav Pixa, Bosch
removed using a vacuum pump. The specialty gases experts also had to choose the right cylinder lining to ensure that no gas molecules would attach to the surface or react with the material. “We had to continually assess our equipment and test every step to ensure we were filling the exact gas volumes every time,” says Hayes.

Filling over 100 substances with ppm accuracy

Petrol and diesel are almost entirely made up of volatile organic compounds. In a car engine, these are combusted to other compounds such as carbon dioxide. However, in the first five minutes after a vehicle has been started, the engine is still cold and cannot burn all of its fuel. Dozens of different pollutants are released in these five minutes, including a lot of VOCs. This is particularly dangerous because many VOCs are carcinogenic. Previously, these compounds were grouped together in emissions testing under one value known as the total amount of hydrocarbons. “The stricter emissions standards now stipulate that values for certain VOCs have to be listed separately,” continues Hayes. As a result, the calibration gas cylinders from Linde’s labs not only contain nitrogen oxides but also carbon dioxide and a wide range of VOCs. The record for the number of different chemical substances in one cylinder currently stands at 110, and each one has a concentration of exactly one ppm less any preparation and analytical uncertainty. It takes two days to fill a cylinder with multiple components to this degree of accuracy. This approach has earned Hayes a lot of respect from his peers and Linde an entry in the Guinness Book of Records. “These are the kinds of precise, complex measurement standards that you would normally only find at state-run calibration and testing institutes such as Germany’s Federal Institute for Materials Research and Testing,” confirms Stephen Harrison, Global Head of Specialty Gases & Specialty Equipment at Linde. “Our SPECTRA® VOC calibration gas mixture under our HiQ® brand places us one step ahead. No other institute can create a calibration gas mixture with this many VOCs and other pollutants to this level of accuracy,” adds Harrison. The team’s success confirms Harrison’s statement – Linde’s lab was the first one worldwide to be accredited to the international standard ISO 17025 for measuring equipment used to detect VOCs.

And the future certainly seems bright for this Linde development. It can also be used to detect other pollutants, for example those generated during the combustion of the eco-friendly biofuel ethanol. Formaldehyde is a prime example here. As ethanol becomes more widely used, this carcinogen is set to become an increasingly important risk factor. In the US, for example, the measurement of formaldehyde levels is already stipulated by health regulation CFR 1065. Ammonia is another case in point. It is used in modern Diesel vehicles to neutralise nitrogen oxide in emissions. If an engine is not working properly, the ammonia can get into exhaust fumes and subsequently the surrounding air. Moving forward, emissions thresholds are set to fall further, making testers’ jobs even more challenging. In the US, for example, environmental regulations already stipulate the measurement of further greenhouse gases such as nitrous oxide. With exact calibration gas mixtures from Linde, however, even these challenges can be easily mastered.

**LINK:**

www.dieselnet.com
Solar goes flexible: Storing heat with molten salt

SOLAR POWER ON DEMAND

Solar power plants do not produce power at night or during bad weather. Demand for renewable energy does not sleep, however. Industry needs new technologies to store solar energy efficiently. One possible answer is latent heat storage solutions based on salt. Linde is working with the German Aerospace Centre (DLR) to advance and establish this technology – and to open it up to other industrial applications.

These sun worshipers have no time for sunscreen. The silver sea of parabolic mirrors reaches up lazily towards the burning sun, catching as many rays as they possibly can. Every year, the sun beams 1.5 sextillion (10 to the power of 21) kilowatt-hours of sunshine down to the earth. The technologies already available today are capable of meeting 380 percent of the world’s energy needs through solar power.

The parabolic mirrors are designed to automatically follow the sun in order to capture as much energy as possible. Shaped like a trough, the curved surfaces concentrate sunlight onto a receiver tube located at the focus of the parabolic mirrors. “A heat transfer fluid flows through these receivers, absorbing the heat from the sun and transferring it from the solar field to the power plant,” explains Stefan Hübner, Project Manager Energy Production and Storage at Linde’s Clean Energy and Innovation Management unit. “The energy stored in the medium can then be used to create power – as long as the sun stays shining at least.”

As soon as the sun sets, radiation ceases and the solar power plant can no longer supply energy. Unless, of course, it stored up excess energy during the day. “With a storage solution, regenerative energy would also be available during the night,” adds Hübner. Working with his colleagues at Linde Group member Bertrams Heatec, Hübner is exploring ways to make solar power more flexible. One of the projects he is working on with DLR is called Direct Steam Generation Store (DSG Store). This involves developing a totally new generation of thermal storage solutions for solar thermal power plants. As Hübner explains: “We hope to gain valuable insights into the potential of this technology for other industrial applications. It could be used for instance to capture process off-heat.”

The heat transfer fluid plays a defining role in the efficiency of solar storage systems. In existing parabolic solar power plants, thermal oil typically flows through the receivers. It is heated to around 390 degrees Celsius as it passes through the solar field. In a second step, the thermal oil heats water, producing steam that drives a turbine to generate electricity. The downside of this oil is that it degrades at temperatures in excess of 400 degrees Celsius. Linde and DLR want to overcome this challenge by replacing oil with water as the direct working medium. As project manager Markus Eck from the DLR Institute for Solar Research explains, water has a number of advantages: “If we supply water under a pressure of up to 120 bar, we can produce superheated steam at a temperature in excess of 500 degrees Celsius.” This would significantly increase the process temperature of the power plant and thus boost efficiency levels. Direct solar steam generation calls for specially adapted storage technologies, however.

Molten salt, for instance, is a suitable medium to store and transfer such heat. “Solar salt – currently the salt mixture of
Rich energy harvest: Parabolic mirrors capture the sun’s rays and concentrate them onto receiver tubes. A heat transfer fluid circulates in these tubes, conveying the sun’s energy to the heat storage system or the power plant.
choice – consists of potassium and sodium nitrate,” explains Markus Weikl, Product Manager at Bertrams Heatec in Switzerland. Both solar salt components must be extremely pure as contaminants such as chloride could result in pipeline corrosion. State of the art solar thermal power plants working with thermal oil use this solar salt to store sensible heat. “Sensible refers to the fact that energy accumulates as the temperature of the storage medium increases,” explains Weikl. Two large tanks hold the molten salt mixtures at different temperature levels. Collectively, the tanks store more than 30,000 tonnes of salt. During the day, the molten salt is pumped from the “cold” tank (290 degrees Celsius) to a heat exchanger, where it absorbs energy from the thermal oil that has been heated by the sun to reach a temperature of around 380 degrees Celsius. During the night, the salts are fed back to the colder tank. Heat exchangers extract the stored energy and feed it to the power plant to generate electricity.

As part of the DSG Store project, Linde and DLR are exploring a different avenue. They are looking to generate steam directly in the solar field and combine this with a latent heat storage system. This approach combines the advantages of high steam temperature, and thus process efficiency, with the benefits of an easy-to-use heat transfer fluid that would not require costly anti-freeze protection. “But even direct steam generation calls for specially adapted storage technologies in order to efficiently store the huge volume of energy contained in the steam,” explains DLR expert Eck. Latent heat is “hidden” energy, which means that energy is accumulated as the storage medium changes phase – from solid to liquid for instance. In other words, it is invisible to a thermometer. Special nitrate salts can act as latent heat stores – which is why they are at the heart of the Linde/DLR cooperation. The storage systems consist of a salt tank fitted with long tubes through which the steam can flow. The exterior of the tubes feature fine aluminium fins. “The

CAPTURING THE SUN’S HEAT

The direct evaporation effect of the sun’s heat uses water as the transfer medium. It flows through receiver tubes, onto which the sunlight is concentrated by means of parabolic mirrors. The sun heats the water up to create superhot steam. Steam turbines and generators turn the energy captured in that steam into electricity. To make solar power available at night, the energy from the superheated steam is collected in several heat storage systems. First, molten salt is used to store the sensible heat via heat exchangers (hot tank). Then the latent heat store, connected to a storage buffer, captures the evaporation heat (intermediate tank). The molten salt which is not charged with heat is stored in the cold tank.
fins allow the steam to transfer its thermal energy most effectively to the salt store,” elaborates Eck. This design increases the effectiveness of the heat transfer process by several orders of magnitude. “The molten salt has to freeze in order to release the energy so it can be used,” continues the DLR expert. The system works in a similar way to reusable hand-warmers based on crystallisation. In the case of solar thermal power plants, the sun heats up the crystallised salts by means of steam. This melts the salt mass. If the energy is subsequently withdrawn, the salt recrystallises and can be powered up with heat from the sun again. The advantage of latent heat storage systems is that they can capture the hidden energy contained in the steam itself – also known as the enthalpy of vaporisation. According to Hübner: “Over 60 percent of the energy absorbed from the sun is concentrated in the phase change from boiling water to saturated steam. And the only way to efficiently capture this energy is with latent salt storage systems.”

