

Oxygen enrichment for intensification of
air oxidation reactions.

Vol. 1. Refineries.



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Preface.

This book focuses on oxidation processes that involve the use or addition of industrial oxygen to optimise processes. In particular, it looks at how oxygen can be used to increase the throughput and/or yield of a target product and make processes more flexible.

This includes oxidation processes in the refining and petrochemical industries. In addition, this book describes the hardware needed to apply industrial oxygen. It also focuses on the mathematical modeling of reaction processes, often used to simulate the effects of industrial oxygen. And it looks at the key risks and limitations of using oxygen enrichment in industrial facilities.

This first volume covers oxygen enrichment applications in refineries. Subsequent volumes will focus on petrochemical production, fluidised beds, and environmental topics.

This book is the result of application-driven work on the possibilities of oxygen at Linde AG and primarily aims at application engineers in the gases and chemicals industries as well as at chemists and engineers who work in chemical facilities.

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Authors Dr Hans-Jürgen Reinhardt, Dr Heinz-Dieter Obermeyer, Dr Bernhard Schreiner, Dr Stefan Wolf

Introduction.

Oxidation reactions are at the heart of countless chemical processes, producing both chemical building blocks and final products. Oxidation, for example, plays a key role in refining crude oil, the most important fossil resource in the petrochemical industry. Other oxidation processes are equally essential, for example, to heat feedstocks, condition catalysts or treat waste streams. In the vast majority of these processes, molecular oxygen is the oxidising agent of choice.

The oxygen is usually supplied in the highly diluted form of process air. Almost 79 percent of air (by volume) is inert and so its oxidation potential is very limited. This extra “ballast” also has to be routed through the different process steps, which usually requires a significant amount of energy. Enriching process air with industrial oxygen is often a simple way of increasing the efficiency of air oxidation processes. O₂ enrichment is typically deployed to overcome limitations in process air supply as well as to increase capacity and relieve bottlenecks in flue gas treatment stages. Oxygen enrichment can also help achieve other goals such as the need to increase energy efficiency or plant flexibility.

O₂ enrichment thus offers technical and financial benefits to air oxidation processes across the widest range of applications – from refinery operations to downstream chemical processes. Depending on individual requirements, industrial oxygen can replace part of the process air feed or it can be added to the existing supply. O₂ enrichment has already proven its value in many thermal and catalytic air oxidation processes.

Purely thermal, non-catalytic oxidation reactions are used in a wide range of chemical processes, including various production steps and the treatment of waste streams. These reactions rarely rely on pure oxygen as the sole oxidising agent. The most important exceptions here are gasification processes that use carbon-based feedstocks to produce synthesis gas (H₂/CO) – most of these utilise pure oxygen.

Overall, however, air oxidation is the more widespread process by far, used, for example, in other partial oxidation reactions such as the recovery of sulfur from gases that contain H₂S.

Process air is also used for a wide range of total oxidation reactions including:

- Regeneration of catalysts by burning off coke deposits (as is the case with fluid catalytic cracking, FCC)
- Roasting sulfide ores
- Recycling used sulfuric acid
- Thermal treatment of highly contaminated wastewater

The high volume of N₂ in process air compromises efficiency in both oxidation reactors and subsequent process steps, regardless of whether an operator is using a furnace with burners or a fluidised bed reactor. The inert gas also has to be heated as it moves through the process. Its extra volume also severely limits system capacity. These negative effects can often be reduced or eliminated in the processes listed above by replacing part of the process air with industrial oxygen.

O₂ enrichment of process air can also bring similar benefits to production processes that use catalytic air oxidation in the gas or gas-liquid phase. These kinds of oxidation processes are typically used in the production of base chemicals such as terephthalic acid, ethylene dichloride, cyclohexanone and acrylonitrile. O₂ enrichment can be used to intensify these and many other processes provided that measures are in place to safely dissipate the extra reaction heat caused by the addition of pure oxygen. Adding oxygen relieves process bottlenecks and, in many cases, enhances product selectivity. It has proven effective on an industrial scale for the processes listed above and is thus already seen as a state-of-the-art technology.

Building on the insights gained from these industrial-scale deployments, detailed investigations were carried out into other air oxidation processes. The findings are presented in this book. The benefits of oxygen enrichment outlined here are based on direct comparisons with air-only oxidation processes. In some cases, the investigations were carried out on pilot scale only. In other cases, however, custom-developed software and hardware enabled test mode at industrial plants and even O₂ enrichment during regular operations.

1. Oxygen.

Figure 1: Composition of dry air

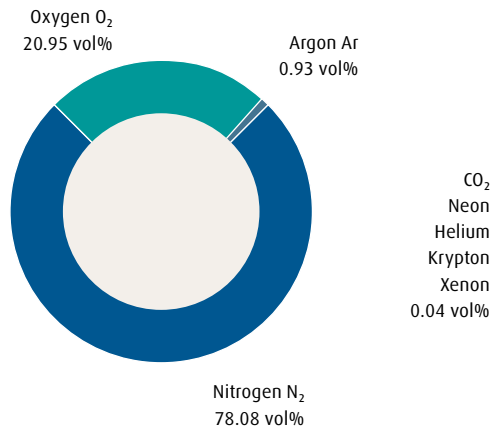


Table 1: Physical properties of oxygen and nitrogen

Gas	Oxygen	Nitrogen
Chemical formula	O ₂	N ₂
Molar mass [kg/kmol]	31.999	28.013
Melting point at 1.013 bar [°C]	-218.8	-210.0
Boiling point at 1.013 bar [°C]	-183.0	-195.8
Heat of vaporisation [kJ/kg]	213.0	198.7
Critical point		
Temperature [°C]	-118.57	-146.95
Pressure [bar]	50.43	34.00
Density at 1 bar and 0°C [kg/m ³]	1.429	1.250
Relative density with respect to dry air (0°C, 1 bar)	1.105	0.967

Oxygen is not very soluble in water. Solubility decreases as temperature increases and pressure drops. At 20°C and normal pressure, for example, its solubility is 44 mg/l.

Figure 2 maps the vapour pressure curve of oxygen against those of the inert gases nitrogen, argon and carbon dioxide.

Oxygen is usually produced via adsorption from gaseous air or from liquid air using fractional distillation and condensation.

Oxygen is very reactive. Despite its ability to react with a wide range of elements, oxygen does not directly react with gold, chlorine, bromine, iodine or the noble gases. Furthermore, it only reacts with nitrogen under certain conditions, for example in combustion engines under high pressure and temperature. Oxygen is an oxidising agent. This means that it takes two electrons from another reactant and is reduced to an oxide. This redox reaction is exothermic.

1.1 Properties of oxygen

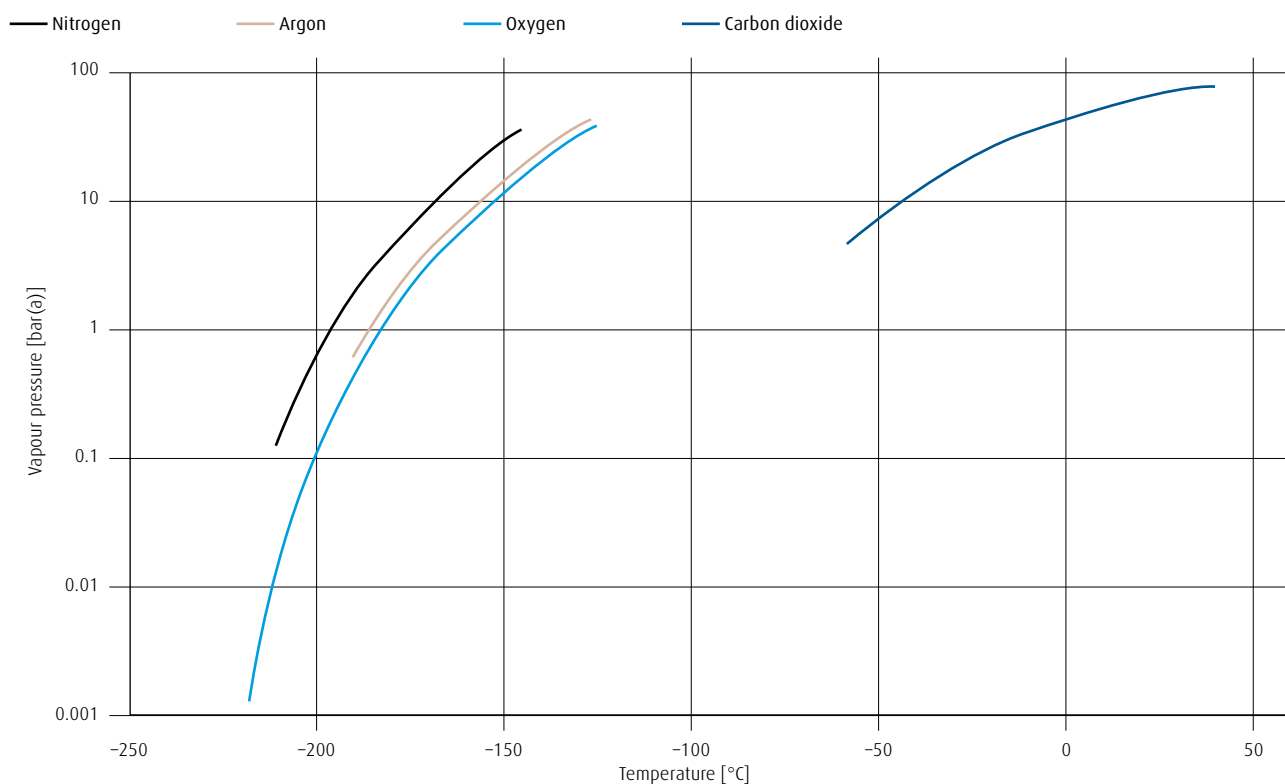
Oxygen is a colorless, odorless and tasteless gas. It is an extremely common element, present in the earth's atmosphere, the lithosphere, the hydrosphere and the biosphere. It is also part of many chemical compounds. Oxygen makes up around 50.5 percent of the earth's crust¹ and 20.95 percent of dry air (by volume). Figure 1 shows the composition of dry air.

Oxygen occurs in a number of different forms:

- Molecular oxygen (dioxygen) has the formula O₂. It is a highly reactive gas that combines with many substances to form oxides. Molecular oxygen also plays a role in combustion and corrosion processes. Oxygen is vital to almost all forms of life. In high concentrations, however, it is poisonous.
- Ozone (trioxygen) has the formula O₃. It is a colorless and highly poisonous gas, and is one of the most powerful oxidising agents.
- Atomic oxygen Atomic oxygen is made up of individual, free radical oxygen atoms. It is only stable under certain conditions, for example, in the hot atmosphere of stars. Atomic oxygen is also a reactive precursor in atmospheric chemistry and plays an important role in many reactions in this area.

Table 1 shows the key physical properties of oxygen compared with the inert gas nitrogen.

Figure 2: Vapour pressure curves of oxygen, argon, nitrogen and carbon dioxide



1.2 Oxygen production processes and supply systems

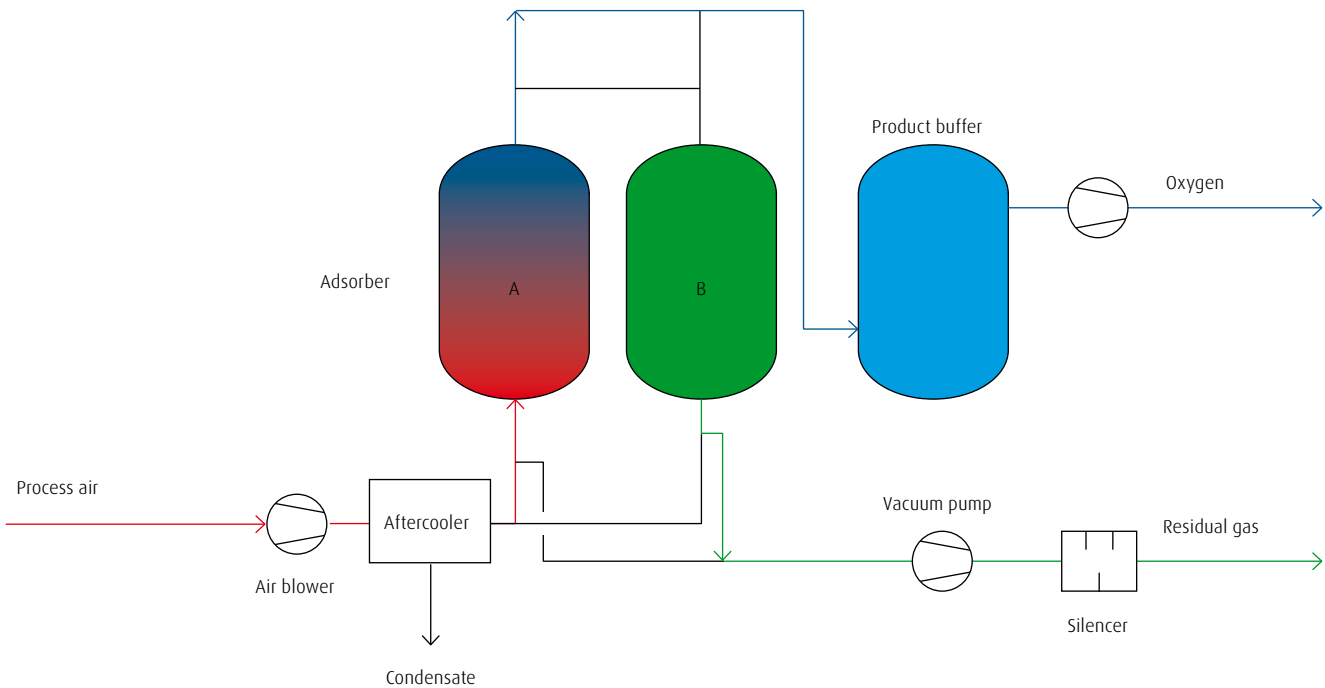
1.2.1 Overview

Oxygen can be delivered to customers on an industrial scale in a variety of ways. It can be supplied in liquid form in tanks; it can be generated at an adsorption plant; or it can be generated on site with a cryogenic air separation facility. Table 2 provides an overview of volumes and different supply options. Oxygen can also be supplied in cylinders or cylinder bundles to low-volume users, for example, laboratories.

