

Industrial gases in the chemical industry



Linde industrial gases – partners to the chemical industry



Industrial gases find vast and versatile application in the chemical industry. They serve as feed materials for synthesis processes, they ensure and improve the economy of processes and plants, they enhance product quality and plant safety, and they help to protect the environment.

Supply of gases must be matched specifically to the diversity of products, processes and production capacities. Essential factors in this are dependability, economy and wide-ranging applications solutions.

Together with optimum supply of a complete selection of gases, Linde provides the chemical industry with comprehensive know-how and extensive supporting services:

- ▶ Process consulting, economic feasibility studies
- ▶ Advice on safety issues
- ▶ Process design calculations
- ▶ Experimental investigations
- ▶ Development of technological and engineering solutions
- ▶ Implementation and start-up
- ▶ Financing, rental and operation of gas production and distribution facilities.

Quality, safety and environmental protection are key ingredients in all of Linde's work. Our integrated QSE management system based on DIN EN ISO 9001, DIN EN ISO 14001 and SCC assures consistently high quality and safety of our products and services as well as environmental compatibility in the application of industrial gases and their disposal where required.



Industrial gases – components for synthesis processes

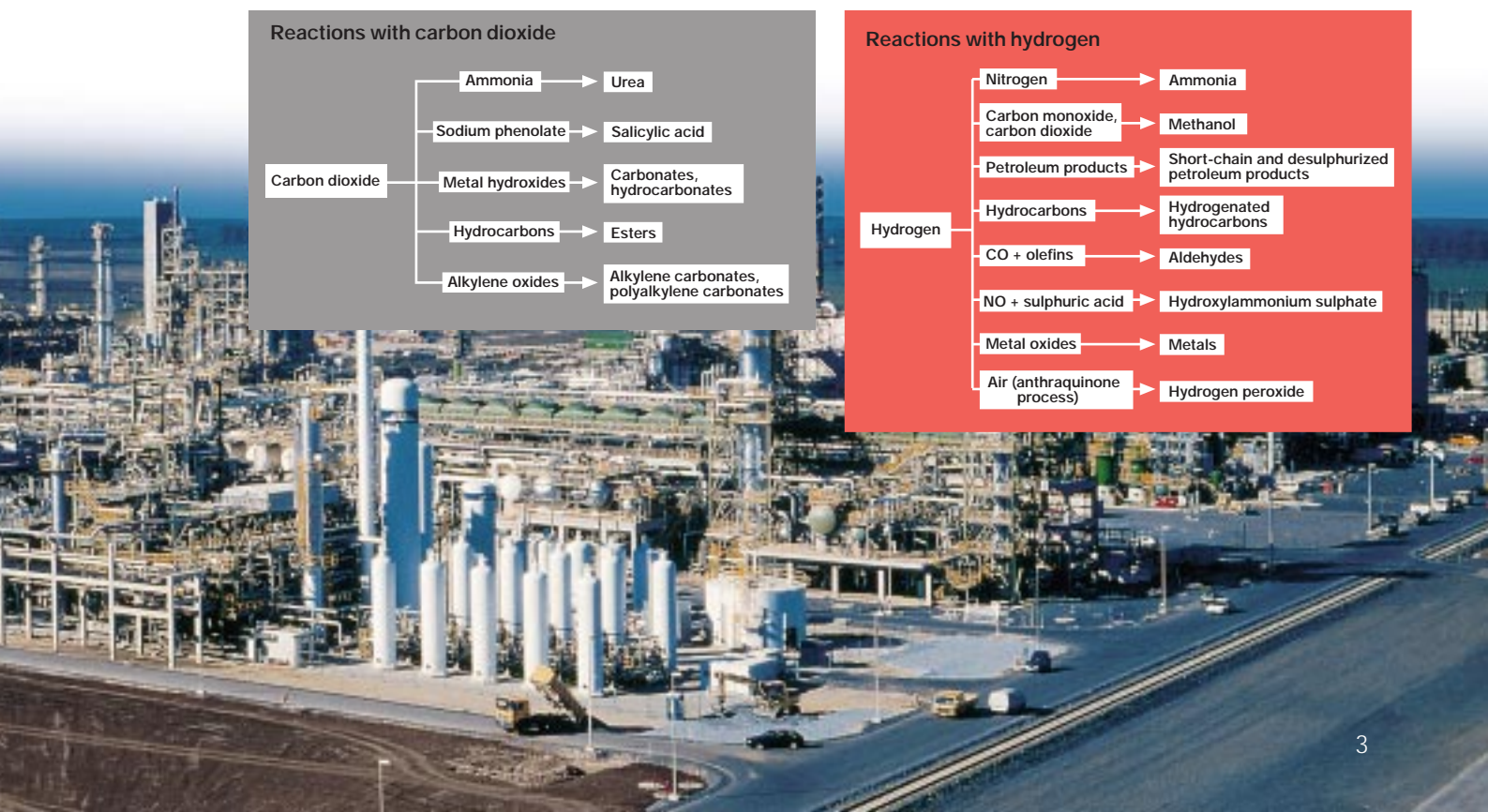
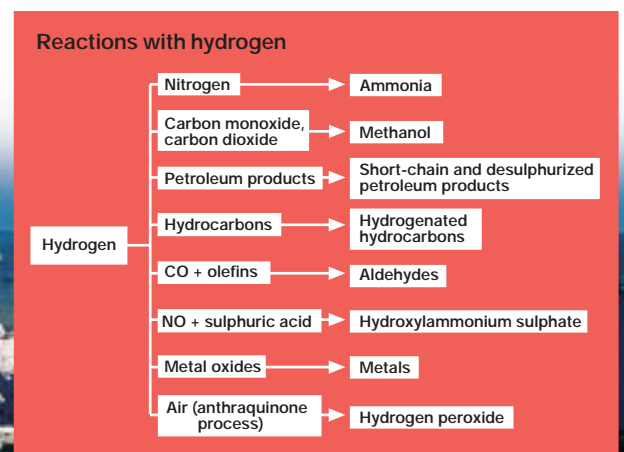
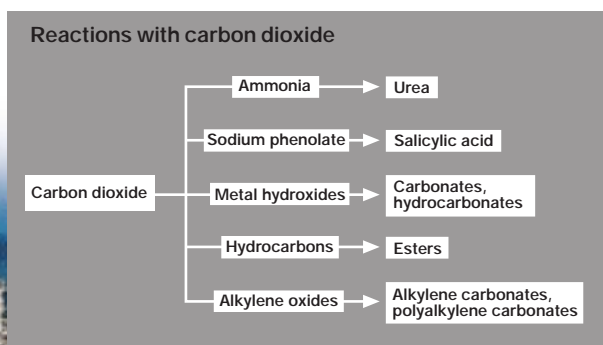
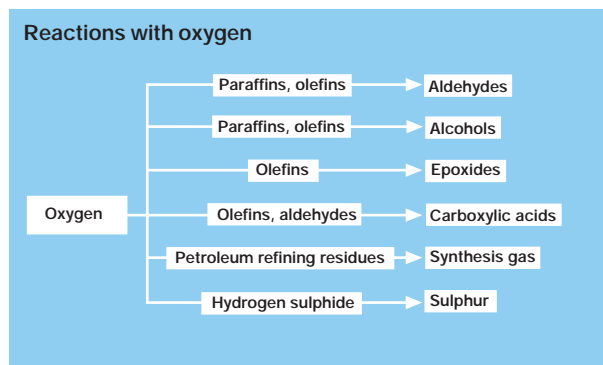
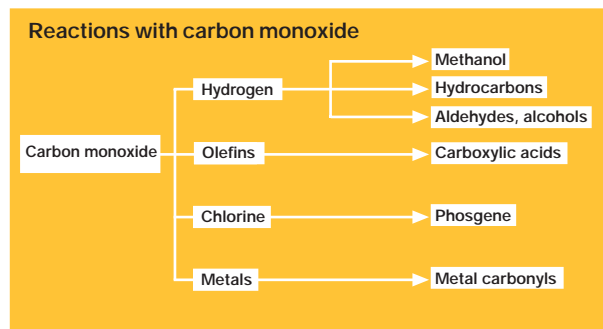


