More than volatile molecules.

Technical gases for the chemical industry.
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Fast, safe and economic supply of technical gases ranging from cylinders to on-site production plants to pipeline networks
Linde Gases supports customers in more than 100 countries, providing not only industrial and medical gases, but also application know-how, extensive services and equipment to help make their operations more profitable, more efficient and more sustainable.

In the chemical industry, technical gases perform a number of tasks acting as “invisible helpers and problem solvers”. They serve as reactants, protectors of production assets and as indispensable tools for quality control, product forming and maintenance as well as for storage and transport operations. Normally, these tasks can be covered by focussing on appropriate gas quality and supply alone – but in addition, they often call for individual solutions as well, in order to ensure safe and reliable gas applications tailored to the customer’s situation.

Correspondingly, Linde Gases offers a wide range of gas-related solutions encompassing hardware for gas supply and application, development tools such as experimental set-ups, calculation programs for process design and other software, e.g. to complement safety competence. Our experts work closely with customers in order to develop optimised gas application solutions – not only during preparation and execution of trial campaigns, but also when it comes to design, implementation and start-up.

In terms of the application of technical gases, Linde can draw upon a wealth of experience and expertise acquired over the course of decades, a body of knowledge which can be transferred, in many cases, from other industries to the chemical industry. Our corresponding know-how enables us to offer solutions tailored to the specific needs of our customers.

### Technical gases – overview

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Enhancing performance and ensuring safety. Gas applications and know-how from Linde Gases.
Low investment costs, significant efficiency boost and more. Oxygen enrichment offers many advantages.

In chemical processing, oxidations are among the most important production technologies. Molecular oxygen clearly predominates as the applied oxidant which is reflected by a broad variety of processes based on oxidation by air only or by pure oxygen. As air is a gas mixture of molecular oxygen and mainly inert components (namely 78 vol.-% of nitrogen), its oxidation potential is rather low and the effluent gas volume downstream of the oxidation reaction is quite high. Both limitations can be remedied to a considerable extent by adding technical oxygen to the process air – the so-called "oxygen enrichment". The latter is a classic option for process intensification and can be applied in many cases. It is often implemented for debottlenecking, e.g. when air blower operation or off-gas treatment capacity is limited. Enhanced oxidation potential – often combined with a reduced nitrogen load of the oxygen-enriched process air – provides the basis for positive effects in terms of productivity and energy efficiency. Beyond the increase of production capacity, there are further advantages of oxygen enrichment that benefit the whole process, but are often overlooked, such as reduced effluent gas streams and thereby decreased disposal effort. The implementation of oxygen enrichment technology at an existing production plant can usually be realised with only minor effort and low investment costs.
Thermal air oxidations
In chemical processing, thermal oxidations are frequently applied, not only for production and recycling steps but also for disposal of effluent streams such as off-gases and wastewater. In these fields, pure oxygen is not used as the sole oxidant very frequently – an exception being gasification of carbonaceous feedstock for the production of synthesis gas (H₂/CO). Air is clearly predominant as the applied oxidant – not only in other partial oxidations such as pyrolysis of heavy hydrocarbons and recovery of sulphur from H₂S gases. Air is also applied for most deep oxidations, e.g.:
→ Regeneration of spent catalysts by burning-off of coke deposits
→ Roasting of sulphidic ore
→ Recycling of spent sulphuric acid
→ Burning of waste material

Irrespective of which technology is used for thermal air oxidation, burner sections and fluidised beds alike are all faced with the high content of nitrogen. This inert gas component inevitably comes with the process air, thus hampering heating and most notably limiting processing capacity by its sheer presence. A versatile and increasingly often applied remedy for limited air oxidation units is oxygen enrichment of the process air, as e.g. in production of carbon black and sulphur as well as in burning of highly contaminated wastewater.