Table 2: Different oxygen supply options (VPSA: vacuum pressure swing adsorption)

Amount of oxygen [Nm ³ /h]	Purity	Supply mode	Supply requirements
0 to approx. 1,000	> 99.5 %	Liquid supply from tank	Demand fluctuates strongly Load range typically between 30 and 100 %
Approx. 300 to 5,000	< 95 %	Adsorption (VPSA)	Load range typically between 60 and 100 %
Approx. 1,000 to 10,000	> 95 %	Cryogenic air separation	

Figure 3: Schematic drawing of a VPSA plant



1.2.2 Adsorption plants

In this process, air is separated using a porous adsorption material such as a molecular sieve. The adsorption process relies on the fact that different parts of air are adsorbed under different pressures and at different temperatures. In vacuum pressure swing adsorption (VPSA) plants, the different components are adsorbed under pressure and desorbed in a vacuum.

An adsorption cycle comprises:

- An adsorption phase
- A desorption phase
- Pressurisation (to prepare for the adsorption phase)

For economic reasons, most adsorption plants produce oxygen with a purity of around 94 percent or less. This is because argon, another component of air, has similar adsorption characteristics to oxygen. The plants have two or three adsorbers and sometimes an extra bed for purifying the air. Figure 3 shows a schematic drawing of a VPSA plant with two adsorbers. In this process, the air is sucked in, compressed and cooled, and then purified using a filter. It is then fed into adsorber A, where the nitrogen is adsorbed under pressure. The stream of oxygen, now free of nitrogen, is then temporarily stored in a product buffer. After this, it is compressed and cooled and ready to be delivered to the point of use. Nitrogen is being adsorbed in adsorber A and desorbed in adsorber B.

There are a number of benefits to using adsorption plants rather than cryogenic air separation facilities. These include:

- Lower investment costs
- Lower energy requirements
- Shorter start-up and shut-down phases

Figure 4 shows a typical adsorption oxygen plant.

1.2.3 Cryogenic air separation plants

Cryogenic air separation plants are used to produce larger amounts of oxygen with higher purity levels. The cryogenic process makes use of the different boiling points of the various components of air (1,013 bar a), above all nitrogen ($-196\text{ }^{\circ}\text{C}$), oxygen ($-183\text{ }^{\circ}\text{C}$) and argon ($-186\text{ }^{\circ}\text{C}$).

Figure 5 shows the most important process steps in cryogenic air separation.

Figure 6 shows a schematic drawing of cryogenic air separation. The air is sucked in, compressed and cooled. The water that condenses during the cooling process is removed from the air stream by the separator.

The air is purified further in a molecular sieve adsorber, which removes the carbon dioxide and hydrocarbon compounds. The air then passes through the refrigerator, the expansion machine and the heat exchanger. After this, it can be rectified.

The rectification process produces liquid oxygen (LOX) and liquid nitrogen (LIN) as well as gaseous oxygen (GOX) and gaseous nitrogen (GAN). Figure 7 shows a cryogenic air separation plant.



Figure 4: Adsorption oxygen plant

Figure 5: Process steps in cryogenic air separation

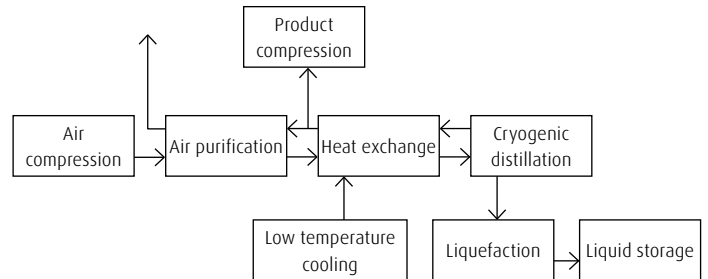


Figure 6: Schematic drawing of the cryogenic air separation process

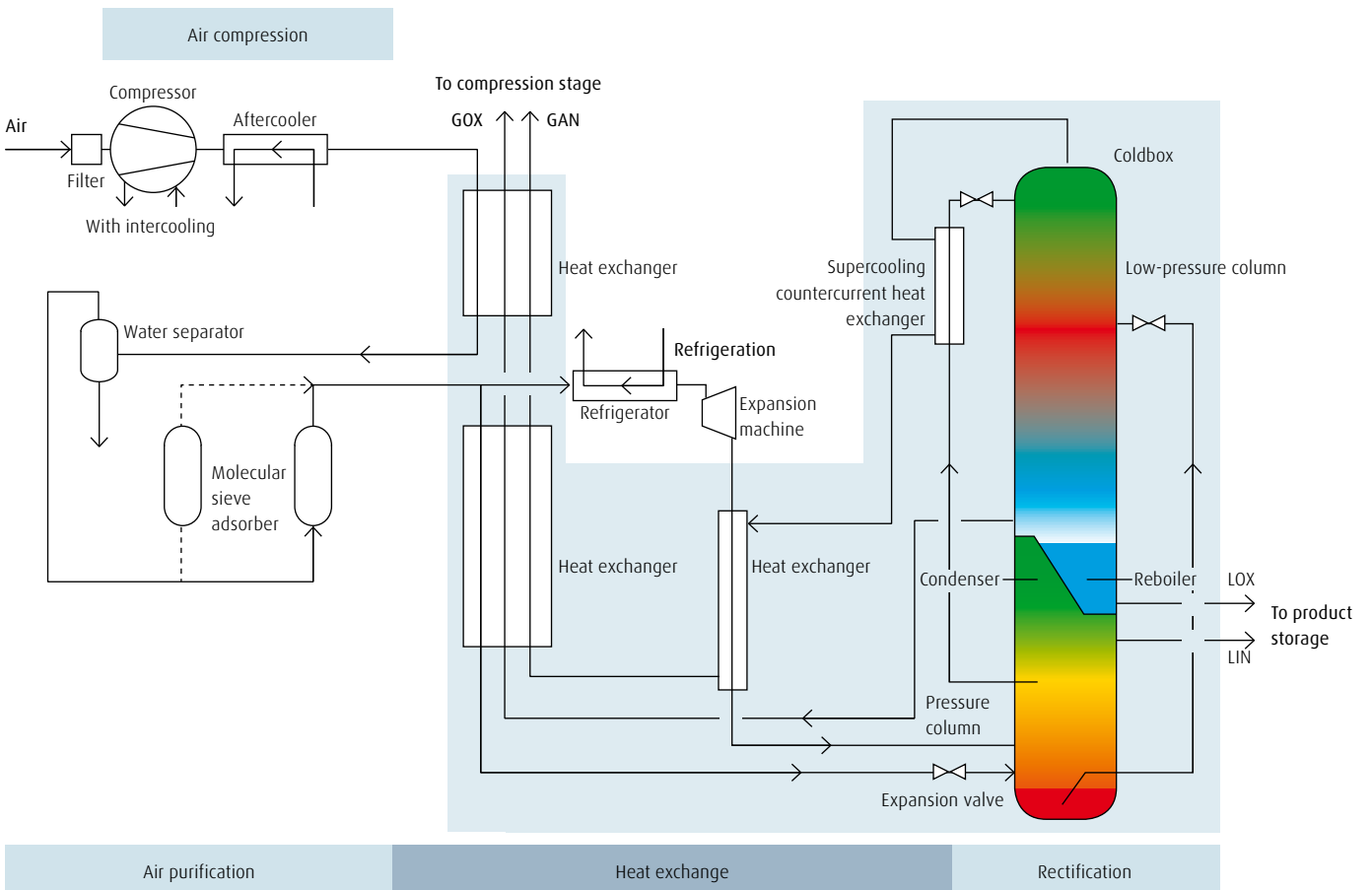




Figure 7: A cryogenic air separation plant



Figure 8: Liquefied gas tanker in front of a filling station

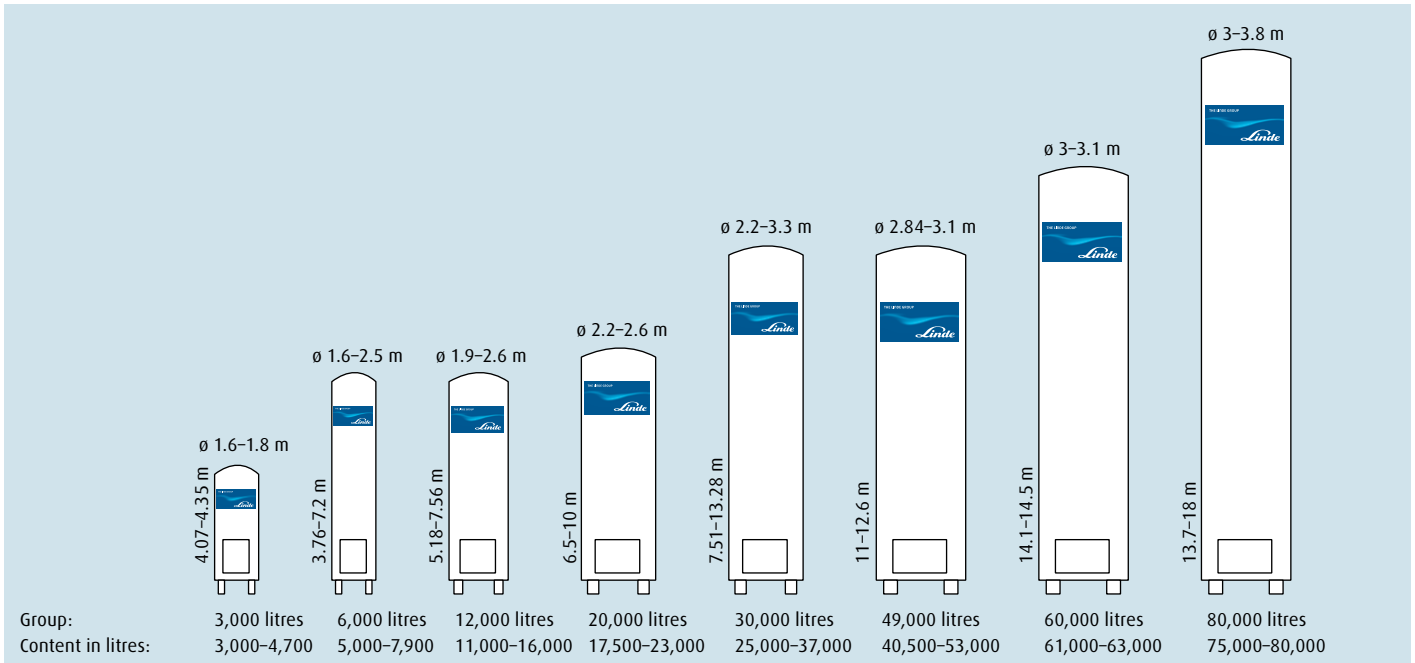


Figure 9: Standard sizes of bulk liquid tanks

1.2.4 Liquid gas supply

Liquefied gas is delivered to customers in tankers and stored on site in bulk tanks (Figure 8).

Tankers are vacuum insulated to prevent pressure levels rising significantly during transport.

A centrifugal pump is used to move the liquefied oxygen from the tanker to the storage tanks (Figures 9 and 10). The pressure in a tank has to remain as stable as possible to ensure that gas can also be withdrawn from the tank while it is being refueled.

To keep boil-off to a minimum, the storage tanks are well insulated using, for example, vacuum-powder insulation. Since the majority of consumers use oxygen in gaseous form, most storage tank systems are connected to either an air-heated vaporiser (Figure 11) or water bath vaporiser.

Air-heated vaporisers make use of heat from the surrounding air while water bath vaporisers use heat from warm water.



Figure 10: Bulk liquid tanks



Figure 11: Air-heated vaporiser

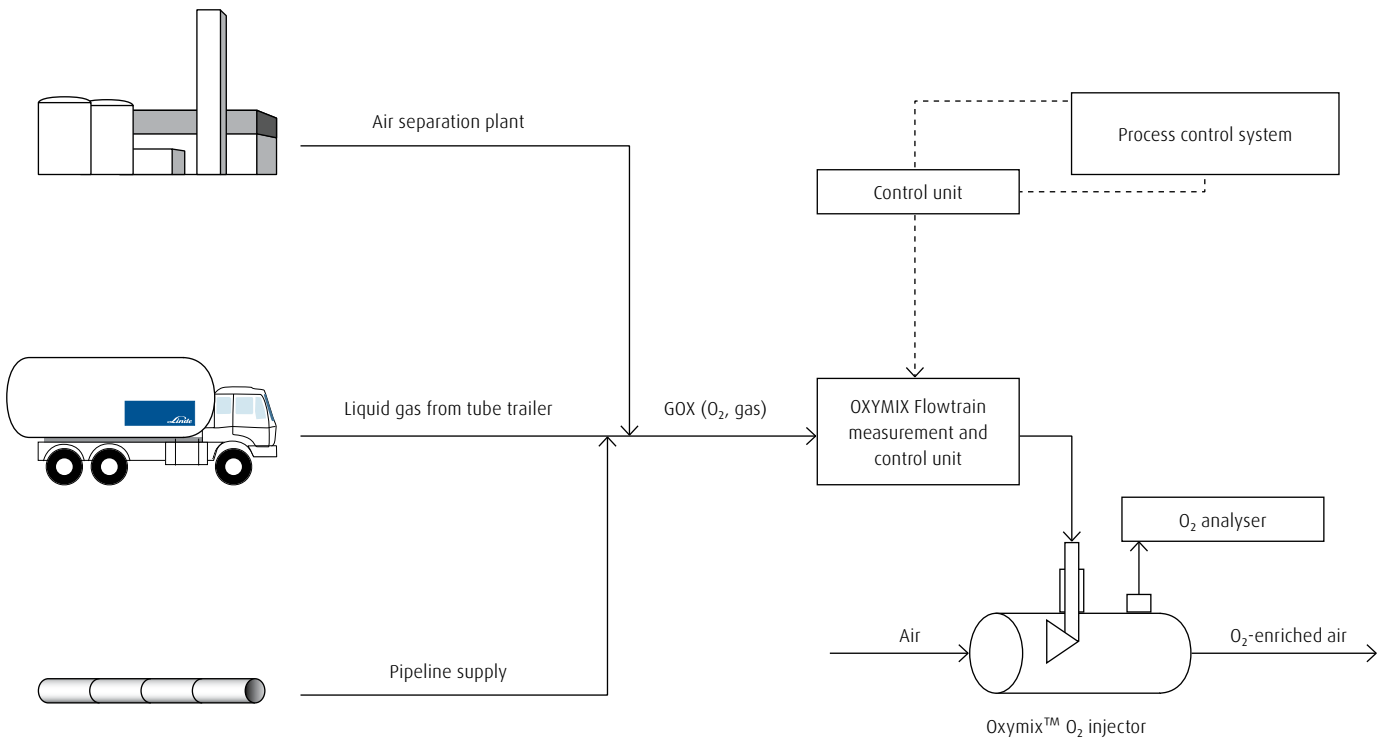
1.2.5 Gas supply from pressurised cylinders or cylinder bundles

Pressurised gas cylinders are usually made of high-tensile chromium molybdenum steel and have a test pressure of 300 or 450 barⁱⁱ. Figure 12 shows a range of different gas cylinders. The maximum permissible filling pressure is 200 and/or 300 bar. Cylinders come in a range of sizes such as 1, 2, 10, 20 and 50 liters. As a rule, these cylinder volumes can carry 1, 2, 10, 20 and 50 m³ of gas stored at 15°C and 1 bar. Cylinder bundles comprising twelve gas cylinders are the preferred solution for higher-volume users. The gas is withdrawn from the cylinders via a pressure regulator.