Applications in general

In the chemical industry industrial gases are used principally

- ▶ as chemical reactants
- ▶ for assuring plant safety
- ▶ for protection of the environment
- ▶ in analytical chemistry
- ▶ for industrial service.

Oxygen, hydrogen, carbon monoxide, carbon dioxide and synthesis gas are reactants in a large number of important synthesis processes. The accompanying charts summarize common reactions working with oxygen, hydrogen, carbon monoxide and carbon dioxide.



Gases for oil refineries – greater efficiency, cleaner environment

Oxygen for oil refineries

Oxygen is used at oil refineries for the partial oxidation of petroleum residues, to regenerate catalysts in FCC plants, and to improve the performance of Claus plants.

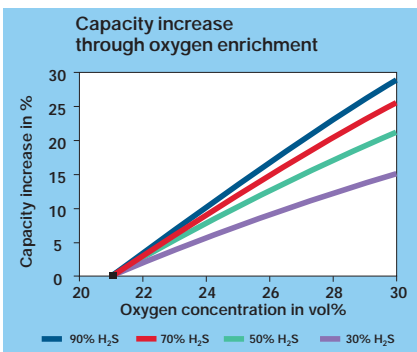
In the Claus process, hydrogen sulphide is converted to elemental sulphur. Removal of sulphur compounds is required in the processing of petroleum, natural gas and coal to motor fuels, synthesis gas and fuel gas.

Its purpose is to ensure compliance with both the emission levels stipulated under environmental laws and the maximum concentrations of sulphur compounds imposed by technological constraints.

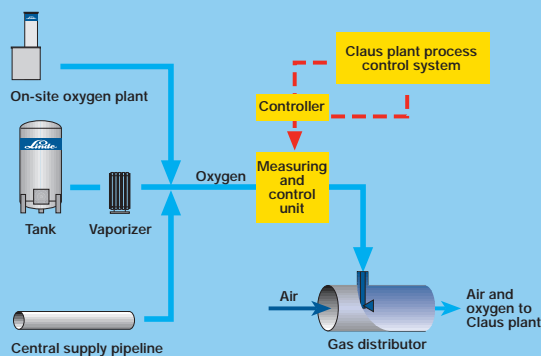
At present, the oxygen content of atmospheric air is primarily utilized for the oxidation of hydrogen sulphide.

Adding oxygen to the air or using pure oxygen results in a number of benefits:

- ▶ Increased plant capacity
- ▶ Higher oxidation temperatures
- ▶ Reduced load on off-gas treatment systems due to lower concentration of inert nitrogen
- ▶ New plants can be built smaller.



Schematic diagram of oxygen enrichment



Claus plant



Linde hydrogen plant

Hydrogen for oil refineries

An oil refinery is both a producer and a consumer of hydrogen, the volumes consumed usually exceeding those internally produced.

Hydrogen is needed as a reactant in hydrorefining and hydrocracking. Since refineries are shifting their output to larger quantities of low-sulphur, low-aromatics and brighter products, demand for hydrogen will continue to grow.

The main processes for production of hydrogen are:

- ▶ Steam reforming of methane
- ▶ Gasification of oil refining residues and recovery from synthesis gas
- ▶ Recovery from refinery off-gases.