But these thermal hotbeds could be of interest to many applications beyond solar power plants. “Latent heat storage systems also offer great potential for conventional power plants, which also work with steam and heat. This technology would be ideal, for instance, for an industrial power plant that might want to separate the delivery of power and heat,” continues the Linde engineer. In addition, many industrial processes generate off-heat. This could be captured with salts and reused.

The experts at Linde, Bertrams Heatec and DLR are already looking beyond the DSG Store project at their next challenge. “Now that DLR has shown that the system works in laboratory tests and a demonstration project, we are keen to further optimise both individual components and the concept overall,” reveals Hübner. This will include computer simulations to optimise the heat transfer process, the development of industrial manufacturing blueprints for the latent heat storage system and the construction of a test module. Linde’s Innovation Management team will be coordinating the project. As Hübner points out: “The bundled know-how of Bertrams Heatec and Linde Engineering means we can rely on the best possible support – covering everything from heat transfer and process blueprinting through tank design to industrial-scale fabrication of tubes equipped with aluminium fins. The depth of Linde’s synergised know-how across the Group never ceases to amaze me.” Hübner is understandably enthusiastic – he is currently working on his PhD and this is his area of specialisation. At the end of 2013, the interdisciplinary team bringing together research and industry received a vote of confidence. “In December, we were awarded funding from the Germany Ministry for the Environment, Nature Conservation, Building and Nuclear Safety – so now we can really press ahead,” enthuses Hübner. The experts are now working flat out on the advancement of this new thermal storage system and alignment of the process technology with the concrete needs of solar power plants. Their ultimate aim is to make sure that solar power can flow at any time of the day or night.

LINK:
www.dlr.de/en
Ultra-clean rooms for electro-mechanical marvels: The delicate microstructures require precise etching with specialty gases.
**Specialty gases for the semiconductor industry**

**DRIVING MICRO-MECHANICS**

From driverless cars to smart logistics flows, machine to machine communication (M2M) is playing an increasingly important role in all walks of life. It relies on microsystems embedded, for instance, in vehicles and smartphones. Micro-mechanics now has the potential to trigger the next leap forward in the semiconductor industry – driven by the specialty gas xenon difluoride and process technology from Linde and its strategic partner Pelchem.

In the aftermath of a serious road accident, every second can make the difference between life and death. This is where an on-board electronics system comes into play: the automatic emergency call system “eCall” will be able to notify the emergency services or traffic control centre within seconds of an accident occurring. This electronic life-saver has already been installed in many luxury models, and it will become mandatory in all new cars in the EU from October 2015. Micro-electro-mechanical systems, or MEMS, is the name of the technology behind these M2M interaction sensors.

“Similar micro-sensors have been a feature of passenger cars for many years now. They measure the level of acceleration on impact, for example, and then safely deploy the vehicle’s airbag,” explains Greg Shuttleworth, Global Product Manager Specialty Gases at Linde Electronics. Now experts are predicting that demand for this technology will explode, not only making cars safer, but also opening up a host of new opportunities in many sectors of industry. Possibilities range from a health diagnostic laboratory on a microchip through ultra-efficient logistics flows to the Internet of Things.

To extend the reach of MEMS technology, the industry not only needs new standards and guidelines, but also improved manufacturing processes. Today’s micro-electro-mechanical systems can consist of up to 20 different elements, and are commonly manufactured using silicon or gallium arsenide substrate. Working with these semiconductor materials requires specialised know-how in order to fabricate such sophisticated, high-tech components. These systems are marvels of electro-mechanical engineering: on a surface area of well under one square micrometre, tiny springs are tensioned, beams move, weights work and gear wheels engage.

Specialty gases are the etchant of choice.” This is a result of the microsystems becoming ever smaller and more complex, so much higher precision is now required in the production process. Weisheit continues: “We have got to the stage where these ultrafine structures can only be created with specialty gases.” In order to etch a movable rotary sensor on a surface made of silicon oxide for example, the specialty gas anhydrous hydrogen fluoride (HF) is needed. However, it takes multiple deposition, etching and doping steps to fully fabricate the fine microstructures. “This

“Specialty gases have no surface tension or static friction, making them ideal for MEMS production.”

Dr Petro Terblanche, Pelchem
works in a similar way to semiconductor fabrication,” says Shuttleworth. Many of the big semiconductor manufacturers are already producing MEMS devices.

**Not every etching gas is suitable for every material**

“The quality requirements placed on the production resources – and hence on the etchants – are very demanding and will become even more so as the systems shrink in size and rely on different materials,” explains Weisheit. Together with his team, he is working on ways to optimise Linde’s specialty gases for the requirements of the electronics industry and the fabrication of MEMS. “Speciality gases have no surface tension or static friction unlike liquid etchants where these properties are capable of destroying the increasingly delicate microstructures while they are being formed,” states Dr Petro Terblanche, Managing Director of Pelchem SOC Ltd. This South African fluorocarbons company has been working closely with Linde to supply a range of fluorinated products including fluorine ($F_2$) and nitrogen trifluoride ($NF_3$) since 2008. The two companies have been working on ways to optimise customer production processes: “Not every etching gas is suitable for every material,” points out Weisheit. In terms of requirements, ultra-high purity is a given. But for the exact fabrication of high-tech products, gases must also be highly selective in terms of their reactivity, i.e. only attacking very specific surfaces of semiconductor materials.

**Xenon difluoride enables uniform etching**

In order to produce the finer mechanical structures on MEMS, it is often necessary to etch silicon oxide. The most common approach is to use high-purity hydrogen fluoride as the etching gas. “We are increasingly finding, however, that for some MEMS, the device needs to be manufactured in pure silicon, for example, pressure sensors,” says Linde’s electronics expert Shuttleworth. For this, the industry is increasingly relying on the specialty gas xenon difluoride ($XeF_2$) – one of the most valuable of the fluorocarbons.

As well as enabling the speedy realisation of complex structures, the gas also has the following advantage: “It allows for very even..."
etching in all directions and is highly selective – especially when working on silicon,” says Shuttleworth. The surrounding structures are not impacted in any way and remain residue-free.

There are very few companies around the world capable of producing and supplying the crucial raw material xenon difluoride in commercial volumes. That is why Weisheit and his team are also working closely with Pelchem to secure supplies of this specialty gas. The South African company has been supplying XeF₂ for the electronics industry since 1998 and has the largest share of the world market. Weisheit elaborates: “Thanks to this collaboration, we can help the electronics industry meet the growing demand for MEMS devices.” The partnership unites Linde’s extensive sales and support network with Pelchem’s high production resources. “Running the world’s largest xenon difluoride production plant, Pelchem can support all application scenarios – from university research projects to industrial scale manufacturing,” says Terblanche. Security of supply will also accelerate the development of microsystems.

Over 100 high-tech sensors in a single car
Currently, many possible applications for MEMS are still at the development stage, often at small universities scattered throughout the world. But in many other cases, the projects are almost ready for series production. “The growth of the Internet, cloud computing and higher-performance semiconductor technologies will give further impetus to the development of MEMS,” maintains Shuttleworth. From connected mobility to augmented reality, micro-mechanical sensors and converters are remotely pulling and analysing data from multiple sources in real time. Automobile manufacturers are already incorporating more than 100 high-tech sensors into new vehicles – and this figure is set to rise. Meanwhile, the MEMS Industry Report predicts that the MEMS market will see annual growth of 13 percent between now and 2017. MEMS devices are a key part of the recent “More than Moore” technology trend. In 1965, the chemist Gordon Moore declared that the number of transistors on a microchip would double roughly every two years. This has largely been maintained by conventional semiconductor technology but manufacturers are now looking to incorporate additional functionalities (such as MEMS) which will not necessarily scale according to Moore’s Law but deliver enhanced capabilities. Now, since the founding of Linde’s exclusive distribution partnership with Pelchem, Weisheit is confident that The Linde Group is well placed to fulfill future requirements of the global electronics industry. Weisheit concludes: “The future of microsystems depends on specialty gases.”