Catalytic air oxidations
The situation is quite similar with air-based processes which imply a catalytically supported oxidation step to ensure a selective reaction. These are applied predominantly for production of commodities and/or intermediates such as terephthalic acid, acetaldehyde, phenol, ethylene chloride, cyclohexanone, benzoic acid and acrylonitrile. In general, for maintaining or exceeding nameplate capacity, the most widely applied technologies – i.e. air oxidations in the gas/liquid phase and, to a more limited degree, in the gas phase – are prone to be intensified by oxygen enrichment if adequate removal of oxidation heat can be realised.

Services
Prior to its implementation, the large-scale realisation of oxygen enrichment calls for various measures to assure safe and successful performance. Correspondingly, Linde offers an extensive service package to effectively support preparation, implementation and execution of the additional application of oxygen. Our offer includes software tools that enable process and safety-related calculations. Moreover, Linde can provide the hardware for appropriate oxygen supply and oxygen injection which paves the way for an easy set-up of trials as well as routinely applied oxygen enrichment at the production plant. In addition, proven pilot units can be used to gain experiment-based results providing the basis for simulation and scale-up calculations for oxidations with molecular oxygen. See the picture on page 13 showing Linde’s “stirred reactor system” for the examination of gas/liquid reactions, such as the oxidation of cumene to cumene hydroperoxide. The diagram above shows the corresponding effects of oxygen-enriched operation in comparison to the air-only mode (i.e. 21 vol.-% O₂).
Invisible but indispensable. Inerting with nitrogen for safe and efficient processing.

Technical gases are often seen as auxiliaries of only minor importance. Without them, however, most processes in the chemical industry wouldn’t be feasible at all, as technical gases help guarantee and improve the economic efficiency of procedures and ensure quality and plant safety.

Inerting
Inerting procedures are among the most important gas applications within the chemical industry. Inert gas displaces inflammable vapours, oxidants such as molecular oxygen or moisture. Nitrogen is by far the most widely used medium applied for prevention of explosive atmospheres, a measure ensuring, for example, the safe start-up as well as shut-down of process plants.

By elimination of any potential for oxidation and humidification, the inert gas protects products during separation and handling processes but also during transport and storage.

The methods applied for inerting are as follows:
→ Dilution purging
→ Displacement purging
→ Pressure-swing purging (pressure build-up, decompression)
→ Blanketing

In many cases, reliable data on flammability characteristics are indispensable for safe processing. They depend not only on the composition of the respective gas phase but also on temperature and pressure. Even though experimental evaluations are sometimes necessary, the application of software tools is usually sufficient for the sourcing of reliable data.
One example is the software “Safety System” developed by Linde. This tool is capable of calculating the characteristics not only of simple systems such as “one kind of fuel in air” but also of complex mixtures as indicated in the exemplary case above. In addition, software has been developed for prognostication of the time frame of different inerting methods and the corresponding gas demand.

For the purpose of safe manual dosing of solids (such as powders etc.) into reaction and other vessels, sluices with incorporated inert-gas locks were developed. When activated, these devices generate a protecting gas curtain within the filling gap, thus preventing the ingress of oxygen and moisture and ensuring product quality as well as the safety of the operating personnel.
Best conditions ensure excellent results. Optimised processing through application of technical gases.

**Process temperature control with liquid nitrogen**

Especially in stirred reactors, multi-step syntheses are often performed which are based on different temperature levels. In the fine and specialty chemistry sector, low-temperature process conditions down to and below -100 °C are not unusual.

For the generation of low temperatures (< -40 °C), cryogenic nitrogen is often the cooling medium of choice. This is not only due to the high cooling power and high flexibility of this liquid. Compared with conventional cooling machines, the liquefied gas also allows for cooling based on lower investment cost.

It is often mandatory to maintain the temperature within a narrow range in order to minimise the build-up of by-products. Temperature control with the CUMULUS® technology meets these demands in most cases due to its characteristic precision of +/-1 °C. The low maintenance effort for the temperature control unit is another compelling argument in favour of this cryogenic application of liquid nitrogen.

In response to the high demands in terms of temperature control of reaction conditions, Linde not only offers cooling units (CUMULUS®) but also combined cooling/heating systems (CUMULUS® CD), hereby answering challenges such as the coverage of a wide temperature spectrum combined with a fast and precise temperature control.