Figure 12: Pressurised gas cylinders from Linde on a truck

Figure 13: Supply and injection of oxygen for oxygen enrichment



1.3 Oxygen injection systems for oxygen enrichment

Linde has developed a general concept for oxygen enrichment tailored to the needs of customers that use oxidation reactions, as shown in Figure 13.

The choice of supply mode (on-site facility, liquid oxygen via a tank and vaporiser, or central supply via a pipeline network) is determined by the specific conditions on site and, most importantly, reflects volume requirements. Economic feasibility studies are carried out where necessary. The concept also incorporates an OXYMIX™ Flowtrain control system (see figure 14) for safely metering the supply of oxygen and an OXYMIX™ injector (see figure 15) that mixes air and oxygen safely within a short distance from the oxygen feed-in point.

Implementing oxygen enrichment up to a level of 28 vol% requires a relatively low capital investment. In addition to an oxygen supply system (liquid oxygen supply, on-site facility or pipeline), operators also require a measurement and control unit and an oxygen injector.

The measurement and control system has to guarantee a secure, reliable supply of oxygen under varying operating conditions in a reactor and/or plant. It therefore features a block-and-bleed system to prevent oxygen in the pipes from reaching the reactor once the air has been switched off. This oxygen metering system here also acts as a link to the process control system.

The OXYMIX oxygen injector is used to feed oxygen into the air pipe, enabling thorough mixing of oxygen with air. It is designed to meet critical criteria for oxygen enrichment: that the oxygen and air are mixed over a short distance, that the mixture is as homogenous as possible and that the oxygen is not injected directly onto the wall.

Gas must be distributed effectively to ensure homogeneity in the reactor. To achieve this, a reactor must be equipped with an effective gas distribution system. The gas and liquid phase must also be thoroughly mixed by the rising bubbles and, if required, by an agitator. In some cases, the gas distribution system may have to be replaced for the reactor to operate safely.



Figure 14: OXYMIX Flowtrain measurement and control unit for safe oxygen metering

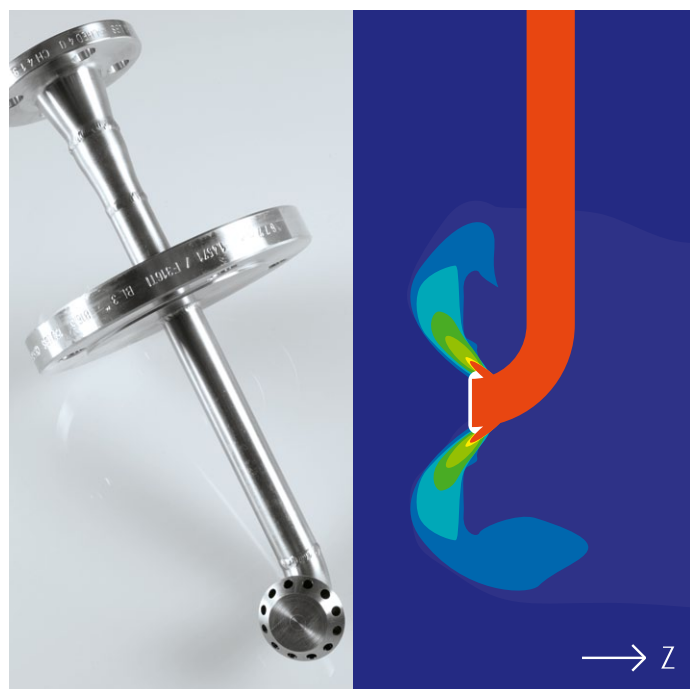


Figure 15: OXYMIX oxygen injector for oxygen enrichment. Photograph (left) and flow pattern (right) of oxygen being fed into the process air pipe

For safety, the care must be taken to prevent reverse flow into the gas distributor. This can be done by feeding nitrogen into the pipe when the air supply stops and by ensuring that the outlet holes are correctly aligned. Furthermore, the air should be fed into the reactor at a temperature below the initialisation temperature of the reaction. This prevents oxidation from taking place in the gas distributor should liquid enter the system.

Oxygen enrichment increases the velocity of a reaction. In exothermic oxidation reactions, this means that more heat is created. To manage the heat balance safely, heat exchanger capacity may have to be increased.

2. Oxygen applications in refineries.



Figure 16: Crude oil refinery in Leuna with hydrogen plant

2.1 Introduction

Crude oil accounts for around 34 percent of primary energy consumption, making it one of the most important sources of fuel. Oil is processed in refineries to produce products such as diesel, gasoline and heating oil. Most of these products are blends of streams from refining processes.

Figure 16 shows a photograph of a refinery. Figure 17 displays the typical process steps carried out in many refineries. It also shows the points at which hydrogen and oxygen are or can be used.

In the early days of oil refining, manufacturers used distillation to separate crude oil into its component parts. The resulting fractions could then be used for different purposes.

Over time, however, it became clear that oil resources were dwindling. This knowledge, coupled with increased focus on environmental protection, sharp rises in the price of oil and continually rising demand, meant that engineers had to get more out of crude oil, especially its heavy fractions.

As a result, refineries have become increasingly complex, incorporating many additional conversion steps capable of converting heavy, long-chain hydrocarbons into lighter, short-chain or branched hydrocarbons.ⁱⁱⁱ

A ban on the use of lead as an antiknock agent is just one example of environmentally motivated restrictions in refining. Sulfur thresholds have also been steadily tightened over the years. Table 3 shows the permitted thresholds of different substances in gasoline and diesel. The figures display how environmental regulations governing fuels have become stricter over time.

Table 3: Changing fuel regulations in the EU

	EURO 2	EURO 3	EURO 4	EURO 5
Introduction	1996	2001	2006	2009
Gasoline		<150		
Sulfur	<300	ppm	<50 ppm	<10 ppm
Benzene	ppm	<2 vol%	<1 vol%	<1 vol%
Aromatic compounds	<5 vol%	<45 vol%	<35 vol%	<35 vol%
Diesel		<350		
Sulfur	<500	ppm	<50 ppm	<10 ppm
Cetane number	ppm	>51 <11	>51 <11	>51 <11
Aromatic compounds	>49	mass %	mass %	mass %

The need to reduce sulfur content in end products meant that refineries had to use increasing amounts of hydrogen. This continuous rise in demand saw refineries switch from hydrogen producers to hydrogen consumers. Table 4 maps hydrogen demand against desulfurization. The shift from lighter to heavier, more sulfurous crude oils also increased demand for hydrogen. Steam reformation is the most common process used to generate extra hydrogen for refineries. In some cases, however, partial oxidation is also used.

Figure 17: Concurrence of typical processes in refineries

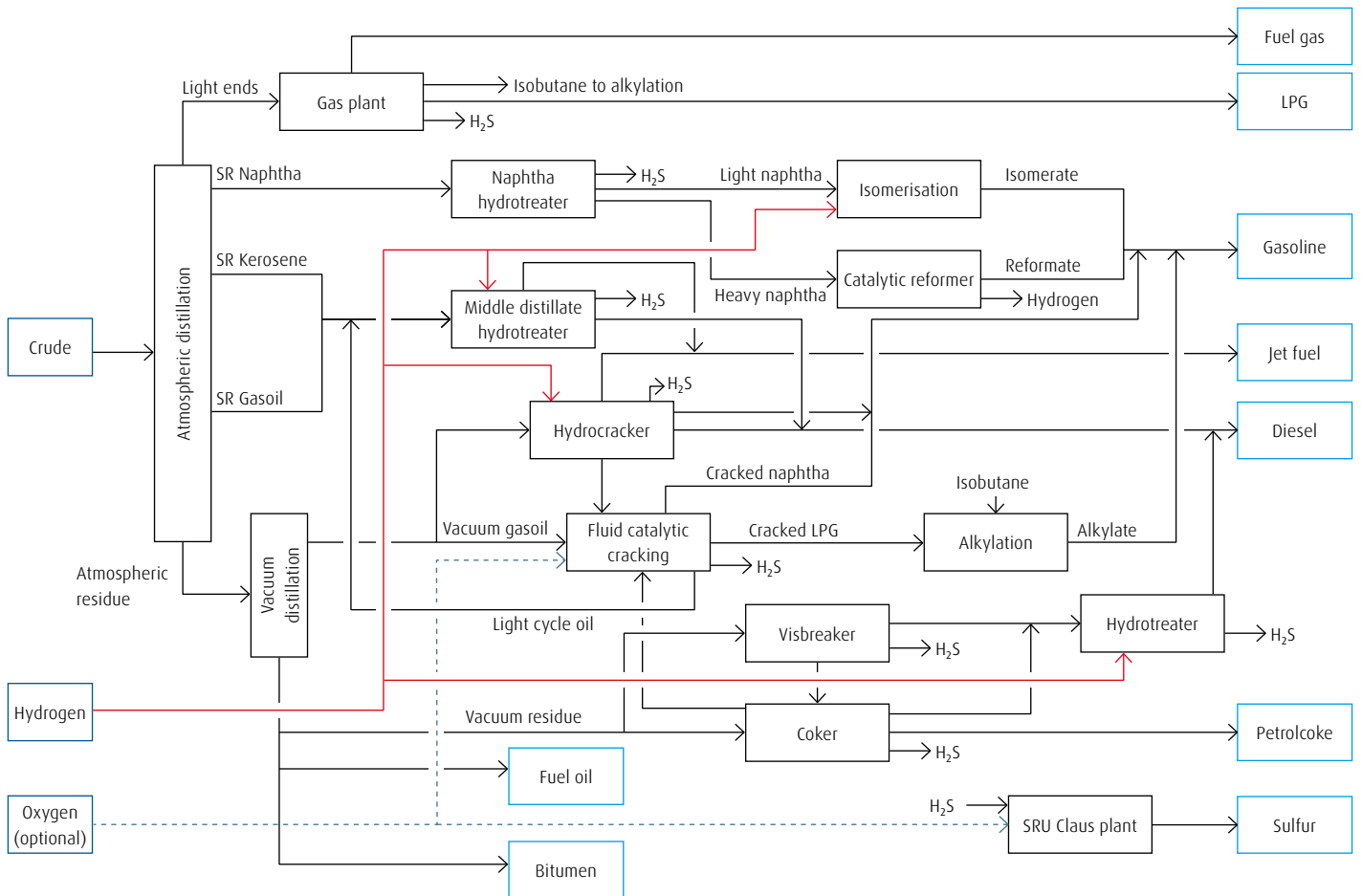


Table 4: Hydrogen demand in relation to desulfurisation

Desulfurization [%]	90	98	99
Addition of H ₂ [mass % of feed]	0.51	0.74	0.94
Hydrogen required for a 10 million t/a ref. [1,000 m ³ /h]	67	97	122

Table 5 lists the most important refinery products and their boiling ranges.

Table 5: Refinery products with the number of carbon atoms and boiling ranges

Product	C number	Boiling range [°C]
Fuel gas	C ₁ and C ₂	
Liquid petroleum gas (LPG)	C ₃ and C ₄	<20
Light gasoline	C ₅ -C ₆	20-80
Heavy gasoline	C ₇ -C ₁₀	80-175
Gasoline	C ₄ -C ₁₂	30-215
Kerosene	C ₁₁ -C ₁₄	150-300
Diesel	C ₁₃ -C ₂₅	180-390
Heating oil (light)	C ₁₃ -C ₂₅	180-390
Lubricant oils	C ₂₀ -C ₃₀	300-500
Heating oil (heavy)	C ₂₀ -C ₄₅	>350
Bitumen	> C ₄₅	>500

Petroleum coke and sulfur are also refinery products. Refinery processes take place at different temperatures and so many feedstocks have to be preheated. This involves all fractionating columns and reactors in which endothermic and exothermic reactions take place. The burners used to heat the feedstocks work with air, which – once it has been filtered and compressed – provides a cost-effective source of oxygen molecules for combustion.

In Claus plants, sub stoichiometric combustion is used to recover elemental sulfur from hydrogen sulfide.

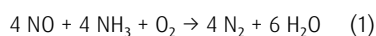
To decoke a reactor, the coke is burnt out using air, and in some cases, steam. Decoking is a continuous part of the FCC process, which is described in detail in Section 2.3.

Wastewater from refineries is also oxidised. Here, biological processes remove substances that are harmful to the water cycle (see Section 2.6).

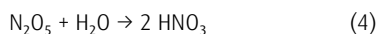
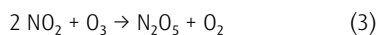
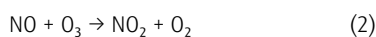
Air is usually a key ingredient for all of these oxidation reactions. However, more and more producers are interested in using oxygen enrichment technologies to optimise and adapt processes and increase capacity. Oxygen enrichment is already widespread in Claus plants and there are also many examples of oxygen being adopted in the FCC process. Wastewater treatment is another area that benefits greatly from the addition of pure oxygen (see Section 2.6). Pure oxygen is a key ingredient in partial oxidation or gasification processes that remove heavy residue from refineries and produce synthesis gases. This approach significantly reduces the size of plants, which in turn keeps investment costs down (see Section 2.5).

Using oxygen enrichment for burners in preheating processes can cut fuel consumption – something that refineries are also becoming increasingly interested in. Adding oxygen reduces the amount of nitrogen in the air, which means that less of this inert gas has to be heated. This reduces the amount of fuel required and cuts costs (see Section 2.4). Using less fuel also cuts CO₂ emissions.

The addition of oxygen to a process has to be planned very carefully, however, to ensure that it does not create additional nitrogen oxide (NO_x) emissions. In fact, careful planning can even help reduce NO_x levels. Over the coming years, NO_x thresholds are set to lower significantly in many locations globally. If a facility cannot comply with NO_x thresholds, the flue gas has to undergo additional treatment to reduce levels further. A reducing reaction such as the Selective Non Catalytic Reduction (SNCR) process is one of the options here. The SNCR process involves injecting ammonia (NH₃) or an ammonia solution into hot flue gas. The resulting reaction (1) converts nitric oxide (NO):



The NO can be oxidised further using ozone (O₃) to produce dinitrogen pentoxide (N₂O₅) (see reactions (2) and (3)). Unlike NO, N₂O₅ dissolves easily in water.