LINK:
www.memsindustrygroup.org
“PUSHING THE BOUNDARIES OF INNOVATION”

What strategies will shape the future of manufacturing? To find out more about some of them, Linde Technology spoke with Sven Godorr from R&D at Sasol, an international, integrated energy and chemical company based in South Africa.

**How do you see the energy mix of the future and what mid-term challenges do you envisage?**

In the very long term, society can only survive if we manage to meet most of our energy needs from renewable sources. In the short to medium term, we will remain dependent on fossil fuels. I suppose we are probably about halfway through the “hydrocarbon age” of cheap fossil fuels, with the shift moving from coal to oil to gas, and potentially back to coal in the absence of alternatives. In my view, the next decades will be shaped by the fascinating challenges of transitioning to an increasingly varied mix of energy sources, integration of energy networks and efficiency. The longer term transition to renewable sources will call for elegant storage options, particularly for electricity in both stationary and mobile applications.

**What role do you see coal and gas playing in this mix?**

Of course in the short term, coal remains a vast and relatively cheap fall-back option, but it is unfortunately difficult to process in an environmentally acceptable manner. Non-conventional gas has provided some much-needed breathing space in the pursuit for competitive renewable alternatives. The spotlight will increasingly be on the effective use of natural gas in various energy applications. I am guessing that it will be critically important for companies such as Sasol and Linde to assess how much natural gas will be used in native form as compressed natural gas (CNG) or liquefied natural gas (LNG) and how much will be converted to other forms of fuel. I see gas challenging the energy role that has been developing for hydrogen, and also displacing some traditional fuels such as diesel, heavy fuel oils and gasoline.

**How is Sasol stepping up to these challenges?**

Sasol is fortunate in that we have a great technology position to produce high-quality liquid fuels (diesel, gasoline, jet fuel) from non-conventional feedstocks such as coal, gas or even biomass and waste. These can be dropped into existing logistics chains or used in dedicated services. A niche application of this very clean diesel is in situations where low particulate emissions are important, such as urban bus fleets or underground mining. Our technology is also well positioned to accommodate shifts in feedstock supply and value, currently precipitated by the shale gas boom in the USA. As a concrete example, we have just kicked off the early engineering work for a large 96,000 barrel-per-day project in Louisiana, where we will be converting readily available natural gas primarily into diesel using our gas-to-liquids (GTL) technology. The resulting diesel has great advantages in terms of low sulfur and aromatic content, as well as high cetane. As part of this project, we are also extracting high-value chemical feedstocks for further processing in special applications.

**What about strategic co-operations and partnerships?**

We have developed many process technologies in-house, but also partner with other players for specific technologies. We tend to keep tight control over our core technologies so that we maintain and build our competitive edge. Early collaboration with an engineering contractor has yielded great benefits for us in the past. For instance, we worked closely with Linde for many of our chemical extraction processes a few years ago.

**How does partnering with an engineering contractor benefit you?**

**Interview**
A partner such as Linde, which has a strong technology culture, adds a lot of value by establishing a solid foundation of good data, powerful models and robust engineering. Making sure that the correct things are measured and checked during piloting is essential for effective scale-up and efficient commercialisation. My time at Linde helped me to appreciate the importance of coupling fundamental thermodynamics, hydraulics and chemistry with strong engineering rigour using disciplined systems. When we partner with Linde, we know that we can rely on engineering excellence, maximum efficiencies and a balanced engineering/operating perspective. This greatly enhances the chances of successful commercialisation.

NEW TECHNOLOGIES ARE THE MOST VALUABLE ASSET FOR ANY SUCCESSFUL COMPANY. HOW DOES SASOL MANAGE R&D?

Sasol has always been prepared to push boundaries in pursuing something new, investing in R&D facilities and in people for the longer term. This is not a fast-moving industry and it takes many years to take an idea or discovery to successful commercialisation. Our successes have always been based on the sweet spot, where the technical team and the business and strategic vision of the company align. We have the usual “stage gate” process to manage our various R&D activities. We also keep a close eye on our research portfolio mix to ensure it aligns with our strategic direction.

WHAT ARE THE MOST IMPORTANT DEVELOPING MARKETS?

The USA is doubtless a special case in the shorter term, but the discovery of massive gas reserves “on our doorstep” in places such as Mozambique is clearly also an opportunity for us. I expect that similar opportunities will arise elsewhere in the world as the technology to access both conventional and unconventional reserves improves and is applied globally. The opportunities to extract valuable chemicals from our GTL technologies and complement these with other chemicals derived from natural gas will be important to keep our chemicals business healthy.

HOW DOES SASOL STEP UP TO THE “CLEANER AND GREENER” TREND?

As a company that processes hydrocarbons and largely specialises in fuel products, this is a very important challenge for us and one we tackle on a number of fronts. This starts with our choice of feedstock – gas in preference to coal. Thermodynamically, one can achieve significantly higher efficiencies when transforming a hydrogen-rich feed material than one that is poor in hydrogen. We invest a lot of energy in the optimisation of our gas loops for maximum conversion efficiency. Not only does this reduce our environmental footprint, but it also makes the business case more attractive. In addition, we try to maximise the positive characteristics of our products. Synthetic diesel for instance is effectively sulfur- and aromatic-free, which significantly reduces particulate emissions from engines. Other contributions in this area include the use of waste and biomass as feedstocks and the development of a number of novel water treatment processes.
Blast furnaces – more efficient, less emissions

LOW-ENERGY OPTION FOR COMBUSTION AIR

Linde and Siemens have developed a flue gas recycling technology for the steel industry that reduces energy consumption and emissions. The new process isn’t just good news for the environment though. Because it pays for itself in a short space of time, it also has a positive impact on operators’ overheads.

Making steel is an energy-intensive process. To produce glowing, liquid pig iron, blast furnaces have to smelt iron ore, coke and flux at temperatures above 1,400 degrees Celsius. The combustion air for these heating processes is provided by cylindrical hot blast stoves that have to be preheated alongside the blast furnace. In addition to producing hot air, however, these blast furnaces and hot blast stoves also generate significant amounts of CO₂. “Blast furnaces and hot blast stoves are responsible for the vast majority of carbon dioxide emissions from steelworks,” explains Andy Cameron, Senior Process Specialist at Linde. And the figures are huge. The global steel industry emits almost two billion tonnes of carbon dioxide each year, more than any other sector of industry. Steel production accounts for over 6.5 percent of global emissions.

However, CO₂ emissions from steelworks could soon be cut drastically thanks to a new flue gas recycling (FGR) system for hot blast stoves jointly developed by Linde and Siemens engineers. This flue gas recycling system could dramatically change the emissions balance in the steel industry. “The process saves thermal energy and can cut CO₂ emissions from a steelworks by at least 30 percent if used in conjunction with carbon capture and storage technology,” elaborates Cameron. Steel already has a number of environmental benefits. It can be easily recycled, for example, and is an indispensable building block in many industries including the manufacturing sector. Steel is also used to construct wind power plants and enables engineers to create innovative, high-tensile, lightweight structures in the automotive and aviation sectors. Optimising the energy footprint of steel production could put an even brighter shine on the already sparkling image of this extremely robust, silver-grey material.

The new process developed by Linde’s experts harnesses the residual heat in the combustion flue gases from hot blast stoves. This air can be as hot as 400 degrees Celsius. Today, in many cases thermal energy is emitted unused into the environment via chimney stacks. Even small blast furnaces lose huge amounts of energy in this way. In fact, according to Cameron, it would take the world’s largest wind turbine to compensate for the rate of energy loss from a modestly sized blast furnace. In the FGR process, Linde engineers add pure oxygen to around one third of the flue gas stream and feed this mix back into the combustion chambers of the hot blast stoves. This hot oxygen-enriched flue gas is then burnt together with scrubbed blast furnace gases, which contain some carbon monoxide generated as a by-product of the iron-making process. Conventional stove operations use air to burn these blast furnace gases. Air, however, primarily comprises nitrogen. Only 20 percent is oxygen, the vital ingredient for boosting burning efficiency. This means that the nitrogen also has to be heated even though it does not aid combustion in any way.