**Cooling/heating system with secondary heating circuit**
Calibration gases for process control
To a high degree, modern process control technology is based on process data gained by sophisticated analytical instrumentation. This is also true for gas phases, and the performance of corresponding analysers greatly depends on qualified calibration procedures in which the application of high-quality gas mixtures is an indispensable necessity.

But gas mixtures also play an important role beyond production. Not only for the surveillance of flue-gas installations, but also for health and safety in the workplace or the determination of permissible concentration values, a great variety of standardised and also tailored calibration gases are available. HiQ® calibration gas mixtures are manufactured to meet your most stringent calibration requirements from binary to multi-component blends, with concentration levels from percent to parts per billion.

High purity grade for measurable success
Analytical services are among the main tasks for laboratories of the chemical industry, not only for quality and process control, but also for optimisation of production steps. Due to this wide range of challenges, the analytical methods applied are manifold.

High-quality utilities such as carrier and make-up gases for gas chromatographs are among the primary preconditions for smooth operation of analytical instrumentation. For sample preparation (a key step in analytical procedures), gases are applied for extraction, stripping and cooling purposes. For these applications, high purity grades can be just as important as for zero gases, which ensure a correct setting of the analytical zero line. But premium quality standards based on minimised impurity levels are also important for precise results substantiated by high reproducibility when gases or gas mixtures are applied as reactants such as fuel or oxidants. HiQ® specialty gases are for reliable and accurate operation of analytical instruments and process gas analysers and are delivered in a cylinder package to suit your individual analytical requirements.
Indispensable in many sectors.
Carbon dioxide opens up a broad range of applications.

Due to its potential as a greenhouse gas, CO₂ is in the focus of widespread discussions about climate change. As our level of industrialisation is closely connected with the usage of fossil feedstock, the generation of CO₂ can not be significantly suppressed, making CO₂ recovery a matter of considerable interest. In this field, Linde is excellently positioned, as its Engineering and Contracting Division has a vast wealth of experience in CO₂ recovery and purification. Linde has erected numerous units providing pure CO₂, e.g. from natural gas sources or off-gases from the chemical industry, as in case of ethylene oxide plants. The unique physico-chemical properties of CO₂ provide the basis for a remarkable variety of applications – most of them of considerable interest to the chemical industry. Moreover, the steady development of new areas of CO₂ usage often allows for the substitution of old-fashioned procedures and utilities which are not up to date anymore in terms of efficiency or sustainability.
CO₂ reacts
Not only in the chemical industry, the weak acid CO₂ is often applied as a neutralising agent. It substitutes mineral acids in many other sectors as well, e.g. in wastewater treatment. In contrast, its application as a synthetic agent in process chemistry is not very widespread, although considerable efforts are being made in CO₂-related development activities. On the industrial level, CO₂ usage is mainly limited to the production of urea (derivatives), carbonates and organic acids.

CO₂ dissolves
Especially in its supercritical phase, carbon dioxide is applied in analytical procedures and for extraction, often allowing for the substitution of classic solvents, most notably of (halogenated) hydrocarbons. As an easily removable solubiliser, supercritical CO₂ moreover comes with many advantages in regard to chemical reactions, advantages which can overcome classic problems such as phase transfer limitations.

CO₂ forms
In polymer production, CO₂ is used in different steps, e.g. as a solvent for polymerisation reactions. Many more variants of its usage, however, can be found among manufacturing technologies. In this field, CO₂ is widely applied as an auxiliary tool for foaming and for the production of small-sized particles.

CO₂ extinguishes, cools and cleans
Under certain circumstances, CO₂ behaves as an inert medium. Because of this, it is also applied in fire fighting, especially when its high gas density is advantageous. Further application potential arises from the possibility to transfer the gas in the solid phase, which is characterised by its low temperature. Application of solid CO₂ not only allows for cooling, the so-called dry ice is also used as a cleaning tool for the removal of problematic material from surfaces – especially hardened or sticky residues.
Hydrogen for hydrogenations. All-purpose potential of a reducing agent.