This then reacts in a scrubber to produce nitric acid (HNO₃) (4). Ozone is produced in an ozone generator by feeding pure oxygen through high-voltage cell, containing dielectrics. The resulting electrical discharge reaction generates ozone.

Over thirty systems with Linde's LoTOX™ technology have been installed, primarily in the US and China, in order to significantly reduce NO_x emissions at FCC plants. This technology is set to become more widespread in response to tightening thresholds.



Figure 18: Modern Claus plant (With kind permission of Bayernoil Raffineriegesellschaft mbH. Photo taken by Jürgen Sturany.)

2.2 Using oxygen in Claus processing

2.2.1 Importance of the Claus process

The energy content and synthetic potential of fossil fuels make them a cornerstone of our modern industrial lifestyle. However, crude oil, natural gas and coal always contain a certain amount of sulfur, accounting in some cases for several percent of overall content. The majority of these raw materials are used as fuels to generate energy. To eliminate SO_2 emissions, the sulfur in each energy carrier has to be removed either before oxidation (usually in the form of hydrogen sulfide (H_2S)) or after oxidation (usually by converting or separating SO_2).

When refining crude oil or cleaning sour natural gas, as well as raw synthesis gas from gasification processes, scrubbing systems are usually used to remove H_2S from the respective gas streams. This produces significant amounts of acid gases, which, depending on their source can comprise up to nearly 100 percent H_2S . Claus plants are designed to process these highly toxic gases, which are extremely foul smelling in low concentrations. They are by far the best option for refineries that produce large amounts of H_2S as an intermediate. Well over 90 percent of sulfur “recovered” from H_2S (127,000 tons per day in 2005) is generated in Claus plants.

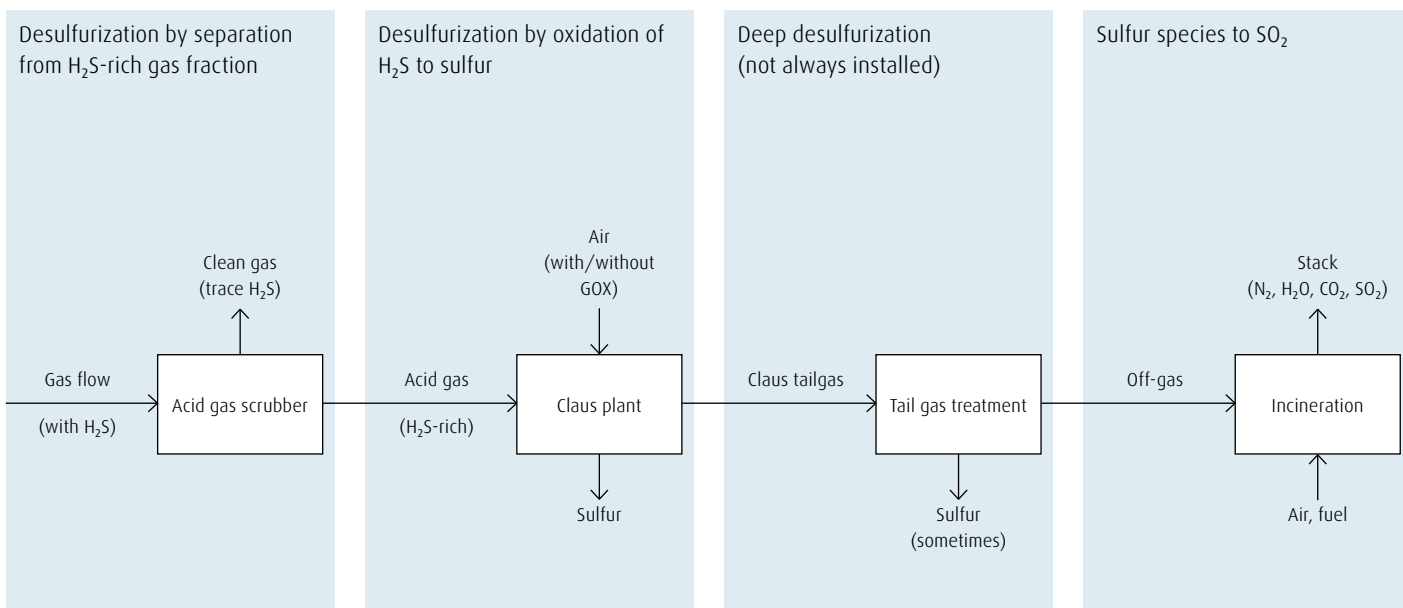
Figure 18 shows a Claus plant built in 2009 with a production capacity of 170 tons of sulfur per day.

Almost every refinery operates at least one Claus plant. These units produce high-purity elemental sulfur, a product that unlike H_2S is not toxic and can be easily transported. Despite ranking among the most important base chemicals, sulfur itself usually fetches a very low price. Therefore, from a financial perspective, sulfur recovery is not an important production process for refinery operators. It is, however, a key disposal process. A reliable Claus plant that operates within legal emissions thresholds is crucial for smooth refinery operations and therefore profitability.

Legal regulations governing sulfur content in many refinery products have become steadily stricter from the mid-1990s on. The EU’s Auto-Oil Programme is a point in case here. Since 2009, it has limited sulfur content in gasoline and diesel to 10 ppm. And this trend is set to continue elsewhere. The International Maritime Organization, for example, is planning to improve the quality of bunker fuels for maritime traffic as the majority of these still contain extremely high levels of sulfur. This is flanked by a clear shift toward processing increasingly sulfur-rich crude oils. These moves will increase the amount of H_2S produced and thus drive the need for extra Claus capacity.

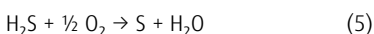
The diagram in Figure 19 shows the typical position of a Claus plant in a refinery’s process flow. Today, most refineries have to incorporate a deep desulfurization step to meet the strict legal requirements governing desulfurization rates.

Figure 19: Typical position of a Claus plant in a refinery's sulfur set up



2.2.2 Molecular oxygen – the key to recovering sulfur

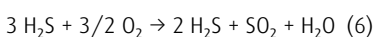
The process of oxidising H_2S to produce relatively harmless and versatile elemental sulfur (S) is often referred to as sulfur recovery. This process is based on the reaction equation shown below (5), in which H_2S reacts with molecular oxygen:



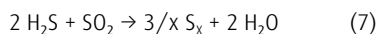
Typically, air (O_2 content (dry): 20.9 vol%) is added to provide the O_2 molecules required for this exothermic oxidation process. Process air admixed to acid gas can be passed through solid catalyst to ensure that the partial oxidation process reaches sufficient speed. This was the case with the original Claus process, which was patented in the late 19th Century. Back then, the Claus process only comprised the catalytic step. It is still used today in this form, although it is now known as: "H₂S direct oxidation" (H₂S DO). The acid gas is oxidised (using air) exclusively over a solid catalyst bed. The heat generated by the reaction as shown in equation (5) means that only acid gases with relatively low H_2S content, preferably below 5 percent, can be treated here.

2.2.3 The Claus process in particular

As the petrochemical industry grew, however, manufacturers were soon processing gases with very high levels of H_2S . The original Claus process had to be modified to meet this challenge. In the early 1930s, an upstream, thermal process step was incorporated that involved the partial oxidation of H_2S using a burner. In this thermal step, the acid gas is partially combusted to SO_2 in a free flame reaction within a combustion chamber and subject to just enough molecular oxygen (usually as a component in process air) to enable one third of the H_2S to be oxidised to sulfur dioxide (SO_2) according to reaction (6):



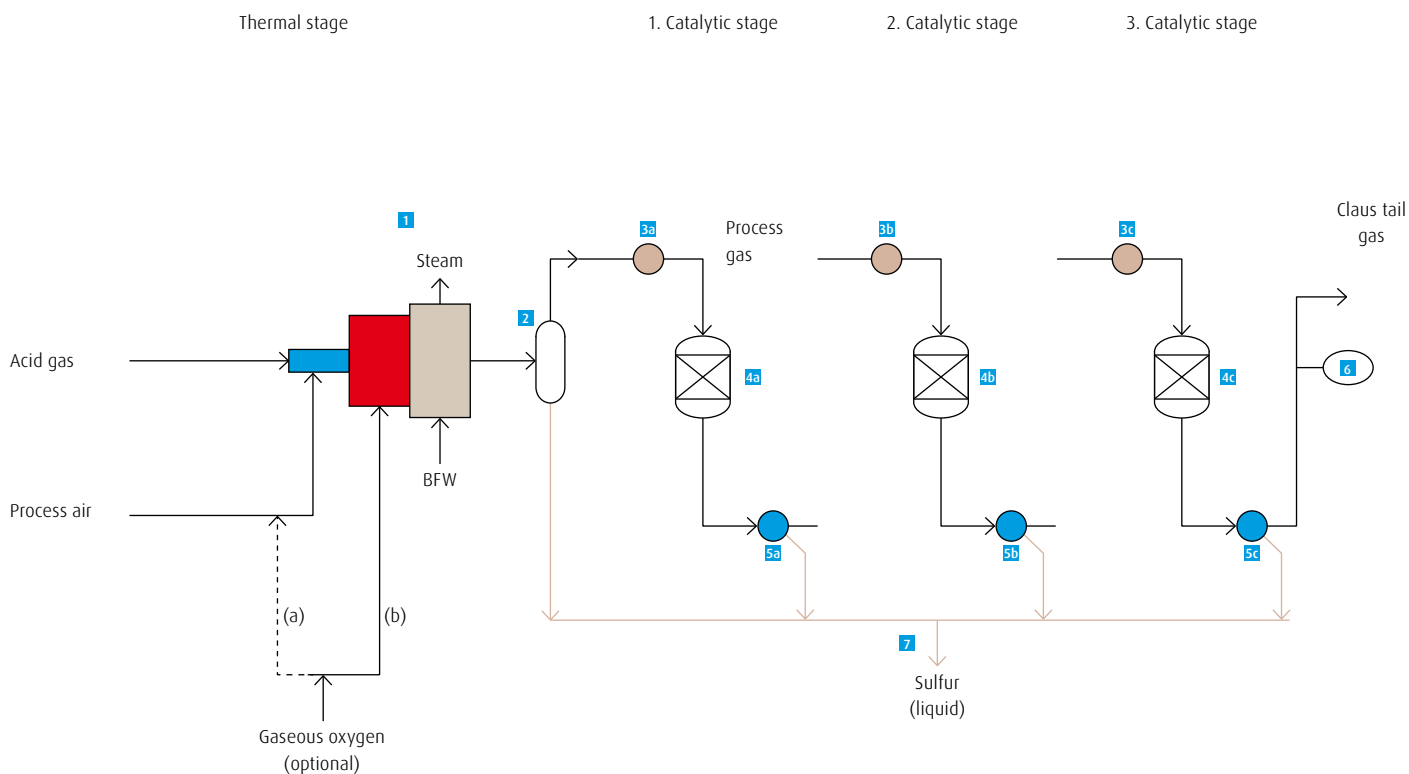
On this basis, some elemental sulfur has already been formed in the thermal step according to the Claus reaction (7):



whereby x means that different sized molecules, for example S_2 or S_8 , may be present.

Especially as a result of the exothermic reaction (6), the resulting gas stream is extremely hot (usually between 950 and 1,200°C). The hot gas is rapidly cooled in a waste heat boiler downstream of the Claus furnace, thereby recovering energy as steam. The resulting sulfur vapour condenses to produce liquid sulfur, which can then be removed from the process. The remaining H_2S and SO_2 sulfur compounds in the process gas (mol ratio 2:1) can then be converted to sulfur at gradually decreasing temperatures in downstream catalytic Claus steps in line with reaction (7). Here again the sulfur is condensed to a liquid and drained out of the system.

Figure 20: Typical set-up of a three-stage Claus plant



1 The thermal step in the Claus process, comprising three main components (left to right): burner, combustion chamber and waste heat boiler where the process gas is cooled by turning the boiler feed water (BFW) into steam i.e. recovering energy., **2** Separator for recovering liquid sulfur, **3** Reheating of process gas, **4** Claus reactors; in other words, containers filled with Claus catalyst (temperature $4a > \text{temperature } 4b > \text{temperature } 4c$; typically between 350°C and 180°C), **5** Process gas coolers (minimum temperature around 130°C) to condense and drain out liquid sulfur, **6** Gas analyser for H_2S and SO_2 ; the concentration ratio of these gases should be between 2:1 and 10:1, depending on the Claus tail gas treatment process installed, **7** Pipes to drain off liquid sulfur to containers

Figure 20 shows the typical set-up of a three-stage Claus plant. Oxygen can be added to the thermal step of the Claus process in two ways:

- Via the process air line
- Direct injection into the flame inside the combustion chamber

During the thermal phase of the Claus process, oxidation is controlled so that only one third of the H_2S in the acid gas oxidised to SO_2 . In Claus plants, this is always achieved by adding gaseous, molecular oxygen. Provided that certain conditions are met, the oxygen molecules can be added as part of air or oxygen-enriched air, or they can be injected as industrial oxygen of varying purity. However, it is very important that furnaces do not get too hot as this could damage structural materials.

2.2.4 Using oxygen or oxygen enriched air in the Claus process

Increasing the concentration of O_2 in oxidation gas decreases the amount of inert gas, primarily nitrogen, which has to be transported through a Claus plant. A Claus plant that uses additional oxygen therefore imports less oxidising gas than one which does not. This reduction in gas is

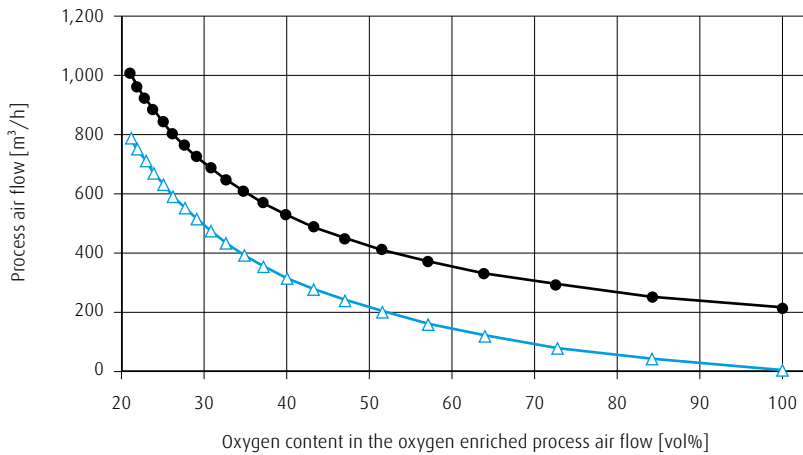
critical to understanding the opportunities and benefits that O_2 -enriched air brings to the Claus process.

As Figure 21 shows, increasing O_2 content reduces the overall amount of oxidation gas fed into a Claus plant and, crucially, cuts the amount of nitrogen ballast transported through the system.