Oxygen-enriched flue gas does not have this nitrogen ballast and its use increases the efficiency of the stoves by bringing extra heat into the combustion chamber and enabling the hot blast stoves to reach their required temperature faster. In addition, the new process generates significantly less nitrogen oxides, which have around 300 times more global warming potential than carbon dioxide. And
Managing molten iron: In future, blast furnaces should consume less energy and have a lower carbon footprint – thanks to Linde flue gas recycling.
because it recovers more of the combustion energy, Linde’s flue gas recycling concept also eliminates the need for additional energy in the form of natural gas or coke oven gases.

Most importantly, however, the flue gas recycling process conserves a huge amount of thermal energy. “A typical European steelworks produces between three and five million tonnes of steel per year. The FGR process could cut thermal energy consumption by up to 60 terajoules compared with air-based combustion,” adds Cameron. This corresponds approximately to the annual energy consumption of almost 4,000 three-person households in Central Europe. The thermal energy from the flue gas could also be used to generate power using steam turbines, although according to Cameron, “the energy efficiency here is much lower.”

Linde’s new flue gas recycling system also enhances the shape of the combustion flame. “An oxygen-rich flame is usually very hot and intense,” explains Cameron. “This may be perfect for some processes such as welding and cutting. In furnaces, however, it can lead to localised overheating and cause damage.” A flame of this kind can cause thermal shocks or melting of the refractory structure of the stoves. In the FGR process, the flue gas stream dilutes the flame, making it so large and diffuse that it becomes invisible to the naked eye, giving rise to the name “flameless” combustion. The large, transparent flame distributes heat evenly throughout a furnace. “This gives manufacturers complete control over the combustion process and enables them to operate their stoves at their maximum service temperatures with none of the risks normally associated with oxy-fuel combustion,” explains the Linde blast furnace expert. The upshot is energy and raw material savings. “If a hot blast stove is heated to higher temperatures, it produces hotter air for the blast furnaces. And this reduces the amount of coal and coke required for iron-making,” continues Cameron.

One of the biggest challenges facing the global steel industry is how to reduce its carbon footprint. Today, established blast furnaces are already extremely energy-efficient. Which means that further improvements can only be achieved by capturing the carbon dioxide and either feeding it into downstream processes or storing it under-

**FACTS & FIGURES ON STEEL**

In 2013, global steel production reached a new record high of 1,607 million tonnes. Almost half of the coveted resource is produced in China (46.3 percent), followed by Europe at 13.5 percent. By comparison, 851 million tonnes were produced in 2001. The world steel industry directly employs over two million people. Not only is steel an important material for the automotive and mechanical engineering industries, 50 percent of the total volume produced worldwide is used in construction of bridges, skyscrapers and other buildings.

Source: World Steel Association

**Birthplace of steel:** Blast furnaces lie at the heart of the steel-making industry – as seen here at Tata Steel (left). During processing, the liquid steel is cast (right) and then solidifies.
The idea behind flue gas recycling stems from another Linde technology that is well established in another part of the steel production chain. Flameless REBOX® oxyfuel burners are used, for instance, in rolling mills to fire the furnaces that preheat steel stock before it is rolled. These burners use oxygen-enriched air and a flame diluted with flue gas. Swedish steel producer Ovako has equipped around 60 furnaces with this flameless oxygen technology. The shorter heating times are a particular plus for the company. “We can heat at least 20 percent more steel in the same timeframe,” explains Anders Lugnet, Technology Manager at Ovako. The Linde process also improves the quality of the steel products by eliminating localised overheating – a problem that can create stress within steel and damage its structural integrity. “We simply integrated the technology into our existing process flow. The investment paid for itself very quickly,” confirms Lugnet.

Operating modes for every eventuality
And this technology pays equal dividends in blast furnaces. Linde’s experts calculate that the cost of the new process can be amortised within two years at most. An FGR system for a standard-sized blast furnace requires an investment of less than ten percent of what a company could expect to pay for a competing technology. The flue gas recycling process was developed using complex computer simulations. All of the simulations confirm that the combustion process runs smoothly and effectively. Nevertheless, Linde’s engineers are prepared for every eventuality and have equipped the system with different operating modes. A steelworks control console will feature three buttons so operators can easily and quickly switch between flue gas recycling mode, conventional combustion and mixed combustion.

Linde expert Cameron does not yet know when the first flue gas recycling system will be actively deployed in a hot blast stove. “In our experience, it takes a while for a new technology to gain a foothold in the steel industry,” he confirms. The industry is, however, showing real interest in this novel concept, and deployment may not be far away. “We are already talking with steel plant operators and things are looking very promising,” he concludes.

WHAT ARE THE BIGGEST CHALLENGES IN STEEL PRODUCTION TODAY?
High carbon dioxide emissions and cost are certainly two major issues. It is becoming increasingly difficult to procure high-quality raw materials at an affordable price. The price for metallurgical coke, for example, has almost doubled in the last 15 years alone.

HOW CAN THESE PROBLEMS BE SOLVED?
Carbon dioxide emissions can be reduced, for example, with carbon capture and storage technologies. However, CCS technologies will have to become more economically viable and more widely accepted by society as a whole. On the raw materials front, the industry will start transitioning from fossil materials such as coal and coke to electrical energy, preferably from renewable sources. The EU project ULCOS, for example, is currently developing a process for smelting chemically reduced iron ore in electric arc furnaces. Previously, these furnaces were used exclusively for recycling scrap. Ore can also be converted to iron using electrochemical processes. However, this technology is still in the very early stages.

HOW IMPORTANT IS OXYGEN HERE?
It is very important. Combustion processes that use high concentrations of oxygen are more efficient and use fewer raw materials. And this reduces greenhouse gas emissions. Oxygen enrichment also increases the concentration of CO₂ in flue gases, making them more suitable for carbon capture and storage. Oxygen can also be manufactured using electrical energy and therefore with a climate-neutral footprint – at least in theory. Economically speaking, it would be good to see more affordable, lower purity oxygen on the market and not just oxygen purities in excess of 99 percent. Researchers are currently looking into this.
Making natural gas fit for LNG carrier engines

FULL STEAM AHEAD

The industry wants LNG carriers to use more of the natural gas that they transport as fuel, reducing their reliance on heavy fuel oil. Linde Group member Cryostar has developed a new compressor technology that makes this transition possible and also increases engine efficiency.

LNG carriers may not be the fastest ships at sea, but they are among the largest. From bow to stern, they can measure up to 300 metres in length – that is as long as the Eiffel Tower is high. A single LNG carrier can hold up to 260,000 cubic metres of cryogenically frozen liquefied natural gas (LNG) – enough to supply a city of 150,000 inhabitants with natural gas for one year. Global demand for natural gas as a source of electricity and heat is also rising. More and more freighters are making their way across the world’s oceans to distribute LNG. According to BP Energy Outlook, over ten percent of all traded natural gas is already transported by sea. This is set to rise to around 20 percent by 2030. This sharp increase is fuelled in part by a rapid rise in demand in two major import countries: Japan and South Korea. “The US is also developing its shale gas reserves and will start exporting LNG to Asia and Europe in the near future,” explains Roger Dambach, Head of LNG Transport and Terminals at Linde Group member Cryostar. Today, around 400 large LNG carriers transport natural gas around the globe. This is around twice as many LNG carriers as ten years ago. Most of these ships’ engines are fuelled by crude oil, but new technologies should enable LNG carriers to use LNG as a fuel. The key to this technology is boil-off gas (BOG). LNG freighters store liquefied natural gas at minus 160 degrees Celsius in well-insulated tanks in the holds. Despite these measures, the cargo will always be subject to a certain amount of heating, resulting in part of the LNG evaporating as BOG. “Reliquefaction is one of the solutions used in ships today – but on-board reliquefaction plants also consume large amounts of energy,” says Dambach.

And there are other reasons why the LNG industry is looking for new solutions. One of these is related to the level of liquid in the tanks. “In the past, LNG carriers carried significant amounts of LNG on the journey home too. This keeps the tanks cool,” continues Dambach. “Economic dynamics have changed, however. Today, almost all of the cargo is unloaded from LNG carriers when they reach their destination port, leaving the ships as good as empty for the journey home.” A small LNG residue cannot be pumped out for technical reasons. This low level of LNG poses a challenge for engineers. If
a tank is almost empty, it heats up faster, causing a lot of warm BOG. “If there is enough LNG in a tank, the temperature of the BOG seldom exceeds minus 90 degrees Celsius,” explains the Linde expert. “At this temperature, the comparatively cold BOG can be compressed to 6.5 bar in two phases using a two-stage compressor. The resulting compressed gas can be used as fuel in a dual-fuel engine,” adds Dambach. In other words, a four-stroke ship’s engine of this kind can burn both a heavy fuel oil and air mixture and BOG.