Apart from its small-scale application as a fuel, which is currently being advanced by Linde and other global companies, hydrogen (H₂) is widely used as a reducing agent in chemical synthesis, ranging from laboratory work to large-scale applications within the petrochemical industry. Here, the most important tasks are hydrogenations, e.g. selective reduction of phenol to cyclohexanone in the production of caprolactam. High amounts of hydrogen are also applied to comply with environmental legislation – most notably for the desulphurisation of fuels in oil refineries.

Moreover, hydrogen is used for activation of catalysts, for quality control and for removal of impurities from product streams. Corresponding applications range from hydrogenation of disruptive aldehydes in the production of polyester monomers to the selective reduction of acetylene (a by-product in steam cracking of hydrocarbons for production of olefins) to ethylene.

Production of hydrogen

On the industrial level, hydrogen production is predominantly based on synthesis gas routes, i.e. sourced from H₂/CO mixtures gained by partial oxidation of carbonaceous feedstock such as coal, or from steam reforming of hydrocarbons. The latter, mainly based on natural gas as a feed, is by far the most important production method. In engineering and the construction of corresponding production plants, Linde is among the leading suppliers. This is also true in respect of purification technologies, when pure hydrogen is obtained from gas mixtures, e.g. certain petrochemical off-gases. After liquefaction, hydrogen is not only ultra-pure. From a supply point of view, it can be transported and kept in stock in a very effective manner – typically when not too large amounts of the gas are needed and high fluctuations in demand are to be expected, i.e. when erection/operation of a dedicated H₂ production unit is not economic. Recent developments allow for the production of “green hydrogen”, e.g. by reforming of glycerol. This alcohol is a co-product of biodiesel production and is currently being developed as a potential platform chemical for the creation of “green” hydrogen. Moreover, when hydrogenated catalytically in the liquid phase, it can yield 1,2-propane diol as shown by experiments at Linde’s test facilities (see the picture on the right).
Due to the increasing world population and global economic growth, our freshwater resources are decreasing. Gaseous emissions from industrial production, traffic and private consumption are the predominating causes for an alarming climate change. Waste disposal is responsible for pollution of air and water. Technical gases can be used to reconcile industrial production with sustainability, and to preserve our natural resources.

**SOLVOX® – accurate dosing of oxygen in wastewater treatment**
Both in industrial and municipal wastewater treatment plants, many problems arise due to oxygen deficiency. Among the consequences are insufficient cleaning performance and anaerobic degradation processes, often accompanied by serious odour troubles.

Targeted introduction of pure oxygen realised at critical points of the wastewater chain solves these kinds of problems quickly, efficiently and in a flexible manner. In this respect, processes of the SOLVOX® family are well-proven. With only low investment cost and minor maintenance effort, SOLVOX® enhances performance – e.g. of aeration basins or pre-cleaning installations – without necessitating major modifications.

**SOLVOCARB® – tailored neutralisation of wastewater with CO₂**
Alkaline wastewaters from chemical production sites may only be fed into municipal canal systems after proper neutralisation. For this purpose – when compared with mineral acids such as sulphuric acid – CO₂ comes with a number of advantages: the carbonate formed during the neutralisation process is not classified as a harmful substance and doesn’t contribute to salt loads which are often subject to a wastewater fee. From a technical point of view, the flatness of carbon dioxide’s neutralisation curve guarantees that over-acidification is safely avoided.
Burning of wastewater with oxygen
Not seldom, highly polluted wastewaters have to be burned – especially in cases when they contain persistent contaminants which can’t be degraded to a sufficient extent by biological treatment. The capacity of air-based combustion processes can often be enhanced by additional use of oxygen. Linde offers engineering services and hardware ranging from classic oxygen enrichment of combustion air to special burners to complete turnkey plants.