This leads to two direct consequences that pave the way for an increase in capacity, flexibility, energy efficiency and availability of Claus plants – and thus make oxygen enrichment a very interesting option for refinery operators.

Figure 21: Drop in air volume and nitrogen ballast as oxygen enrichment increases and total volume of molecular oxygen remains constant.

● Process air flow, ▲ Nitrogen content in process air flow



Less nitrogen means:

1. Less process gas – which, in turn, leads to the following benefits:

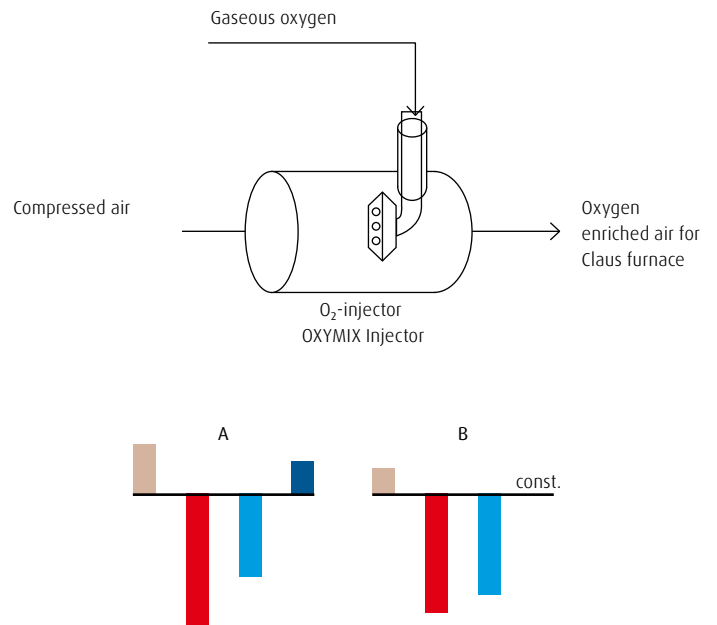
- Higher acid gas throughput is possible, resulting in increased capacity.
- Longer residence time for the process gas, which benefits kinetically-limited reactions in all reactors.
- Less energy and fuel required to preheat the process gas.

2. Higher combustion temperature in the Claus furnace:

- This speeds up kinetically-limited reactions, which means that unwanted elements in Claus feed such as ammonia (NH_3) and BTX (benzene, toluene, and xylene) aromatics are broken down more efficiently.
- It boosts endothermic reactions in the Claus furnace, such as thermal H_2S splitting, which increases H_2 content in the process gas.

Based on the most common type of oxygen enrichment, low-level enrichment as per Figure 20 (GOX option (a)), Figure 22 shows the most common operating modes as reflected in variations in gas flows.

Figure 22: Injecting oxygen into process air – flow effects



— Supplied industrial oxygen
 — Compressed air from the compressor
 — Oxygen enriched air for the Claus furnace
 — Additional absolute amount of molecular oxygen (Total oxygen amount increased (A) or unchanged (B))
 The vertical bars highlight the different gas flows for operational modes A and B, whereby the horizontal baseline represents air-only combustion.

The O₂ enrichment modes shown in Figure 22 (A and B) are described in detail below:

A (increased acid gas throughput)

The extra oxidation potential and lower overall volume of oxidation gas increases capacity. By increasing acid gas flow beyond design load, both the temperature in the Claus furnace and the amount of elemental sulfur recovered are increased.

B (no change to acid gas throughput)

As the conditions in Figure 21 show, mode B has the same oxidation potential as an air-only system (without additional GOX). As a result, no additional H₂S-carrying gas is added to the process. This means that the sulfur production rate is the same as air-only combustion. As in mode A, however, due to the decreased nitrogen load, the temperature in the Claus furnace increases and the amount of process gas in the Claus plant decreases.

2.2.5 Adding oxygen to Claus feeds with varying hydrogen sulfide content

Using lean H₂S gases as feedstock in Claus plants

It is relatively rare for refineries to produce acid gases with H₂S content in the low double-digit percentage range (typically 20 to 40 vol%). If these “lean gases” are produced at all, then normally as a result of the partial oxidation of sulfur-rich feedstocks such as high-viscose refinery residue or petroleum coke. Any inert gas (almost exclusively CO₂) in acid gas has to be heated in the thermal Claus step by heat of reaction. Therefore, if the percentage of inert gas rises, the temperature in the Claus furnace falls. In extreme cases, insufficient fuel content (H₂S) can destabilise the combustion process to such a degree that the burner extinguishes – a situation that has to be avoided. Furthermore, if the thermal step is too “cold”, problematic compounds such as BTX aromatics that are often found in the acid gas can no longer be sufficiently oxidised. This can disturb plant processing significantly in the catalytic step of the Claus process, causing, for example, coke to build up and deactivate Claus catalysts and, in the extreme case, resulting in unwanted discoloring of the sulfur, which is light yellow in its pure, solid form. These effects can be eliminated by increasing the temperature of the furnace. There are a number of ways of doing this and often these methods can be combined for more effective results. Oxygen enrichment is one of these options.

Processing lean gases in Claus plants without industrial oxygen

If air, which has a high percentage of inert gas, is used exclusively as the oxidising agent, part of the acid gas stream can be diverted away from the Claus furnace to a downstream process step. Up to two thirds of the acid gas can be diverted in this way, leaving just one third of the H₂S to be oxidised to SO₂ (see equation (6)). Since a large part of the acid gas no longer has to be heated, the flame and subsequently the furnace can reach much higher temperatures. This acid gas bypass method is often deployed in Claus plants that purify acid gas from sour natural gas close to natural gas wells. These facilities are usually built in remote locations and do not have access to industrial oxygen.

Processing lean gas in Claus plants with industrial oxygen

The situation is very different in gasification plants as these use extremely large amounts of industrial oxygen to partially oxidise

carbon-based feedstocks. Therefore normally large-scale air separation units are required, typically operated nearby. Industrial oxygen here is a cost-effective means of reducing inert gas content in the combined Claus feed. The oxygen replaces part of the process air and thus reduces N₂ content. Depending on the amount of H₂S in the acid gas, industrial oxygen can even be used to replace air entirely. In this case, however, operators must ensure that the temperature of the Claus thermal step does not exceed maximum heat thresholds for furnace materials. This is the most important restriction when using high levels of oxygen enrichment up to 100 percent (no process air at all). Under stable operating conditions and based on the configuration shown in Figure 20 (option (b)), 100 percent oxygen enrichment can enable operators to feed all acid gas into the Claus burner. Unlike the bypass process described above, this variant ensures that all contaminants in acid gas such as aromatics are subject to high flame temperatures and therefore destroyed more efficiently.

Using H₂S-rich gas as feedstock in Claus plants

Acid gases with H₂S content in the high double-digit percent range (typically between 80 and 99 vol%) are usually a by-product of many processes operated in oil refineries. Sulfur is almost always present in crude oils, predominantly in the form of carbon-containing sulfide compounds. The corresponding organic sulfides, disulfides, thiols and thiophene release H₂S under conditions present in numerous refinery processes – in other words, whenever oil fractions are heated under reducing conditions. As a result, gaseous mixtures containing H₂S are generated along with fractions with higher boiling points not only during processes where hydrogen is fed to the system (for example, hydrotreatment and hydrocracking), but also during many other important conversion processes (in particular cracking processes such as fluid catalytic cracking, visbreaking and coking). H₂S has to be separated from the gaseous fractions which the abovementioned processes generate. This is usually done by chemical scrubbing. The gas scrubbing units usually use alkaline solutions of alkanolamines. The scrubbing process produces a desulfurized gas stream and an acid gas stream with high H₂S content (see Figure 19). The latter stream is the major feed component routed to the Claus facility, often combined with a comparably low flow of so-called sour-water-stripper gas, typically composed of similar contents of H₂S, NH₃ and water.

Processing rich gases without industrial oxygen

The vast majority of Claus plants in refineries use air. Today, new plants are still designed and built for use with air as the oxidising agent. One reason for this is, of course, that air is a ubiquitous resource and can be used without pre-processing. Another reason, however, is that air ensures a stable thermal reaction in Claus furnaces when it is used to partially oxidise rich gases in the configuration shown in Figure 20 (in contrast to using air with lean gases). With hydrodesulfurization processes becoming more intense and refiners converting increasingly heavy oil fractions with high sulfur content, the amount of acid gas and ammonia that needs to be processed has risen considerably over the last two decades. This trend has brought many air-based Claus plants to their limits in the past, and continues to do so today.

Figure 23: Capacity increase in the Claus process due to oxygen enrichment

● 90% H₂S in the acid gas to the Claus plant,
 ▲ 50% H₂S in the acid gas to the Claus plant

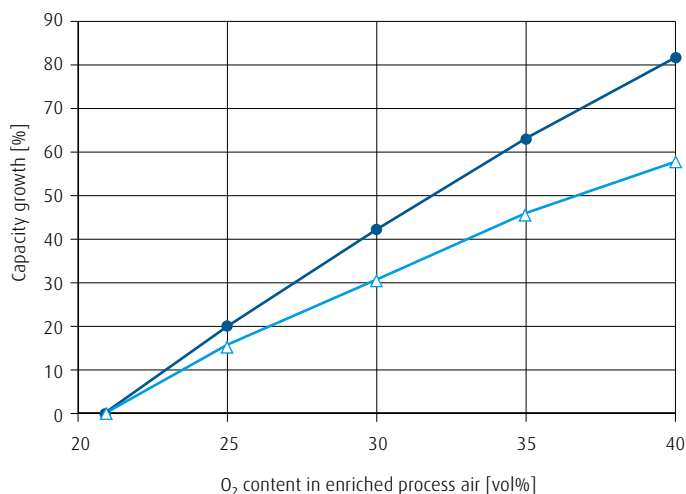


Figure 24: SURE™ burner

2.2.6 Limits to the capacity of Claus installations

Claus plants are not usually limited by the amount of liquid sulfur that they can produce. Gas throughput is the main factor that limits their capacity. Once the plant is operating at 100 percent capacity, the pressure drop across the plant – which in theory increases by the square of the process gas flow – will have grown to such an extent that no more acid gas can be routed through the Claus unit. Increasing the pressure of the acid gas would be an obvious way of overcoming this limitation. However, increasing the pressure of acid gases from amine scrubbing processes is not an easy task. Operators often consider building a new Claus plant to cope with increased volumes of acid gas. However, O₂ enrichment – an inherently low-investment solution – is an interesting alternative that can increase the throughput of existing facilities.

2.2.7 Using oxygen enrichment to increase the capacity of Claus plants

Increasing capacity typically involves increasing the throughput of acid gas feed. The key to doing this is to decrease the amount of air which, in turn, reduces the amount of nitrogen ballast. This can be realised by replacing part of the process air with industrial oxygen. If the oxygen enrichment increases the amount of molecular oxygen in process gas (Figure 22, mode A), the Claus plant can process more acid gas, and therefore convert more H₂S into elemental sulfur.

The diagram in Figure 23 has been verified by numerous field tests. It shows that O₂ enrichment offers huge potential to increase the capacity of Claus plants when it is used especially with H₂S-rich acid gases – in other words under typical refinery conditions.

Low-level enrichment

Figure 23 also shows that O₂ enrichment by amounts of up to 28 vol% (low-level enrichment) can push total capacity beyond 130 percent. This is point up to which the O₂ enrichment method outlined in Figure

20 (GOX option (a)) can be implemented without having to replace a Claus burner designed for use with process air only. This method of intensifying the Claus process requires very little adjustment to existing facilities, which makes it a cost-effective and widely used option.

Mid-level enrichment

If oxygen accounts for over 28 vol% of process air, additional measures – beyond gaseous oxygen supply and related controls installation – have to be taken to introduce the oxygen into the Claus process. If the operator wishes to increase O₂ content up to around 45 vol%, at a minimum the plant's air burner has to be replaced. The new burner must be able to deal with higher O₂ concentrations without being damaged and ensure that the feed gases are mixed well. Depending on the burner technology installed, O₂ can be added to process gas in line with GOX option (a) or (b) in Figure 20. The SURE multiple-lance burner in Figure 24 is suitable for option (b). It can inject industrial oxygen directly into the furnace, thus eliminating the need for it to be mixed with the process air in a separate step.

This type of Claus burner is installed in many Claus plants. Particularly when handling H₂S-rich feedstocks, it is a popular choice irrespective of oxygen enrichment. In other words, similar to low-level enrichment, it also supports air-only oxidation.

Although low-level O₂ enrichment is the most common method of intensifying the Claus process, mid-level enrichment is becoming increasingly widespread. Figure 25 shows a Claus plant that has been modified accordingly to increase capacity. The plant's original burner, which was designed to work with air only, was replaced by a SURE burner (Figure 24). This modification enables the plant to process 50 percent more acid gas.

A Claus plant with a SURE burner installed for mid-level oxygen enrichment is shown in Figure 25. Linde AG developed another burner suitable for O₂ enrichment levels of up to approximately 40 vol%. Its light, compact design makes it ideal for retrofitting existing Claus furnaces. The burner has been designed to deliver outstanding mixing quality over a wide load range and to produce a shorter flame. Figure 26 shows the results of a CFD simulation to support burner customisation.

Ignition is a serious issue for operators as many burners are difficult to ignite. As a result, Linde engineers also carried out ignition tests while developing the burner (see test equipment in Figure 27).

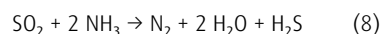
High-level enrichment

SURE burners (see Figure 24) can be configured to work with high-level O₂ enrichment for maximum capacity gains. If the burner is used with rich feed gases and up to 100 percent industrial oxygen, overall capacity of the respective Claus unit can be increased up to 250 percent.

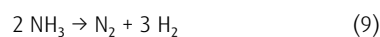
Intensifying the sulfur recovery process to such an extent also requires other extensive alterations to existing plants. The industrial oxygen, for example, has to be added not in a single injection step but at different stages. For this kind of oxidation, a second gas cooler has to be connected downstream of the first waste heat boiler, and the two oxygen streams have to be introduced before these points in the system. This ensures that the furnace does not get too hot. If oxygen content above approximately 45 vol% (above mid-level enrichment) would be used in the Claus thermal step based on the set-up in Figure 20, the furnace would overheat.

2.2.8 Processing ammonia in Claus plants

In refineries, ammonia (NH₃) stems from hydrocarbon compounds that contain nitrogen. These are produced in almost all process steps that generate H₂S, including purely thermal processes such as coking, visbreaking and partial oxidation, and catalytic processes such as fluid catalytic cracking (FCC), hydrocracking and hydrotreatment. This last process is typically used for the desulfurization (HDS) and denitrification of fractions. The amount of ammonia produced increases with the severity of the hydrogenation process conditions, for example deep desulfurization of fractions that produce “sulfur-free” diesel (sulfur content of max. 10 ppm). Since ammonia (NH₃) is very soluble in water, it is mainly found in aqueous process condensates. These are collected and fed into sour water strippers where the NH₃ and co-adsorbed H₂S are removed. Isolating pure NH₃ for sale in most cases is not economically viable here. The gas streams containing NH₃ and H₂S (sour water stripper (SWS) gases) are therefore usually fed into Claus plants to be processed with the acid gas from chemical scrubbing processes. The aim here is to fully oxidise ammonia to nitrogen. This is a relatively effective process that takes place exclusively in the Claus furnace based on reaction (8):



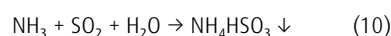
and reaction (9):



NH₃ often accounts for up to ten percent of acid gas/SWS gas mixtures. This concentration is reduced to a few hundred, and often less than one hundred, vol ppm in the thermal Claus step under the normal conditions used for the Claus process (air oxidation of rich gas).

Problems caused by ammonia

Ammonia is the only base component in Claus process gas. Acid-base reactions, especially reaction (10), can cause salt, solidifying in “cold” parts in the Claus plant:



These sulfide deposits generally occur at temperatures < 150°C, for example when the process gas is on its way through the sulfur condensers. They can also form in the pipes that drain off liquid sulfur or in process gas analysers, which regulate the air supply to the Claus burner.

This often causes a number of problems, ranging from reduced capacity, operational disruptions and downtime to corrosive damage to materials and lower desulfurization rates.

Figure 28 shows ammonia salt deposits on a device used to capture sulfur vapour or droplets. It clearly shows the degree to which ammonia can disrupt the process gas flow and the serious consequences for a Claus plant when the pressure drop is a limiting factor.

Using O₂ enrichment to minimise problems with ammonia

In light of these problems, it is particularly important that Claus plant operators success in maximizing NH₃ oxidation in Claus furnaces. There are a number of approaches that can be taken here, typically in the design phase:

- Increasing flame and/or furnace temperature
- Increasing the mixing efficiency of the Claus burner
- Increasing the residence time of the gas mixture in the furnace

As Figure 22 shows, O₂ enrichment reduces the amount of oxidation gas, which means that the reaction gas mixture has a longer residence time in the Claus furnace. The increase in temperature that results from substitution of air with industrial oxygen is particularly important here. The graph in Figure 29 provides quantitative information on this based on field data collected during low-level oxygen enrichment trials. O₂ content is increased gradually in small steps in this approach.



Figure 25: Claus plant with SURE burner

Figure 26: Gas velocities in the new burner
(calculated using CFD simulation)

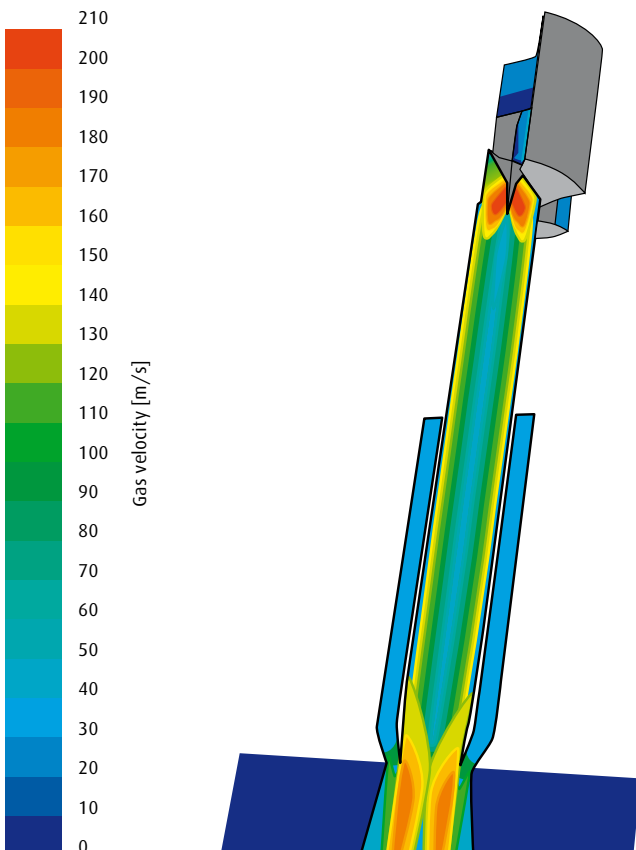


Figure 27: Burner test installation in Pullach, Germany



Figure 28: Demister with major ammonium salt deposits

Figure 29: Increase in temperature in a Claus furnace mapped against different oxygen contents in process air

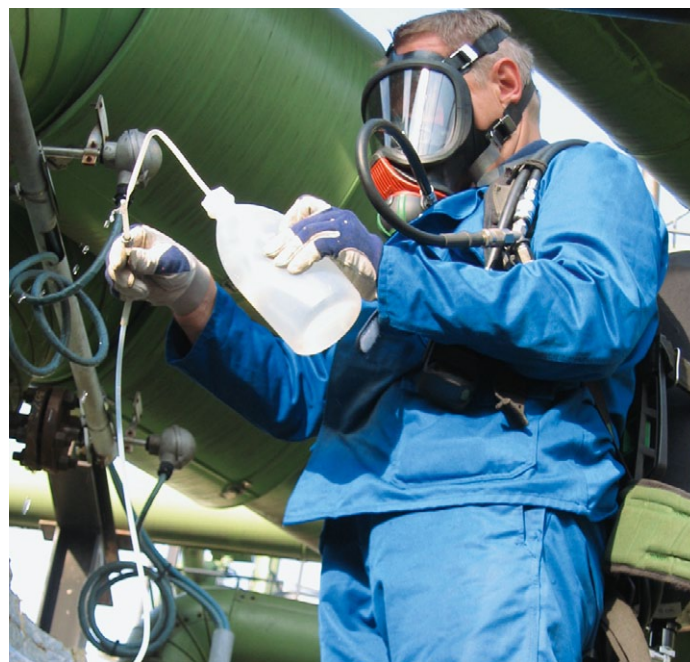
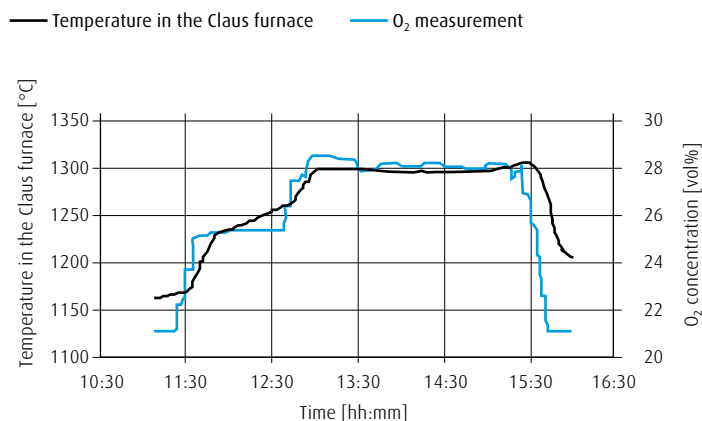


Figure 30: Sampling of Claus process gas for ammonia measurement

Experience has shown that the efficiency of ammonia destruction in the Claus furnace increases with increased furnace temperature. Reaching approximately 1,300 °C often provides residual ammonia concentrations low enough for proper Claus operation.

The degree of NH₃ destruction cannot be reliably determined using calculations alone. Measurements based on process gas sampling downstream of the waste heat boiler are therefore recommended in order to get a clear picture of the Claus furnace's performance. NH₃ content in process gas is an impartial indicator of how much NH₃ has been destroyed during the thermal step of the Claus process. To determine NH₃ content, a small sample gas stream (measured volumetrically) is removed immediately after the thermal step and fed through a mineral acid solution. The NH₃ dissolves into ammonium (NH₄⁺) in this solution. The concentration of the latter can be measured using photometric or ion chromatography analysis methods, for example.

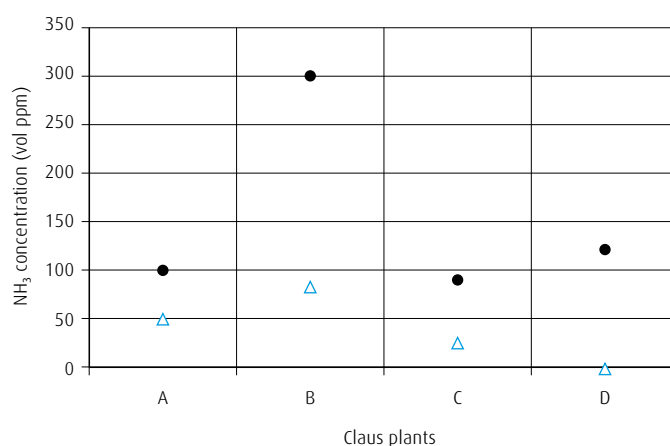
Such manual sampling and analysis has to be applied as automatic instruments like on-line NH₃ analysers are not state-of-the-art at Claus process conditions (see Figure 30).

To quantify the effects of temperature increases in Claus furnaces, NH₃ content was measured in over a dozen O₂ enrichment field tests (low- and medium-level enrichment). At each site, the residual concentration of NH₃ with O₂ enrichment was compared against NH₃ values from air-based combustion. Figure 31 shows the results for selected Claus plants with burners configured for use with air. The plotted values clearly shows that there are big differences between the burners' abilities to reduce residual NH₃ content, also following the addition of extra O₂, however in all cases O₂ enrichment causes a significant drop in residual NH₃ content. In some cases, depending on the individual furnace conditions, almost all of the NH₃ was destroyed. These values do not necessarily mean that

a decomposition factor of three, for example, will increase the period until operators can expect major NH₃ salt problems by a factor of three. However, they are convincing enough to have already persuaded many operators to install permanent O₂ enrichment solutions. This move has most likely also been prompted by other benefits associated with O₂ enrichment. These are described below.

Figure 31: Comparison of residual ammonia content in different plants following air and oxygen combustion in Claus furnaces

● Air (21 vol% O₂), △ 27-28 vol% O₂



2.2.9 Impact of oxygen enrichment on Claus tail gas treatment and waste gas incineration

In many cases, the output of Claus plants is not limited by processes in the plants themselves but by bottlenecks in downstream processes such as tail gas treatment or in subsequent incineration systems. Reducing the amount of transit gas can also help increase capacity in these processes. O₂ enrichment can also lead to a number of other appreciably beneficial consequences, which, in turn, can reduce consumption of resources (oxidation air, fuel, energy consumption and in many cases H₂) and lower repair and maintenance costs at plants.

Processing Claus tail gas

Today, almost all Claus plants feature process steps for treating tail gas in order to minimise SO₂ emissions. These treatment processes typically increase a plant's sulfur recovery rate from a maximum of 98 percent (i.e. a performance achievable by a 3-stage Claus unit as shown in Figure 20) to between 99 and 99.8 percent. Different technologies are used to achieve different maximum rates.

The most effective among the most widely applied Claus tail-gas treatments is based on SCOT (SHELL Claus: Off-gas Treatment) technology. This method initially converts all sulfur species in the Claus tail gas (SO₂, S vapour, COS and CS₂) into H₂S. The H₂S is then separated and concentrated in a gas scrubbing system. The resulting H₂S-rich stream is then fed back into the thermal step of the Claus process. To fully hydrogenate sulfur vapour and SO₂ to H₂S in the first step, however, a reducing gas often has to be added. In many cases, hydrogen, a valuable resource, is used for this.

The higher temperatures generated by O₂ enrichment upstream within the Claus furnace cause significantly more H₂ to be generated than with air-only operation. This is primarily caused by a shift in balance in the following endothermic reaction (11) in favor of the products:



The hydrogen is not depleted to any great extent in the subsequent catalytic Claus process step. It therefore remains in the process gas and progresses to the afore-mentioned hydrogenation step in the Claus tail-gas treatment process. This increased hydrogen content reduces the amount of additional H₂ that has to be imported for this step. Field tests show that under the right conditions, O₂ enrichment pays for itself on the basis of this effect alone. Low-level enrichment (O₂ content of just 26 vol% in process air), for example, was found to cut H₂ import by one third. Another plant that used GOX option (b) in Figure 20 was able to eliminate hydrogen import entirely by increasing O₂ content to approximately 44 vol% (mid-level enrichment).

Sub dew point (SDP) processes are also used for treating Claus tail gas. With well over a hundred installations, they are similarly as important as the SCOT process described above. The benefits of O₂ enrichment are somewhat different with SDP processes. Here, the catalyst beds are periodically set to a relatively "cold" temperature (~130°C), which causes the balance of the Claus reaction (7) to shift significantly toward sulfur production. It also causes the pressure of the sulfur vapour to drop significantly. The drop in temperature causes ammonia salt deposits to form. This often brings a range of problems such as corrosion (in a short



Figure 32: Ammonia salt deposits in a pipe



Figure 33: Corrosion caused by ammonia salt deposits

space of time), limited availability and decreased yield. Field tests have shown that these problems are especially prevalent in systems where the regeneration gas from the sulfur-containing catalyst beds contains up to several percent of NH₃.

Figures 32 and 33 show ammonium salt deposits inside piping in a Claus tail-gas treatment plant using SDP processes. These installations react particularly strongly to NH₃ in process gas. Case studies have shown that O₂ enrichment can almost entirely eliminate ammonia salt deposits and the associated operational and maintenance issues.

In general, O₂ enrichment does not have any negative impact on desulfurization rates in Claus plants or in tail-gas treatment processes.

Thermal oxidation

Thermal oxidation of off-gas is an integral downstream component of every Claus plant and tail-gas treatment unit. It is primarily used to eliminate odors from flue gases before they are released into the atmosphere (see Figure 19). Legal regulations therefore require that all reduced sulfur species in flue gas (in particular H₂S) are fully oxidised to SO₂. Usually, only very small amounts of H₂S emissions are permitted, typically around 10 ppm in the gas stream to stacks. Operators use catalytic or thermal oxidising processes to meet these regulations. Thermal oxidation is better equipped to deal with systems that experience relatively frequent changes in load. Since these are often the conditions in refineries, thermal oxidation is frequently used downstream of Claus plants in refineries. Fuel is an important issue here due to the relatively high combustion temperatures of around 600–800°C.

Field tests have shown that O₂ enrichment and the resulting reduction of Claus process gas combined with increased H₂ content can also lead to significant savings in resource consumption in this step. Two Claus plants with an O₂ concentration of 26 vol% in their process air streams were able to cut heating gas consumption by almost 20 percent in their joint thermal oxidation steps compared with air-only combustion. This drop in consumption for heating gas can, under the right conditions, more than make up for the extra resources required for the import of industrial oxygen, enabling the system to pay for itself based on this benefit alone.

2.2.10 Outlook

Using O₂ in Claus processes is a success story that started in the mid-1980s. Since the 1990s this technology has become more widespread in refineries due to the increasingly stringent legal regulations regarding deep desulfurization of engine and heating fuels. These developments have driven demand for additional sulfur recovery capacity and presented Claus plants with a range of new challenges.

Introducing oxygen to the Claus process can help operators master these challenges efficiently and without having to invest in expensive installations. O₂ enrichment also increases energy efficiency and reduces CO₂ emissions. In light of this long list of benefits, it is not surprising that this method of intensifying Claus processes has already been installed in around 20 percent of all Claus plants. Oxygen enrichment systems are also being incorporated into new plant designs (see Figure 18) – a clear sign that this technology is widely accepted across the industry.

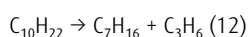
Legal regulations governing sulfur content in mineral oil products will continue to be tightened across the globe. Additionally, refiners are increasingly forced to convert heavy products into lighter, more valuable products in order to operate profitably. In light of these developments, and the fact that sulfur content in crude oil is slowly but surely rising, O₂ enrichment is set to play an increasingly important role in Claus plants in crude oil refineries.

2.3 Using oxygen in FCC processes

A number of methods can be used to convert long-chain hydrocarbons to short-chain hydrocarbons. The following processes are used to split long-chain hydrocarbons:

- Thermal cracking
- Hydrocracking
- Fluid catalytic cracking

In the case of the alkane cracking reaction (12) decane (C₁₀H₂₂) is cracked to a short-chain paraffin (hydrocarbon with single bonds, in this example, heptane (C₇H₁₆)) and an olefin (hydrocarbon with at least one double bond, in this example propene (C₃H₆)):



In the early days of chemical conversion, thermal cracking was found to be the simplest way of creating light distillates from heavy products. Cracking takes place at temperatures above 370°C. Thermal cracking is still used today to process residue from vacuum distillation. It generally involves using a coker that produces light distillates and petroleum coke at temperatures in excess of 500°C.

Hydrocracking is the process best suited to meet current demand for lighter and middle products. This is because the sulfur and nitrogen compounds are hydrogenated and removed in one go.

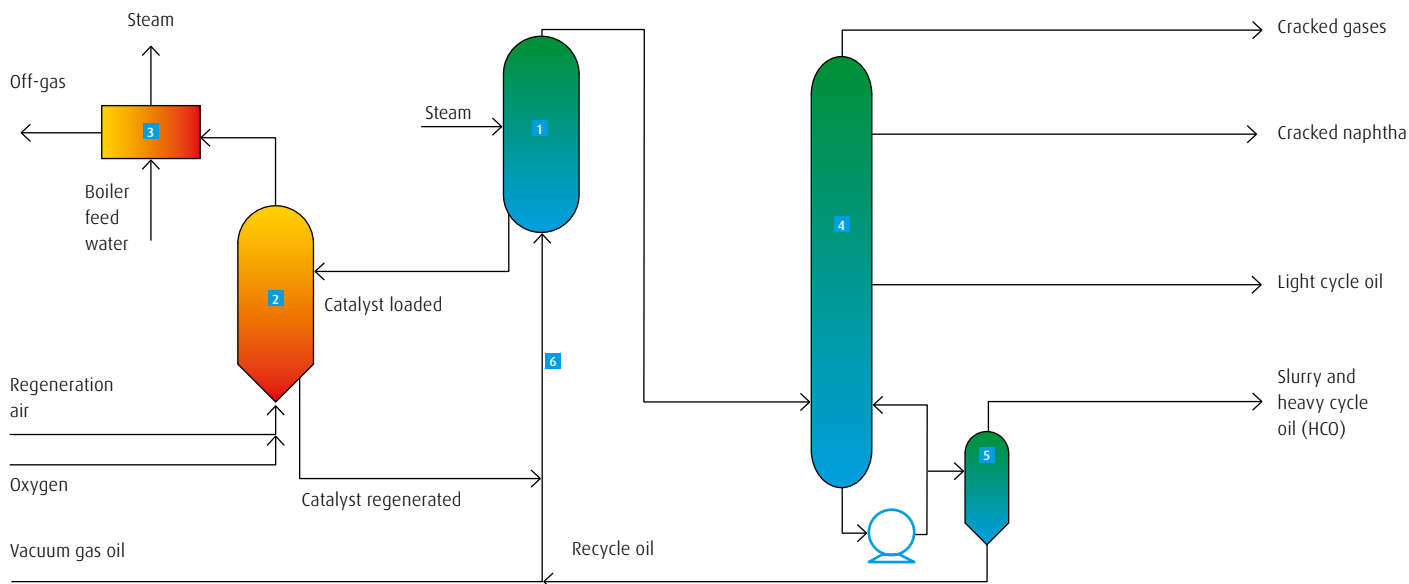
Fluid catalytic cracking (FCC) is an older process that dates back to the 1930s but is still widely used today. This is in part due to the number of existing plants that are still in operation today. Another main factor, however, is that FCC plants are significantly more cost effective to build and run than hydrocrackers. The two processes do not have the same product spectrum. The FCC process produces more gasoline than hydrocracking. It also produces more olefins, which means that the percentage of propene in the petrochemical FCC process can be as high as 20 percent. To combat the disadvantages of the high sulfur content, the FCC feed is pre-treated in a process that is similar to mild hydrocracking.

Figure 34 shows a schematic drawing of a FCC plant. Vacuum gas oil is usually used as the feedstock for the FCC process. This is fed into the riser where it is vaporised using steam and immediately mixed with the catalyst. The main part of the cracking reaction takes place in the riser in just a few seconds. Today, reactors are primarily used to separate the gaseous product and solid catalyst. Steam is also used to strip the products from the catalyst. Cyclones in the headspace of the reactor are used to retain the catalyst.

The product is then broken down into individual fractions in a distillation column. Table 6 lists the typical concentrations of FCC products.

The FCC products are added to the refinery products. LPG, for example, is used to produce propene. Cracked naphtha is an important source of gasoline and the cracked gas oil or light cycle oil (LCO) is added to diesel or light heating oil. The reactions in the FCC reactor are endothermic. The catalyst supplies the requisite reaction heat. During the reaction,

Figure 34: Basis schematic of a FCC plant



1 FCC-Reactor, 2 Regenerator, 3 Boiler, 4 Fractionation, 5 Recycle oil, 6 Riser

coke deposits form on the catalyst and deactivate it. The coke must be burnt off in order to regenerate the catalyst. This takes place in the regenerator. Burning off the coke also heats the catalyst providing it with new energy for the reaction.

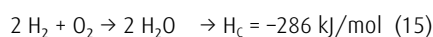
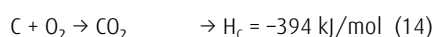
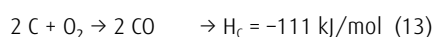
Table 6: FCC products

Product	Description	Percentage [mass %]
Refinery gas	C ₂ and lighter	4
Liquid petroleum gas (LPG)	C ₃ and C ₄	20
Cracked naphtha	C ₅ -C ₁₂	48
Light cycle oil (LCO)	C ₁₃ -C ₂₅	18
Slurry and HCO	>C ₂₅	5
Coke	On the catalyst	5

The regenerator comprises a fluidised bed. Pressurised air is fed in from below and keeps the catalyst suspended. The acidic catalyst is a powder. It primarily comprises zeolites (aluminum oxide Al₂O₃ and silicon dioxide SiO₂) and minor components that stabilise the structure and promote certain reactions. The average particle diameter is around 75 µm. The crude oil contains metals such as vanadium and nickel. Over time, these form irreversible deposits that deactivate the catalyst. Around one percent of the entire catalyst mass is replaced with fresh catalyst each day to ensure a consistent level of activity and to replace losses resulting from catalyst attrition.

A cyclone system is also used to keep the catalyst in place in the regenerator and to ensure that only hot air leaves the headspace. The amount of air determines a regenerator's mode of operation. In "full burn" mode, the coke on the catalyst is fully converted to CO₂. In "partial burn" mode, part of the coke leaves the regenerator as CO. In this case,

the CO has to be fully combusted to CO₂ in a CO boiler. In partial burn mode, the energy supply can be reduced to prevent the catalyst from overheating. As reactions (13), (14) and (15) show, significantly less heat is gained by burning coke to CO than to CO₂.



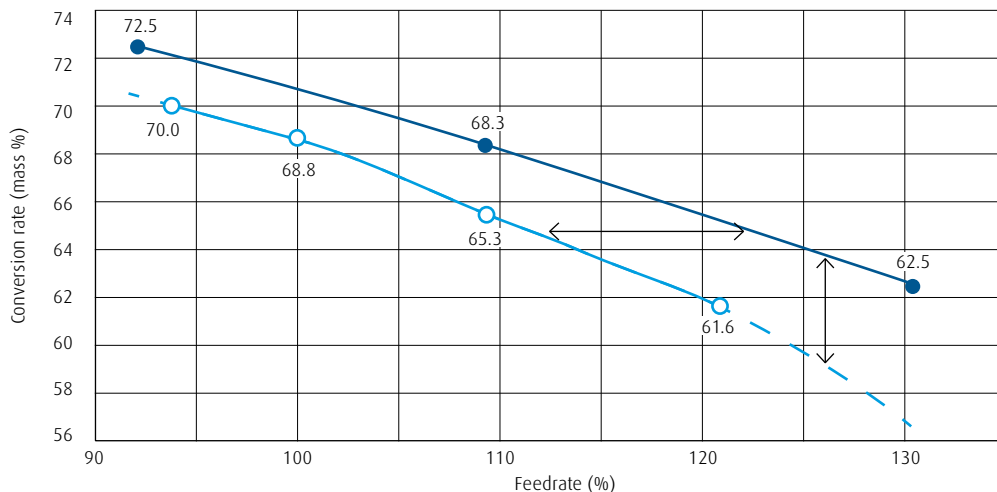
Applying the enthalpy of combustion to the oxygen used here yields the following results:

1 mole of oxygen delivers 394 kJ of heat during the reaction to CO₂, and 222 kJ of heat during the reaction to CO.

Partial burn mode can therefore accommodate more coke and thus handle, for example, heavy feedstocks. CO content in flue gas in partial burn mode is between 3 and 10 vol%. Coke deposits on the catalyst are polymerised hydrocarbons, not pure carbon. As such, a certain amount of hydrogen always remains. This hydrogen must be taken into consideration in the heat balance as it can account for up to 9 mass% of the coke. The valve-regulated catalyst is fed from the regenerator to the riser. In the riser, the preheated feedstock is vaporised by the catalyst and reacts immediately. The temperature at the riser outlet is between 480 and 530°C. Temperatures in the regenerator reach between 650 and 750°C.

The FCC process is very flexible. The adjustments in Table 7 can be made to achieve different results.

Figure 35: Increased conversion efficiency and capacity resulting from oxygen enrichment in the regeneration process



● Conversion rate at 27% by vol. O₂, ○ Conversion rate at 21% by vol. O₂

↔ Increase in Load ↑ Increase in conversion

Table 7: Adjustable operating parameters in FCC process

Increase in feed temperature	More cracked naphtha
Increase in riser temperature	More cracked naphtha
Lower reactor pressure	More light olefins
Higher catalyst/feed ratio	More light olefins
Lower catalyst/feed ratio	More middle distillates
Lower catalytic activity	More middle distillates

A variety of catalysts or catalyst compositions can also be used to achieve the desired results, for example, to produce more cracked naphtha or light olefins. Adding industrial oxygen to the air in the regenerator can also make the FCC process more flexible. The oxygen can be used to burn off coke deposits on the catalyst and does not increase the amount of inert gas. This increases burn-off efficiency and makes the catalyst more active. O₂ enrichment can play a particularly important role if an air compressor has reached its limits and capacity can no longer be increased. This is a particular problem on hot summer days when air pressure is lower and compressors can no longer process the same amounts of air.

Oxygen can increase the capacity of a regenerator that has already reached its limit with regard to fluid dynamics. What this actually means is that if the fluidising gas reaches a certain velocity in the regenerator, the height of the catalyst bed is too high and the cyclones can no longer cope with the resulting amount of catalyst. As a result, too much catalyst leaves the system. Replacing this lost catalyst increases costs. This burden on the cyclones as a result of excess catalyst can also speed up erosion and cause unscheduled downtime and replacements. The resulting repair work drives up costs for operators and also reduces production rates. FCC is still a central and relatively profitable process step in many refineries.

Enhancing catalyst burn-off in this way can be used to improve throughput (horizontal arrow in Figure 35). It can also be used to increase activity and therefore conversion in the riser (vertical arrow in Figure 35).

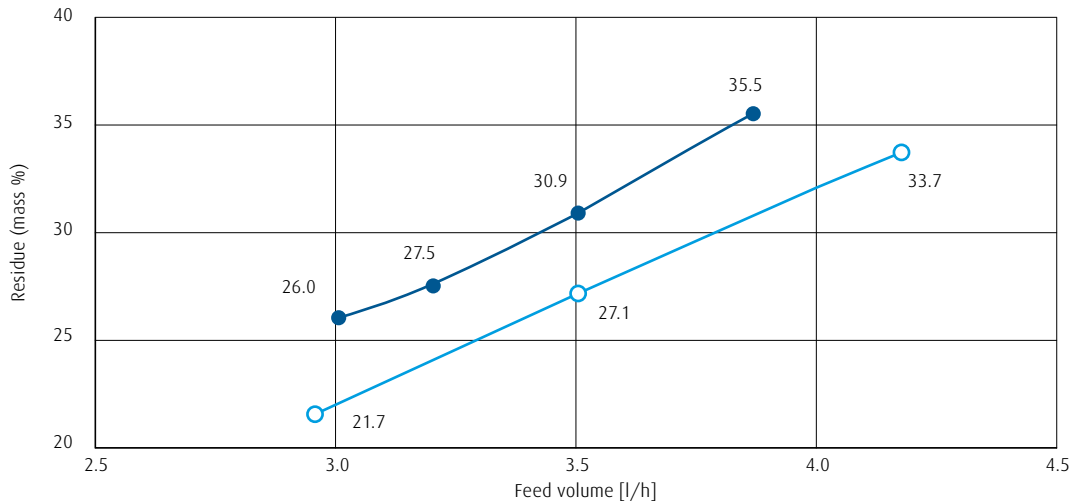
These results were recorded in a test plant. The vacuum gas oil was sourced from a neighboring refinery. Raising oxygen content to 27 vol% increased capacity by 10 to 14 percent. In refinery units, these capacity increases can be achieved by raising the proportion of oxygen in air to just 22.5 to 23.5 percent.

Oxygen enrichment also reduces residue. In tests, 3.5 to 5 percent less residue was generated (Figure 36). This makes the FCC process significantly more cost efficient and ensures that oxygen enrichment pays for itself within a few weeks or months. The expected changes in the process can be accurately simulated. The latest data can be used to predict the changes to the product composition and temperatures that occur when the feed is modified and oxygen added. The simulation tool from EUROTEK Refining is based on Excel and is relatively easy to use.

Oxygen can also be an efficient way of resolving performance bottlenecks in the wet gas compressor. Wet gas compressors compress the cracked gas from the distillation column so that it can be further broken down into its constituent parts in the FCC gas plant. Increasing pressure in the reactor enables the wet gas compressor to process more air. The rise in pressure reduces the flow rate of air blowers. However, industrial oxygen can be used to compensate for this drop in blower capacity.

Cyclones in a regenerator are configured to work within specific ranges. If the gas flow is higher than this optimum cyclone range, catalyst losses increase significantly. Adding oxygen to the fluidisation air keeps the FCC

Figure 36: Reductions in residue following oxygen enrichment



● Residue at 27% by vol. O₂, ○ Residue at 21% by vol. O₂

process flexible and enables the cyclones to work in their design range with minimum catalyst losses. Gas usually travels at 20 m/s at cyclone inlets. Cyclone outlet flow usually ranges from 25 to 30 m/s.

The following two case studies are examples of oxygen enrichment in FCC plants. Figure 37 shows a FCC plant with oxygen enrichment.

Case 1:

The first FCC facility is a UOP plant with the reactor located above the regenerator. The throughput is 3,300 m³/d (20,000 bbl/d). The feed comprises 65 mass% vacuum gas oil, 25 mass% coker gas oil and 10 mass% hydrogenated gas oil. Density ranges between 21 and 22° API (between 0.9279 kg/l and 0.9218 kg/l). Based on the Conradson carbon calculation (a method of determining the amount of heavy residue in a heavy oil), the feed's residue is 0.3 mass%, which is in the standard range for a gas oil. Sulfur content is 0.65 mass%. The FCC process is operated in partial burn mode. Oxygen content at the outlet is therefore zero; CO accounts for between 3 and 4 vol% and CO₂ content is 14 vol%. Around 100 t of catalyst is used at a circulation rate of 15 t/min. nickel and vanadium content is within the standard ranges at 800 ppm and at 1,700 ppm respectively. Nickel is a catalyst for dehydrogenation while vanadium aids the deactivation of the catalyst. Both of these processes are undesired yet unavoidable due to the presence of the metals in the crude oil.

The aim of enrichment was to increase yield by 10 percent. To achieve this, the coke on the regenerated catalyst (CRC) first had to be reduced from the very high value of 0.5 percent to below 0.1 percent. Table 8 shows the differences between air-only mode and oxygen-enriched mode.



Figure 37: Refinery with oxygen enrichment for FCC

Table 8: Using oxygen enrichment in an FCC plant to increase capacity

	Air-only	Enrichment to 22.2 vol% O ₂	Change [%]
Feed [m ³ /d]	3,242	3,650	+12.6
Products [m ³ /d]			
LPG	1,044	1,054	+1.0
Cracked naphtha	1,652	1,971	+19.3
LCO	845	840	-0.6
Slurry and HCO	356	340	-4.5
Temperatures [°C]			
Feed	288	275	
Reactor	524	524	
Regenerator	710	724	
Regenerator flue gas	700	730	
Reactor pressure [bar]	1.70	1.73	
Regen. pressure [bar]	2.04	1.99	

The resulting capacity increase exceeded the original goal. The amount of coke on the regenerated catalyst was reduced to 0.05 percent. The overall investment had paid for itself in less than three months. The amount of slurry produced also fell. As a result, more of the valuable product was produced, which helped make the plant much more profitable.

Case 2:

This FCC facility is an UOP side-by-side plant. The regenerator and reactor are located next to each other. The plant is operated in full-burn mode

and has a catalyst circulation rate of 25 t/min. The amount of feed was increased from 4,200 to 6,000 m³/d, which led to bottlenecks in the air blowers. This problem was overcome using oxygen enrichment.

The following results were recorded:

- Raising oxygen content by one percent increased capacity by six percent.
- Raising oxygen content by one percent helped increase temperatures in the regenerator by 2°C. This rise in temperature was due to more intense coke burning.
- Oxygen reduced FCC slurry and HCO
- Oxygen enrichment enabled heavier feeds to be processed.

Overall, the findings show that oxygen enrichment in the regenerator of an FCC plant makes the process more flexible and that it pays for itself in a very short time. The following improvements could be achieved by adding oxygen:

- Higher capacity due to increased oxygen availability in the regenerator
- Increased conversion
- Reduction of residue in the FCC process
- Alleviation of problems with air blowers, especially in the heat of summer
- Reduction of gas flow in the regenerator and downstream cyclones; this reduced catalyst losses and erosion
- Higher capacity by increasing pressure in the reactor and subsequently increasing the performance of the wet gas compressor; oxygen compensates for reduced air blower performance.



Figure 38: Furnaces for pre-heating products in a refinery

2.4 Oxygen enrichment for burners

All key processes in refineries require hydrocarbons to be heated and partially vaporised in fired heaters. Adding oxygen to combustion air or directly injecting oxygen to the combustion chamber can cut fuel consumption and increase heat transfer. And this, in turn, cuts CO₂ emissions.

In many cases, catalysts become less active over time, for example in hydrotreaters. Increasing temperature, however, can boost their activity again. This can be useful to synchronise operations across multiple units. Adding oxygen to combustion air can reduce the length of the burner flame, which means that the temperature increase can be maintained for a longer time. Shortening the burner flame is particularly important if there is a risk of it coming into contact with the internals of the furnace or with the wall of the furnace itself. Materials can be irreversibly damaged if they come into direct contact with the flame. Flame damage also shortens the lifetime of a furnace. Figure 38 shows furnaces in a refinery.

The diagram in Figure 39 shows how these furnaces work.

Figure 39: Structure of a furnace for preheating refinery feed products

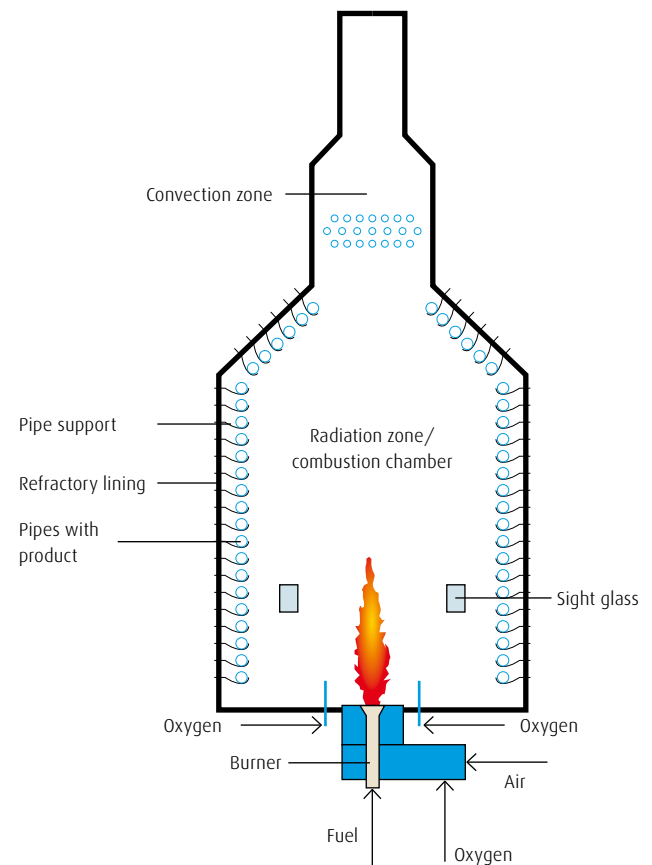
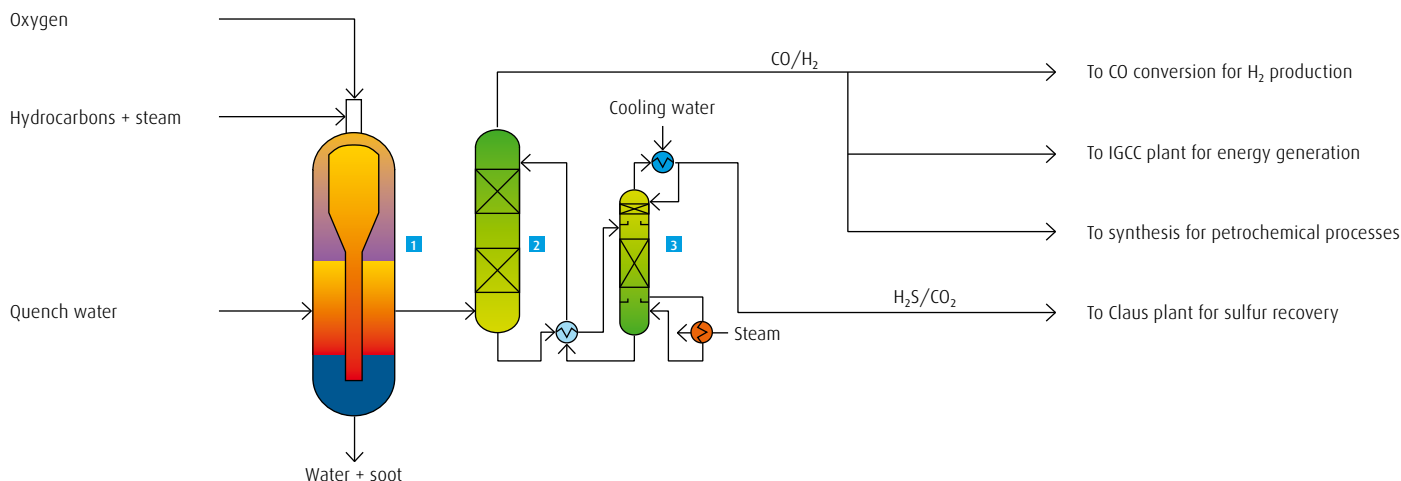


Figure 40: Gasification of liquid hydrocarbons



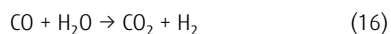
1 Gasifier, 2 Gas scrubber, 3 Regeneration of scrubbing agent

2.5 Gasifying refinery residue

Partial oxidation uses gasification to convert solid or liquid hydrocarbons to hydrogen, carbon monoxide and carbon dioxide at high temperatures and under high pressure (approximately 1,350°C and 85 bar).

Figure 40 illustrates the principle of gasification. Hydrocarbons are oxidised with steam and oxygen under sub stoichiometric conditions. The high temperatures break down the long chain molecules to form carbon monoxide (CO), hydrogen (H₂) and carbon dioxide. The resulting gas is cooled and cleaned in a number of scrubbing steps. This removes all impurities to produce a synthesis gas comprising CO and H₂. The H₂/CO ratio in liquid refinery residues is between 1.3 and 1.8.

If hydrogen is the only end product required, the CO can be reacted with water vapour to produce CO₂ and H₂. This reaction (16) is also known as the shift reaction:



The hydrogen is then concentrated to a typical purity of 99.9 percent in a PSA unit.

Gasifying vacuum residue enables refiners to use every ingredient of crude oil (bottom of the barrel conversion) and eliminate all residues from refinery processes. Synthesis gas can be converted to hydrogen or used for other applications:

- Synthesis gas can be converted to methanol in a process known as methanol synthesis.

- Fischer-Tropsch synthesis can be used to convert synthesis gas back to longer-chain hydrocarbons, which are more valuable than the original feed.
- Synthesis gas can be used to generate power in an integrated gasification combined cycle (IGCC) power plant.

A gasification plant can significantly expand a refinery's capabilities, enabling operators to process a range of crude oils, including heavier crude oils, and thus expand the refinery's economic base. However, gasification also requires substantial investment, which is why many refineries do not use it. The photograph in Figure 41 shows a gasification unit for producing hydrogen and carbon monoxide.

2.6 Wastewater treatment

Oxygen deficits cause a lot of problems in wastewater treatment. Refineries are particularly susceptible to this issue. They produce highly contaminated wastewater which can quickly push their treatment capacities to the limit. And when this happens, processes in activated sludge tanks become anaerobic, causing odors and floating sludge to form. Floating sludge does not settle in final clarifiers and so the discharged water will not be clean enough. Odors lead to complaints from the surrounding area. Together, these problems attract the attention of the authorities, who will insist that they are resolved. In many cases, industrial oxygen can help resolve these issues by increasing capacity and making processes more flexible. Pure oxygen is already used in the following applications:

- Peak load deployment: Pure oxygen is used at peak times when ventilation systems reach their limit



Figure 41: Gasification plant for the production of H_2 and CO from naphtha



Figure 42: Using pure oxygen for intermittent denitrification in the wastewater treatment plant of a refinery

- Denitrification: Pure oxygen is used to reduce nitrate via intermittent (Figure 42), simultaneous or upstream denitrification
- Emergency deployment: Oxygen is used, for example, if a ventilation system fails or a wastewater treatment plant is being converted to oxygen-only operation
- Pretreatment: Pretreating wastewater with pure oxygen
- Pressure pipelines: Oxygen is added to wastewater at different points in a pipeline to prevent hydrogen sulfide from forming.

One of the main benefits of using pure oxygen in wastewater treatment is that it enables operators to upgrade existing facilities and increase purification levels with little investment. Adding oxygen has the same effect as enlarging the treatment basins.

Oxygen can be added via gas hoses or by using a Venturi system, which also mixes the oxygen with wastewater (Figure 43).

The following example explains intermittent denitrification at a refinery wastewater treatment plant. In this mode of operation, oxygen is added in cycles. These can be, for example, forty minutes of oxygen enrichment and twenty minutes of mixing without oxygen. During this time, microorganisms use oxygen from the dissolved nitrate (NO_3^-) in the wastewater to metabolise. The nitrate is reduced to molecular nitrogen (N_2), which escapes into the air. This prevents over-fertilisation at water receiving. If air were to be used for this concept, the treatment basins would still have to be enlarged by 50 percent. With pure oxygen, however, the existing ponds can be used.

The refinery can continue to comply with the legal discharge values of $N_{total} < 5 \text{ g/m}^3$ and the BOD_5 discharge value of $BOD_5 < 3 \text{ g/m}^3$. The BOD_5 value is the amount of oxygen consumed in a sample of water incubated at a certain temperature over five days.



Figure 43: Venturi system for injecting oxygen into stabilisation ponds

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