*Above:
Gasification of oil
residues with oxygen*



*Left:
Production of syn-
thesis gas and
methanol from oil
refining residues*

Economical reactants for production of basic chemicals and intermediates

Oxidation of ammonia for production of nitrogen monoxide



Oxygen: Improving economy – reducing investment costs

Increasing use is being made of industrial oxygen in oxidation processes for the manufacture of oxides, aldehydes, and also acids and alcohols. It can greatly improve the economy of existing plants and reduce capital expenditure for new plants. The methods used are oxygen enrichment of the oxidizing air, adding oxygen to the feed stream and substituting pure oxygen for air.

The benefits of oxygen are:

- ▶ Larger throughput in the same size of plant by lowering the concentration of inert nitrogen
- ▶ Higher temperatures in the reacting stream
- ▶ Accelerated reactions due to higher oxygen concentration
- ▶ Higher selectivity of the oxidation process in parts
- ▶ Smaller off-gas flows
- ▶ Lower energy consumption.

Oxidation processes using oxygen

Product	Feed	Air	Oxygen	Enriched air
Acetaldehyde	Ethylene	●	●	●
Benzoic acid	Toluene	●		
Cyclohexanone	Cyclohexane	●		●
Acetic acid	Acetaldehyde	●		●
Ethylene oxide	Ethylene		●	
Propylene oxide	Propylene	●	●	
Nitrogen monoxide	Ammonia		●	
Terephthalic acid	p-Xylene	●		●
Vinyl acetate	Ethylene, acetic acid		●	
Vinyl chloride	Ethylene, hydrogen chloride		●	
Hydrogen peroxide	Hydrogen	●		●

Hydrogen: Basic chemicals, hydrogenation, catalyst production

Hydrogen is a reactant in the manufacture of basic chemicals and intermediates as well as specialty chemicals and pharmaceuticals. Synthesis gas, a mixture of hydrogen and carbon monoxide, is employed above all for synthesis of methanol and in the hydroformylation of olefins to aldehydes and alcohols. Ammonia is manufactured from a different synthesis gas mixture of hydrogen and nitrogen.

Another process of considerable importance is hydrogenation, which involves the homogeneous or heterogeneous catalytic addition of hydrogen to organic compounds.

Examples are:

- ▶ Hydrogenation of adipic acid dinitrile to hexamethylene diamine
- ▶ Hydrogenation of benzene to cyclohexane
- ▶ Hydrogenation of phenol to cyclohexanone.

Industrial hydrogen is also used in the manufacture of catalysts for reducing metal oxides to the active metallic form and to regulate chain length in the polymerization of propylene to polypropylene and in the manufacture of polyethylene.

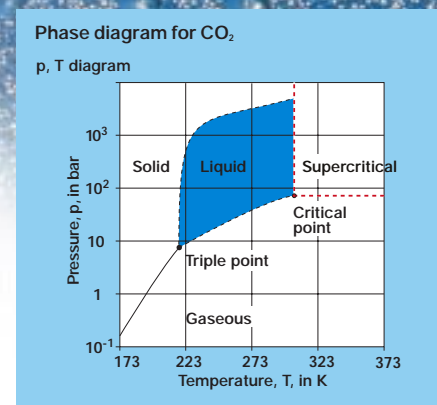
*Hydrogenation
of phenol to
cyclohexanone*

Carbon dioxide: reactant, solvent, pH control agent

Carbon dioxide is used, for example, in the manufacture of urea, salicylic acid, carbonates and polyalkylene carbonates, and in several other organic chemistry synthesis processes.

Supercritical carbon dioxide is a prospective replacement for environmentally hazardous solvents as currently required in a number of chemical synthesis reactions and is capable of improving the properties of some products made by polymerization.

Beyond that, carbon dioxide is widely used for pH-value control and neutralization of liquids.



*Production of
epoxy resins
using carbon
dioxide*



Environmental protection and resource recovery – reliable, efficient, economical

Neutralization with a SOLVOCARB® reactor in a chemical plant



Neutralization of alkaline effluents with carbon dioxide (SOLVOCARB® process)

Before alkaline effluents from an industrial plant can be discharged to the municipal sewage system, they must be neutralized.