In an almost unloaded ship making its way home, however, the temperature of the BOG rises up to 40 degrees Celsius. This is too warm for the two-stage compressor – due to thermodynamics the power needed for compressing warm gases is higher. Engineers at Cryostar in Hésingue, France, were among the first to step up to these challenges. “We wanted to develop a compressor that would be more powerful but not much larger than the previous system,” explains Dambach. The engineers turned to their proven centrifugal compressor technology in their search for a solution. The centrifugal system uses blades to compress the warm BOG during a four-step process, similar to aircraft turbines. The gas is gradually compressed as it moves from one chamber to the next.

**Centrifugal compressors to boost efficiency**

The centrifugal technology has a number of benefits over conventional compressors that use pistons. “The unit is very stable. Unlike piston compressors, it doesn’t have to deal with changing pressures and this makes it lighter and more compact,” elaborates Dambach. Most crucially, however, the four-step centrifugal compressor can process warm BOG with temperatures up to 40 degrees Celsius without an intermediate cooling step. The centrifugal technology also requires much less maintenance than piston compressors. Cryostar’s development has also won over LNG freight companies. Over one hundred four-step centrifugal compressors have been delivered since the system was launched in December 2010.

The LNG transport business faces further challenges. The industry has to reduce fuel consumption, not least through the introduction of more efficient engines. This applies to two- and four-stroke engines alike. Most large merchant ships are powered by two-stroke engines and although they consume less fuel than their four-stroke counterparts, they usually run exclusively on heavy fuel oil. 2011 saw the launch of a number of dual-fuel two-stroke engines capable of burning BOG as well as oil. The BOG has to be injected at an extremely high pressure of 300 bar. Cryostar offers an elegant cryogenic pump solution for this problem. Since then, however, another manufacturer has developed a new two-stroke engine that only requires input pressure of around 16 bar. The Cryostar experts are currently adapting their four-step compressor to work with the same pressure level. The design of the compressor chambers plays a key role here. A diffusor at each outlet converts the kinetic energy of the exiting gas into pressure. “If we fed the gas directly from one centrifuge to the next, this would create unwanted spin and destroy valuable energy,” elaborates Dambach. The new system means that a multi-step centrifugal compressor can compress the gas to the requisite 16 bar. It also reduces energy consumption. This development would be a dream come true for many LNG ship-owners as it means that natural gas freighters could be equipped with two-stroke engines capable of processing warm BOG, creating the most energy-efficient way of transporting natural gas.
Fresh produce often has an eventful life before it makes its way into your supermarket trolley. Bananas cross the high seas, prawns are cryogenically frozen, and salads, cheese and fish are protected in modified atmosphere packaging. Extending along the entire food and beverage value chain, Linde’s gas applications are as colourful and varied as the produce itself.
Water is essential to life – and is the basic ingredient in all drinks. Gas applications from Linde play a key role before, during and after the bottling of water, soft drinks and fruit juices. Even wine-makers and beer dispensers rely on Linde’s food and beverage solutions.
Food-grade gases from Linde are used at all stages of the food and beverage chain – from production through processing to supermarket.

**Cultivation & ripening**

It’s all about getting the balance right. Gases assist not only in the cultivation of fruit and vegetables, but also in fish farming.

- **Greenhouse tomatoes** grow much better when the air has a higher concentration of carbon dioxide. In the Netherlands, purified CO₂ from refineries is piped to massive greenhouse developments.
- In fish farming, the right gas composition is important to ensure that farmed fish stay healthy. Our SOLVOX® system ensures even distribution of oxygen while ozone keeps bacteria under control.

**Acidification and attaining the right pH value are important in cheese production.** Carbon dioxide helps get the balance right and control the cultures of the various microorganisms.

- **Bananas** are usually green when they are harvested. Ethylene is later used to speed up their ripening. This gas can also process pellets – of quick-frozen spinach for example.

**Pressure-sensitive products like marinated steaks or fish fillets are individually fed into our CRYOLINE® SC Super Contact freezer from a conveyer belt with disposable film.**

**Dough mixing machines** produce a lot of heat. Dry ice pellets are added to the dough to maintain an optimum temperature. The dry ice evaporates without residue to form CO₂.

**Herbs and spices** contain beneficial essential oils which remain in the milled or ground product if cryogenic gases are used in the milling machine. The addition of these gases also prevents clumping.

**Processing**

Longer shelf life, protection against spoilage, preservation of flavour and greater production efficiency – gases are indispensable in the food industry.

- **Nitrous oxide** is used to whip cream to an airy yet firm consistency. The volume-increasing effect of this gas is also used for creamy desserts and aerated chocolate.

**Grinders shred cuts of meat to produce sausage meat.** They are cooled efficiently with LIXSHOOTER®, which works by injecting liquid coolant from below. The coolant evaporates and the cold gas cools the product.

**To prevent high-grade edible oils from becoming rancid,** their storage tanks are inerted using nitrogen. Hydrogen is used to hydrogenate, i.e. solidify fats and oils.

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**Cooling & freezing**

Extreme below-zero temperatures prolong the shelf life of foods. The method used to drop the temperature plays a key role in maintaining quality.

- **Freezing** portions of vegetables, sauces and purées for ready-made meals is easy with CRYOLINE®. These customisable cryogenic freezers can also process pellets – of quick-frozen spinach for example.

**Pressure-sensitive products like marinated steaks or fish fillets are individually fed into our CRYOLINE® CW CRYOWAVE freezer.** A wave-shaped conveyer prevents the prawns from clumping together, making it easier for the consumer to thaw them out separately.
Fruit juices and wines are especially prone to oxidation. To prevent this, nitrogen is used to displace humid air in the headspace of the carton or bottle. When combined with a precise valve control system, this process is also suitable for large storage tanks.

Inerting
Fruit juices are rich in vitamins and flavour. To retain the fresh flavour and nutritional value as long as possible, juice containers are inerted with nitrogen. This displaces the oxygen, which destroys beneficial vitamins. The inerting process also helps the juice maintain its colour for longer.

Sparging
Bubbling nitrogen through a liquid is an effective way to remove undesired oxygen.

Stabilisation
PET bottles are becoming ever lighter in an effort to use less plastic. The problem with thin walls though is that the bottles are unable to withstand the pressure exerted during the transport and storage of heavy pallets. If a drop of liquid nitrogen is added to the bottle before sealing the cap, it will evaporate and create a stabilising internal pressure.

Carbonation
Whether lemonade, mineral water or sparkling wine – the ingredient that gives all of these drinks their sparkling fizz is carbon dioxide. The process involves dissolving CO₂ in the beverage under high pressure. This also increases the shelf life of the drink and inhibits oxidation.

Purification of drinking water
There is an increasing need to desalinate seawater for drinking. Unwanted ions are eliminated with oxygen (SOLVOX®), whereas carbon dioxide (SOLVOCARB®) helps to control the pH value and hardness of the water.

In the beverage industry, a fast bottling process is crucial. Gases play an important role at several key stages.

**Quality assurance**
Many of the measurements carried out in the analytical laboratories of food manufacturers and test institutes rely on high-purity gases.

**Packaging**
Special protective gas mixtures ensure that pre-packaged foods stay fresh for longer — reaching the consumer in optimum condition.

**Transport & storage**
High-quality, fresh supermarket produce hinges on a number of factors – including an unbroken cold chain.

**Gas mixtures**
- CO₂
- Ar
- N₂
- O₂
- H₂
- NH₃

**Refining**
- CO₂
- O₂
- N₂
- Ar

**Gases in wine and beer**

**Wine production**: Cryomaceration is an important step in wine-making. It involves adding liquid carbon dioxide to the grape must. This results in the formation of CO₂ snow, which has the desired cooling effect. This also preserves colour and flavour as the carbon dioxide displaces any oxygen present.

**Dispensing gases**: When beer and soft drinks are dispensed at a bar, they are often enhanced with carbon dioxide from BIOGON® gas cylinders. Depending on the drink, the BIOGON® cylinders contain either pure carbon dioxide or a mixture of nitrogen and carbon dioxide.