CIRRUS® units – off-gas purification and resource recovery by cryocondensation
Condensation is an elegant and efficient option for cleaning effluent gas streams containing volatiles such as organic compounds, as their recovery provides the basis for re-use within the process or – e.g. in case of hazardous substances – for appropriate disposal measures. By passing heat exchangers, the raw gas is cooled down in order to undercut the dew point of the contaminant(s) – which in many cases are valuable material – thereby condensing as a liquid. As a coolant, liquid nitrogen (-196 °C) is applied which opens up temperature levels which are not achievable otherwise, e.g. when using conventional refrigerating machines. Therefore, even off-gases with very low-boiling gas components can be eliminated, which in many cases allows for compliance with regulations concerning off-gas quality. Gaseous nitrogen gained by the cooling process is often re-used within the process – e.g. for inerting purposes after injection into the nitrogen network of the respective site.

Exemplary scheme: Cryocondensation
Industrial services in every dimension. Shortened revisions, less risk of fire, non-polluting processes.

Linde offers a comprehensive portfolio of service processes. Their main purpose is the minimisation of downtime in case of revision or maintenance activities. But increasing demands in terms of environmental protection are covered as well: the applied gases are neither toxic nor inflammable, thereby eliminating fire and explosion hazards especially during start-up and shut-down operations of process plants. The following examples of applications which we can realise for our customers illustrate the breadth of our service portfolio:

**Drying of process plants**
For drying and purging with nitrogen, Linde offers valuable assistance. In many cases – not only in restored plants, but in new plants as well – significant amounts of humidity are accumulated, which is unacceptable because this delays start-up or – if not rectified – inhibits maximum product yield for an extended period of time. Through the purging of installations with nitrogen heated up to 400 °C, the unit can be dried in a controlled manner. Delay of operational action until start-up or maximum capacity can often be reduced by several days. For this purpose, nitrogen flows of up to 25,000 m³/h and pressures of up to 700 bar can be provided on site. Nitrogen temperatures can be set within a wide range.

**Reactor cooling**
The cooling of hot operation sections such as catalytic reactors can be very time-consuming and often causes considerable loss of production. By application of the CATCOOL™ process – a targeted injection of considerable amounts of cold nitrogen – Linde offers the possibility to reduce the cooling phase of reactors by days. This of course allows for a considerable reduction of downtime expenses.
Cleaning with CRYOCLEAN®
In the application of the CRYOCLEAN® process, particles of dry ice are accelerated and “shot” onto the surface to be cleaned. The thermal effect of deep cooling of the impurity combined with the high-velocity impact of the pellets in many cases allows for the removal and proper separation of solids as well as sticky residues of various kinds. In the process, dry ice sublimates, producing gaseous CO₂ which naturally separates from the pollution material, leaving it in a concentrated form. Accordingly, no further handling of large amounts of used blasting agents, such as polluted liquids or abrasives – as after cleaning with water or by sand jet – is necessary. Typical CRYOCLEAN® applications are the cleaning of heat exchangers, pipelines and stirrer systems.

Pigging and pipeline maintenance
For emptying, cleaning or inspection of pipelines, so-called pigs are widely applied. In order to propel this equipment through the respective duct, sufficient pressure has to be exerted. Very often, this pressurisation is realised by use of gaseous nitrogen which also ensures inert conditions as well as corrosion protection.

Intermediary supply of natural gas
From time to time, regional or long-distance gas supply lines are taken out of operation, e.g. due to maintenance activities or renewal. In chemistry, as well as in many other industries, such interruptions can cause the shut-down of production units. In order to avoid such inconveniences, intermediary gas supply can be realised, using mobile units with high safety standards which – from an energy point of view – are self-sustaining.

Leak testing
Under operating conditions with pressures of up to 375 bar, very small leaks and their precise leakage rates can be determined with a special leakage test method. The leaks are repaired immediately if possible. With a nitrogen/helium mixture, the inert and diffusible helium is used as an easily detectable tracer gas component. Compared with a standard helium leakage test, using a gas mixture makes this procedure much more interesting from an economical point of view. After the test, the client receives a detailed report which enables him to remedy deficiencies prior to commissioning. In addition to the protection of personnel and the plant itself, this test procedure also contributes to environmental protection and, not least, economical operation.
Reliable gas supply by Linde. Comprehensive, fast, flexible.

With its tightly knit production, sales and distribution network, Linde can guarantee fast, reliable and economical supply of gases. This capability is based on supply options and facilities ranging from pressurised 1-litre MINICAN® gas cans and gas cylinders to tanks filled with liquefied gas to on-site production units to pipeline supply. Linde’s strong market presence, combined with short delivery distances and high supply chain reliability, also contributes significantly to the high availability of the entire gases portfolio.

Gas cylinders
Linde Gases delivers gases as well as gas mixtures packaged for convenient application. Based on a modern and continually renewed cylinder park, Linde guarantees highest gas availability. In order to provide our customers at all times with an accurate overview that shows the whereabouts of rented cylinders, Linde offers the tracking system ACCURA®, which allows for an efficiently run cylinder management.

Tanks for liquefied gas
Customers whose requirements exceed the capacity of cylinder-based deliveries are supplied with liquefied (cryogenic) gases. The liquids, a highly efficient transport form, are transported by tanker trucks and stored for use in tanks installed on the customer’s premises. Available tank sizes range from 3,000 to 80,000 litres and provide liquefied gases such as oxygen, nitrogen, hydrogen, argon and carbon dioxide in the immediate vicinity of the respective gas use. Linde – being competent in terms of all areas of operation, including installation, maintenance and inspection – also provides peripheral but indispensable equipment such as vaporisers which are attached to the tanks and transform the cryogenic liquid into the gas phase. Furthermore, in order to ensure uninterrupted gas supply, Linde offers a modem-based remote level control and monitoring system.

MINICAN®, ACCURA® and ECOVAR® are registered trademarks of The Linde Group.
High-performance on-site supply by ECOVAR® units

Beyond a certain consumption rate, supply of gases by road tanker is not a satisfactorily economical solution. In cases where larger gas volumes are required, Linde offers the ECOVAR® solution – a supply concept which is especially interesting when fluctuations in gas consumption are not too pronounced. ECOVAR® gas production units are typically dedicated to a customer’s process and installed nearby, usually in combination with a back-up tank installation for cases of peak consumption or emergency situations. Examples for this combined supply solution are widespread and can be found in (petro)chemistry, semiconductor production, metallurgy, waste treatment, food production, research and science etc. In terms of gas type, production volume and specified gas purity, the customer can choose between three different types of units: ECOVAR®-C (cryogenic process), -A (adsorption) or -M (membrane). Among the characteristics of these gas production plants are typically long periods of uninterrupted service, low production costs and a high degree of flexibility.

Pipeline network

In case of high gas demand of a customer, a direct pipeline connection fed by a nearby gas production centre normally is the most economic supply solution. Especially when more than one consumer is connected to the pipeline (as often is the case in chemical clusters), this mode of supply proves to be very advantageous. In terms of this pipeline supply business, Linde is in an excellent position, as its Engineering and Contracting Division offers an entire portfolio of gas production plants. Apart from air separation units for pipeline supply with air gases – namely nitrogen and oxygen – Linde has the necessary know-how and experience for the planning, design, delivery and construction of units producing hydrogen (H₂), carbon monoxide (CO) and mixtures of the latter gases (synthesis gases).
Getting ahead through innovation.

With its innovative concepts, Linde is playing a pioneering role in the global market. As a technology leader, it is our task to constantly raise the bar. Traditionally driven by entrepreneurship, we are working steadily on new high-quality products and innovative processes.

Linde offers more. We create added value, clearly discernible competitive advantages, and greater profitability. Each concept is tailored specifically to meet our customers’ requirements – offering standardised as well as customised solutions. This applies to all industries and all companies regardless of their size.

If you want to keep pace with tomorrow’s competition, you need a partner by your side for whom top quality, process optimisation, and enhanced productivity are part of daily business. However, we define partnership not merely as being there for you but being with you. After all, joint activities form the core of commercial success.

Linde – ideas become solutions.