Carbon dioxide has several advantages over mineral acids in neutralizing alkalies. To begin with, it is not classified as a material which is hazardous to water. Moreover, it is not associated with high salt loads, which may be penalized by special charges, and the flat neutralization curve excludes risk of over-acidification.

Neutralization of wastewater with carbon dioxide is carried out with the Linde SOLVOCARB® process.

Oxygen for wastewater treatment (SOLVOX® process)

Many problems occurring in the treatment of wastewater are due to a deficit of oxygen. In the chemical industry especially, where effluents are usually heavily contaminated, this can cause considerable trouble such as degraded treatment performance or appreciable odor nuisance due to anaerobic decomposition processes.

Industrial oxygen is often capable of remedying such situations.

The necessary oxygen is injected into the wastewater by the Linde SOLVOX® process. Particular advantages of this process are its low investment costs and flexible adjustment of oxygenation to actual needs.

Oxygenation of wastewater using the SOLVOX®-B process



Recovery of valuable organic materials and waste air purification by cryocondensation

Cryocondensation works with liquid nitrogen as a low-temperature refrigerant. The polluted air stream is cooled in heat exchangers to below dewpoint temperature, causing contaminants or recoverable materials present in vapor form to condense. Liquid nitrogen achieves condensing temperatures well below those attainable with conventional refrigerating machines.

Benefits

- ▶ Convenient adjustment of process temperature to changed conditions
- ▶ Regulation of condensation performance over a broad range
- ▶ Treatment of highly contaminated waste air streams
- ▶ Reduction of residual contaminant levels to parts per million.

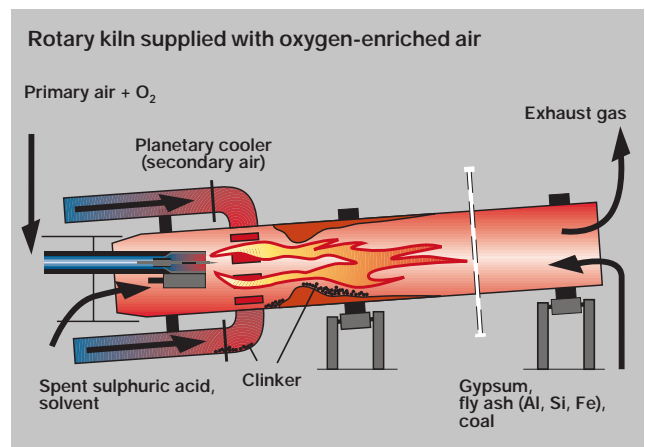
Oxygen in processing of spent sulphuric acid

Mineral wastes and spent sulphuric acid can be processed in rotary kilns. For example, gypsum is processed in these rotary kilns jointly with spent sulphuric acid and coke, followed by conversion of sulphur dioxide to sulphuric acid.

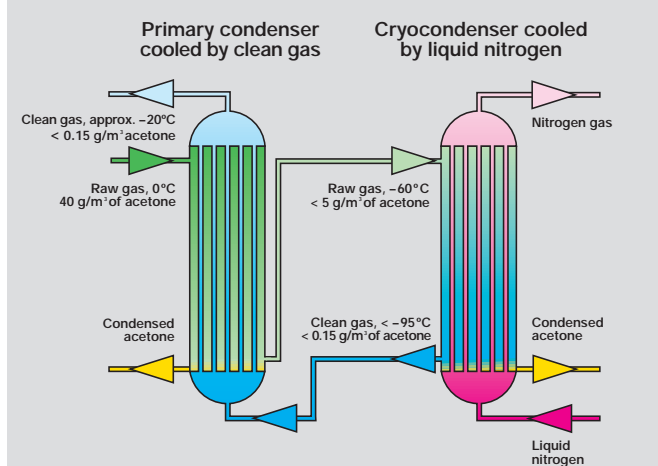
Enriching the air supplied to the kiln with oxygen achieves the following benefits:

- ▶ Increased processing capacity
- ▶ Combustion of solvents containing higher levels of water.