**Blanketing**
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COLD BLAST FOR BACTERIA

The poultry market is booming right across the world. Still, however, an invisible danger lurks beneath the surface: around three quarters of fresh slaughtered poultry carries Campylobacter bacteria. These can cause serious food-borne illnesses. Now experts from Linde Group member BOC UK have teamed up with turkey producer Bernard Matthews Ltd. to develop the Rapid Surface Chilling™ technology to kill these bacteria effectively.

Eating meat is no longer the preserve of the rich and privileged. Right across the world, demand is rising for animal protein – especially poultry. Over the last decade, production of chicken legs, broilers and chicken wings has increased by around four percent. By comparison, in the same period production of the world’s most popular meat, pork, only grew by roughly two percent. Today, 93 million tonnes of chicken meat are produced each year. There are good reasons for this rising demand: not only is poultry leaner and lower in calories than pork and beef, it can also be produced very cheaply. This makes it affordable for just about everybody.

Fresh poultry does have a drawback, however. When the birds are slaughtered, Campylobacter bacteria living in the gut often escape and can make their way to the surface of the skin. If the chicken is not subsequently cooked-through or if infected meat juices come into contact with other food or with kitchen surfaces, the consumer runs the risk of campylobacteriosis, a food-borne infection.

Salmonella is undoubtedly the best-known type of food bacteria. “But a much more common cause of infection is the group of bacteria known as Campylobacter,” declares Cedric Hanson, Business Development Manager Applications Technology at Linde Group member BOC UK. The European Food Safety Authority (EFSA) estimates that in the European Union alone nine million cases of campylobacteriosis occur each year. This makes it one of the most common food-borne infections in the EU, costing the public health authorities and industry EUR 2.4 billion in healthcare and lost production.

The symptoms of campylobacteriosis include stomach cramps, lingering diarrhoea and a high fever. In a small proportion of cases, infection may result in death, or long-term illness from irritable bowel syndrome, reactive arthritis, and Guillain-Barre syndrome which affects the nervous system. In the UK alone, around 100 people every year are killed by the infection.

In a Europe-wide investigation of freshly slaughtered chickens in 2008, researchers identified Campylobacter in three out of every four carcasses tested, 27 percent of which had dangerously high levels of the bacteria above 1,000 colony forming units per gram. According to the EFSA, chicken meat is the main source of campylobacteriosis in humans. These figures caused alarm not only for the EFSA, but also for national food authorities. In 2009, the UK Food Standards Agency (FSA) was prompted to take action and the Joint Industry-Government Working Group (JWG) on Campylobacter was formed. Its objective was to reduce the share of freshly slaughtered birds carrying the highest levels of contamination from 27 percent to ten percent by 2015. However, this seemingly easy target was not straightforward as Campylobacter is a highly complex organism.

Reducing bacteria significantly

In partnership with Bernard Matthews Ltd., the leading turkey producer in the UK, Linde has developed a breakthrough new technology to significantly reduce Campylobacter in poultry by up to...
95 percent. Known as Rapid Surface Chilling™, this technology uses a very cold nitrogen vapour to rapidly chill the surface of the skin of the birds to kill the Campylobacter. To date, over 6,000 birds have been successfully treated during industrial trials using a new, in-line cryogenic tunnel designed by Linde. The Rapid Surface Chilling™ technology has also been independently validated in tests carried out on behalf of the FSA by Campden BRI, the UK’s largest independent food and beverage R&D organisation. “This technology represents a key milestone in the fight against one of Europe’s most serious health concerns,” comments Jeremy Hall, Technical Director of Bernard Matthews Ltd.

Targeting bacteria – maintaining meat quality
An added advantage of the technology is that the use of liquid nitrogen to chill the meat has no impact on its quality. “Texture, taste and nutritional value remain unaffected since it is only the surface of the flesh that is chilled – and only for a matter of seconds,” explains Hanson. The results of the trials have captured the attention of food safety authorities. In recent years, numerous different methods to reduce Campylobacter have been tested. “These have failed either on account of not meeting EU regulations or not being sufficiently effective,” points out the Linde expert.

Economic efficiency also adds to the appeal of this new technology. Around 180-250 carcasses per minute can be cryogenically treated, which equates to 11,000-15,000 birds per hour. A patent application for the Linde technology has been submitted and steps to further develop the cryogenic equipment are underway. In early 2014, plans were drafted to design and build a commercial machine, with the first commercial trials scheduled to start as early as this summer. “If everything runs smoothly, we expect to see our cryogenic system available on the European market sometime in the second half of the year,” maintains Hanson. “This would be a major milestone in the FSA’s mission to effectively reduce Campylobacter to the 2015 targets,” he concludes.

The three main food poisoning bacteria are Campylobacter, Salmonella and Escherichia coli. Campylobacter primarily occurs in raw poultry. Salmonella is usually harboured on egg shells and in raw pork and poultry. Most strains of Escherichia coli are harmless. The bacteria are even part of the intestinal flora of the human gut. The dangerous strains are known as enterohemorrhagic Escherichia coli, or EHEC. They are transmitted by consuming raw meat or unpasteurised milk products. The EHEC outbreak in Europe in 2011 was, by contrast, traced back to contaminated fenugreek seeds.
Processing wet shale gas: Shale oil reserves also contain products such as wet shale gas. It can be efficiently processed with CRYO-PLUS™ technology as seen here at the Linde plant in North Dakota, USA.
Efficiently producing feedstocks for the petrochemical industry

UNLOCKING THE TREASURE IN SHALE

The petrochemical industry is booming in the US – largely fuelled by the low cost of shale gas as a feedstock. New drilling and exploration techniques enable this natural gas to be extracted cost-effectively from shale rock. Linde’s CRYO-PLUS™ technology means that even wet shale gas basins can now be developed efficiently to deliver valuable natural gas liquids for various industries.

Across the American continent, natural gas reserves lie deep below the earth’s surface. They occur in many other parts of the world too, but it is in the US where industry is most determined to develop unconventional sources of natural gas – known as shale gas – in order to reduce dependence on energy imports. But shale gas is a lot more than just a source of energy. Not only is it an ideal fuel for power plants and district heating, it also delivers valuable feedstock such as ethane for the petrochemical industry. “Natural gas can be easily converted into base chemicals such as ethylene, which is a hydrocarbon compound and precursor of many common chemicals. The best known are probably the plastics found in everything from packaging and cable insulation through car seats to toys,” explains Thomas Rings, A.T. Kearney partner and expert for energy and utilities. The American Chemistry Council (ACC) estimates that by 2020, the shale gas boom will fuel investments to the tune of almost USD 70 billion in the American petrochemical industry alone. Yet gas fields that will be of real interest to ethylene producers are still at the very early stages of development. Ethylene from shale gas has the potential to unleash a new industrial revolution in the US.

Before that can happen, however, there are hurdles to overcome. “The shale gas liquid recovery processes typically used thus far are not the most efficient,” explains Ron Key, Vice President Technology and Sales at Linde Process Plants in the US. Efficient processing of these valuable raw materials calls for highly specialised know-how as the quality of shale gas reserves can vary significantly from one well to another. Experts differentiate between dry and wet shale gas reserves. Up until now, extraction efforts have focused on dry shale, which is an excellent source of energy containing almost pure methane with a small share of longer-chain hydrocarbons. Wet shale is a much more interesting prospect for industry, however, as these reserves contain extremely valuable raw materials. Their composition can vary dramatically. As Key explains: “Wet shale gas contains less methane, but higher concentrations of ethane (C₂) and longer-chain hydrocarbons such as propane (C₃) and butane (C₄) and higher molecular weight hydrocarbons. These are referred to as natural gas liquids (NGL). They are the perfect feed for gas crackers, which produce ethylene.” This translates into a huge market opportunity. Chemical insight and forecasting company IHS Chemical predicts that global demand for ethylene will rise to around 160 million tonnes a year by 2017.

Unconventional reserves present a number of challenges to chemical engineers, however. “The wet shale gas is occasionally contaminated with impurities such as trace amounts of mercury and sometimes hydrogen sulfide,” outlines Key. These substances must be almost completely removed before the ethane and propane in the shale gas can be fed to an olefin plant. The engineers at Linde Process Plants have now found a way to recover valuable NGLs by evolving their proven CRYO-PLUS™ technology. Plants that previously compressed and cryogenically cooled conventional raw natural gas only in order to crack it into its constituent parts can now also

NATURAL GAS LIQUIDS CONTAIN UP TO 45 PERCENT ETHANE.
easily handle wet shale gas. “Our aim was to adapt CRYO-PLUS™ to meet evolving market demands; in other words: increase plant flexibility and recover more liquid hydrocarbons,” continues Key.

This involved quite a few technical refinements. The higher concentration of hydrocarbons with a high molecular weight in wet shale gas made it necessary to modify the feed treatment process. “This enabled us to reduce coke formation during regeneration of the dryers,” elaborates Key. Also, the hydraulics of the facility required a thorough review and were adapted to better support turndown cases of the design. Competing recovery methods such as the Gas Sub-cooled Process (GSP) – widely regarded as the industry standard in the US – can provide high levels of combined ethane/propane recovery. “However, these processes fall short if the demand changes to a product with high levels of propane recovery with limited or no demand for ethane recovery, for instance,” continues Key.

When refining the design, Linde engineers were able to build on the vast experience they had already gained with CRYO-PLUS™ in the field. This technology is already successfully deployed in over 20 refineries and petrochemical plants, where it is used to recover ethane, propane and hydrocarbons with a higher molecular weight from refinery and petrochemical off-gases. And demand for this technology is rising around the world, driven in particular by growing concerns over climate protection. In Iraq, for instance, almost 60 percent of the off-gases from oil production – many of which are rich in ethane – are flared. The region around Basra alone flares enough ethane to produce as much as two megatonnes of ethylene every year. “That ethane could be easily captured with CRYO-PLUS™,” says Key. “Our plants provide proven performance in multiple shale gas basis.”

**Successful due to production synergies**

The US natural gas boom is providing strong momentum for the petrochemical industry. Many North American refineries are already extracting so much feedstock from shale gas that US oil companies are thinking about exporting crude oil for the first time since the oil crises at the start of the 1970s. Integrated crude oil refineries and petrochemical plants have the strongest prospects of increased profits due to production synergies, coupled with integrated, more cost-effective utility systems. “In addition, integrated designs have a greater ability to control the risk of fluctuations in demand for either fuel or petrochemical production,” says Key. The naphtha cracker run by BASF-TOTAL Petrochemicals in Port Arthur, Texas, is a good example. Linde engineers will soon be finished upgrading the facility so it can process more ethane. Since April 2013, the cracker has been meeting 40 percent of its ethylene needs from ethane and another 40 percent from butane and propane. Supported by Linde, BASF-TOTAL Petrochemicals has also commenced work on another ethane cracking furnace. It is set to go on stream in 2014 and will increase

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**US PRODUCTION OF NATURAL GAS LIQUIDS**

![Graph showing US production of natural gas liquids (NGL) from 2005 to 2012.](source: U.S. Energy Information Administration)

The shale gas boom in the United States is driving production of natural gas liquids (NGL). The light hydrocarbons ethane and propane/propylene have been the primary vehicles behind expansion of the NGL offering since 2005. NGL refers to a wide range of components generated during natural gas treatment and crude oil refining. These liquids serve as feedstock for many different industries, including the plastics and fuel sectors.
cracker capacity by an additional 15 percent. According to Patrick Pouyanné, President of TOTAL Refining and Chemicals, TOTAL is also looking at a project to build a new ethane cracking furnace, which would be attached to the original Port Arthur cracker. So it seems that many operators in the US are already in the process of upgrading their cracker systems.

Shale gas production will continue to rise
Looking also to the longer term, shale gas is set to keep the US in pole position. In just a few years, it has turned the country from one of the world’s most expensive chemical hubs into one of the world’s cheapest. In its 2014 report, the US Energy Information Administration (EIA) projects that shale gas production will continue to rise up until 2040. “The existing exploration infrastructure puts the US in a unique position,” adds Rings. Which is why sizeable shale gas reserves in regions such as China or South America will not have the same impact as shale gas in the US in the foreseeable future. One thing is sure, however, the shale gas market will remain dynamic, thanks in part to innovative technologies from Linde.

**LINK:**
www.eia.gov/naturalgas/

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**SHORT INTERVIEW**

“**MASSIVE SHIFT IN THE CHEMICAL INDUSTRY**”

Linde Technology talked to Thomas Rings, A.T. Kearney partner and expert for energy and utilities, about the impact of the US shale gas boom on industry.

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**WHY DOES THE POTENTIAL OF SHALE GAS EXTEND BEYOND SECURING ENERGY SUPPLIES?**

Originally, shale gas was not a significant petrochemical feedstock. But the situation changed dramatically with the increased recovery of wet shale containing oil. These reserves also contain a high proportion of natural gas liquids (NGL). And a single barrel of NGL comprises 40 to 45 percent ethane. So instead of simply flaring this “by-product”, as was previously often the case, we can put it to good use as a cost-effective chemical feedstock, together with other NGL components such as propane.

**SHOULD WE EXPECT TO SEE SIMILAR DEVELOPMENTS WITH SHALE GAS OUTSIDE THE US?**

The US benefits from a unique position – it is currently the only place that covers the entire process chain. After a hundred years of intensive exploration, no other country has as clear a picture of its crude oil and natural gas reserves. Equally, the pipeline network is highly developed. Many disused crackers were easy to bring back on stream, while operational facilities had the flexibility to accommodate changes in raw material composition. Other countries, such as China, usually lack more than just the necessary pipeline network – know-how in essential exploration and production technologies like horizontal drilling and fracking is often also lacking.

**WHAT IMPACT WILL US SHALE GAS HAVE ON THE PETROCHEMICAL SECTOR IN FUTURE?**

Shale gas will trigger massive shifts in all areas of the chemical industry. In the medium to long term, this cost-efficient US resource looks set to put a lot of pressure on petrochemical plants and crackers in regions such as Europe, Japan and Korea.
Steel is at the heart of the construction industry. When it comes to joining the massive metal structures required to build bridges or high-rise buildings, the spotlight shifts to modern welding technology. The success of welding processes hinges on a stable, consistent gas flow. Linde experts have developed a novel gas pressure regulator that sets a new landmark.

Megacities are growing the world over – and not just outwards, but also upwards. The cityscapes of Tokyo, New York and Hong Kong are now dominated by breath-taking skyscrapers. Hundreds of cranes can be seen lifting steel girders into the air. They are joined by kilometres of weld seams, ensuring a stable, durable steel framework. These welded joints must be able to withstand high tensile, compressive and sometimes centrifugal forces. So high quality standards are required at all stages of construction – welding included. For steel construction workers, a good head for heights is just the start. Producing a stable welded joint also requires experience and the best technology available. Even small variations in the gas mixture, for example, can seriously undermine the strength of a weld seam. Various factors have to be taken into consideration when welding or cutting with an oxy-fuel mixture using acetylene for instance. For starters, the nozzle of the burner has to deliver a consistent mixture at a constant gas flow and pressure. Pressure must also be maintained to avoid safety hazards such as flashbacks, where the flame burns back up into the equipment and causes damage or explosions. Gas pressure regulators, or just regulators, are used to control the gas flow and pressure. “Cylinders containing oxygen are main-
"SMART" GAS CYLINDERS

With carbon fibre wrapping, an electronic display and ergonomic design features, GENIE® proves that gas cylinders no longer need to be huge, unwieldy and hard to operate. GENIE® is an innovative range of composite cylinders for welding gases. Lightweight and stable, they also come with additional user-friendly features. The electronic display shows the type and the volume of gas left in the cylinder as well as the flow rate and remaining operating time. Finally, an alarm sounds when the cylinder is almost empty. GENIE® can be used for all compressed gases, from argon and nitrogen to hydrogen and oxygen.

Steady pressure and precise flow

This welding innovation also resolves another common challenge; namely the need to maintain a constant gas pressure throughout the day without constant readjustments – even as the cylinder content, and hence the pressure, drops. This is not the case when using SMOOTHFLO™. As the cylinder pressure drops, the outlet pressure rises. Afrox resolved this by designing SMOOTHFLO™ as a single-stage regulator (i.e. with one chamber) with the features of a multi-stage model, which typically works with two pressure chambers. Other plus points are pressure stability and a precisely controlled gas flow. Naidoo adds: “The cutting process is not only faster, saving us on production time, but we are also achieving much cleaner cuts.”

For the Linde team, solving the technical challenges of the SMOOTHFLO™ project was just half the story. “Different time zones and contrasting customer expectations make it more difficult to develop products for the international market. We wouldn’t have managed it without a large, well-coordinated global team,” maintains Dionisio. At present, SMOOTHFLO™ is only suitable for oxygen and acetylene and a cylinder pressure of 230 bar. But there are plans to develop new variants suitable for argon, nitrogen and liquid petroleum gas (LPG). These will open up a range of new applications for the gas pressure regulator.

www.linde-gas.com
The spread of hydrogen mobility continues to gather pace. The foundations and strategies for a future H₂ ecosystem are largely in place, and engineers around the globe are now closing the technical gaps with dedicated solutions to advance the infrastructure for this clean fuel. This entails looking at the path from the source to the point of use. “It’s a question of ensuring hydrogen deliveries to refuelling stations are as energy-efficient as possible,” explains Dr Andreas Opfermann, Head of Clean Energy and Innovation Management at Linde. At present, Linde transports this eco-friendly fuel to the pump by truck, either as a cryogenic liquid (LH₂) or as a compressed gas (CGH₂).

“Up to now, we had to choose whether to transport relatively small amounts of gas or liquefy the hydrogen beforehand, consuming extra energy,” outlines Dr Helmut Hönnicke, Project Manager for Linde’s Innovation Management. However, thanks to Hönnicke and his colleagues, it is no longer a case of either or. The Linde engineers have spent three years working on an innovative storage technology to enable transport of larger volumes of H₂ by increasing compression. As a rule, trailers carry the pressurised gas in multiple upright cylinders linked together to form a connected storage system. “Previously, the hydrogen was pumped into the trailers at a pressure of 200 bar,” states Hönnicke, which meant a truck could transport 6,000 normal cubic metres of gaseous hydrogen per trip. But that was not enough for the project team, as Hönnicke recalls: “We set out to double the possible payload.” Reaching this target meant the H₂ specialist and his colleagues needed to overcome various hurdles. “On one hand, the weight and dimensions of a trailer are subject to legal limits. And on the other, the materials themselves restrict the pressure we can exert on hydrogen storage elements.”

So the Linde engineers were challenged to develop a hydrogen storage solution with an improved payload-to-mass ratio. To achieve this, they collaborated with storage element specialists from xperion Energy & Environment and gas transport experts from Wystrach.

**Boosting H₂ infrastructure efficiency**

**THE PRESSURE IS ON**

An effective refuelling network is a key success factor in the widespread commercialisation of hydrogen mobility. And an efficient network calls for an energy-optimised supply chain. Linde’s engineers have now developed a new storage technology to ensure that hydrogen reaches the filling station more efficiently than ever before.
“The key to our solution lay in increasing the working pressure from 200 to 500 bar,” reveals Hönnicke. The higher gas pressure significantly improves the ratio of mass to volume. In economic terms, too, a 500 bar working pressure proved ideal: “It meant we could keep the material and development costs for the storage elements within reasonable limits, while still considerably increasing the storage capacity,” Hönnicke reports. The resulting technology also substantially reduces the overall costs of CGH₂ transport. “A trailer equipped with the new 500 bar storage technology currently costs as much as three conventional trailers,” acknowledges Herbert Schenke, Head of Bulk Product and Supply Chain Management for Linde’s Continental and Northern Europe region. “But the associated running costs are significantly lower.”

Carbon fibre shell for robust storage elements
The storage elements form the all-important core of the new 500 bar hydrogen trailer. Engineers from xperion and Linde have developed lighter cylinders featuring a carbon fibre shell, which are strong enough to support the load and withstand the high pressure. “In the new storage technology, the sole function of the inliner – a special inner cylinder made of high-pressure polyethylene – is to make the container gas-tight,” explains Hönnicke. The previous trailers used storage systems consisting of steel cylinders, which were only wrapped in carbon fibre as reinforcement.

Assembling the storage solution and attaching it to the truck also presented its own technical challenges. “We have to ensure that cylinders will not be damaged in transit,” confirms the engineer – which is why Linde decided to bring in experts from Wystrach for this part of the project. The Wystrach gas transport specialists built a steel superstructure for the semi-trailer so that the storage elements could be mounted on the chassis, fitting their attachment points with articulated joints. “This ensures the elements are securely attached to the chassis while remaining mobile enough to absorb bumps and movements,” explains Walther Ambros from Central Technical Services at Linde Gas Germany.

To increase the safety of the trailer still further, the entire structure is subdivided into eight storage segments, which can be individually sealed off from one another. A further benefit of the 500 bar technology is revealed when discharging the load at the refuelling station: thanks to new, specially designed fittings and a high-pressure hose, it now takes just one hour to completely empty the entire hydrogen storage system. The old trailers managed just a quarter of the amount in that time.

This new H₂ tank concept not only increases efficiency in transport logistics, it also paves the way for higher pressures at stationary hydrogen tanks. As things stand, the 200 bar trailers are still supplying gas tanks that only work at a pressure of 45 bar. As Hönnicke emphasises, “Increasing the storage density would save space at the filling station.” It also means that storage tanks that currently rise metres above the ground could disappear below ground, as is usual with petrol and diesel. This development would resonate strongly with station operators. “This way, the technology is not only safely integrated but also barely visible,” Opfermann confirms. And he has no doubts: “Details such as this also help to enable an efficient hydrogen infrastructure.” Various car manufacturers have already announced the launch of series production for fuel-cell vehicles on the German market in 2015. Alongside attractive purchase prices and running costs, enough refuelling stations to keep pace with demand is one of the most important success factors – and it goes hand in hand with the ability to supply them efficiently.
Cryochamber for elite athletes

COLD PATH TO THE TOP

Getting to the top requires dedicated and consistent training. It is important to keep injury and rehabilitation periods to a minimum. Cryotherapy helps athletes to get fit faster. Linde Group member BOC UK has now developed the world’s first mobile cryotherapy chamber.

Rugby is often described as a hooligan’s game played by gentlemen. Fair play is very much to the fore, but the on-field battle is so intense that injuries are inevitable. Long recovery lay-offs are something the modern professional can ill afford, however. Coaches and sports therapists are always on the look-out for ways to shorten rehabilitation periods. It is well known that the application of ice helps to ease bruises and sprains. Going a step further with extremely cold temperatures should therefore speed up recovery even more. The cryogenic specialists from Linde Group member BOC UK have developed the world’s first mobile cryotherapy chamber to meet this need. “We use liquid nitrogen to cool down the temperature inside the chamber – to as low as minus 135 degrees Celsius to be exact,” explains Michael Toole, Cryotherapy Business Development Manager at BOC.

“I feel much more refreshed after the cryochamber and my recovery time is shorter,” maintains Kevin Sinfield, captain of the England rugby league team. The squad headed by coach Steve McNamara embraced “whole body” cryotherapy towards the end of 2012. Since then, a BOC expert has been making regular trips to the training ground with a state-of-the-art mobile cryotherapy chamber. “During the World Cup, we used this chamber up to three times per week with around three treatments every day after field and gym sessions,” explains McNamara. Whenever two of his squad enter the cryochamber they are kitted out in personal protective equipment and a BOC expert is always on hand to supervise. “First of all, the players spend thirty seconds in a -60°C pre-chamber to get used to the cold, before entering the main chamber at -135°C,” explains Toole. While the players are walking around for two minutes, the BOC expert checks that the temperature, pressure and humidity are all within safe limits. One of the factors that makes cryotherapy so appealing is the fact that it replaces an unpopular alternative – ice baths, which were typically used to accelerate recovery. “Ice baths are a thing of the past and players are more willing to use cryotherapy than submerge themselves in ‘wet’ ice cold baths,” says Toole.

Even though the skin rapidly cools down to -15°C, the core body temperature is maintained. The overall physical effect is impressive, however: the peripheral blood vessels constrict, blood is directed to the core of the body and the supply of blood to the muscles is enhanced. The body’s hormone system also reacts by releasing endorphins to alleviate pain. Adrenaline increases the flow of anti-inflammatory substances. After the cryochamber, athletes report that they feel both invigorated and relaxed. A study carried out by the French National Institute of Sport, Expertise and Performance (INSEP) has demonstrated that cryotherapy is more efficient than other recovery methods. Just one hour after a treatment, participants demonstrated complete regeneration of maximum muscle strength and an improved sense of physical wellbeing. The optimum exposure time to influence physiological changes is two minutes at -135°C, according to pioneering international research by the University of Central Lancashire (UCLan). The shorter recovery periods help to enhance sporting performance in the long term. The England rugby league players now feel ideally prepared for their next campaign.

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