Processing spent sulphuric acid in rotary kiln



Flowsheet for cryocondensation



Cleaning acetone-contaminated waste gas by cryocondensation with liquid nitrogen

Safe inerting and efficient cooling

Inerting in storage of chemical products



Inerting in chemical processes

Lowering oxygen concentrations to a safe level by inert gases (nitrogen and carbon dioxide) is a proven method of preventing oxidation, fires and explosions.

A cushion of inert gas is frequently placed over liquids in storage tanks. Silos are purged with inert gas as a precaution against dust explosions.

Another important application is for explosion protection on reactors in which oxidation takes place in the liquid phase. Due to the risk of an explosive mixture forming in the head of the reactor, it must be purged continuously with inert gas so as to dilute the gas mixture below its explosion limit.

Cooling vessels and reactors

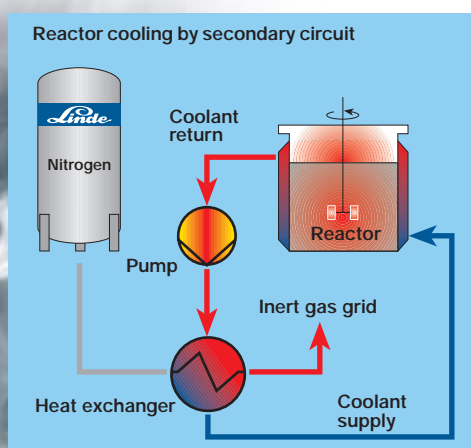
Control of temperature is often vital to achieving high yield and good quality of chemical compounds manufactured by synthesis. Liquid nitrogen enables low-temperature synthesis of chemical and pharmaceutical products to be carried out conveniently at $-80\text{ }^{\circ}\text{C}$ or such other temperature as may be required.

Cooling can be performed by three methods:

- ▶ Injecting liquid nitrogen directly into the reactor.
- ▶ Cooling the reactor contents by nitrogen flow through an external jacket or an internal cooling coil.
- ▶ Indirect cooling by a secondary circuit.

The benefits of liquid nitrogen cooling are:

- ▶ Cooling capacity variable over a wide range
- ▶ Low investment and operating costs
- ▶ Absence of environmentally damaging refrigerants or noise nuisance .



Reactors cooled with liquid nitrogen

Other gas applications for the chemical industry

Deoxygenation of boiler feedwater (SOLVOGEN® process)

Because it corrodes piping and vessels, oxygen must be removed from boiler feedwater, hot water system recirculating flows and chemical process water. The SOLVOGEN® process has been designed for this purpose.

The process is based on converting dissolved oxygen with hydrogen over a palladium catalyst at ambient temperature.

Linde supplies SOLVOGEN® systems to treat water flows as small as 10 m³/h in the food industry or as large as 1000 m³/h in power stations.



Catalytic reactor for deoxygenation of boiler feedwater

Gas and equipment supply for laboratories and pilot plants

Ultra-pure gases, gas mixtures and calibration gases are required by laboratories and pilot plants in the chemical industry for analytical and measuring applications and test operation.

Linde has a stock range of standard gas mixtures.

Calibration gases – precision gas mixtures of customer-specified composition and certified analysis for use in calibrating measuring and analytical instruments – are supplied in pressure cylinders.

Gases of high-grade quality are essential for reliable and accurate operation of gas analyzers. Linde supplies operating gases for gas chromatography, flame photometry, chemiluminescence, spark spectroscopy, ECD analysis and atomic absorption, and filling gases for counter tubes.

Linde designs and builds complete gas supply systems for laboratories and pilot plants as either standard or customized units.



SOLVOGEN® control panel



Laboratory in the chemical industry

Service processes – quicker inspections, reduced fire risk, environmentally compatible

*Leak test on piping
assembly for
hydrogen plant*



All of the comprehensive services and service processes available from Linde are designed to minimize the time required for inspection and maintenance of complete systems, equipment and components.

They also satisfy increasingly stringent environmental demands. All gases employed are non-flammable, non-toxic and non-corrosive. Moreover they reduce fire and explosion risks, permitting safe start-up of equipment.

Services available are:

Piping and pipeline cleaning by the Sandjet® process

This is a blast cleaning method using nitrogen to force the abrasive through the piping system. The abrasive is recovered for re-use.

Leak testing

A nitrogen-helium gas mixture is used for leak testing of complete systems or individual components at operating pressure.

System drying

Drying of pipings, complete production systems or individual components is carried out with nitrogen, which may be heated to relatively high temperatures as required.

Reactor cooling

Rapid cooling of reactors is achieved by controlled injection of liquid nitrogen to prepare them for servicing. Time saved for cooling greatly reduces the duration of system shutdown.

*Pig trap and
nitrogen feeding
point in Rongellen,
Switzerland*



Pigging and pipeline renewal

A pig is a mechanical device forced through a pipeline system by introducing nitrogen at high pressure, displacing the oil or other fluid into a receiving tank and cleaning the pipe. At the same time the pipeline is inertized by the nitrogen. Cleaning can be combined with remote visual inspection by video camera.

Mobile natural gas supply

Long-distance or regional gas pipelines have to be taken out of service when modernization, rerouting or repairs become necessary. For the chemical industry this may normally necessitate temporary shutdown of production facilities. During such times, continuous supply of gas can

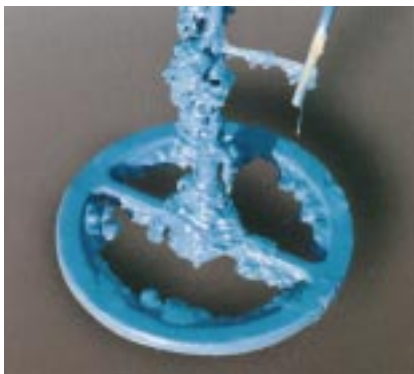
be maintained with Linde mobile natural gas stations, self-contained units operating at a high level of safety and reliability.

Blast cleaning with dry ice

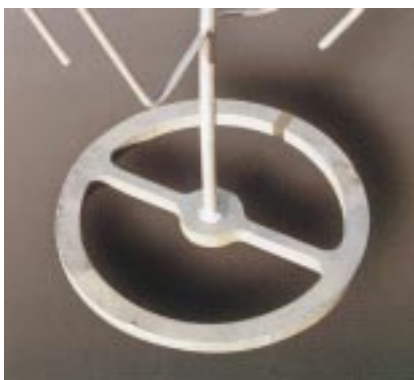
In the CRYOCLEAN® process, dry ice pellets frozen to -78°C are propelled at high velocity onto the surfaces of work to be cleaned. On impact, the dry ice immediately vaporizes, removing dirt and impurities while leaving the cleaned surface clear of grit or sludge residue. Typical applications in the chemical industry are for cleaning heat exchangers, piping and agitators.

Cleaning molds used in production of polyurethane foam

Agitator used in paint manufacture prior to being cleaned



Agitator after being cleaned by the CRYOCLEAN® process



Gas supply – complete and functional

With our tightly knit production, sales and distribution network we can guarantee fast, reliable and economical supply of gases to users by facilities ranging from two-litre steel cylinders to on-site units, from 75,000-litre liquid tanks to direct pipelines.

Gas cylinders

Upwards of four million gas cylinders displaying the Linde name are in circulation in Europe. They are delivered to users by road truck or trailer, depending on the quantities required. To enable customers to maintain a running inventory of gases, Linde provides the LIBAS® cylinder tracking system, which continuously monitors movement of all cylinders.



*Gas cylinders
in various sizes*

Liquefied gas tanks

Customers whose requirements exceed the capacity of cylinder deliveries are supplied with liquefied gases transported by tanker truck and stored for use in tanks installed on their premises.

Linde furnishes vaporizers and all other associated equipment together with the storage tanks and assumes responsibility for the entire installation, maintenance and inspection work. Electronic remote monitoring of tank level ensures that an adequate supply of gases is available at all times.

ECOVAR® on-site units

Above a certain consumption rate, supply of gases by road tanker is not a satisfactorily economical proposition. In such instances we recommend installation of a plant for on-site production.



ECOVAR®-A plant



ECOVAR®-M plant



*Tanker delivering
liquid hydrogen*



ECOVAR®-C plant

The ECOVAR® supply concept combines an on-site production unit and liquid storage tank for supply of nitrogen or oxygen. Basic demand is covered by the capacity of the production unit with a reserve supply available in the storage tank to meet peak consumption and emergency situations. Customers can choose among three alternatives according to the required product, purity and production capacity: ECOVAR®-C (cryogenic process), ECOVAR®-A (adsorption process) or ECOVAR®-M (membrane process). All three types are marked by high reliability of supply, economical production cost and a high level of flexibility.

Pipeline grid

Direct delivery by pipeline from one of our production centers is the most economical form of supply for companies using large tonnages of gases. A growing number of high-volume users have endorsed this option by reason of its obvious advantages. Linde puts up the capital for new plants, invests its many years of experience acquired in operation of numerous comparable facilities, and moreover guarantees reliable supply in times of peak demand or emergencies through its backup resources of large tank farms and extensive distribution capabilities.

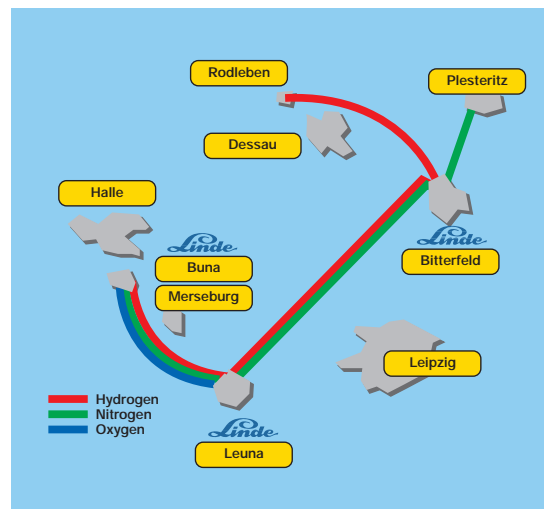
Pipeline supply is particularly economical in industrial regions where several users are linked to a supply grid served by a central production facility.

Linde is well positioned for pipeline business. Through its Process Engineering and Contracting Division the company has access to an extensive range of equipment. Air separation plants are designed and built for pipeline supply of oxygen and nitrogen as well as plants for production of hydrogen, carbon monoxide and synthesis gas.



Steam reformer producing hydrogen in Milazzo, Sicily

Linde pipeline system in Germany totalling more than 400 kilometres supplies hydrogen, nitrogen, carbon monoxide and oxygen to high-tonnage users



Performance on site – Linde Industrial Gases



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Linde industrial gases are encountered in applications as varied as welding, freezing, propulsion, heating, industrial cleaning, respiration or testing. They improve the quality of life and they help to secure the future by making production operations more efficient and economical.

Supply of the gases themselves is supported by expert counselling and know-how, customised hardware, custom-application testing, and the complete handling associated with industrial gases.

Gases can be supplied in any form appropriate to customers' requirements: in cylinders or multi-cylinder batteries, from liquefied gas tanks, through ECOVAR® on-site production units, by pipeline.



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Your local supply center: