Making our world more productive

Oxygen enrichment for intensification of air oxidation reactions.

Contents.

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 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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Kaufbeuren and Unterschleissheim, January 2015

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. O_2 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.

O_2 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. O_2 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 (H_2/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 H_2S.

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 N_2 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.

O_2 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. O_2 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 O_2 enrichment during regular operations.

1. Oxygen.

Figure 1: Composition of dry air

Oxygen O_2
20.95 vol%

Argon Ar
0.93 vol%

CO_2
Neon
Helium
Krypton
Xenon
0.04 vol%

Nitrogen N_2
78.08 vol%
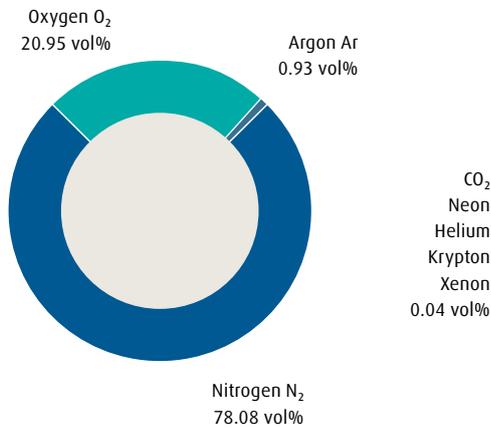
1.1 Properties of oxygen

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 crust 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 O_2. 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 O_3. 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.

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/m³]	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.

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

| — Nitrogen | — Argon | — Oxygen | — Carbon dioxide |
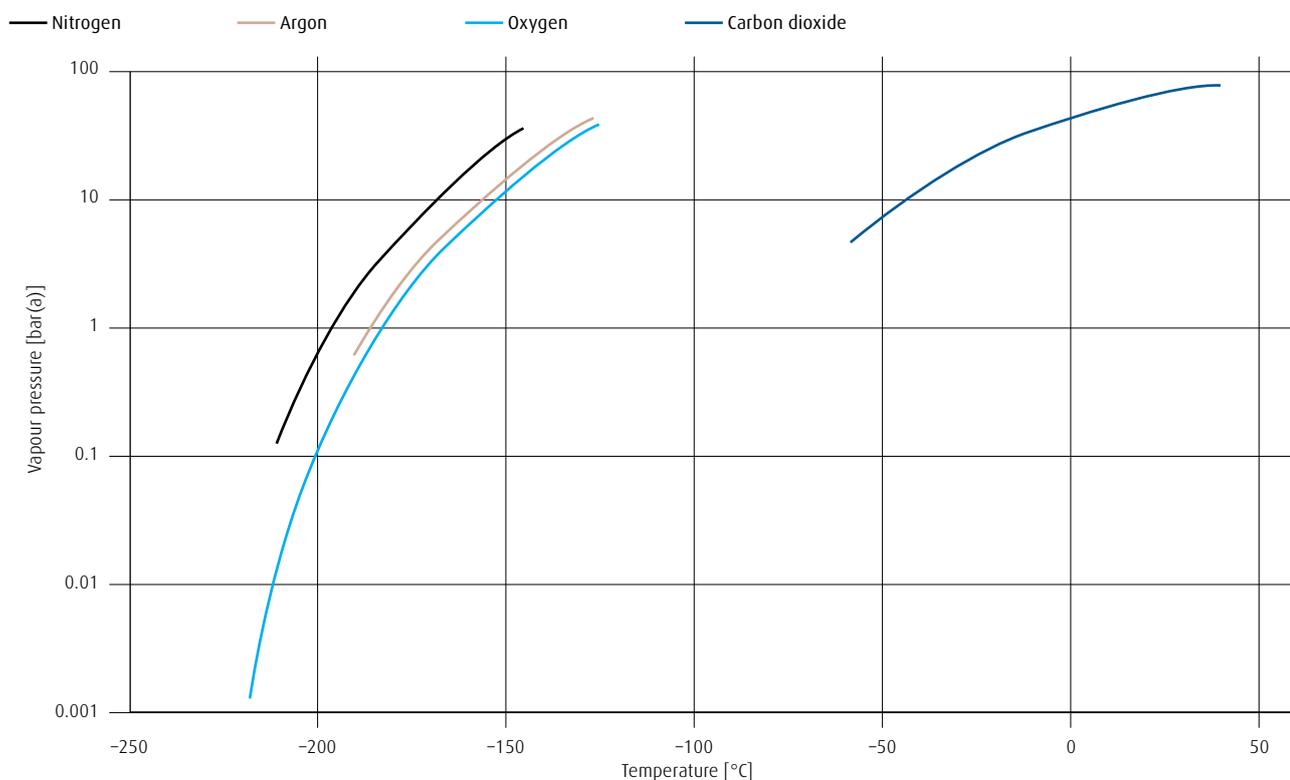
1.2 Oxygen production processes and supply systems

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 [Nm³/h]	Purity	Supply mode	Supply requirements
0 to approx. 1,000	> 99.5%	Liquid supply from tank	Demand fluctuates strongly
Approx. 300 to 5,000	< 95%	Adsorption (VPSA)	Load range typically between 30 and 100%
Approx. 1,000 to 10,0000	> 95%	Cryogenic air separation	Load range typically between 60 and 100%

Figure 3: Schematic drawing of a VPSA plant
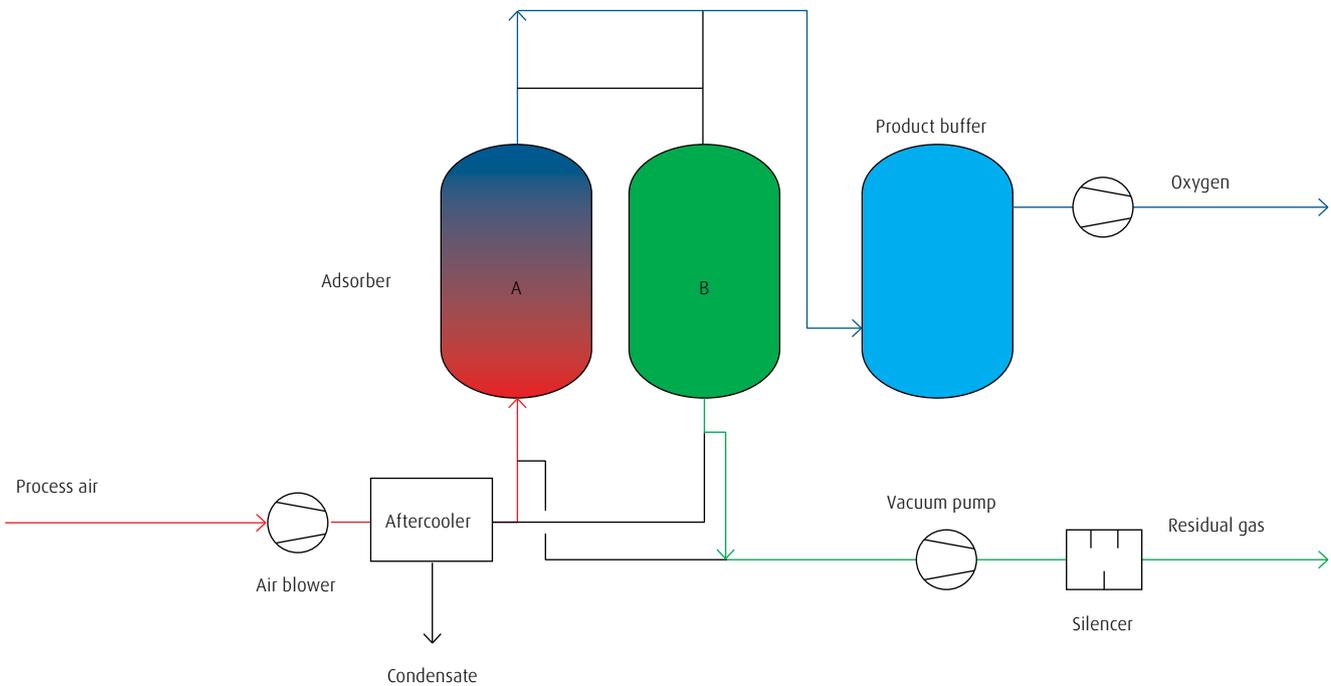
1.2.2 Adsorption plants

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 °C), oxygen (−183 °C) and argon (−186 °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
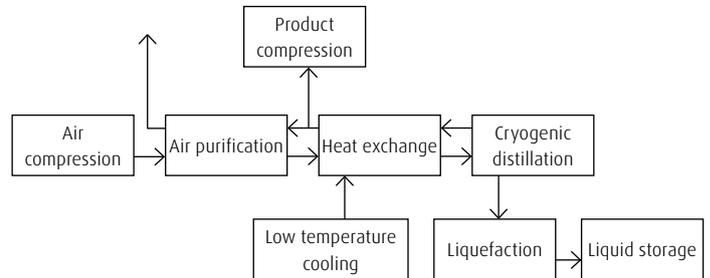
Figure 6: Schematic drawing of the cryogenic air separation process
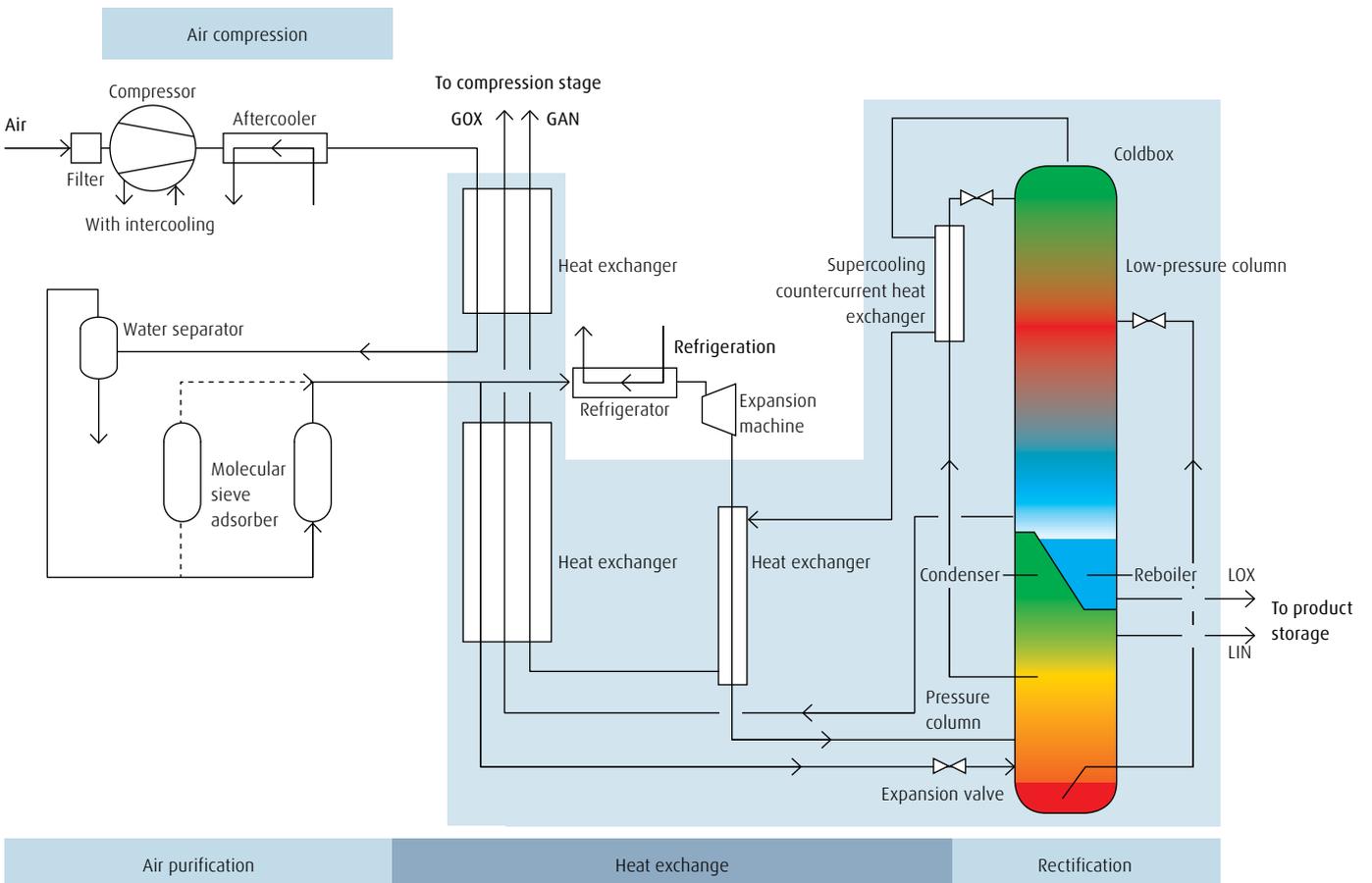
Figure 7: A cryogenic air separation plant

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

Group:	3,000 litres	6,000 litres	12,000 litres	20,000 litres	30,000 litres	49,000 litres	60,000 litres	80,000 litres
Content in litres:	3,000–4,700	5,000–7,900	11,000–16,000	17,500–23,000	25,000–37,000	40,500–53,000	61,000–63,000	75,000–80,000
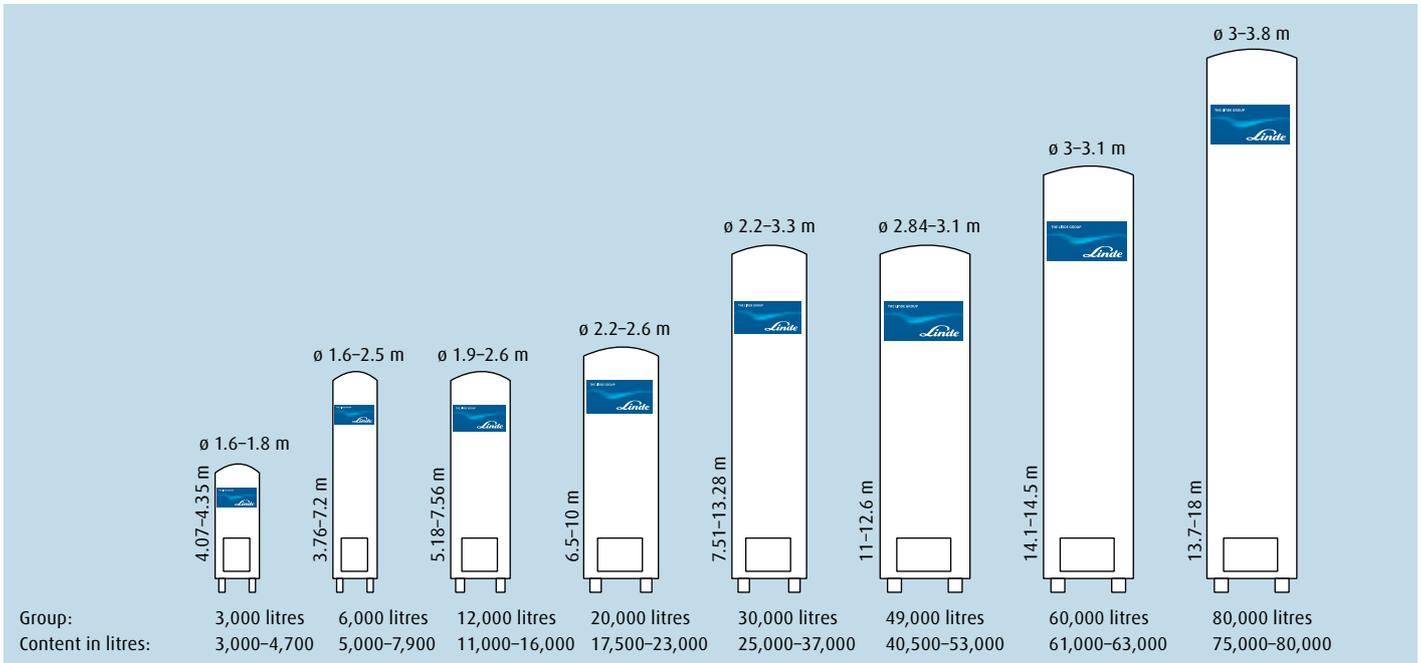
Figure 9: Standard sizes of bulk liquid tanks

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 bar. 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 m^3 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

Air separation plant

Process control system

Control unit

Liquid gas from tube trailer
plus vaporiser

GOX (O$_2$, gas)

OXYMIX Flowtrain
measurement and
control unit

O$_2$ analyser

Air

O$_2$-enriched air

Pipeline supply

Oxymix^{TM} Injector
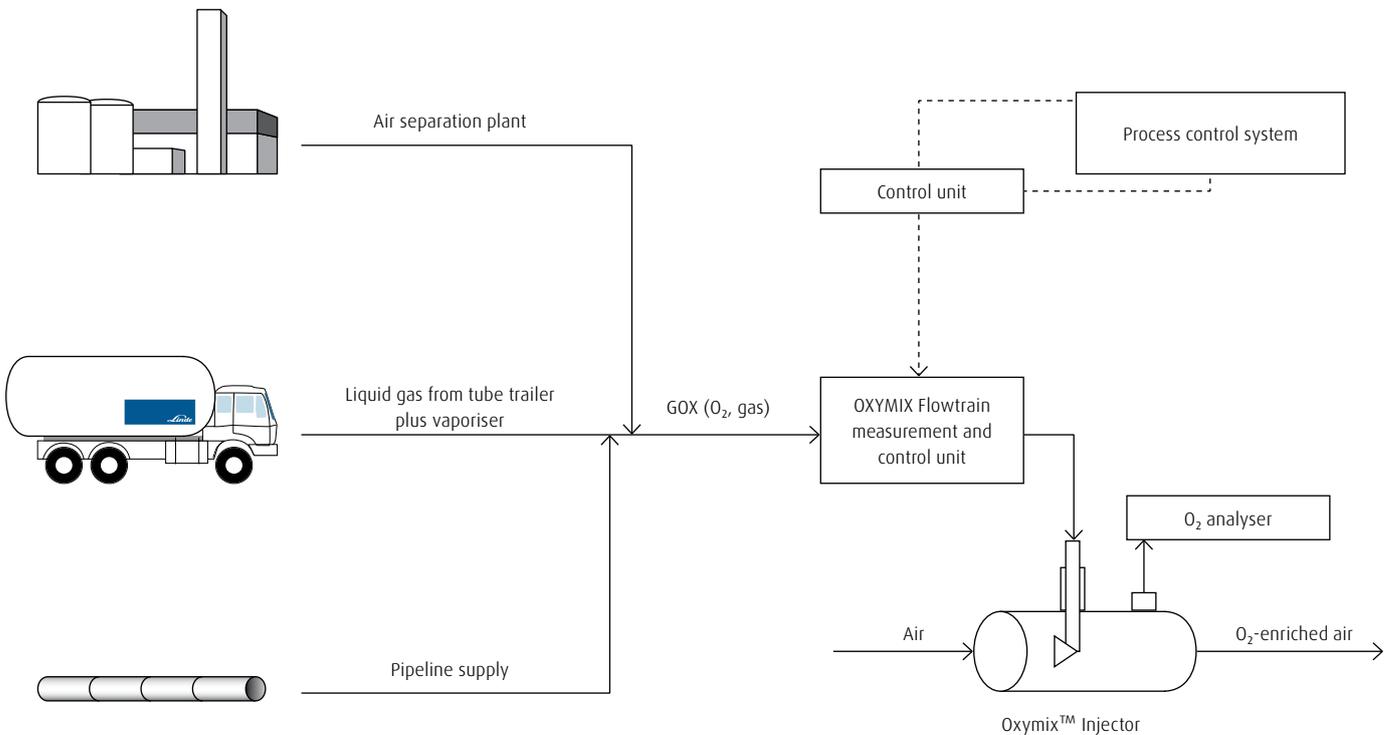
1.3 Oxygen injection systems for oxygen enrichment

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 a OXYMIX^{TM} Flowtrain control system (see figure 14) for safely metering the supply of oxygen and an OXYMIX^{TM} 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 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 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.

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				
Sulfur [ppm]	<300	<150	<50	<10
Benzene [vol%]	<5	<2	<1	<1
Aromatic compounds [vol%]	–	<45	<35	<35
Diesel				
Sulfur [ppm]	<500	<350	<50	<10
Cetane number [vol%]	>49	>51	>51	>51
Aromatic compounds [mass%]	–	<11	<11	<11

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 desulfurisation. 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
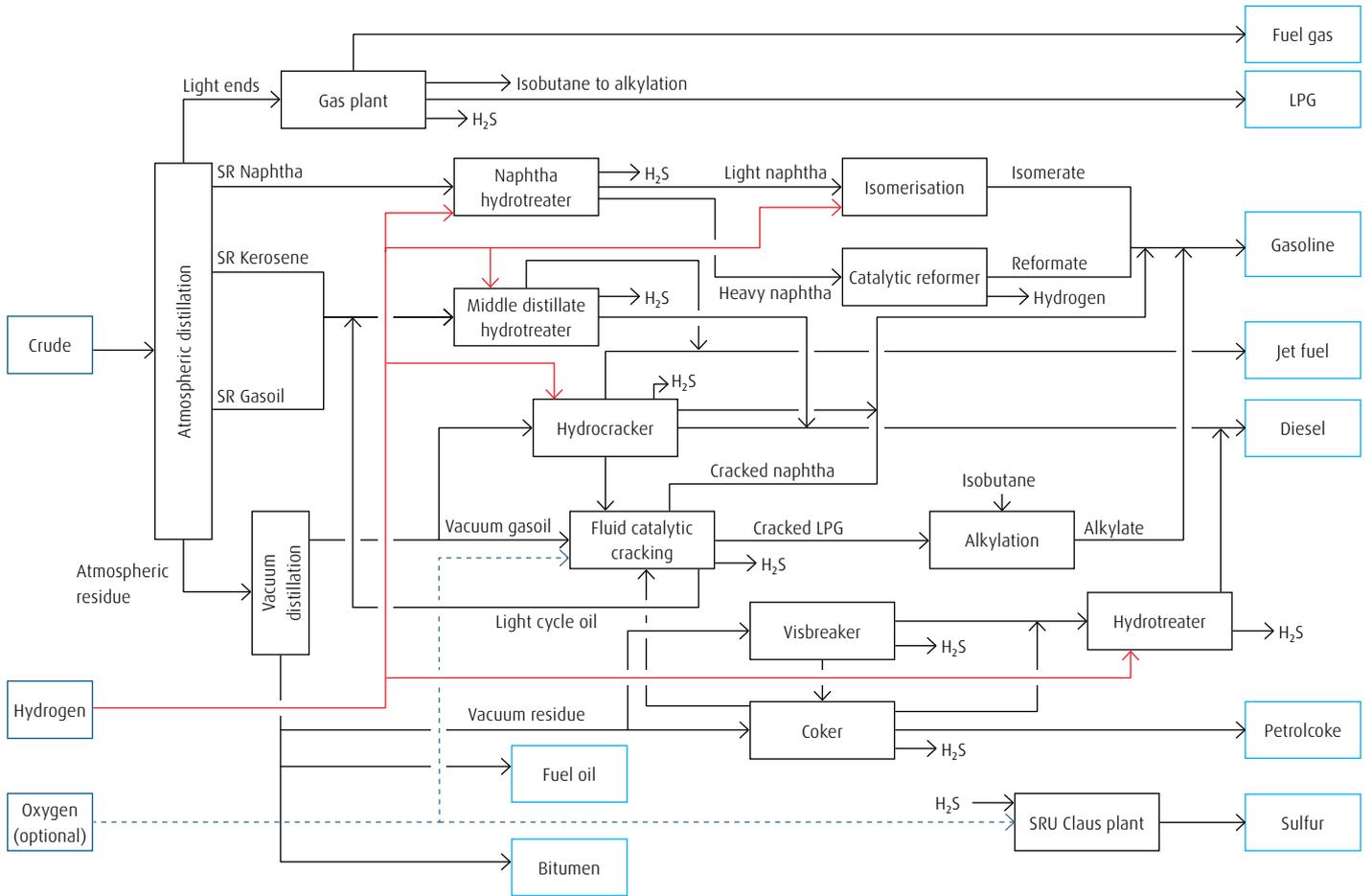
Table 4: Hydrogen demand in relation to desulfurisation

Desulfurisation [%]	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 m³/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

Petrolcoke 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 CO_2 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 (NH_3) or an ammonia solution into hot flue gas. The resulting reaction (1) converts nitric oxide (NO):

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O \quad (1)$$
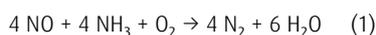
Instead of using ammonia for the reduction of NO, a powerful oxidant can be injected into the NO bearing gas stream. Accordingly the LoTOx™ process applies ozone (O_3), which oxidises NO to produce dinitrogen pentoxide (N_2O_5) (see reactions (2) and (3)). Unlike NO, N_2O_5 dissolves easily in water.

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (2)$$

$$2\ NO_2 + O_3 \rightarrow N_2O_5 + O_2 \qquad (3)$$

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3 \qquad (4)$$
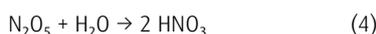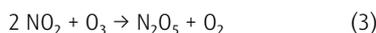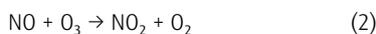
N_2O_5 then hydrolyses in a scrubber to produce nitric acid (HNO_3) (4). Ozone is produced in an ozone generator by feeding pure oxygen through high-voltage cell, containing dielectrics. The resulting electrical discharge reaction generates ozone.

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 desulfurisation step to meet the strict legal requirements governing desulfurisation rates.

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

Desulfurisation by separation from H_2S-rich gas fraction	Desulfurisation by oxidation of H_2S to sulfur	Deep desulfurisation (not always installed)	Sulfur species to SO_2
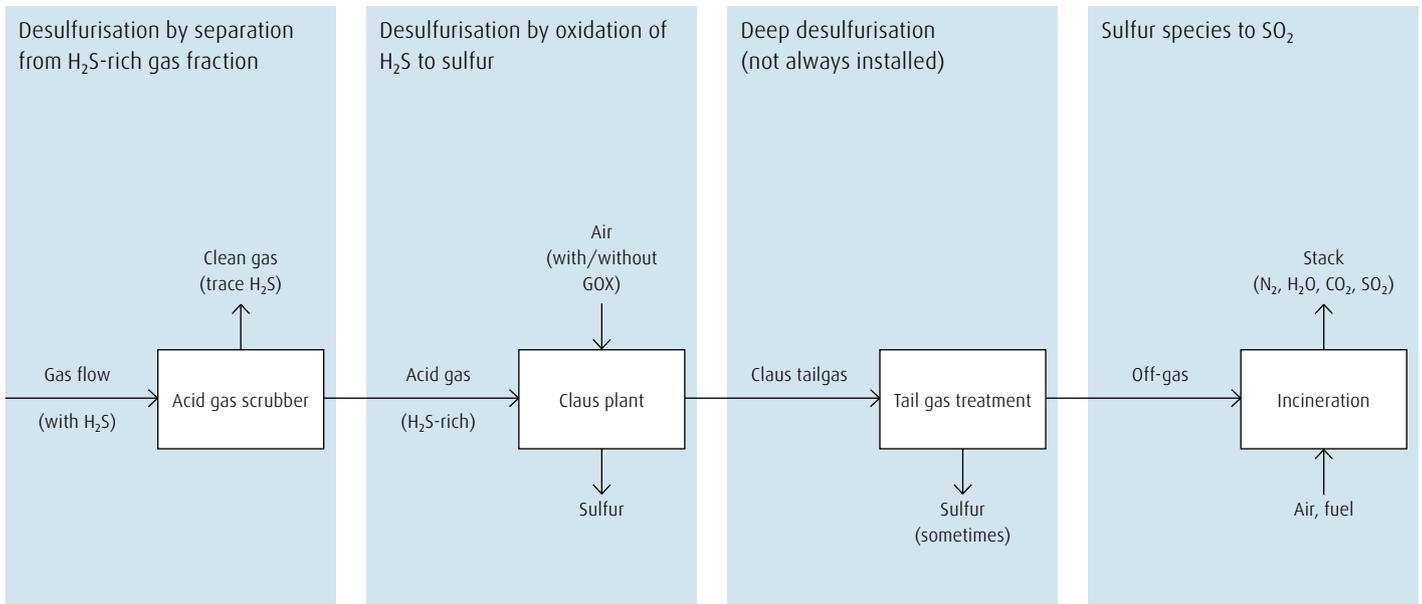
2.2.2 Molecular oxygen – the key to recovering sulfur

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:

$$H_2S + \tfrac{1}{2}\,O_2 \rightarrow S + H_2O \qquad\qquad (5)$$
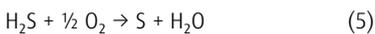
Typically, air (O_2 content (dry): 20.9 vol%) is added to provide the O_2 molecules required for this exothermic oxidation process. Process air admixed to acid gas can be passed through solid catalyst to ensure that the partial oxidation process reaches sufficient speed. This was the case with the original 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: "H_2S direct oxidation" (H_2S 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):

$$3\,H_2S + 3/2\,O_2 \rightarrow 2\,H_2S + SO_2 + H_2O \quad (6)$$
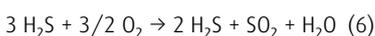
On this basis, some elemental sulfur has already been formed in the thermal step according to the Claus reaction (7):

$$2\,H_2S + SO_2 \rightarrow 3/x\,S_x + 2\,H_2O \qquad (7)$$

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

| Thermal stage | 1. Catalytic stage | 2. Catalytic stage | 3. Catalytic stage |
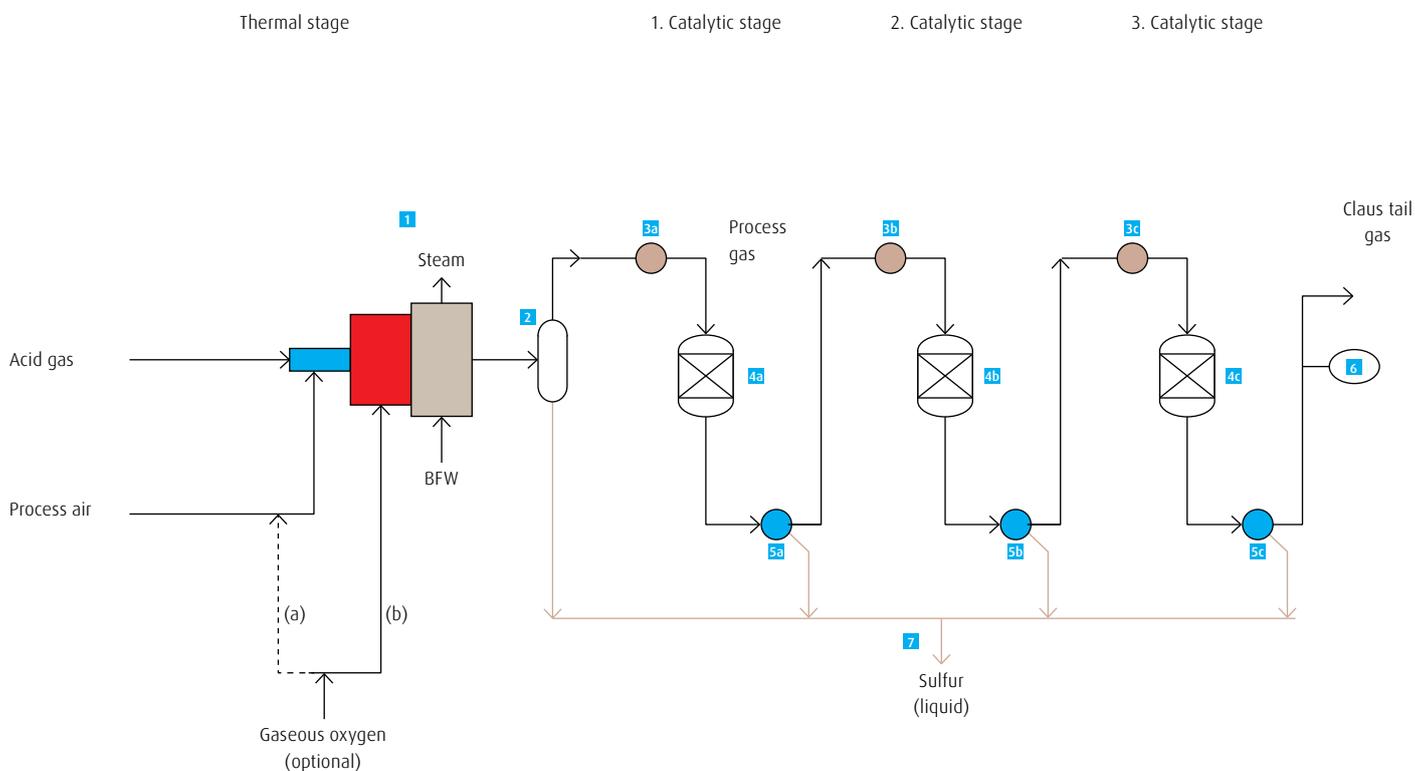
1 The thermal step in the Claus process, comprising three main components (left to right): burner, combustion chamber and waste heat boiler where the process gas is cooled by turning the boiler feed water (BFW) into steam i.e. recovering energy., **2** Separator for recovering liquid sulfur, **3** Reheating of process gas, **4** Claus reactors; in other words, containers filled with Claus catalyst (temperature 4a > temperature 4b > 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
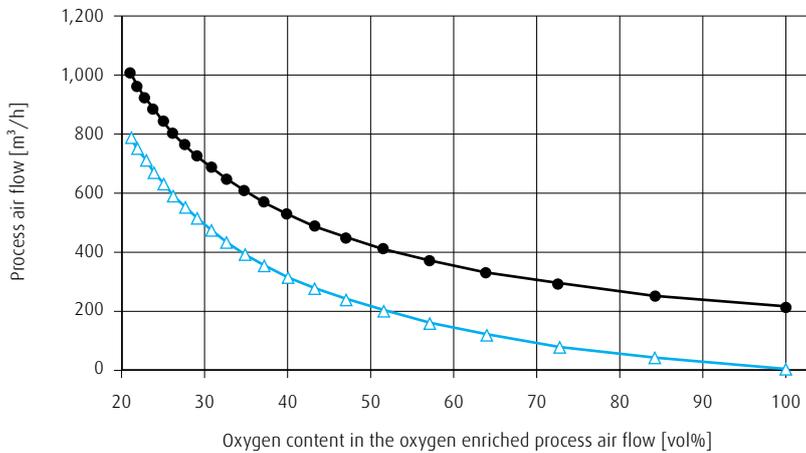
Less nitrogen means:

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

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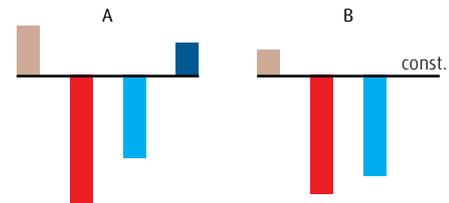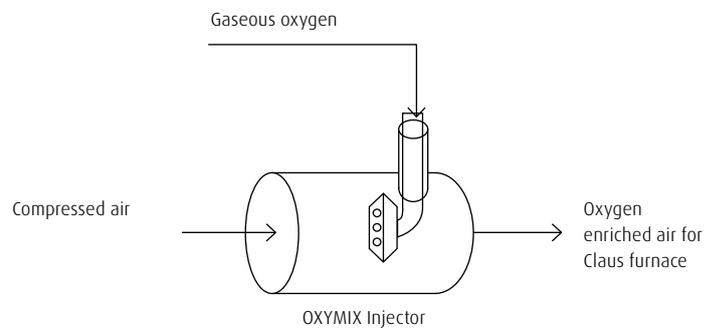
—— Supplied industrial oxygen
—— Compressed air from the compressor
—— Oxygen enriched air for the Claus furnace
—— Additional absolute amount of molecular oxygen
(Total oxygen amount increased (A) or unchanged (B))
The vertical bars highlight the different gas flows for operational modes A and B, whereby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

The O_2 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 H_2S-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 H_2S gases as feedstock in Claus plants
It is relatively rare for refineries to produce acid gases with H_2S 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 CO_2) 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 (H_2S) 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 H_2S to be oxidised to SO_2 (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 N_2 content. Depending on the amount of H_2S 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, 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 contaminates in acid gas such as aromatics are subject to high flame temperatures and therefore destroyed more efficiently.

Using H_2S-rich gas as feedstock in Claus plants
Acid gases with H_2S 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 H_2S under conditions present in numerous refinery processes – in other words, whenever oil fractions are heated under reducing conditions. As a result, gaseous mixtures containing H_2S 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). H_2S 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 H_2S 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 H_2S, NH_3 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 hydrodesulfurisation 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% H_2S in the acid gas to the Claus plant,
△ 50% H_2S in the acid gas to the Claus plant

O_2 content in enriched process air [vol%]
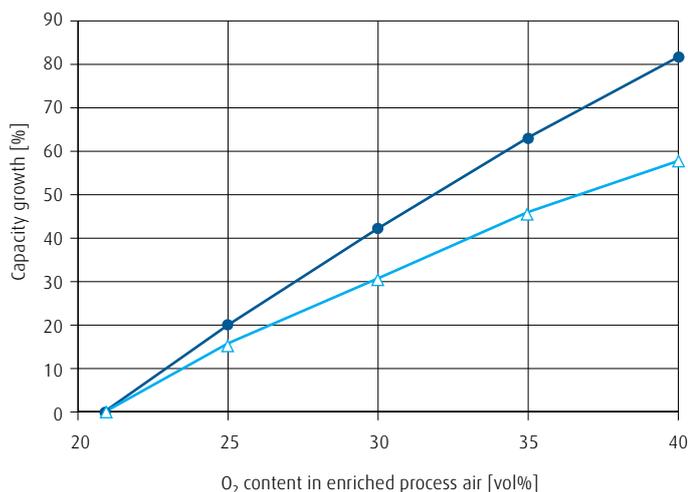
Figure 24: SURE™ burner

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, O_2 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 H_2S into elemental sulfur.

The diagram in Figure 23 has been verified by numerous field tests. It shows that O_2 enrichment offers huge potential to increase the capacity of Claus plants when it is used especially with H_2S-rich acid gases – in other words under typical refinery conditions.

Low-level enrichment

Figure 23 also shows that O_2 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 O_2 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 O_2 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 O_2 concentrations without being damaged and ensure that the feed gases are mixed well. Depending on the burner technology installed, O_2 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 H_2S-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 O_2 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 O_2 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 O_2 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 (NH_3) stems from hydrocarbon compounds that contain nitrogen. These are produced in almost all process steps that generate H_2S, 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 desulfurisation (HDS) and denitrification of fractions. The amount of ammonia produced increases with the severity of the hydrogenation process conditions, for example deep desulfurisation of fractions that produce "sulfur-free" diesel (sulfur content of max. 10 ppm). Since ammonia (NH_3) is very soluble in water, it is mainly found in aqueous process condensates. These are collected and fed into sour water strippers where the NH_3 and co-adsorbed H_2S are removed. Isolating pure NH_3 for sale in most cases is not economically viable here. The gas streams containing NH_3 and H_2S (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):

$$SO_2 + 2\ NH_3 \rightarrow N_2 + 2\ H_2O + H_2S \qquad (8)$$
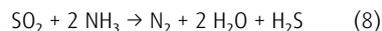
and reaction (9):

$$2\ NH_3 \rightarrow N_2 + 3\ H_2 \qquad (9)$$

NH_3 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:

$$NH_3 + SO_2 + H_2O \rightarrow NH_4HSO_3 \downarrow \qquad (10)$$

These sulfite 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 desulfurisation 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 O_2 enrichment to minimise problems with ammonia
In light of these problems, it is particularly important that Claus plant operators success in maximizing NH_3 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, O_2 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. O_2 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)
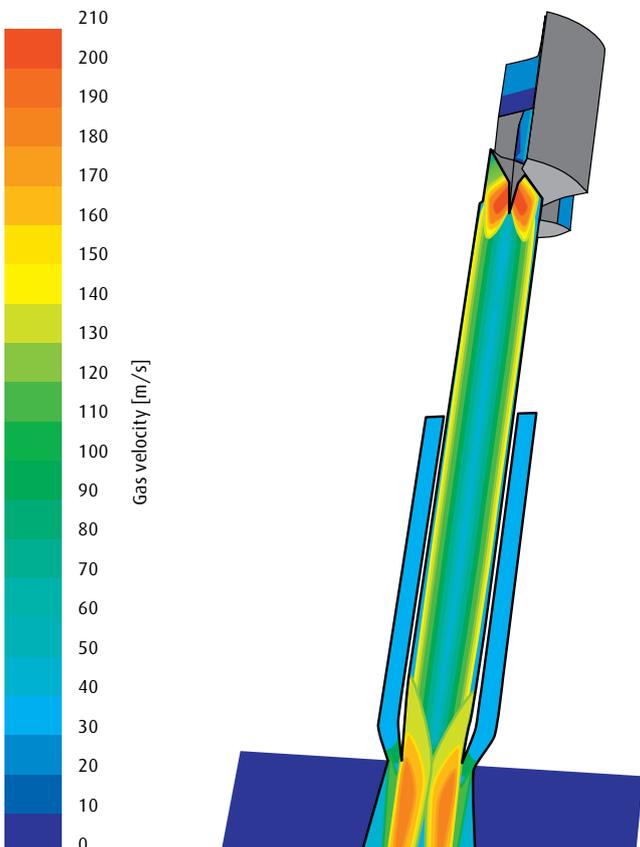
Figure 27: Burner test installation in Pullach, Germany

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

— Temperature in the Claus furnace   — O$_2$ measurement
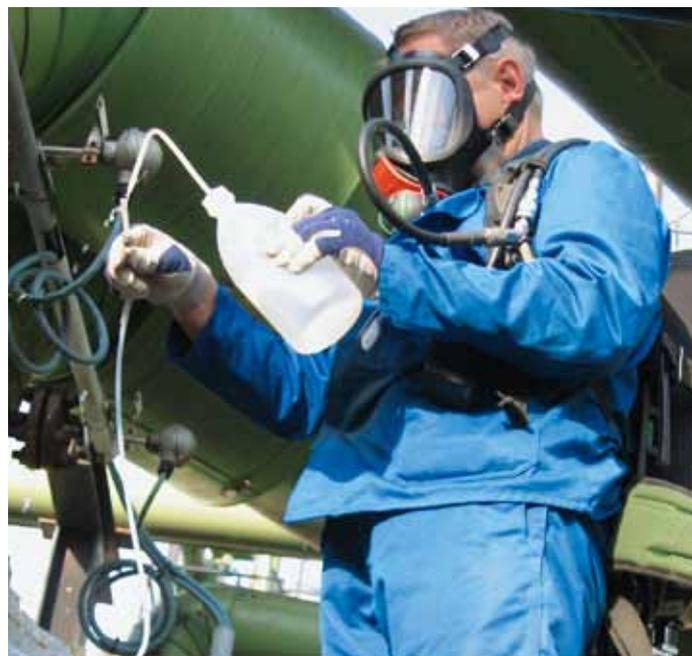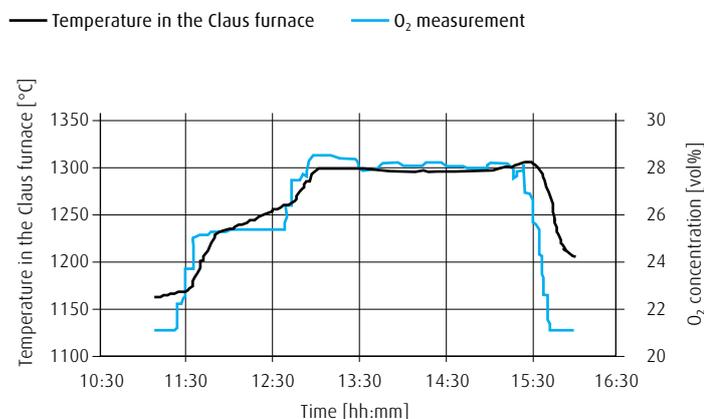
Figure 30: Sampling of Claus process gas for ammonia measurement

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 NH$_3$ 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. NH$_3$ content in process gas is an impartial indicator of how much NH$_3$ has been destroyed during the thermal step of the Claus process. To determine NH$_3$ content, a small sample gas stream (measured volumetrically) is removed immediately after the thermal step and fed through a mineral acid solution. The NH$_3$ dissolves into ammonium (NH$_4$+) 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 NH$_3$ analysers are not state-of-the-art at Claus process conditions (see Figure 30).

To quantify the effects of temperature increases in Claus furnaces, NH$_3$ content was measured in over a dozen O$_2$ enrichment field tests (low- and medium-level enrichment). At each site, the residual concentration of NH$_3$ with O$_2$ enrichment was compared against NH$_3$ 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 NH$_3$ content, also following the addition of extra O$_2$, however in all cases O$_2$ enrichment causes a significant drop in residual NH$_3$ content. In some cases, depending on the individual furnace conditions, almost all of the NH$_3$ 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 NH$_3$ salt problems by a factor of three. However, they are convincing enough to have already persuaded many operators to install permanent O$_2$ enrichment solutions. This move has most likely also been prompted by other benefits associated with O$_2$ 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% O$_2$), △ 27–28 vol% O$_2$
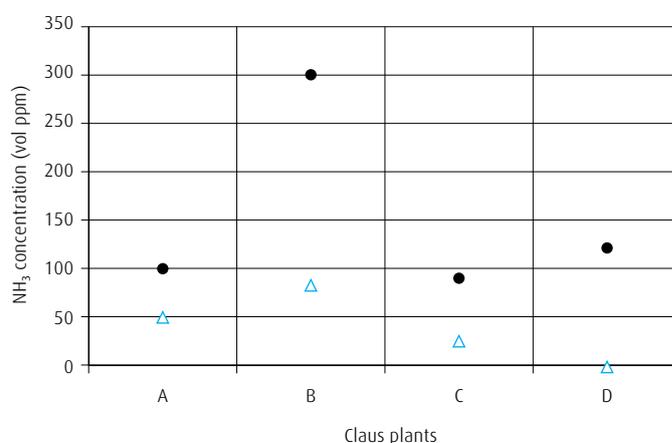
2.2.9 Impact of oxygen enrichment on Claus tail gas treatment and waste gas incineration

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. O_2 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 H_2) 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 SO_2 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 (SO_2, S vapour, COS and CS_2) into H_2S. The H_2S is then separated and concentrated in a gas scrubbing system. The resulting H_2S-rich stream is then fed back into the thermal step of the Claus process. To fully hydrogenate sulfur vapour and SO_2 to H_2S 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 O_2 enrichment upstream within the Claus furnace cause significantly more H_2 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:

$$2\,H_2S \rightarrow 2\,H_2 + S_2 \qquad (11)$$

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 H_2 that has to be imported for this step. Field tests show that under the right conditions, O_2 enrichment pays for itself on the basis of this effect alone. Low-level enrichment (O_2 content of just 26 vol% in process air), for example, was found to cut H_2 import by one third. Another plant that used GOX option (b) in Figure 20 was able to eliminate hydrogen import entirely by increasing O_2 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 O_2 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 NH_3.

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 NH_3 in process gas. Case studies have shown that O_2 enrichment can almost entirely eliminate ammonia salt deposits and the associated operational and maintenance issues.

In general, O_2 enrichment does not have any negative impact on desulfurisation 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 H_2S) are fully oxidised to SO_2. Usually, only very small amounts of H_2S 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 O_2 enrichment and the resulting reduction of Claus process gas combined with increased H_2 content can also lead to significant savings in resource consumption in this step. Two Claus plants with an O_2 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 O_2 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 desulfurisation 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. O_2 enrichment also increases energy efficiency and reduces CO_2 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, O_2 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 ($C_{10}H_{22}$) is cracked to a short-chain paraffin (hydrocarbon with single bonds, in this example, heptane (C_7H_{16})) and an olefin (hydrocarbon with at least one double bond, in this example propene (C_3H_6)):

$$C_{10}H_{22} \rightarrow C_7H_{16} + C_3H_6 \quad (12)$$
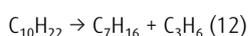
In the early days of chemical conversion, thermal cracking was found to be the simplest way of creating light distillates from heavy products. Cracking takes place at temperatures above 370 °C. Thermal cracking is still used today to process residue from vacuum distillation. It generally involves using 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
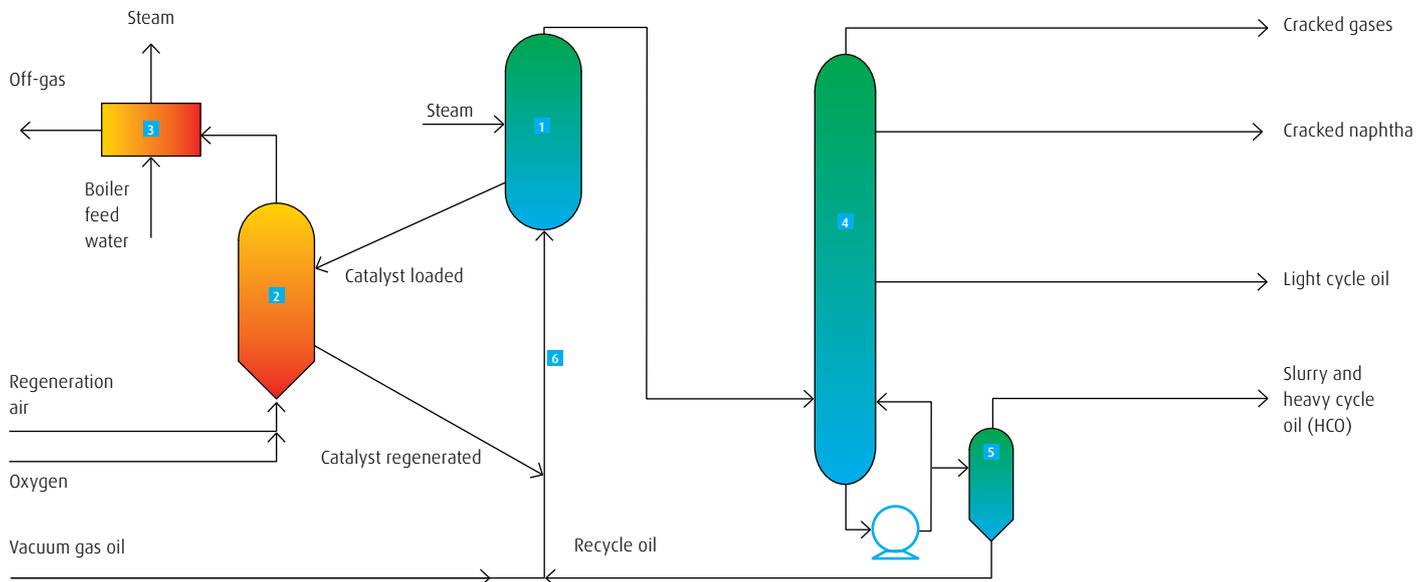
1 FCC-Reactor, **2** Regenerator, **3** Boiler, **4** Fractionation, **5** Recycle oil , **6** Riser

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 Al_2O_3 and silicon dioxide SiO_2) 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 atrition.

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 CO_2. In "partial burn" mode, part of the coke leaves the regenerator as CO. In this case,

the CO has to be fully combusted to CO_2 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 CO_2.

$$2\,C + O_2 \rightarrow 2\,CO \qquad \rightarrow H_C = -111 \text{ kJ/mol} \quad (13)$$

$$C + O_2 \rightarrow CO_2 \qquad \rightarrow H_C = -394 \text{ kJ/mol} \quad (14)$$

$$2\,H_2 + O_2 \rightarrow 2\,H_2O \quad \rightarrow H_C = -286 \text{ kJ/mol} \quad (15)$$
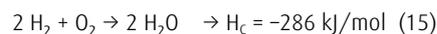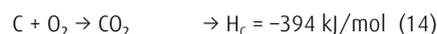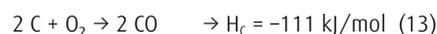
Applying the enthalpy of combustion to the oxygen used here yields the following results:

1 mole of oxygen delivers 394 kJ of heat during the reaction to CO_2, 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
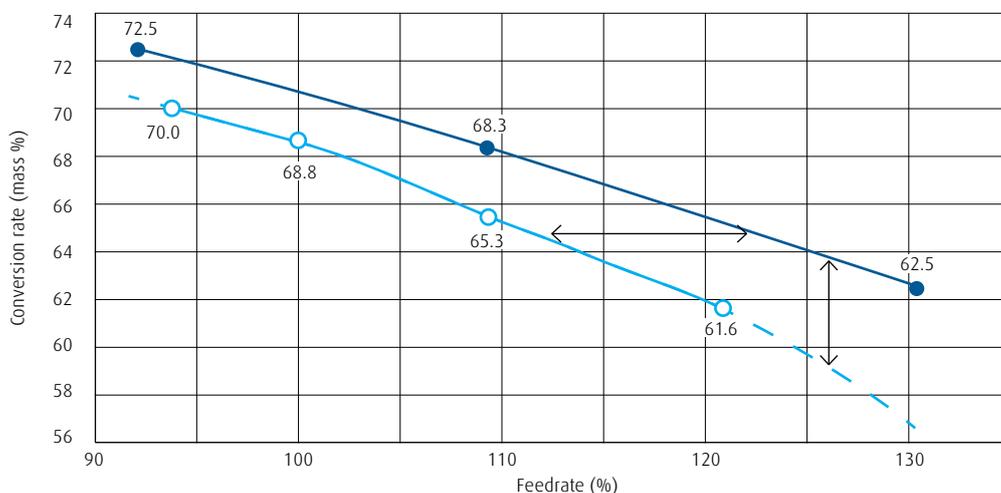
● Conversion rate at 27% by vol. O_2, ○ Conversion rate at 21% by vol. O_2

⟷ 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 catalyctic 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. O_2 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
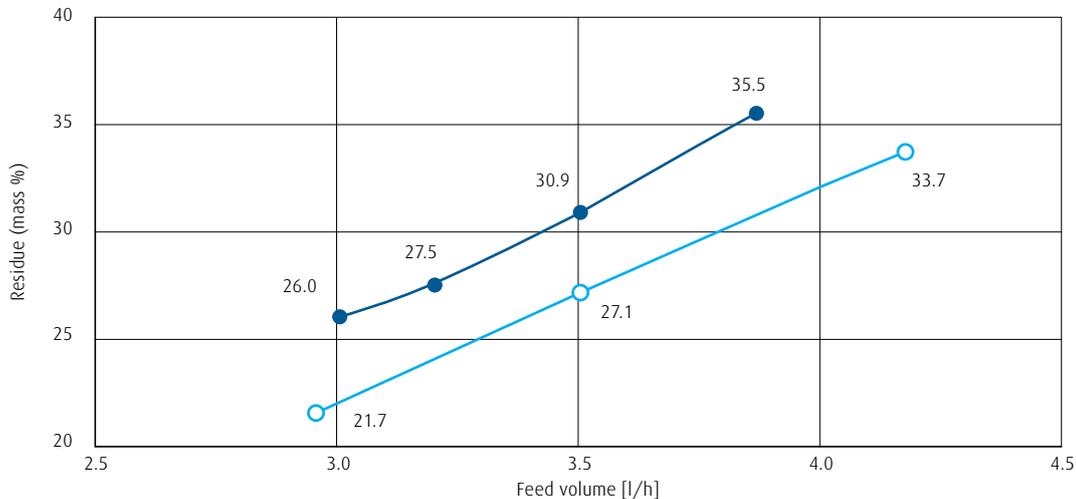
Residue at 21% by vol. O$_2$, ○ Residue at 27% by vol. O$_2$

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.

Figure 37 shows the two-pronged core of an FCC unit: The slender riser reactor wherein heavy hydrocarbons are cracked (within the scaffold left) and the more bulky regeneration reactor where by air oxidation coke is burnt off from the catalyst particles separated down-stream of the cracking section. The following two case studies are examples of oxygen enrichment in FCC plants.

Case 1:
The first FCC facility is a UOP plant with the reactor located above the regenerator. The throughput is 3,300 m^3/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 CO$_2$ 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: FCC unit in a German refinery (with kind permission of TOTAL Raffinerie Mitteldeutschland GmbH)

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

	Air-only	Enrichment to 22.2 vol% O_2	Change [%]
Feed [m³/d]	3,242	3,650	+12.6
Products [m³/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 CO_2 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
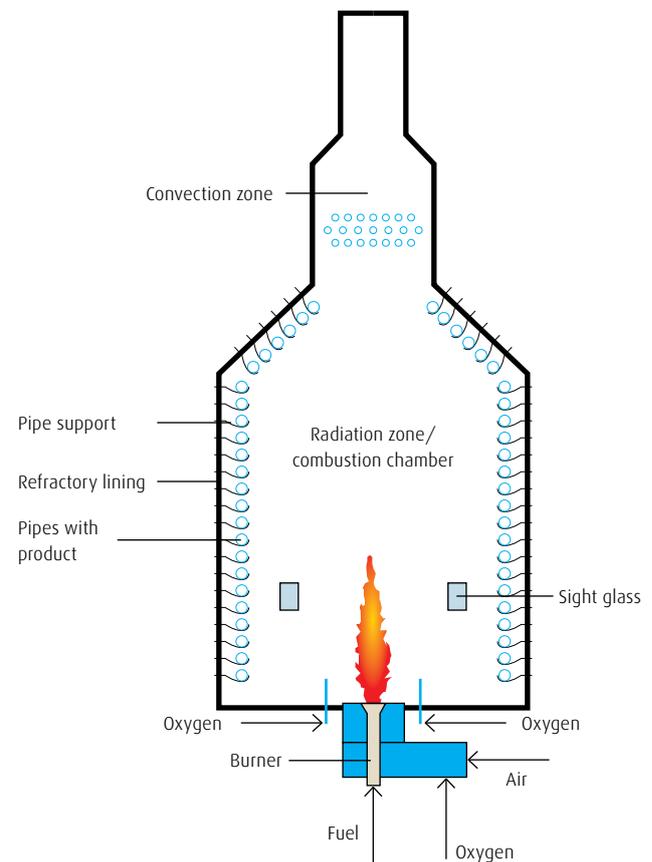
Figure 40: Gasification of liquid hydrocarbons
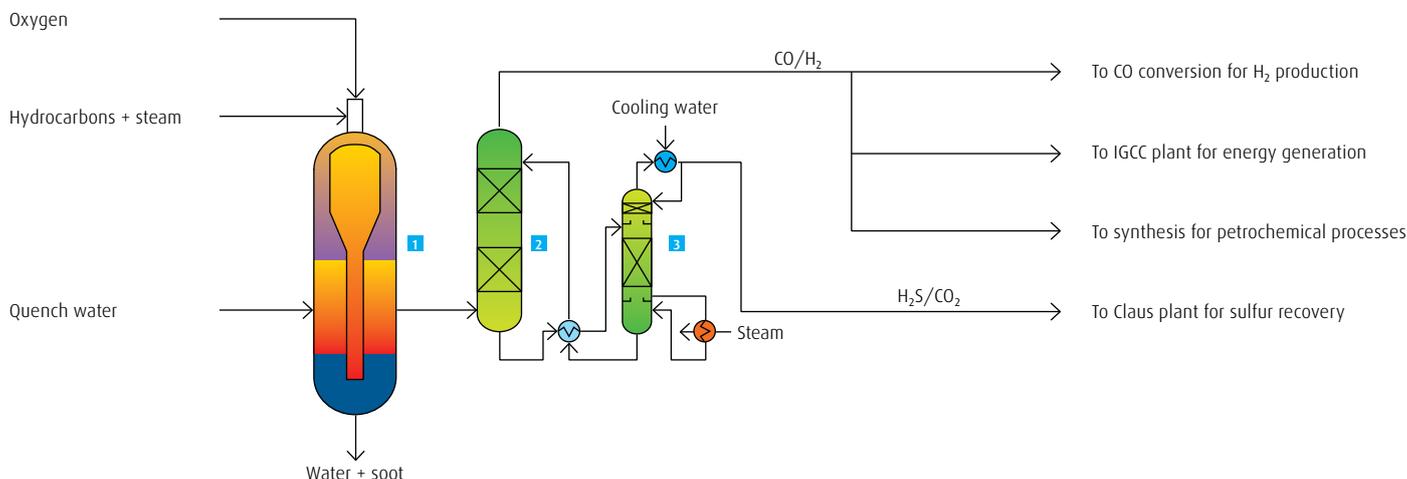
1 Gasifier, 2 Gas scrubber, 3 Regeneration of scrubbing agent

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 (H_2) 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 H_2. The H_2/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 CO_2 and H_2. This reaction (16) is also known as the shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (16)$$
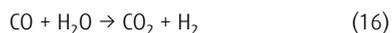
The hydrogen is then concentrated to a typical purity of 99.9 percent in a PSA unit.

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 g/m^3 and the BOD$_5$ discharge value of BOD$_5$ < 3 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

3. Oxygen applications in gas-liquid oxidations.

3.1 Introduction

Gas-liquid reactions play an extremely important role in the chemicals industry. The oxidation of hydrocarbons using oxygen is a central process here. It is used to manufacture mass products and also plays a key role in the fine and specialty chemicals industry. Table 9 provides an overview of the most important reactions and their global demand.

The majority of oxidation reactions use the oxygen contained in air for oxidation. However, industrial oxygen is growing in popularity. Engineers deploying innovative process technologies often prefer to use pure oxygen. It is also being used increasingly to enrich process air with a view to improving the performance of existing processes.

Deploying oxygen can result in a number of effects including:

- Lower investment costs in new plants due to more compact footprint
- Improved energy efficiency
- Increased capacity
- Higher conversion
- Improved selectivity (in many cases)
- Significant reduction in waste gas

This chapter provides an overview of the different ways industrial oxygen can be used in gas-liquid oxidation reactions and outlines the associated problems. The focus is primarily on increasing oxygen content to 28 vol% in process gas as this has a particular impact in industrial applications.

Experiments are presented and evaluated which investigate the effect of oxygen enrichment in the oxidation of cumene, toluene and p-xylene.

The technical measures and safety issues involved in implementing oxygen enrichment are also covered.

Table 9: Important gas-liquid oxidations and their production capacities

Oxidation of	Product	Global demand [kt/a]
p-xylene	Terephthalic acid	43,700
p-xylene	Dimethyl terephthalate	1,800
Cyclohexane	KA oil (cyclohexanol/ cyclohexanone mix)	4,400
Cumene	Acetone	5,500
	Phenol	8,600
Cyclohexane	Adipic acid	2,800
Ethylene	Acetaldehyde	1,300
Oxo aldehydes	Oxo carboxylic acids (e.g. butyric acid, iso-octane acid)	9,600

Figure 44: Reduction in off-gas stream in response to higher oxygen content in the oxidation air for the oxidation of toluene, p-xylene and cumene

○ p-Xylene   □ Toluene   ▲ Cumene

3.2 Benefits and problems of using oxygen in gas-liquid oxidations

Pure oxygen is used in a range of important industrial processes and oxygen is often added to process air in many more (Table 10). In addition, more and more reports detailing investigations into the impact of oxygen enrichment on air oxidation processes are being published.

Table 10: Selected gas-liquid oxidations and their oxidising gases

Oxidation product	Air	Air enriched or pure O_2
Terephthalic acid	I	$O_2e(I)$
Dimethyl terephthalate	I	$O_2e(E)$
KA oil[1]	I	$O_2e(I)$
Cumene hydroperoxide	I	$O_2e(E)$
Acetaldehyde	I	$O_2(I)/O_2e(I)$
Acetic acid	I	$O_2(I)/O_2e(I)$
Benzoic acid	I	$O_2e(E)$

The abbreviations used in the table have the following meanings:
I: Used industrially, $O_2e(I)$: Oxygen enrichment used industrially, $O_2e(E)$: Experimental work on oxygen enrichment carried out $O_2(I)$: Pure oxygen used industrially.
[1] Cyclohexanol/cyclohexanone mixture

Oxygen enrichment increases the partial pressure of oxygen and significantly reduces product streams. This is because dry air contains 78 percent nitrogen. Figure 21 illustrates how the amount of air and nitrogen decreases as oxygen enrichment increases.

Figure 44, for example, shows that the amount of waste gas resulting from the oxidation of cumene, toluene and p-xylene decreases as oxygen content in the oxidation gas increases. Increasing oxygen content to 24 vol% causes the waste gas stream to shrink by around 15 percent. An O_2 content of 27 vol% causes it to drop by between 25 and 30 percent.

Adding oxygen to oxidation air usually only requires minor investment but it can have the following effects on waste gas streams:

· Reduced waste gas volume; reduced hydrocarbon losses and lower carbon dioxide emissions
· Higher energy content in waste gas, in some cases enabling it to be used as a fuel for burning waste gas

Oxygen enrichment provides the following economic benefits:

· Reduced investment costs in new plants
· Reduced operating costs, in particular energy costs for compression and waste gas treatment
· Increased productivity due to higher yields and throughput
· Better balance for trade with CO_2 certificates

Experiences in industrial-scale processes, including the Claus process, FCC process and the oxidation of p-xylene to terephthalic acid, show that oxygen enrichment up to 28 vol% can be implemented with little effort and run safely and easily.

Figure 45: Diagram of the stirred tank reactor test plant
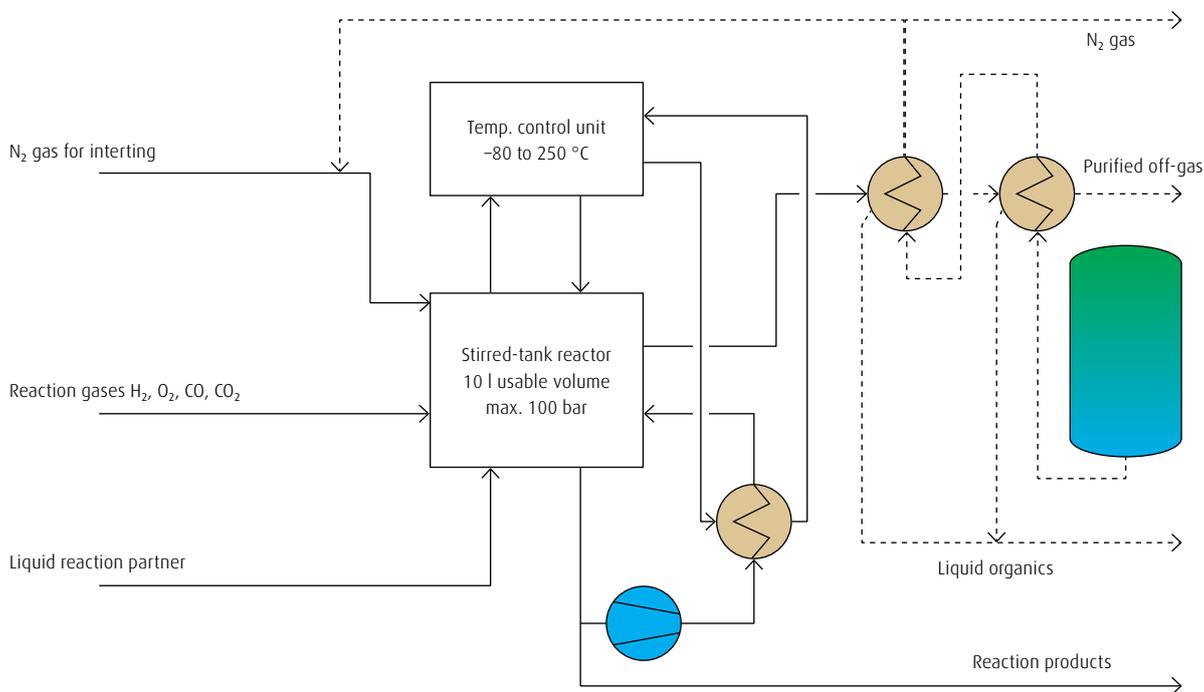
3.3 Experimental equipment

A stirred tank reactor system was developed and built by Linde to investigate the impact of gas in gas-liquid reactions (in particular the oxidation of hydrocarbons using air and oxygen-enriched air). Figure 45 shows a flow diagram of the test plant.

The stirred tank reactor test plant comprises the following main modules:

· A supply system
· Gas metering and supply tank with high-pressure feed pump (5 to 50 l/h) for liquids
· A stirred tank reactor with an external loop (10 litres, –80 to +250 °C, up to 100 bar)
· Temperature control unit (–80 to +250 °C)
· Vessel for the product
· Measurement and control installation and electrical switchbox
· Operating panel with process control system

Figure 46 gives an overall view of the test plant. The stirred tank reactor is at the center of the system. However, this can be replaced by another reactor. The test plant can be operated in batch, semi-batch, and continuous mode.

Figure 46: The stirred tank reactor test system

3.4 Oxidation of cumene to cumene hydroperoxide

3.4.1 Introduction

The oxidation of cumene to cumene hydroperoxide is an intermediate step in the manufacture of phenol and acetone. It is an extremely important air oxidation process in the industry. Global demand for cumene hydroperoxide is difficult to determine as it is an intermediate product, used for example in the manufacture of phenol.

The three most important processes for producing phenol are:

· The reaction of benzene and propene to form cumene, which is then oxidised to cumene hydroperoxide. Cumene hydroperoxide is then cleaved to produce phenol and acetone.
· The hydrolysis of chlorobenzene
· The liquid phase oxidation of toluene to benzoic acid and subsequent oxidation to phenol

New technological developments aim to either eliminate the coproduction of acetone from phenol manufacturing or to develop a way of directly processing phenol. Despite these new developments, the first route is still the most commonly used process.

As phenol is the most important product made from cumene hydroperoxide, market figures for phenol can be used as a baseline for calculating market demand.

Phenol is primarily used in the production of bisphenol A, phenolic resins, caprolactam and alkylphenol.

Diverse end products include aspirin, construction materials, DVDs, vehicles, textiles, cleaning agents, and paint.

Oxygen enrichment also brings a range of economic benefits to this air oxidation process, especially in cases where it increases performance from 7 to 15 percent. The benefits include:

· Higher conversion
· Increased yield (end product)
· Increased throughput
· Less effort required for cleaning waste gas
· Less energy required to compress air

The following work was carried out on cumene oxidation:

· Experiments in the stirred tank reactor pilot system
· Evaluation of test results and development of a kinetics model that takes into consideration the impact of oxygen
· Development of a simulation model and program for bubble columns and stirred reactors for gas-liquid reactions
· Comparison of simulated and actual results from an industrial bubble column
· Predictions of how oxygen influences the reactions and cost effectiveness of industrial oxidation processes. The oxygen content was kept between 21 and 27 vol%.

3.4.2 Technology

This section briefly describes the cumene-phenol process. It is a three-step process (see reactions (17) to (19)), whereby cumene oxidation is the second step:

Alkylation of benzene with propene to produce cumene (17):
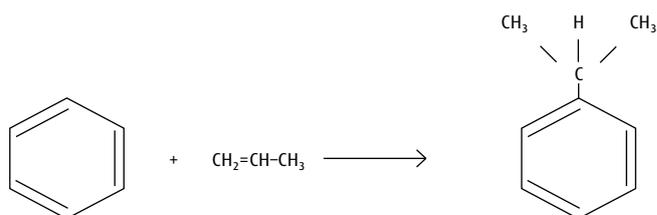
Oxidation of cumene to produce cumene hydroperoxide (18):
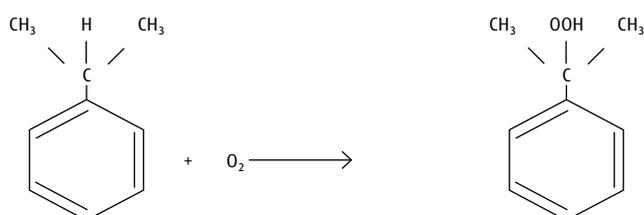
Cleavage of cumene hydroperoxide to give phenol and acetone (19):
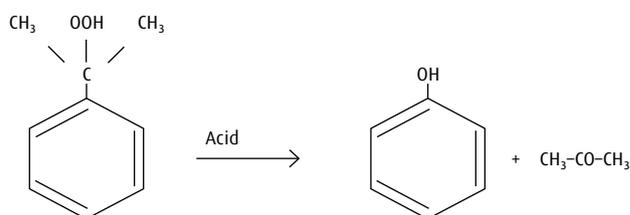
This process was developed by Hock and Lang in 1944. Figure 47 shows the complex technology involved in manufacturing phenol using a stirred reactor for oxidation.

Figure 47: Cumene-phenol process with a stirred tank reactor
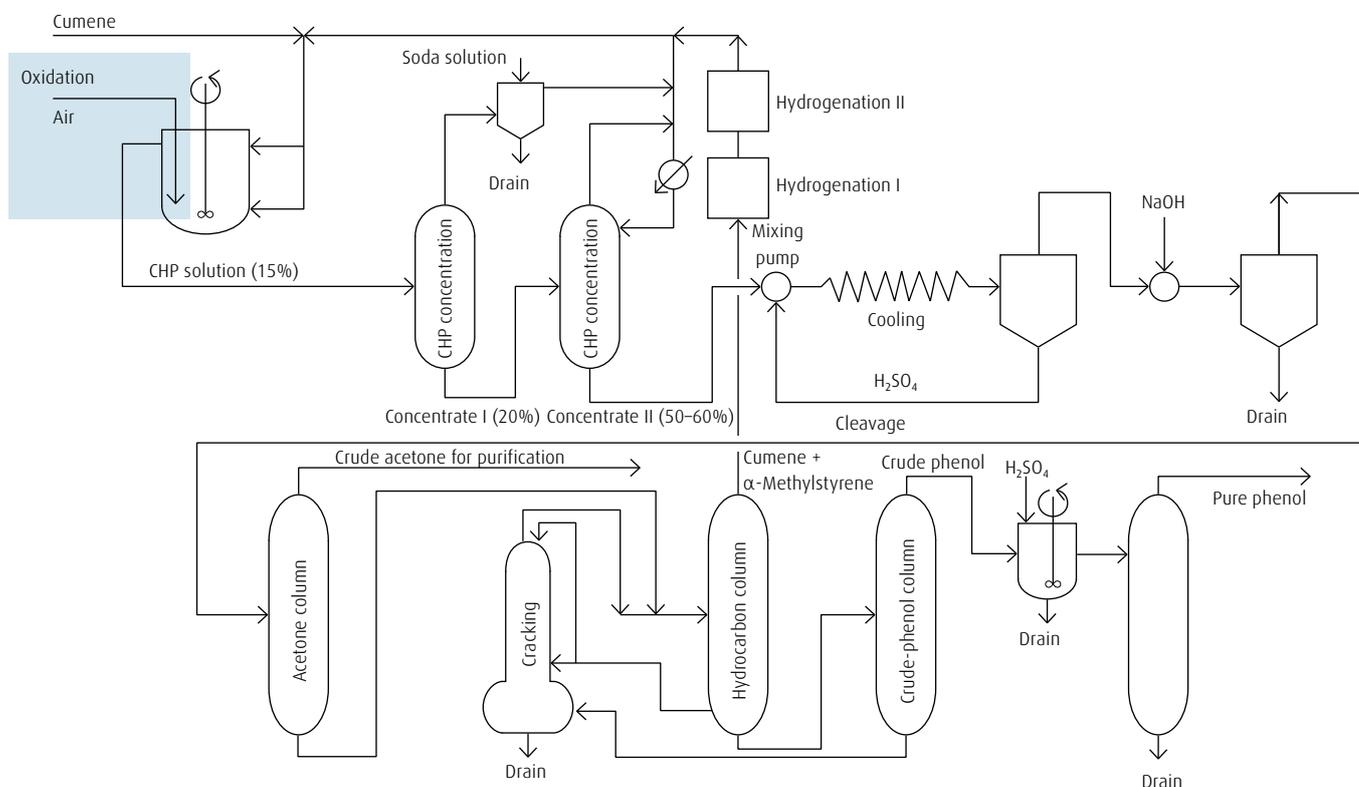
The first plant was built in Canada in 1953 with a capacity of 8,000 t/a. The process is still widely used today despite the unavoidable production of 0.62 tons of acetone for every ton of phenol.

Cumene oxidation is an autocatalytic process, which means that the rate of the reaction increases as the concentration of cumene hydroperoxide rises.

The key characteristics of the process include:

- Feeds: Cumene, air, cumene hydroperoxide as the initiator
- Temperatures: 100–130 °C
- Pressure: 2–7 bar, usually 3–5 bar
- Residence time: 3–5 hours

The conversion rate is generally kept to between 15 and 25 percent (at times between 35 and 40 percent) to minimise unwanted subsequent reactions to dimethyl phenyl carbinol and acetophenone.

In systems that have been stabilised by the addition of soda, the reaction takes place at a pH of between 7 and 8. In destabilised systems, the pH level is between 3 and 6. It is an exothermic reaction that produces around 800 kJ per kg of cumene hydroperoxide.

The off-gas comprises 2 to 6 vol. percent oxygen. The oxygen concentration limit is around 8.5 vol%, depending on the actual conditions.

Bubble column reactors are also often used for the reaction step. Figure 48 is a flow diagram that illustrates phenol production with two bubble column reactors, showing the process steps executed after the feed has been oxidised in the reactors

Particular attention should be paid to the off-gas for reasons of safety. Oxygen content should never exceed the oxygen concentration limit.

Permissible oxygen content values are often between 4 and 6 vol%.

Figure 48: Flow diagram showing phenol production with two bubble column reactors
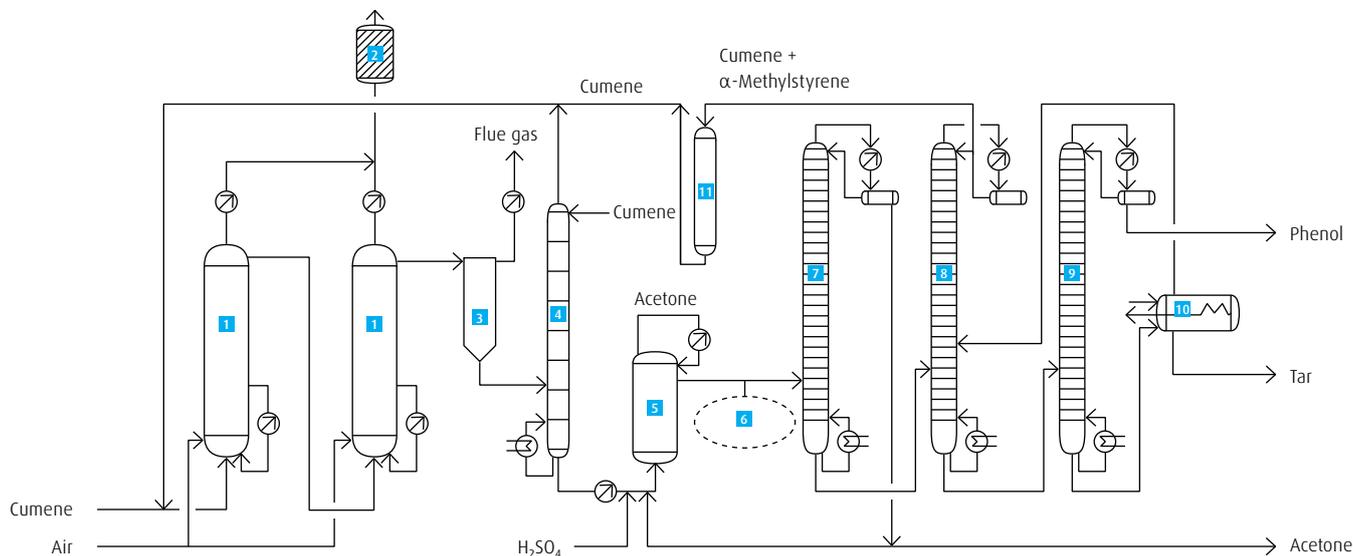
1 Bubble column reactors, 2 Waste gas purification, 3 Gas separator, 4 Concentration of cumene hydroperoxide to between 50 and 60 percent, 5 Cleavage of cumene hydroperoxide with sulfuric acid, 6 Separating the catalyst, 7 Acetone column, 8 Cumene column, 9 Phenol column, 10 Cracking the residue, 11 Hydrogenation of α-methylstyrene to cumene

Weber carried out experiments using large bubble columns for the oxidation of cumene. His report focuses primarily on the kinetics of cumene oxidation as well as gas holdup, the thermal decomposition of cumene hydroperoxide, free convective heat transfer in unmixed reactors (lack of air) and back mixing.

Scientists have reportedly developed a one-step catalytic oxidation process that uses a palladium catalyst to convert benzene directly to phenol. Hydrogen and oxygen are required for this reaction channel. It is unclear if this process has been deployed commercially.

Kusakari et al. carried out experiments of selective oxidation of benzene to phenol with molecular oxygen and rhenium/zeolite catalysts. Attempts at direct oxidation have also been carried out using H_2O_2 and N_2O_5 as oxidising agents. These have not yet resulted in a process that is more cost-effective or more environmentally friendly than the Hock process.

Figure 49: Bubble column reactors
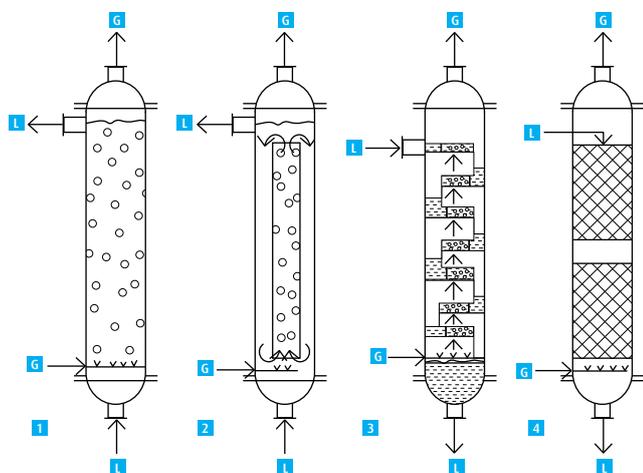
1 Gas bubble column, **2** Bubble column reactor with internal liquid circulation,
3 Tray column, **4** Packed column, **L** Liquid, **G** Gas

Figure 50: Impact of oxygen content on cumene hydroperoxide yield; experimental values for 120 °C and 3 bar

● 21 vol% O_2 △ 24 vol% O_2 □ 27 vol% O_2

3.4.3 Reactor

Bubble column reactors and stirred tank reactors are used in this process. A system can comprise an individual reactor or several reactors arranged in series. For example, a plant may have two to five bubble reactors in sequence, which can then be operated at different temperatures to keep the production of by-products to a minimum. A reactor can be up to twenty meters high. Figure 49 shows a number of typical bubble column reactors.

Sieve-plate columns and bubble column reactors with liquid circulation are most commonly used models for the oxidation of cumene to cumene hydroperoxide.

Cumene oxidation is an exothermic reaction. To minimise the production of by-products and prevent thermal runaway, the temperature has to be reliably managed. To ensure this is the case, plate columns are equipped with heat exchangers between the trays. In the case of bubble column reactors with external liquid circulation, the heat exchangers are positioned outside the reactor in the liquid cycle.

One of the benefits of a plate column is that temperatures remain more or less stable in the reactor. This is because the heat transfer coefficient between the phases and on the walls of the heat exchangers and the reactor is usually high, which, in turn, means that the temperature can be easily controlled. Furthermore, reliable temperature control can be achieved with temperature-critical reactions.

Nevertheless, simple bubble columns with sieve plates are the more commonly used reactors.

3.4.4 Experimental work

The impact of oxygen on cumene oxidation was investigated using a stirred tank reactor system in the test plant. Section 3.3 contains further information on the test plant.

The majority of tests were carried out under the following conditions:

· Temperature: 105–125 °C
· Pressure: 3–5 bar
· Gas throughput: 250–660 l/h
· Oxygen content: 21–27 vol%
· Presence of cumene hydroperoxide: 3–5 mass%
· Gas throughput: 240, 480, 650 l/h

A total of eighteen experiments were carried out to determine the influence of the different parameters on oxidation, conversion and selectivity. Five samples were taken over a period of four hours. To eliminate errors, tests were repeated in every series of experiments.

Cumene, cumene hydroperoxide, acetophenone, dimethyl phenyl carbinol and dicumyl peroxide were analytically determined. The flue gas was also analysed, with a view to assessing the oxygen content in particular. Figure 50 displays the impact of oxygen content on concentrations of cumene hydroperoxide (CHPO) in the reaction mixture for a selected number of results.

Temperature: ■ 110 °C   ■ 115 °C   ■ 120 °C   ■ 125 °C

Figure 51: Calculated impact of oxygen content in the oxidation gas and of temperature on cumene conversion. Reference value: Air oxidation at 110°C
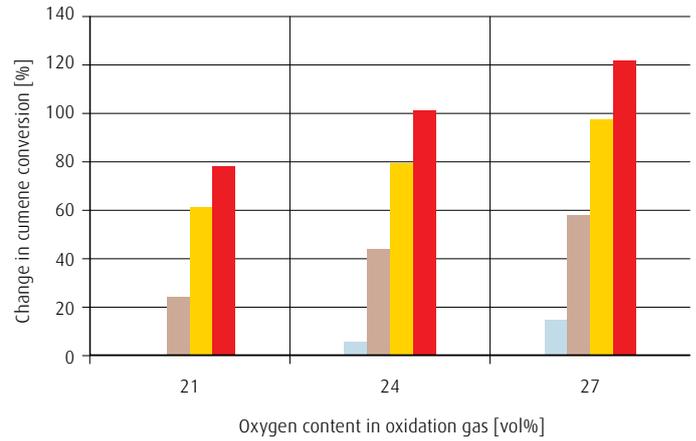
3.4.5 The kinetics of cumene oxidation

The kinetics were determined on the basis of the test results, assuming the following three main reactions (20) to (22):

Cumene + O_2 $\xrightarrow{\quad r_1 \quad}$ cumene hydroperoxide
(CUM)   (CHPO)   (20)

Cumene + 0.5 O_2 $\xrightarrow{\quad r_2 \quad}$ acetophenone + methane
(CUM)   (ACP)   (21)

Cumene hydroperoxide $\xrightarrow{\quad r_3 \quad}$ dimethyl phenyl carbinol
(CHPO)   (DMPC) + 0.5 O_2 (22)
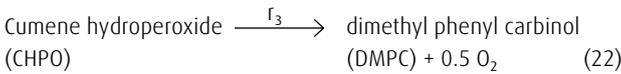
where r_1, r_2 and r_3 denote the rate of these three reactions.

Hattori derived a kinetic model for the reaction rates of the three reactions in his report.

This model was expanded to include the impact of oxygen on the reaction system:

$$r_1 = \exp\left(k_1 - k_2 \cdot \left(\frac{T_r}{T} - 1\right)\right) \cdot \frac{c_{CUM} \cdot {}^*\sqrt{c_{CHPO}} \cdot P_{O2}}{P_{O2} + k_7 \cdot c_{CUM}}$$

(23)

$$r_2 = \exp\left(k_3 - k_4 \cdot \left(\frac{T_r}{T} - 1\right)\right) \cdot c_{CUM} \cdot c_{CHPO}$$

(24)

$$r_3 = \exp\left(k_5 - k_6 \cdot \left(\frac{T_r}{T} - 1\right)\right) \cdot c_{CHPO}$$

(25)

where

k_i: Reaction rate constant (i = 1...7)
c_i: Concentration of component (i = CUM, CHPO)
P_{O2}: Partial pressure of oxygen
T: Temperature
T_r: Reference temperature
$^*\sqrt{\ }$: Modified root function

The experiments were used to determine the reaction rate constants and assess the validity of the kinetic model in collaboration with Linde Engineering. The computer program SIAMoD was used to determine the constants. It was possible to accurately emulate the experiments. The average deviation amounted to around 17 percent, whereby the largest deviations occurred in the by-products. Building on this, the conversion and yield of cumene hydroperoxide was calculated for four temperatures and three oxygen concentrations. The conversion results are shown in Figure 51.

The results show that increasing the partial oxygen pressure leads to a significant rise in conversion. Furthermore, increasing partial oxygen pressure was found to have almost no impact on selectivity. In contrast, an increase in temperature reduced selectivity.

3.4.6 Reactor simulation

A reactor model for a stirred tank reactor and a bubble column were developed and programmed in collaboration with Linde Engineering. The program was tested using the air oxidation values from an industrial bubble column. Once the model and program had been successfully validated, it was possible to predict the impact of oxygen-enriched air.

Mass transfer resistance plays an important role in industrial bubble columns. It is this resistance that prevents the liquid phase from being saturated with oxygen. Oxygen concentration decreases approaching the gas-liquid interface.

The concentration at the gas-liquid interface is calculated using equation (26):

$$k_L \cdot a = \frac{P_{O2}}{H_{O2}} - c_{O2} = r_1 + 0.5 \cdot r_2 - 0.5 \cdot r_3 \tag{26}$$

where

k_L: Mass transfer coefficient for the liquid phase
a: Specific gas-liquid interface
H_{O2}: Henry's coefficient for oxygen
c_{O2}: Concentration of dissolved oxygen in the liquid

The reduction in oxygen concentration resulting from mass transfer resistance is given by:

$$P_{O2} = H_{O2} \cdot c_{O2} \tag{27}$$

These equations can be used to modify equation (23), which defines the rate of reaction (20) (oxidation of cumene to cumene hydroperoxide), to create equation (28):

$$r_1 = \exp\left(k_1 - k_2 \cdot \left(\frac{T_r}{T} - 1\right)\right) \cdot c_{CUM} \cdot {}^*\sqrt{c_{CHPO}} \cdot \frac{H_{O2} \cdot c_{O2}}{H_{O2} \cdot c_{O2} + k_7 \cdot c_{CUM}} \tag{28}$$

Incorporating equations (24), (25) and (28) into equation (26) creates a quadratic equation (29) for oxygen concentration c_{O2} in the form of:

$$A \cdot c_{O2}^2 + B \cdot c_{O2}^2 + C = 0 \tag{29}$$

where A, B and C are coefficients in the quadratic equation.

The mass transfer coefficient k_L is calculated in line with the correlation (30) defined by Akita. Mass transfer resistance only has an impact in the liquid phase. All data thus refers to the liquid phase.

$$\frac{k_L \cdot d_{32}}{D_L} = 0.5 \cdot \left(\frac{\mu_L}{\rho_L \cdot D_L}\right)^{0.5} \cdot \left(\frac{g \cdot d_{32} \cdot \rho_L^2}{\mu_L^2}\right)^{0.25} \cdot \left(\frac{g \cdot d_{32} \cdot \rho_L}{\sigma}\right)^{0.375} \tag{30}$$

where

D_L: Liquid phase diffusion coefficient
μ_L: Liquid phase dynamic viscosity
ρ_L: Liquid density
σ: Surface tension
g: Gravitational constant
d_{32}: Sauter mean diameter.

The sauter mean diameter d_{32} of the bubble was selected at 1.6 mm and tested using Akita's correlation (31):

$$\frac{d_{32}}{D_R} = 26 \cdot \left(\frac{g \cdot D_R^2 \cdot \rho_L}{\sigma}\right)^{-0.5} \cdot \left(\frac{g \cdot D_R^3 \cdot \rho_L^2}{\mu_L^2}\right)^{-0.12} \cdot \left(\frac{u_G}{\sqrt{g \cdot D_R}}\right)^{-0.12} \tag{31}$$

where

D_R: Diameter of the bubble column
u_G: Superficial gas velocity with respect to the total cross section of the bubble column

A constant of 0.36 was chosen for the gas holdup ε_G (see equation (35)). This value corresponds well to the value calculated by Wilkinson. In Wilkinson's model, the interfacial area consists of small bubbles. Larger bubbles only form after a certain gas velocity has been reached.

The rise velocity u_{sb} of the small bubbles can be calculated using equation (32):

$$\frac{u_{sb} \cdot \eta_L}{\sigma} = 2.25 \cdot \left(\frac{\sigma^3 \cdot \rho_L}{g \cdot \eta_L^4}\right)^{-0.273} \cdot \left(\frac{\rho_L}{\rho_G}\right)^{0.03} \tag{32}$$

where

η_L: Kinematic viscosity of the liquid
ρ_G: Gas density

The transition velocity u_{tr} at which larger bubbles start to form is determined using equation (33):

$$\frac{u_{tr}}{u_{sb}} = 0.5 \cdot \exp\left(-193 \cdot \rho_G^{-0.61} \cdot \eta_L^{0.5} \cdot \sigma^{0.11}\right) \tag{33}$$

The rise velocity u_{lb} of the large bubbles is calculated using equation (34):

$$\frac{u_{lb} \cdot \eta_L}{\sigma} = \frac{u_{sb} \cdot \eta_L}{\sigma} + 2.4 \cdot \left(\frac{\eta_L \cdot (u_{G} - u_{tr})}{\sigma}\right)^{0.757} \cdot \left(\frac{\sigma^3 \cdot \rho_L}{g \cdot \eta_L^4}\right)^{-0.077} \cdot \left(\frac{\rho_L}{\rho_G}\right)^{0.0077} \tag{34}$$

Gas holdup ε_G can be calculated for two different states. In the homogenous state $u_G < u_{tr}$, equation (35) is used to calculate gas holdup:

$$\varepsilon_G = \frac{u_G}{u_{sb}} \tag{35}$$

In the heterogeneous region, gas holdup is calculated using equation (36):

$$\varepsilon_G = \frac{u_{tr}}{u_{sb}} + \frac{u_G - u_{tr}}{u_{lb}} \tag{36}$$

The interfacial area can be determined with equation (37):

$$a = \frac{6 \cdot \varepsilon_G}{d_{32}} \tag{37}$$

All component data on substances was taken from Linde Engineering's GMPS database. The model assumes that the phases are in equilibrium in every section of the bubble column, with the exception of oxygen, which is not in equilibrium due to the reaction. Every section was treated as if it comprised an isothermal stirred reactor with a downstream flash unit. Figure 52 shows the alternative layout of the industrial bubble column. The reaction takes place in the continuous stirred tank reactor (CSTR). The reaction products are separated into a liquid phase and a gas phase in the flash unit. The gas is fed into the column from below and the liquid from above. Equation (38) is used to calculate the material balance of every element in the cascade:

$$\dot{n}_{i,in} - \dot{n}_{i,out} = \sum_{j=1}^{3} \gamma_{ij} \cdot r_j \tag{38}$$

where

$\dot{n}_i$: Amount of component i
γ_{ij}: Stoichiometric coefficient of component i in the reaction j.

The chemical equations for all components are solved simultaneously in all sections. This is necessary because the material balances have strong, nonlinear links due to the autocatalytic kinetics.

The cooling energy ($\dot{Q}_i$) required to maintain the predefined temperature is determined using the enthalpy (H) balance for every section. See equation (39):

$$\dot{Q}_i = \sum H_{in} - \sum H_{out} \tag{39}$$

Figure 52: Alternative layout for the industrial bubble column
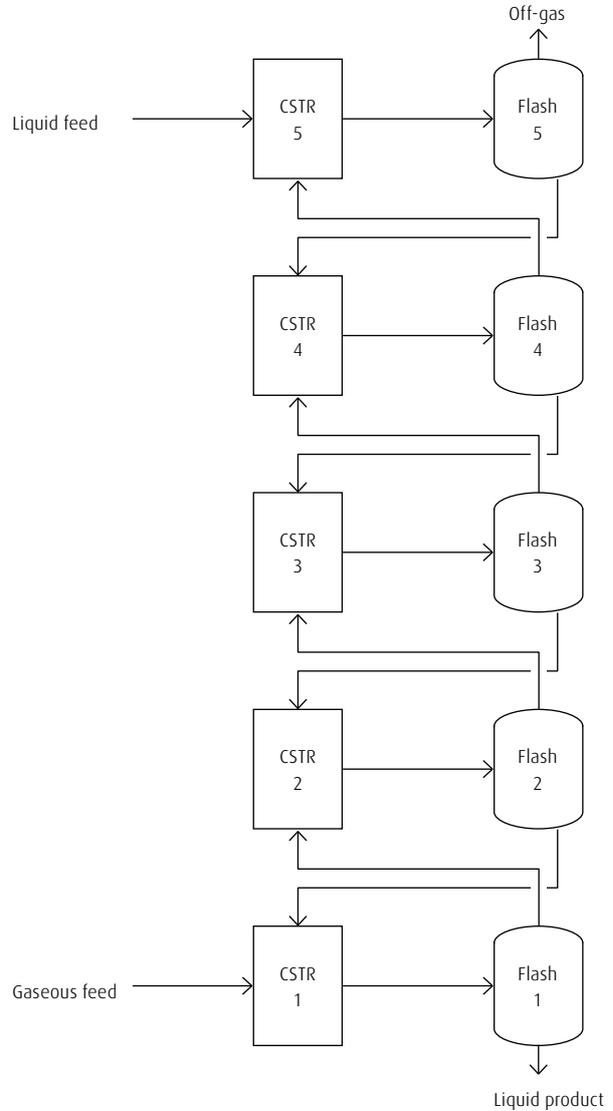
Figure 53: Bubble column operating principle
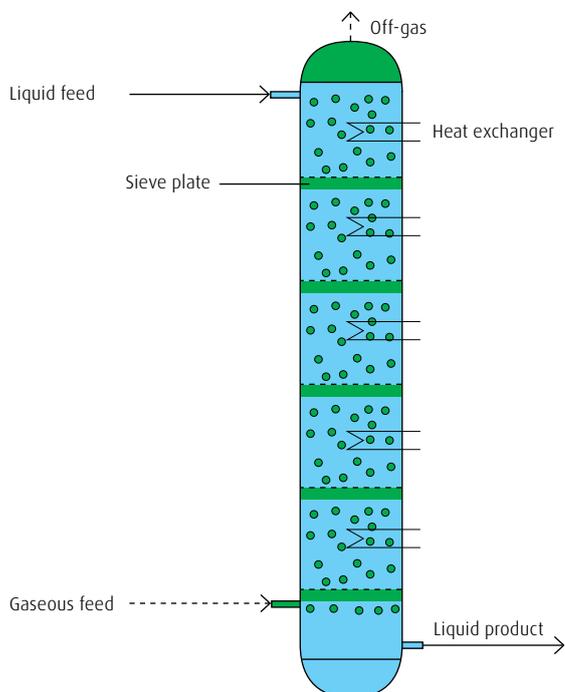
Figure 53 shows the principle and layout of the bubble column.

Table 11 shows the measured and calculated values. The amount of cumene hydroperoxide produced by the reaction is a particularly important indicator, as is the cooling energy required to maintain the predefined temperature during each step.

Table 11: Comparison of measured values and calculated values

Product	Measured values [mass%]	Calculated values [mass%]	Difference
Cumene	83.0	81.7	−1.6%
Cumene hydroperoxide	15.7	14.4	−8.3%
Acetophenone	0.25	0.26	4.0%
Dimethyl phenyl carbinol	1.05	1.07	4.8%
Off-gas	[vol%]	[vol%]	
Oxygen content	4.2	4.2	0%

Given their obvious suitability, the kinetics and bubble column model were used to predict the impact of oxygen enrichment on an industrial bubble column under selected operating conditions. First of all, the oxygen content was increased to 24 and 27 vol%. The flow of oxidation gas and other parameters were not changed. With oxygen content at 27 vol% and an unchanged feed gas stream, the amount of cumene hydroperoxide in the product rose by around 20.9 percent. The volume of by-products, acetophenone and dimethyl phenyl carbinol also increased, albeit by a much smaller step. The amount of cooling energy required rose by 30 percent.

With an oxygen content of 27 vol% in the oxygen-enriched air, the waste gas comprises 6.2 vol% oxygen. Although the oxygen concentration limit is 8.5 vol%, oxygen content is often limited to between 5 and 5.5 vol% for safety reasons. This means that, under these conditions, oxygen enrichment has to be kept below 27 vol% in industrial applications. 24 vol%, for example, would be an acceptable level. With oxygen content at 24 vol%, around 11 percent more cumene hydroperoxide is produced.

3.4.7 Safety factors

Production facilities that utilise cumene oxidation have to meet strict security requirements. This is because the reaction product cumene hydroperoxide (CHPO) decays at room temperature at speeds that can lead to an explosion. The safety of a plant comprising five bubble column reactors connected in series has been analysed. Air is injected at the bottom and in the middle of the reactor at a pressure of 6.33 bar. The reaction temperature is between 115 and 125 °C. The causes of ignition during the oxidation of liquid phases are well documented. A report of accidents that occurred between 1962 and 1982 shows that none of the accidents were caused by the reactor. The majority of incidents took place in storage tank areas. Analysis of 65 accidents that occurred between 1978 and 1996 shows that out of the thirteen peroxide accidents, only two involved cumene hydroperoxide.

Table 12 provides a summary of selected key safety indicators. Table lists the upper (UEL) and lower (LEL) explosion limits for cumene oxidation mixtures. Results shown are due to different test procedures.

Table 12: Selected safety indicators

Components	Flash point [°C]	Autoignition temperature [°C]	Temperature class	Explosion group
Methane			T1	II B
Acetophenone	77	535	T1	II A
Cumene	31	420; 425	T2	II A
Cumene hydroperoxide	79.5	149		

Table 13: Autoignition thresholds for cumene oxidation

Components	LEL [vol%]	UEL [vol%]	P [bar]	T [°C]
	0.8	6.0		
Cumene-air	0.88	6.5		
Cumene-air	2.82	18.26		75
Cumene-O_2	1.93	23.26		75
Cumene-air	0.88	6.5	1.013	100
CHPO-air	6.05	27.1		
CHPO-O_2	2.71	29		130–135
CHPO-cumene-air	2.56	21.74	1	130–135
				85–90
CHPO-cumene-O_2	1.60	23.01		
Dimethyl phenyl carbinol	< 1	< 6.2		

3.4.8 Summary

The tests and calculations carried out for cumene oxidation in various industrial reactors show that adding oxygen to the oxidation air can deliver cost benefits. Oxygen-enriched air with O_2 contents of 24 and 27 vol% were investigated in detail. Table 14 contains a number of results for selected industrial conditions.

Table 14: Calculated difference in a bubble column with oxidation gas containing 24 and 27 vol% oxygen

	Case A		Case B	
Oxygen enrichment [vol%]	24	27	24	27
Oxidation gas				
Flow rate	Constant	Constant	−11.0%	−19.6%
Production				
Production of cumene hydroperoxide	+11.0%	+20.9%	+4.7%	+8.7%
Production of acetophenone	+4.8%	+11.3%	+2.6 %	+5.3%
Production of dimethyl phenyl carbinol	+6.7%	+13.0 %	+3.1%	+5.7%
Off-gas				
Flow rate	−2.7%	−5.3%	−15.2%	−25.8%
Oxygen content [vol%]	5.2	6.2	4.2	4.2

The above table focuses on two cases (A and B):

Case A: The flow rate (volume) of the oxygen-enriched air is that same as in air-only mode.

Case B: The flow rate (volume) has been lowered relative to air-only mode. This was done to keep the oxygen content in the off-gas constant.

In Case A with oxygen enrichment of 27 vol%, the oxygen content in the off-gas exceeds the threshold stated above. As a result, 24 vol% oxygen enrichment is the only viable option for industrial purposes here. It increases the production of cumene hydroperoxide by around 11 percent.

In Case B, the oxygen content of the off-gas was kept to 4.2 vol% with both 24 and 27 vol% oxygen enrichment levels. This case delivers the following effects:

· 4.7 to 8.7 percent increase in cumene hydroperoxide production
· 15.2 to 25.8 percent reduction in off-gas

Although the results shown here only apply to the selected bubble column and the corresponding operating conditions, they nevertheless give an impression of the overall trend and scope of the efficiency gains.

A further benefit of oxygen enrichment is that it can also make plants more flexible.

Due to the properties of cumene hydroperoxide, safety must be prioritised when using oxygen enrichment for industrial applications.

3.5 Oxidation of toluene to benzoic acid

3.5.1 Introduction

Benzoic acid is produced primarily through the oxidation of toluene with air. Benzoic acid is a precursor for example for the manufacture of phenol and caprolactam. It is also traded as a product in its own right.

Industrial plants that harness toluene oxidation for phenol production are concentrated in the US, Canada and the Netherlands.

Benzoic acid is primarily used for the following:

· Benzoate plasticiser
· Sodium and potassium benzoate
· Benzoyl chloride
· Alkyd resin
· n-Butyl benzoate

The toluene oxidation process used to produce benzoic acid is a gas-liquid oxidation reaction that uses air and takes place in stirred tank reactors or bubble columns. Adding oxygen to the oxidation air increases conversion and yield. Oxygen enrichment thus enables operators to intensify this industrial process without having to make major investments.

3.5.2 Technology

The air-based oxidation of toluene in the liquid phase is the most important process in the production of benzoic acid. It requires temperatures between 120 and 180°C and pressures of up to 10 bar.

The main reaction equation is as follows (40):

Toluene   Benzoic acid
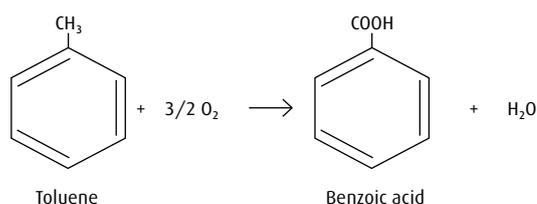
The diagram in Figure 54 illustrates industrial-scale production of benzoic acid. Fresh toluene and circulated toluene, which also contains benzaldehyde, are added at the oxidation step together with a cobalt catalyst (e.g. 0.1 to 0.3 percent cobalt naphthenate) and air. Oxidation then takes place at between 120 and 180°C and 2 and 10 bar. Toluene conversion is around 40 percent. Reaction heat is dissipated via cooling water tubes. Toluene and benzaldehyde are separated from the reaction product in the toluene column and fed back to the oxidator. The acid dissolves in the hot water used to extract the mixture from the bottom of the column. When it cools, the benzoic acid crystallises. It is then filtered and purified in water to produce benzoic acid in a quality suitable for industrial use. This process has a yield of around 90 percent.

Toluene oxidation can be used as the first step in the production of phenol. Figure 55 shows the technology involved. The process was developed by DOW in the US.

The Mid-Century Corporation, SNIA VISCOSA and DSM developed the process further with the aim of achieving:

· High toluene conversion
· High benzoic acid yield
· High purity levels.

Figure 54: Diagram of benzoic acid production

Off-gas (N_2+CO+CO_2+some O_2)

Circulated toluene + benzaldehyde

Toluene cooler

H_2O

Reactor, 5 atm, 160°C
Residence time 6 hours

Sewer

Fresh toluene

Catalyst

Air

Toluene column

Hot water

Extractor

Cooler

Benzoic acid
solution

Filter

Benzoic acid

Oxidation product

Residues
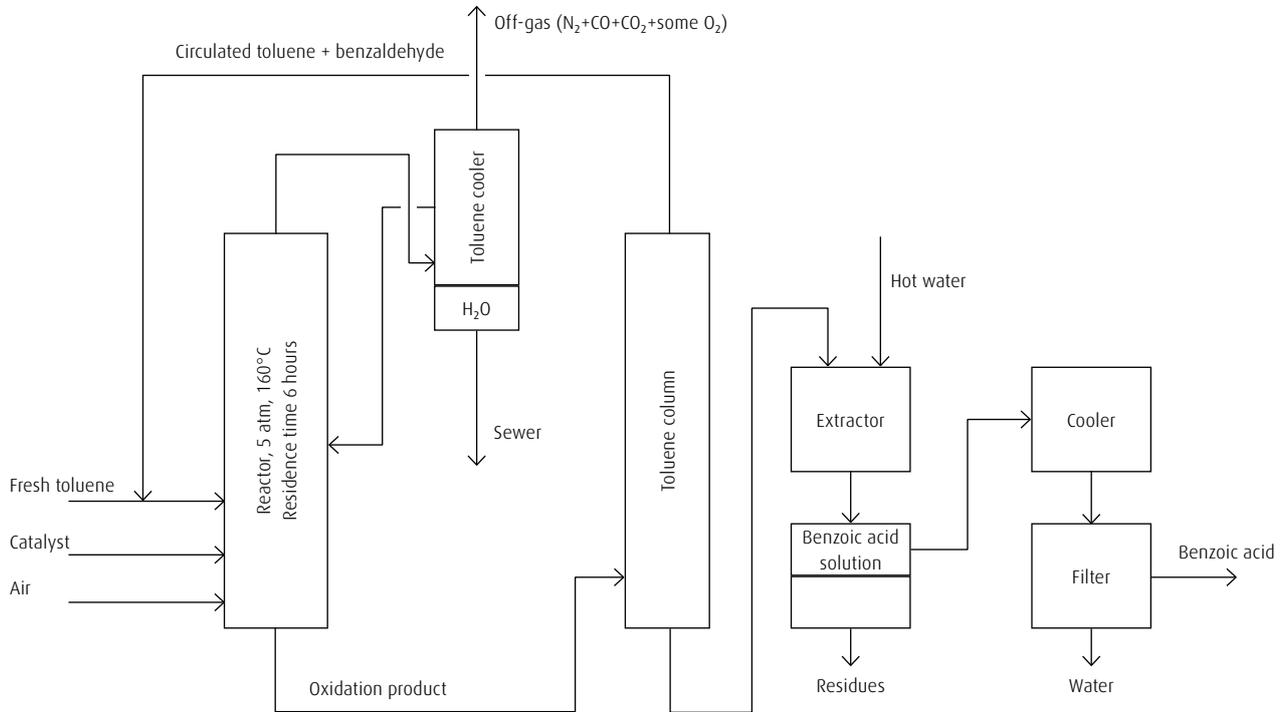
Water

Figure 55: Phenol production by toluene oxidation

Catalyst

Toluene

Air

Catalyst

Benzene

Phenol

Tar

Waste
water
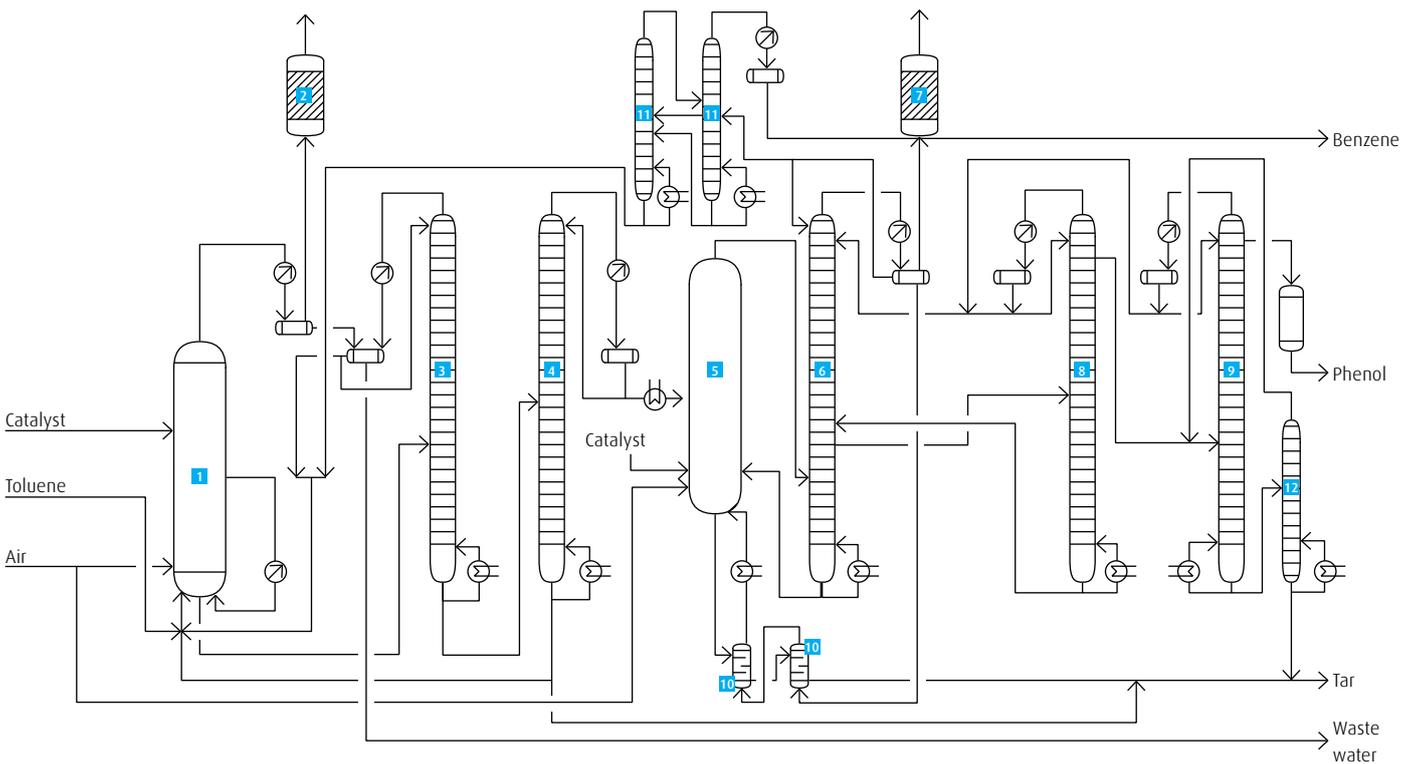
1 Toluene oxidation reactor, 2 Off-gas purification, 3 Toluene stripping column, 4 Benzoic acid column, 5 Benzoic acid oxidation reactor, 6 Water hydrocarbon stripping column, 7 Off-gas purification, 8 Crude phenol column, 9 Phenol column, 10 Residue extraction, 11 Benzene column, 12 Phenol residue column

Figure 56: Diagram of the mid-century benzoic acid process

Figure 57: Measured impact of oxygen content in oxidation gas on benzoic acid yield at 160°C and 9 bar

● 21 vol% O_2 △ 24 vol% O_2 □ 27 vol% O_2
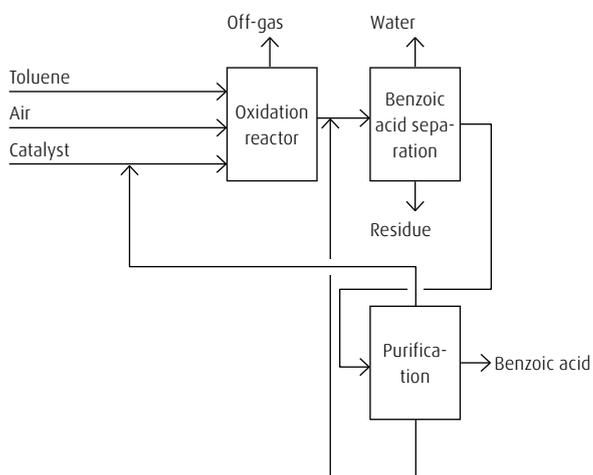
Figure 56 shows a process flow chart. A purification step, for example, was added to increase the purity of the benzoic acid produced to around 99.5 percent.

Toluene oxidation can also be carried out in Amoco plants designed for producing terephthalic acid via p-xylene oxidation. This is because the reaction conditions are very similar. Adding bromine compounds can increase toluene conversion to 96 percent. Benzoic acid yield is around 90 percent.

The SNIA process is another method that harnesses toluene oxidation, in this case to produce caprolactam. It comprises the following reaction steps:

· Catalytic air oxidation of toluene to benzoic acid
· Hydrogenation of benzoic acid to hexahydrobenzoic acid
· Nitrosing decarboxylation of hexahydrobenzoic acid to caprolactam in the presence of fuming sulfuric acid

Toluene is also oxidised to benzoic acid in the following processes:

· Direct oxidation in the gas phase
· Decarboxylation of phthalic anhydride
· Oxidation with nitric acid

However, none of these methods were ever used on a wide scale.

In 2001/2002, DSM built a new facility that featured a new technology for producing benzoic acid and sodium benzoate. The company tripled production capacity for benzoic acid and increased the purity of the products significantly, achieving purity of 99.9 percent for benzoic acid.

The high purity products are used in the food and beverage industry and in the pharmaceutical sector.

3.5.3 Experimental work

Experiments on the oxidation of toluene to benzoic acid were carried out in a stirred tank reactor system. The main aim of the tests was to find out how adding oxygen to the air affects toluene conversion, benzoic acid yield and the production of by-products. Section 3.3 contains information on the test system used. The experiments were carried out in the test plant using the following test parameters:

· Temperature: 115–160 °C
· Pressure: 3–9 bar
· Oxygen concentration: 21–27 vol%
· Reaction time: 2–7 h
· Catalyst: Co(II) naphthenate, 0.1 mass% of Co
· Stirring speed: 1,000 rpm

The following analytical techniques were used:

· Benzoic acid:
  HPLC with gradient elution and UV detection
· Benzaldehyde, benzyl alcohol, methyl benzoate:
  Capillary gas chromatography
· Toluene in off-gas:
  Adsorption with activated carbon tubes and solvent extraction
· CO_2 and CO:
  Gas chromatography
· Water:
  Karl Fischer titration

The test results can be summarised as follows:

Figure 58: Yield of benzoic acid, benzaldehyde, benzyl alcohol and benzoic acid benzyl ester during toluene oxidation at 160 °C, 9 bar and 27 vol% oxygen enrichment

● Benzoic acid, ○ Benzaldehyde, △ Benzyl alcohol, ☐ Benzoic acid benzyl ester
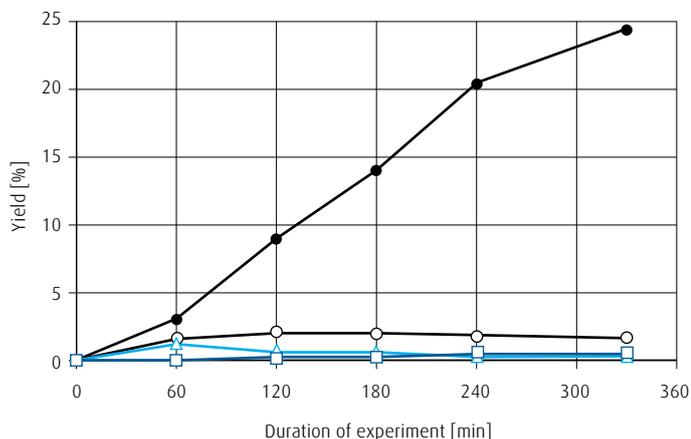
Figure 59: Oxygen consumption and oxygen content in off-gas produced by toluene oxidation at 160 °C, 9 bar and 27 vol% oxygen enrichment

○ O_2-content in flue gas, ■ Total O_2 consumption

* and/or O_2 consumption [mol]
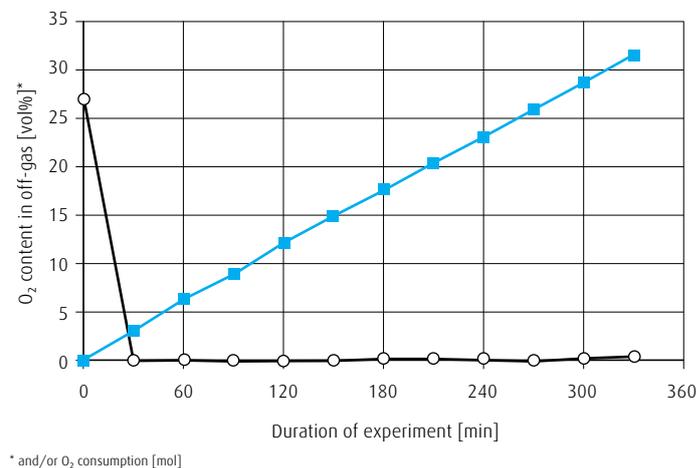
1. Increasing the concentration of oxygen in the oxidation gas from 21 vol% to 24 and 27 vol% resulted in higher reaction rate and increased yield of benzoic acid (Figure 57) at temperatures of 160 °C and a pressure of 9 bar.
2. Different oxygen concentrations in the oxidation gas only have a minimum impact on benzaldehyde and benzyl alcohol selectivity. In the case of benzoic acid benzyl ester, selectivity decreases as the concentration of oxygen in the oxidation gas rises. Figure 58 shows by-product production is low and that two by-products peak at a low level.
3. The amount of by-products also remains low if more oxygen is added to the oxygen-enriched air.

Figure 59 shows that oxygen content in the off-gas falls to a low concentration very rapidly, and is thus well below the oxygen concentration limit.

Oxygen enrichment thus delivers major benefits to toluene oxidation and that any safety risks (compliance with permitted thresholds) can be managed.

3.5.4 Kinetics and reactor calculations
Toluene oxidation with air follows a radical chain reaction. The catalyst shortens the start phase and delays the creation of inhibitors.

Based on publications and the components determined during experiments, the following nine reactions (41) to (49) were chosen as the basis of the kinetic model:

$$2 \text{ toluene} + 3 \text{ O}_2 \xrightarrow{\ r_1\ } 2 \text{ benzoic acid} + 2 \text{ H}_2\text{O} \quad (41)$$

$$1 \text{ toluene} + \text{O}_2 \xrightarrow{\ r_2\ } 1 \text{ benzaldehyde} + 1 \text{ H}_2\text{O} \quad (42)$$

$$2 \text{ toluene} + \text{O}_2 \xrightarrow{\ r_3\ } 2 \text{ benzyl alcohol} \quad (43)$$

$$2 \text{ benzaldehyde} + \text{O}_2 \xrightarrow{\ r_4\ } 2 \text{ benzoic acid} \quad (44)$$

$$2 \text{ benzyl alcohol} + \text{O}_2 \xrightarrow{\ r_5\ } 2 \text{ benzaldehyde} + 2 \text{ H}_2\text{O} \quad (45)$$

$$1 \text{ benzyl alcohol} + \text{O}_2 \xrightarrow{\ r_6\ } 1 \text{ benzoic acid} + 1 \text{ H}_2\text{O} \quad (46)$$

$$1 \text{ toluene} + 9 \text{ O}_2 \xrightarrow{\ r_7\ } 7 \text{ CO}_2 + 4 \text{ H}_2\text{O} \quad (47)$$

$$2 \text{ toluene} + 11 \text{ O}_2 \xrightarrow{\ r_8\ } 14 \text{ CO} + 8 \text{ H}_2\text{O} \quad (48)$$

$$\begin{array}{l} 1 \text{ benzyl alcohol} + \\ 1 \text{ benzoic acid} \end{array} \xrightarrow{\ r_9\ } \begin{array}{l} 1 \text{ benzoic acid benzyl ester} \\ + 1 \text{ H}_2\text{O} \end{array} \quad (49)$$

Table 15 contains the chemical formulas of the individual components.

Table 15: Chemical formulas of the most important components of the reaction system

Component	Chemical formula
Toluene	C_6H_5-CH_3
Benzoic acid	C_6H_5-$COOH$
Benzaldehyde	C_6H_5-CHO
Benzyl alcohol	C_6H_5-CH_2-OH
Benzoic acid benzyl ester	H_5C_6-H_2C-OOC-C_6H_5

As with cumene oxidation, various programs (SIAMoD and Athena) were used to determine the parameters of the kinetic model. Figure 60 shows the quality resulting from the simulation with the kinetic model, which is built on the nine reactions given above, and with the constants

Figure 60: Measured time-dependent formation of benzoic acid with oxygen enrichment of 24 vol%, at 160 °C and 9 bar compared with calculated values

● Measurement, □ SIAMoD, △ Athena weighted, ○ Athena unweighted

According to Yantovskii, pressure has little impact on the lower explosive limits in a pressure range between 2 and 20 atm. The value that the Linde software program Safety System determined (approximately 2 vol% oxygen at atmospheric conditions tallies with this information. In contrast to the lower threshold, the upper explosive limit increases significantly as pressure rises.

Yantovskii et al. report an oxygen concentration limit of 6 vol% in off-gas. This value applies to the following conditions:

· Temperature range from 20 to 200 °C
· Pressure range from 2 to 20 atm

As yet, there are no suitable calculation methods for determining explosive limits. In most cases, measured data must be used. Goethals et al. provide the following temperature-dependent values for the upper explosive limit:

At T = 225 °C, the upper explosive limit rises from 7.9 vol% at p = 1 bar to 9.4 vol% toluene at p = 9.4 bar; in other words by around 20 percent. And at T = 120 °C, from 7.3 to 7.9 vol%; in other words by around 8%. Yantovskii gives a value of 7.5 vol% at 2 bar for T = 180 °C.

Table 16 provides a summary of some key safety indicators.

determined using a range of methods. The graph shows that the kinetic model fits the oxidation of toluene to benzoic acid even for oxygen enrichment.

Building on the kinetic model described above, a corresponding reactor model was used to calculate a continuous stirred tank reactor with ChemCAD software.

The following data was used in the calculation:

Reactor:

· Reactor volume: 40 m^3
· Pressure: 9 bar
· Temperature: 140 and 160 °C

The results show, for example, that at 160 °C, benzoic acid yield can rise by 30 percent if the oxygen content of the oxidation gas is increased from 21 to 27 vol%.

Toluene oxidation is carried out in stirred reactors and bubble columns. Experiments in a bubble column are also described by Lemoine et al.

3.5.5 Safety factors
The most important safety parameters include:

· Limiting oxygen concentration (LOC)
· Lower explosive limit (LEL)
· Upper explosive limit (UEL)
· Flash point

The explosive limits also expand as oxygen content increases. The explosive ranges for oxygen contents of 21, 24 and 27 vol% at standard pressure (one bar) were calculated with the Linde software program Safety System. The results are displayed in Figure 61.

The graph in Figure 61 shows that, as oxygen content rises, the lower explosive limit remains unchanged while the upper explosive limit increases significantly.

Very little safety information is available on the substance mixtures produced during toluene oxidation. Table 17 shows the upper (UEL) and lower (LEL) explosion limits.

3.5.6 Summary
Oxygen enrichment thus delivers major benefits to toluene oxidation and that any safety risks (compliance with permitted thresholds, for example) can be managed. The results show, for example, that at 160 °C, benzoic acid yield can rise by 30 percent if the oxygen content of the oxidation gas is increased from 21 to 27 vol%. Selectivity to benzoic acid remains largely unaffected.

Table 16: Safety indicators for pure substances under standard conditions (1 bar)

	M [g/mol]	Melting point [°C]	Boiling point [°C]	Density at 20°C [g/m³]	Flash point [°C]	Autoignition temp. [°C]
Toluene	92.1	−95	111	0.87	6	535
Benzoic acid	122.1	122	250	1.27	121	570
Benzaldehyde	106.1	−26	179	1.05	64	190
Benzyl alcohol	108.1	−15	206	1.04	94	435
Benzyl benzoate	212.2	21	323	1.12	148	480
Carbon monoxide	28.0	−205	−192	1.17	−191	605

	LEL [g/m³]	UEL [g/m³]	LEL [vol%]	UEL [vol%]	LOC [vol%]
Toluene	42	300	1.1	7.8	~ 9.6 at 100 °C
Benzaldehyde	60		1.4		
Benzyl alcohol	55	584	1.2	13.0	

Figure 61: Relation between explosive limits and oxygen content, calculated using Safety System
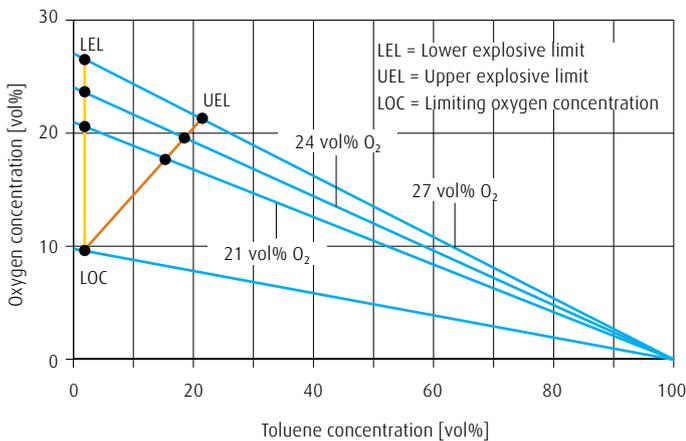
Table 17: Lower (LEL) and upper (UEL) explosion limits for the oxidation of toluene with air

Component	LEL [vol%]	UEL [vol%]	P [bar]	T [°C]
Toluene-air	1.1	7.8		
	1.2	7.1	1	25
Toluene-air	1.2			
	7.0			
Toluene-air	1.17–1.3			25
	0.99			100
	0.82	6.75–7.0	1	200
Toluene-air	1.24		1	30
	1.2		1	100
	1.07	7.1	1	200
Toluene-air	> 0.8	< 8.4	1	25; 50
Toluene-air-N₂	1.0–1.2		1–20	20–200
Benzaldehyde-air	1.4			
Benzyl alcohol-air	Approx. 1.2			
Diphenyl-air	0.6	5.8		

Figure 62: Main reactions in the Witten process (production of DMT)

p-Xylene
(p-X)

p-Toluic acid
(p-TA)

Methyl p-toluate
(MPT)

Mono-methyl terephthalate
(MMT)

Dimethyl terephthalate
(DMT)
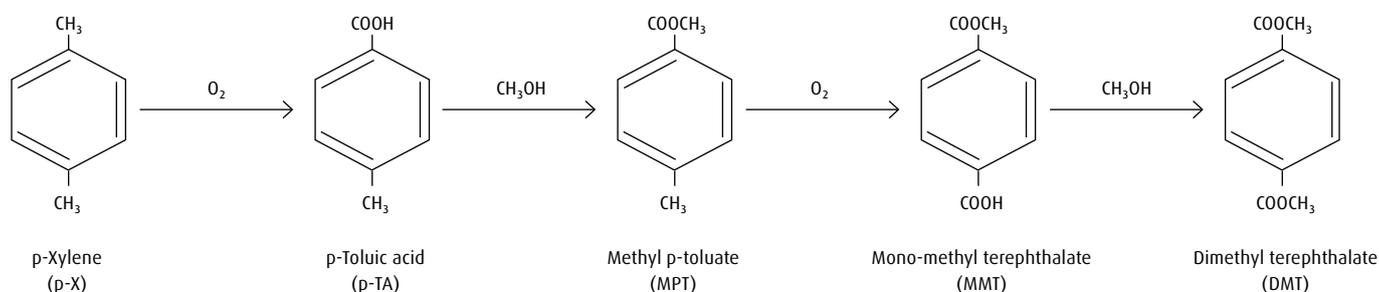
3.6 Oxidation of p-xylene

3.6.1 Introduction

Terephthalic acid and dimethyl terephthalate (DMT) are important raw materials for the production of polyester. Demand for PTA continues to rise steadily.

Terephthalic acid is primarily used in the production of polyester fibres and reusable PET bottles. Both of these processes require purity of 99.99 percent.

At this highest purity level, terephthalic acid is known as purified terephthalic acid (PTA). Medium purity terephthalic acid (MTA) also exists.

The first commercial process for oxidising p-xylene was developed in 1951. It is known as the Witten process (Dynamit Nobel process) and involves the oxidation of p-xylene and esterification using methanol. The resulting dimethyl terephthalate can then be used to produce terephthalic acid.

Later, this process was used to create the Amoco process. Oxidation also takes place in the liquid phase here. In this process, however, the catalyst also contains bromine as an initiator, in addition to cobalt and manganese. 95-percent acetic acid is used as the solvent. This process is widely used across the globe.

3.6.2 Technology
Witten process for producing dimethyl terephthalate
The Witten process comprises four main reactions: two oxidations and two esterifications with methanol. Figure 62 shows a simplified representation of the chemical reactions.

A mixture of p-xylene and recycled methyl p-toluate is oxidised with air in a continuous reactor, usually a stirred reactor. The oxidation of p-xylene remains at the p-toluic acid stage. Following the esterification to methyl p-toluate, however, it can be further oxidised with air to produce monomethyl terephthalic acid (MMT). This MMT can then be esterified to DMT using methanol.

The reaction conditions for the oxidation step are as follows:

· Temperature: 150–170 °C
· Pressure: 4–10 bar
· Catalyst: Co-Mn catalyst that is fed into reactor as an aqueous solution.

The heat from the reaction is dissipated by heat exchangers and by the evaporation of p-xylene and reaction water.

There are two different types of esterification carried out under the following conditions:

Medium-pressure process
· Temperature: 140–240 °C
· Pressure: 0–40 bar
· Acid catalyst

Figure 63: Witten process for producing dimethyl terephthalate
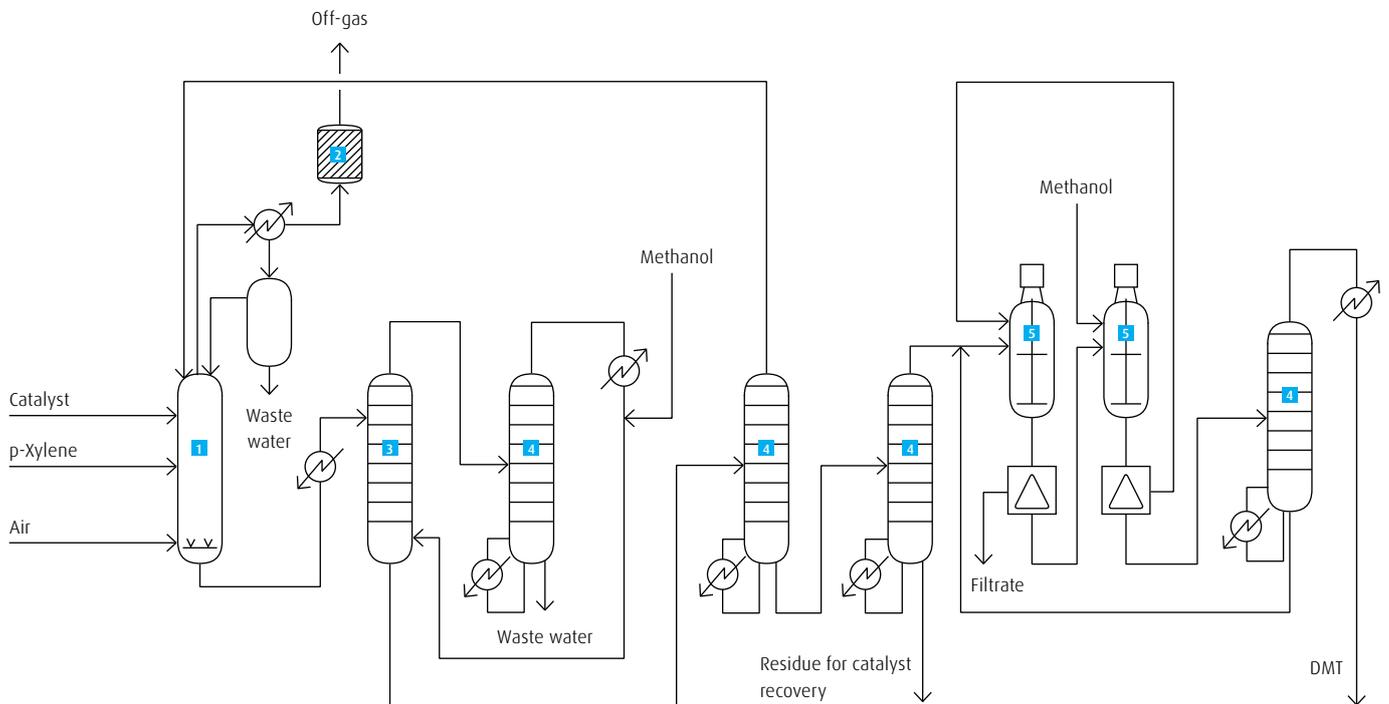
1 Oxidation reactor, 2 Off-gas purification, 3 Esterification column, 4 Distillation column, 5 Crystalliser

- High-pressure process
- Temperature: 240 °C
- Pressure: 97 bar
- No catalyst
- Supercritical methanol is used for this esterification process.

Figure 63 shows a technical flow chart of the Witten process. Once the methanol has been separated and the raw product processed, this process delivers yields of 88 to 89 percent dimethyl terephthalate with a purity of 99.99 percent.

The process has the added benefit of enabling the plant to be built with normal pressure-resistant steel as no corrosive substances are used.

The drawbacks include:

- Increased investment costs as oxidation and esterification are carried out separately in two reaction steps
- Increased operating costs due to the use of methanol for esterification

DEGUSSA-Hüls is the most important licenser. Glitsch Technology Corp. (GTC) specialises in modernising DMT plants. The company reported that it has developed a technology that enables upgraded DMT facilities to competitively produce PTA.

Sulzer Chemtech and H&G Hegmanns have also developed improved DMT technologies. Hegmanns primarily focuses on the reaction step and also holds patents from Dynamit Nobel.

The Japanese company Teijin has also unveiled a new process for producing DMT from recycled PET containers at the same cost as from p-xylene.

Figure 64: Amoco process
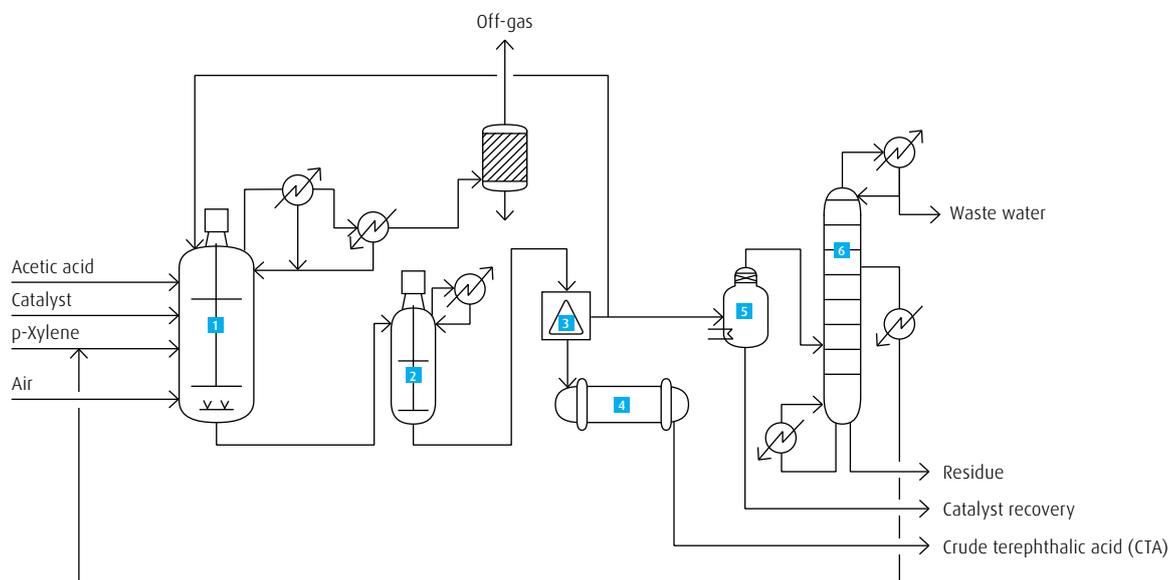
1 Oxidation reactor, 2 Stirred-tank cascade, 3 Centrifuge, 4 Dryer, 5 Pot still, 6 Distillation column

Amoco process for producing terephthalic acid

p-Xylene is air-oxidised to terephthalic acid in a reactor – usually a stirred tank reactor – in the presence of a Co/Mn/Br catalyst dissolved in acetic acid. This is a complex exothermic reaction. The main reaction (50) is as follows:

$$+ 3O_2 \longrightarrow +2H_2O \tag{50}$$
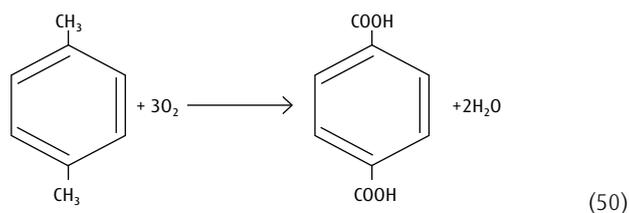
The reaction process parameters are as follows:

- Feed: p-Xylene, air, acetic acid
- Catalyst: Co/Mn/Br
- Temperature: 175–225 °C
- Pressure: 7–30 bar
- Residence time: 1–3 h
- Yield: > 95 mol%
- Conversion: > 98%

Material requirements
- Reactive section: Hastelloy C, titanium and/or titanium lining
- Heat dissipation: Via evaporating solvent and heat exchangers in the reactor

Figure 64 shows a basic set-up of the Amoco process. Amoco, Eastman/Lurgi and Interquisa are the most important licensors.

The companies Lurgi, Eastman Chemical Company and SK Chemicals formed an alliance in order to distribute and license Eastman's terephthalic acid technology. Figure 65 shows the technology involved. This approach has a number of benefits. First and foremost are the mild oxidation conditions and exclusive oxidation reactor, which does not have any internal mechanical parts or stirring equipment.

There are also many other processes for producing purified terephthatic acid (PTA). However, none of these are very widespread:

- Toray process
- Teijin process
- Mitsui process
- Mitsubishi process
- Interquisa process

Figure 65: Technology from Lurgi/Eastman/SK Chemicals used to manufacture PTA
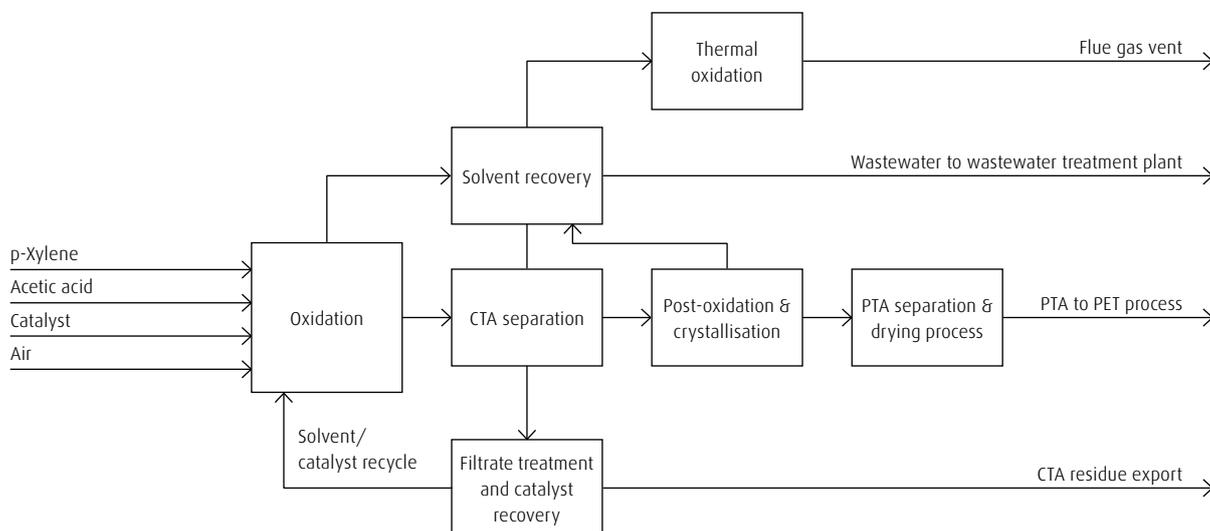
Oxygen enrichment during the production of terephthalic acid

Oxygen enrichment is used on an industrial scale during oxidation of p-xylene in Europe and in Asia, e.g. by Tuntex Petrochemicals in Fujian/China.

Oxygen enrichment is limited by the production of by-products, which can lead to discoloration. A wide range of information has been published on this subject together with advice on how to solve the problem.

Table 18 contains an example of how capacity can be increased at a 500,000 t/a plant by raising oxygen content in the oxidation gas up to 28 vol%.

Table 18: Increases in capacity at a PTA plant resulting from higher oxygen concentrations in the oxygen-enriched air

PTA capacity increase [%]	12.5	20	30	46
Increase in PTA production [kt/a]	62.5	100	150	230
Amount of oxygen required [kt/a]	36	58	87	133
Oxygen concentration in the oxygen-enriched air [vol%]	23.0	24.2	25.7	28.0

Experiments have been done using pure oxygen for the oxidation of p-xylene to terephthalic acid.

Table 19: Comparison of results from a reactor using oxygen only with results from a conventional reactor using air

Parameter	Pure oxygen	Conventional
Oxidising agent	100% O_2	Air
Temperature [°C]	180	200
Pressure [bar]	9	17
Reaction time [h]	1	1
Conversion [%]	100	100
Selectivity [%]	98.2	96.2
Loss of acetic acid [kg/100 kg PTA]	< 3	5–7
4-Formylbenzoic acid [ppm]	1,500	3,000

Table 19 compares the results of tests carried out by Kingsley and Roby with pure oxygen and a conventional air-only oxidation.

Other gases such as nitrogen and hydrogen are required in addition to oxygen. The crude terephthalic acid is purified via hydrogenation in liquid phase using Pd/active carbon catalysts. Nitrogen, and sometimes carbon dioxide, is used to dry crude terephthalic acid and for inerting processes.

Engineers and chemists are looking to develop new processes in order to:

· Create more efficient catalyst systems that do not require acidic solvents or bromine catalysts
· Optimise oxidation conditions and increase the purity of the crude product
· Increase partial oxygen pressure in the reactor through oxygen enrichment

Figure 66: Measured relationship between yield of MMT and O_2 content in the oxidation gas at 170 °C and 6 bar

● 21.0 vol% O_2, △ 24.3 vol% O_2, □ 27.3 vol% O_2
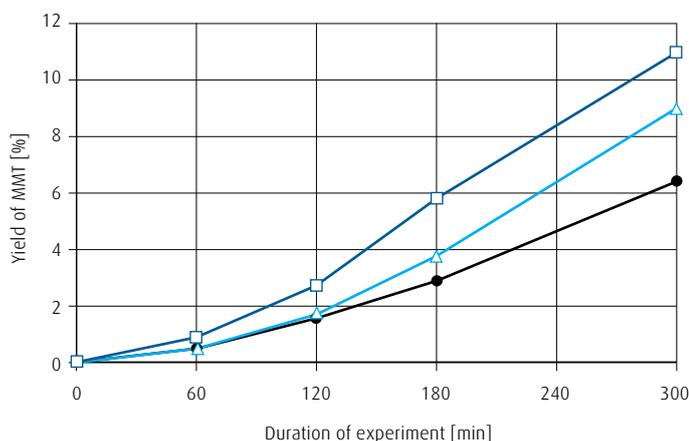
Figure 67: Relationship between yield of p-TA and oxygen content in the oxidation gas

● 21.0 vol% O_2, △ 24.3 vol% O_2, □ 27.3 vol% O_2
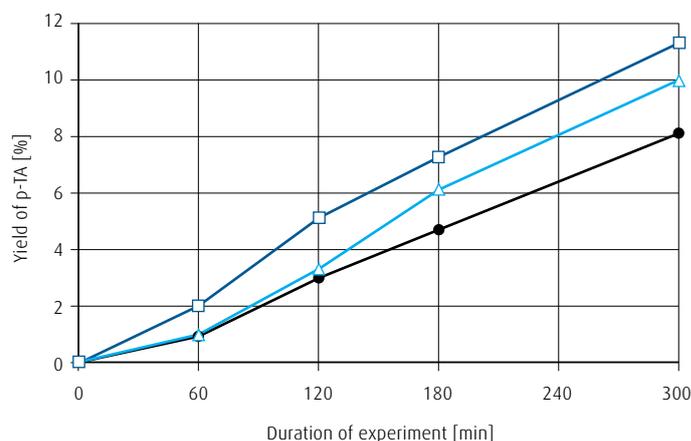
3.6.3 Experimental work on production of DMT

Oxidising p-xylene to produce DMT and terephthalic acid is an important process. Furthermore, demand for these products is rising sharply. For this reason, Linde investigated the impact of oxygen enrichment on p-xylene oxidation. The aim here was to collect initial information and to find out more about the possibilities and limitations of oxygen enrichment. A stirred tank reactor test plant was used for these experiments (see Section 3.3). Since the test system is made of stainless steel, it was only possible to investigate oxidation in line with the Witten process (for DMT production). The Amoco oxidation process (for PTA production) uses a catalyst that contains bromine compounds as well as acetic acid solvent. Both substances are very corrosive and would therefore require a reactor made of Hastelloy or with titanium lining.

After evaluating the literature cited by Brandes et al., taking into account safety aspects, the tests were planned and carried out in the stirred tank reactor system.

A mixture of p-xylene and methyl p-toluate (MPT) was used for oxidation to reflect typical industrial-scale DMT manufacturing processes. The catalyst comprised cobalt(II) acetate and manganese(II) acetate.

The reaction conditions were as follows:

- Temperatures: 150 and 170 °C
- Pressure: 6 and 10 bar
- Oxidation gas flow: ~ 520 l/h
- Oxygen concentrations in oxidation gas: 21–27.3 vol%
- Liquid content (p-xylene + MPT): 3.2 kg p-xylene + 4.8 kg MPT (mass ratio 2:3)
- Stirring speed: 1,000 rpm
- Reaction time: 5 h

- Catalyst: Co(II) acetate/tetrahydrate (1,000 ppm for Co) Mn(II) acetate/tetrahydrate (250 ppm for Mn)

The reaction products were analytically determined using high performance liquid chromatography (HPLC) and UV detection. Water content was determined using the Karl-Fischer method and the acid value in line with DIN 51778. Gas chromatography–mass spectrometry (GC-MS) was used to detect p-xylene and methyl p-toluate in the waste gas composition. Gas chromatography was used to detect CO_2 and CO. The oxygen content in the waste gas was continually measured on basis of the paramagnetic properties of the O_2 molecule.

The tests showed that oxygen enrichment can increase conversion and yield significantly. Figures 66 to 68 show selected test results.

The results of the tests can be summarised as follows:

- Raising the concentration of oxygen in the oxidation gas from 21 vol% to 24.3 and 27.3 vol% at temperatures between 150 and 170°C and pressures between 6 and 10 bar increases reaction rates and yields of monomethyl terephthalate (MMT) and p-toluic acid (p-TA).
- Selectivity of MMT and p-TA increases with conversion, peaking at 27.3 vol%.
- In all tests, oxygen content in the waste gas fell to below the oxygen concentration limit, which is usually between 5 and 8 vol%. The actual values measured were between 0 and 1 vol%. This means that the oxygen concentration limit in waste gas is not an obstacle to introducing oxygen enrichment.

Figure 68: Development of oxygen content in oxidation reactor off-gas and oxygen consumption during the test

● O_2 content in off-gas at 21.0 vol%, ▲ O_2 content in off-gas at 24.3 vol%, ■ O_2 content in off-gas at 27.3 vol%, ○ Accumulated O_2 consumption at 21.0 vol%, △ Accumulated O_2 consumption at 24.3 vol%, □ Accumulated O_2 consumption at 27.3 vol%
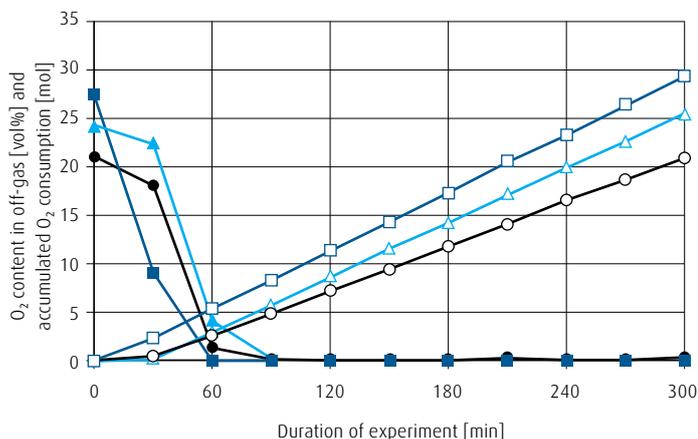
3.6.4 Kinetics of oxidising p-xylene during the production of dimethyl terephthalate

A kinetic model for the oxidation of p-xylene and methyl p-toluate with oxygen enrichment was developed based on the values determined from the experiments.

Kinetic equations were drawn up based on information published by Cao et al. and Cincotti et al. Out of the five mathematical models developed, model 4 corresponds most accurately to the test data. This model is thus used as a basis for the following observations. The following reaction equations (51) to (55) form the basis of the kinetic model:

1. Oxidation of p-xylene

$$p\text{-}X \xrightarrow{r_2} P\text{-}Tal \xrightarrow{r_4} p\text{-}TA$$

$$p\text{-}X \searrow^{r_1} \quad \nearrow^{r_3}$$

$$MBA \qquad (51)$$
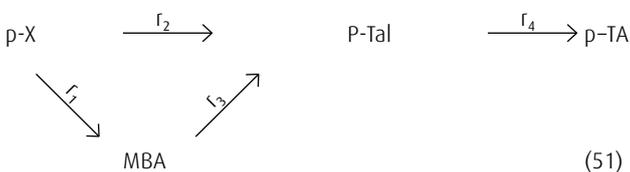
2. Oxidation of methyl p-toluate

$$MPT \xrightarrow{r_6} MFB \xrightarrow{r_8} MMT$$

$$\searrow^{r_5} \quad \nearrow^{r_7}$$

$$HM\text{-}BME \qquad (52)$$
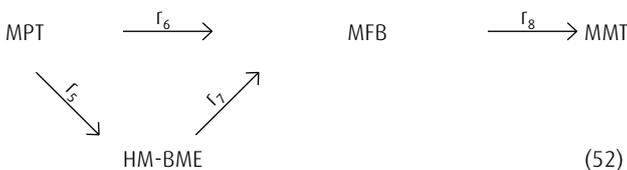
3. Terephthalic acid is produced from the oxidation of p-toluic acid

$$p\text{-}TA \xrightarrow{r_9} TA \qquad (53)$$

3. The kinetics of CO and CO_2 formation

$$MBA \xrightarrow{r_{10}} CO_2 \qquad (54)$$

$$MBA \xrightarrow{r_{11}} CO \qquad (55)$$

The abbreviations are explained in Table 20.

Table 20: Abbreviations of the chemical components and chemical formulas used in the kinetic model

Component	Abbreviation	Chemical formula
p-Xylene	p-X	C_8H_{10}
Methylbenzyl alcohol	MBA	$C_8H_{10}O$
p-Toluylaldehyde	p-Tal	C_8H_8O
p-Toluic acid	p-TA	$C_8H_8O_2$
Terephthalic acid	TA	$C_8H_6O_4$
Methyl p-toluate	MPT	$C_9H_{10}O_2$
Hydroxymethylbenzoic acid methyl ester	HM-BME	$C_9H_{10}O_3$
Methylformylbenzoate	MFB	$C_9H_8O_3$
Mono-methyl terephthalate	MMT	$C_9H_8O_4$

Figure 69: Parity diagram for p-TA yield
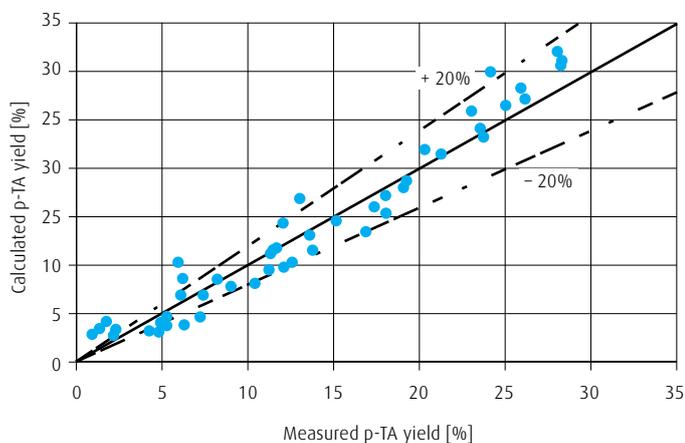
Figure 70: Parity diagram for MMT yield
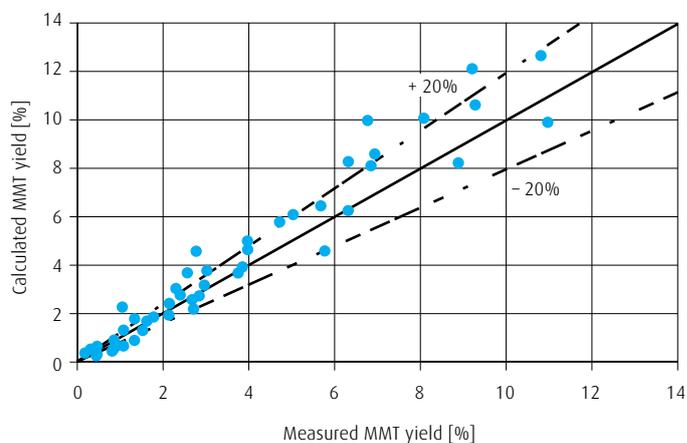
Parity diagrams can be used to assess the quality of the model, which was selected from a total of five models. In these diagrams, the calculated values are plotted against the measured values. All measured values are included. Figures 69 and 70 display the results for p-TA and MMT. They show that the model is of a high quality.

This kinetic model can thus be used to investigate the impact of oxygen in industrial reactors.

Figures 71 and 72 show p-TA and MMT yields and how they are affected by oxygen.

p-TA yield increases by 13.6 and 23.6 percent and MMT yield by 28.1 and 48.4 percent when oxygen content in the oxidation gas is increased to 24 and 27 vol%.

3.6.5 Safety factors

The autoignition temperatures and explosive limits of the reaction mixture as well as the oxygen concentration limit are all important aspects that have to be taken into consideration when assessing process safety.

Table 21 shows the typical composition of waste gas from a plant that produces dimethyl terephthalate (DMT).

Table 21: Composition of waste gas stream from a DMT plant with a flow of 67,000 m³/h

Component	Chemical formula	Concentration
Xylene	$CH_3C_6H_4CH_3$	17–20 g/m³
Methyl acetate	CH_3COOCH_3	2–4 g/m³
Methyl formate	$HCOOCH_3$	2.5–4 g/m³
Acetic acid	CH_3COOH	Trace
Formic acid	$HCOOH$	Trace
Acetaldehyde	CH_3CHO	Trace
Dimethyl ether	CH_3OCH_3	0.6–0.9 g/m³
Methanol	CH_3OH	0.3–0.7 g/m³
Water	H_2O	6.0–11.0 g/m³
Formaldehyde	$HCHO$	0.05 g/m³
Oxygen	O_2	3–4 vol%
Nitrogen	N_2	90–96 vol%
Carbon monoxide	CO	0.7–1.1 vol%
Carbon dioxide	CO_2	2–4 vol%

Figure 71: Calculated impact of O$_2$ enrichment on p-TA yield

■ p-TA yield   ■ Change in p-TA yield
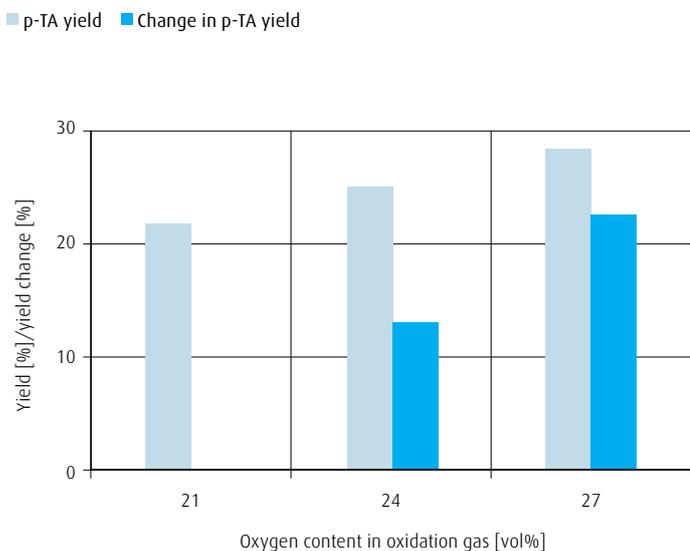
Figure 72: Calculated impact of O$_2$ enrichment on MMT yield

■ MMT yield   ■ Change in MMT yield
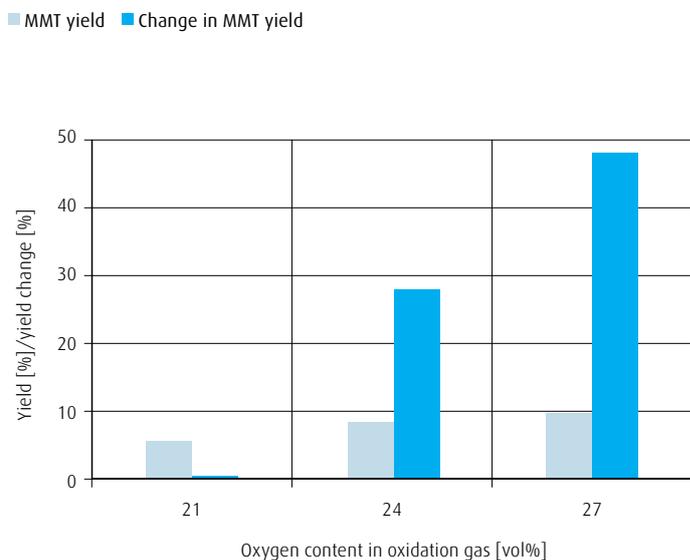
Table 22: Upper and lower autoignition limits for substance mixtures in xylene oxidation processes

Component in air	LEL [vol%]	UEL [vol%]	P [bar]	T [°C]
p-Xylene	1.1	7.0	1	100
Acetic acid	4	17		
Methyl bromide	8.6	20		

Table 22 contains upper (UEL) and lower (LEL) explosion limits for selected mixtures. Further data on these aspects can be found in "Petrochemical Processes". Oxygen concentration is relatively low in this case at between 3 and 4 vol%. This is far enough below the oxygen concentration limit for oxygen enrichment to be used.

3.6.6 Summary

Based on Linde experiments and evaluation of available literature, introducing oxygen enrichment to the oxidation step in the production of dimethyl terephthalate and terephthalic acid results in higher reaction rates and yields. It also increases selectivity to the requisite oxidation products. Oxygen enrichment is thus used in a number of major facilities and has a particularly important role to play when increasing the capacity and flexibility of production plants.

3.7 Reactors and gas injection systems for gas-liquid reactions

3.7.1 Reactors for gas-liquid reactions

Gas-liquid reactions are mainly carried out in stirred tank reactors and bubble columns. Other types of reactors have been developed and built for specific processes, including loop reactors, plug-flow reactors, thin-film reactors, jet scrubbers, jet reactors and packed columns.

Figure 73 lists the properties of the most important ideal reactor types.

The rest of this chapter focuses on stirred tank reactors and bubble columns as these are the most widespread models used. Their most important properties are listed in Table 23. The ideal discontinuous stirred tank reactor ensures perfect mixing.

There are no localised differences in concentration or temperature with this kind of reactor. The fluid particles therefore spend the same amount of time in the system (residence time).

Table 23: Characteristics of stirred tank and bubble column reactors

Reactor type	Amount of gas [m³/m² h]	Disperse phase	Size of bubble [µm]
Stirred tank	250	Gas	100–1,000
Bubble column	1,000	Gas	> 1,000

The reaction mass is stirred by agitators. Many different kinds of agitators are used for this including:

- High viscosity: Helical and anchor agitators
- Medium viscosity: Impeller, cross-beam and blade agitators
- Low viscosity: Propeller, pitched blade, disc and impeller agitators

The following agitators are particularly suited to dispersing gas in a liquid:

- Disc agitators
- Cross-beam agitators
- Self-priming hollow agitators

In the case of gas-liquid reactions, the gas is usually fed into stirred tank reactors below the agitator via a gas injection system.

The gas injection system has to ensure that the gas is evenly distributed within the liquid. In stirred tank reactors, agitators aid this process.

The mass transfer from the gas to the liquid phase is determined by the following:

- Reactor design
  - Stirred-tank reactor (height/diameter), agitators, gas injection system, heat exchangers
  - Bubble column (height/diameter), gas injection system, plates or packing, heat exchangers

- Operating conditions:
  - Pressure, temperature, liquid flow rate, gas volumetric flow rate
- Properties of the liquid and gas:
  - Density, viscosity and solubility

All of these factors influence gas holdup, bubble distribution, bubble size distribution and bubble coalescence. And these, in turn, have a significant impact on mass transfer.

Discontinuous stirred tank reactors are often used for small production volumes, for example, in the specialty and fine chemicals industry. They are also widely used in labs and test/pilot plants. The tanks range from less than one liter to several hundred liters in size.

Continuous stirred tank reactors are generally assumed to deliver perfect mixing. However, residence time behavior varies significantly. This variation is wide as some particles leave the tank very quickly while others stay in the reactor. This means that particles with different residence times come into contact, which can negatively impact selectivity in the reaction. In a perfectly mixed reactor, there are no spatial or temporal differences in concentration. The concentration in the reactor is identical to the concentration in the output flow.

If high yields and/or low residence time variations are required, several continuous stirred tank reactors can be combined in a cascade.

Bubble column reactors are used for gas-liquid reactions, whereby the gas and liquid phase flow can run in the same or opposite directions. Gas is generally fed in from below and moves upwards in the form of bubbles. The bubbles increase in size due to coalescence. They also stir the liquid phase. Different components, often sieve plates, are installed in bubble columns to intensify the mixing process and increase the interfacial area of mass transfer between the gas and the liquid. The gas injection equipment also plays an important role. One of the benefits of bubble column reactors is their simple design. They are often used when the liquid phase requires a long residence time.

3.7.2 Gas injection systems for gas-liquid reactions

Gas-liquid reactions are very common in the chemicals industry. High mass transfer rates are required to ensure that this process runs smoothly, and these can only be achieved by creating a large interfacial area between the phases in the reactors. In addition to these phase-related requirements, the geometry of the components and any agitators used, as well as the type and amount of gas fed into the apparatus are all important factors.

In stirred tank reactors and bubble columns, the liquid is in the tank and the gas is injected via a nozzle or a bar or ring of nozzles using a pressure system. The following is a list of the most commonly used gas injection systems:

- Insertion pipe
- Nozzle ring
- Concentric nozzle rings
- Porous gas distributor made of metal, plastic or glass

Figure 73: Properties of ideal reactor types

Type of reactor	Characteristics	Concentration profile over time	Concentration profile over location	Residence time distribution
	Discontinuous stirred tank (batch reactor)			
	Continuous steady-state plug-flow reactor			
	Continuous steady-state stirred tank (tank reactor)			
	Cascade of continuous steady-state stirred tanks			
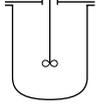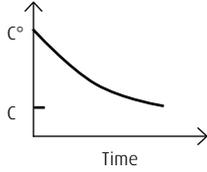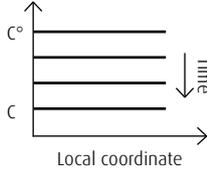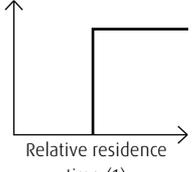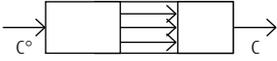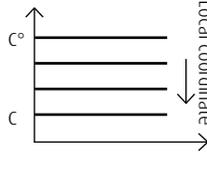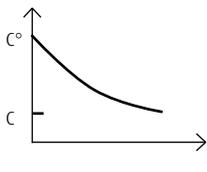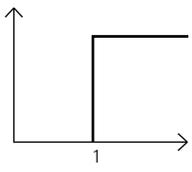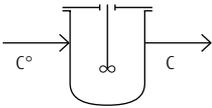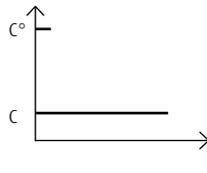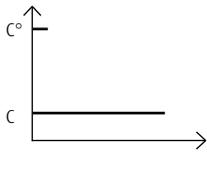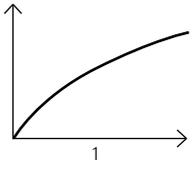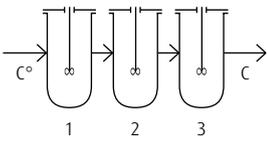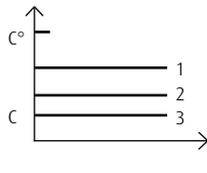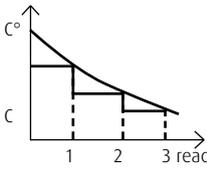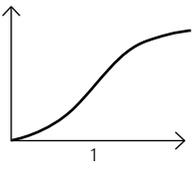
For an optimum reaction and good mixing, the gas mixture has to be distributed as evenly as possible over the height and the cross section of the reactor. The gas can be fed via a number of systems including nozzle rings. These rings comprise a number of openings, in some cases at different angles to the vertical direction of the system. The gas openings usually have a diameter between 1 and 6 mm and are positioned at the top or the bottom of the ring. Nozzle bars can be used instead of rings. As with a ring design, nozzle bars have a lot of openings to feed in the gas. These openings face upwards or downwards.

The size of the gas bubbles in the liquid has a direct impact on the phase boundary and gas holdup. Bubble size is determined to a certain extent by the diameter of the holes in the nozzle bar or ring. However, the flow regime in the reactor also has an influence on bubble size. If the interfacial area is too small and the phases are not mixed sufficiently, this leads to conversion losses and localised overconcentration. This, in turn, can increase the production of by-products and/or lead to localised overheating.

The patent cited under H.-R. Himmen, H. H. Lux, H.-J. Reinhardt, Vorrichtung zur Durchführung von Gas-Flüssig-Reaktionen (Equipment for gas liquid reactions) German patent number DE 10 2010 053 289 A1, 2 December, 2010 contains suggestions and design improvements for gas distribution equipment. These focus on improving mass transfer between the gas and liquid phases and ensure a more even distribution of gas in the liquid across the height and the cross section of the apparatus. The suggested changes also make it easier to adapt the gas distribution system to changes in process conditions and prevent liquid or reaction mass from backing up into the gas injector.

Figure 74 shows the cross-section of a stirred tank reactor with a gas injection system. To provide a clear view of the system, the agitator is not shown. The gas injection system comprises four pipes or half pipes that are fitted to the inside of the tank or held by rings. The tubes extend vertically into the reaction mass and are equipped with holes or nozzles that distribute the gas. The pipes can be raised or lowered in order to change the number of holes used, their diameters, or the number of nozzles to align with volume requirements.

Figure 74: Cross-section of a stirred tank reactor showing the position of the nozzle bars
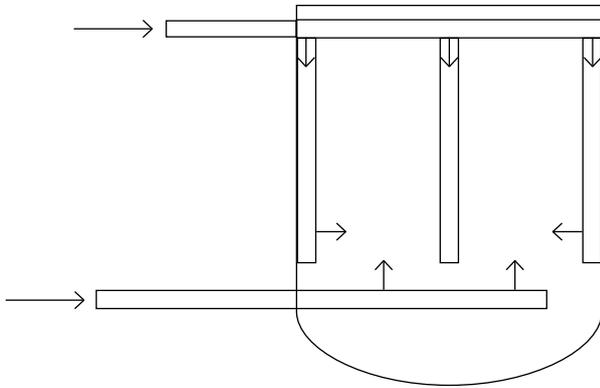
Figure 75: View of the nozzle bars under the agitator and the position of the nozzle bars relative to the reactor shell
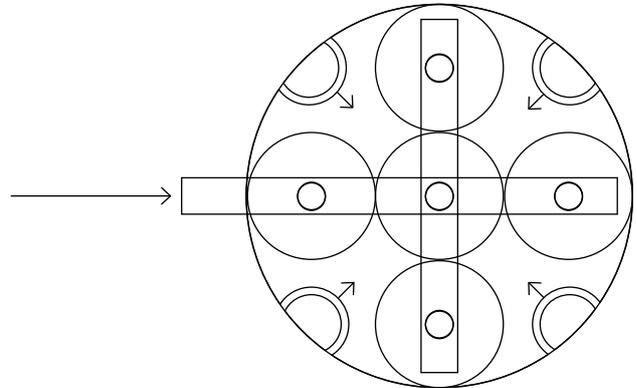
Gas is also fed in via nozzles under the agitator. The nozzle bars also have holes or nozzles. Figure 75 shows the position of the nozzle bars.

Figure 76 shows the different nozzles that can be screwed into a nozzle bar. These solutions offer a number of benefits: they can be easily adapted to the mixing system, for example, and the gas can be evenly distributed across the entire reaction space.

Figure 76: Different types of nozzle
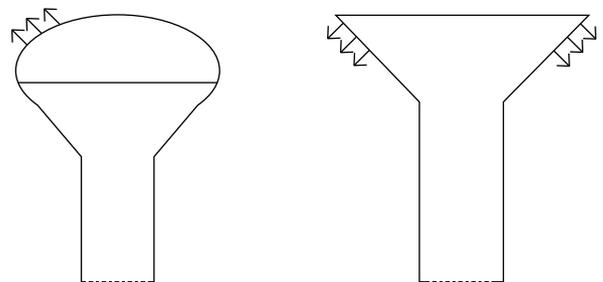
3.8 Safety issues when using air and oxygen enrichment for gas-liquid oxidations.

The majority of gas-liquid oxidations are carried out with air. As described previously, adding oxygen to this air can often increase conversion and yield and can also help resolve capacity bottlenecks. However this higher oxygen content usually leads to faster and more intensive oxidation reactions. Measures must therefore be taken to counter any potential hazards. These measures include:

· Deploying the right technology, equipment and automation solutions
· Choosing appropriate material and resources for the specific parts of plants

The following areas should be given particular attention when deploying oxygen enrichment:

· Injecting oxygen into the air stream
· Distributing oxygen-enriched air in the reactor
· Preventing heterogeneities in the reactor, in particular hot spots
· Compliance with oxygen concentration limits in the gas phase, in particular in reactor off-gas
· Start-up and shut-down of the process step

Safe injection of enriched oxidation gas requires equipment controls that have been designed with these safety issues in mind, such as Linde's OXYMIX Injector and OXYMIX Flowtrain, which enable the following:

· Thorough mixing of air and oxygen over a predefined distance between the oxygen feed-in point and the reactor to prevent the forming of zones where oxygen concentration is too high

· Compliance with requisite oxygen concentrations with varying air flow rates
· Safe shut-down in the event of a malfunction

Oxygen enrichment increases the risk of explosions. Although the lower explosive limit (LEL) remains almost unchanged, adding oxygen pushes the upper explosive limit (UEL) upwards.

The autoignition temperatures as well as the upper and lower flammability limits of hydrocarbons are also important factors. Oxygen enrichment, for example, reduces autoignition temperature by 10 to 30 °C relative to air. Despite this shift, autoignition temperatures remain significantly higher than reaction temperatures in almost every case.

The following is a list of main risks and limits that have to be taken into consideration when analysing safety factors of air oxidation processes, especially when introducing oxygen enrichment:

· Prevention of uncontrolled reactions, in particular oxidation processes and the thermal decomposition of peroxides, which can occur during cumene oxidation.
· A large volume, inflammable gas phase must not be allowed to form under any circumstances. This especially applies to the reactor headspace, where oxygen concentration limits must not be exceeded. Although these are often between 9 and 11 vol%, concentrations of ≤ 5 vol% are often specified for industrial operations for safety reasons.
· In a bubble column, it is assumed that bubbles can be allowed to explode as this produces only a small amount of energy, which is adsorbed by the liquid phase. Care must be taken, however, to ensure that the reaction conditions in the reactor are such that the oxygen concentration in the bubbles as they expand into the large volume,

pure gas phase remains below the defined oxygen concentration limit (e.g. 5 vol%).

- If liquid enters the gas distribution area, there is a risk that oxidation may take place here. To eliminate this risk, the temperature of the oxygen-enriched air should be lower than the initialisation temperature of the reaction when the air mixture enters the reactor. It is recommended that the temperature is kept 30 to 40 °C lower than the reactor temperature.
- Potentially dangerous situations can occur when starting up or shutting down oxidation reactors. Specific measures should therefore be taken to eliminate these risks, including, for example, the use of nitrogen during the start-up or shut-down of a reactor.
- When introducing oxygen enrichment, special consideration should be given to the materials and seals used in the pipes and equipment that will be affected by this transition. As a rule, oxygen enrichment of up to 28 vol% of the oxygen-enriched air does not require any major technical modifications.

In bubble columns where gas is dispersed into liquids, the bubbles should not be allowed to get too big as this might cause localised volumes of flammable mixtures to form. This risk is usually eliminated by installing additional mixing equipment (for example gas nozzles, sieve plates, baffles or cooling and heating coils) that reduces the size of the bubbles and thus ensures that they are evenly dispersed. This equipment counters the risk of autoignition of too big gas volumes.

However, there is also a gas phase above the liquid in the bubble column that comprises nitrogen, hydrocarbons and oxygen. Temperatures and pressures in this area are high and explosive gas mixtures can easily form. The relevant oxygen concentration limits have to be observed to prevent explosions in the gas phase at the headspace of the reactor. To ensure this is the case, safety equipment has to be installed at the headspace of the column. Usually, this includes oxygen measurement and equipment for quickly injecting inert gas whenever required. The oxygen sensors must be accurate. If there is a risk of combustion inside the reactor (corresponding damage has been observed on gas distributors, for example), it is advisable to install both oxygen and carbon dioxide sensors. Measuring carbon dioxide, usually with relative low down time, can provide valuable information on the presence of unwanted oxidation processes in a reactor.

Oxygen content in the oxidation gas does not impact oxygen concentration limits. However, increasing temperature and pressure does cause concentration limits to fall. Computer programs (such as EPSIM 2) that calculate oxygen concentration limits are available.

There are a number of national and international committees and research institutes that deal with safety issues in this area. In Germany, one of the most important of these is Department 2 (Chemical Safety Engineering) of the Federal Institute for Materials Research and Testing (BAM). This department deals with dangerous substances, dangerous chemical reactions, plants, units and safety equipment for handling dangerous substances and substance systems. The European Industrial Gases Association (EIGA) is another important body that focuses on all safety issues regarding the use of oxygen and organises corresponding workshops.

The CHEMSAFE database, which is organised by DECHEMA and developed by the BAM in Berlin and the Physikalisch-Technische Bundesanstalt (PTB) in Braunschweig, is often an extremely useful source of information on engineering safety.

4. Using oxygen enrichment to intensify air oxidation in fluidised beds.

4.1 Introduction

Oxidation reactions performed in the gasphase are a major cornerstone in chemical processing. Besides fixed bed oxidations fluidised bed reactors are successfully deployed for many catalytic air oxidations.

They are also ideal for oxygen enrichment thanks to the range of benefits that they offer over packed bed reactors. Adding oxygen to the oxidation air can increase conversion and yield and also improve catalyst activation. Oxygen enrichment also increases the flexibility of the fluidised beds, overcoming performance limitations of fans in air in-feed systems, for example.

Furthermore, reducing the nitrogen content also reduces the volume of off-gas.

4.2 Properties of fluidised beds

When compared to fixed bed reactors, fluidised bed reactors deliver a number of important benefits:

- The intensive mixing in the fluidised bed ensures good heat transfer. The axial and radial temperature profiles are more or less balanced.
- The catalyst can circulate continuously. This is particularly important if a catalyst becomes inactive relatively quickly.
- The contact load is evenly distributed as the core of the catalyst is constantly moving in the bed.

- The pressure drop per unit of length is lower than with a packed bed and is not dependent on throughput.
- Catalyst addition resp. exchange can be realised on the run, i.e. without a shut down period of the whole plant.

There are, of course, disadvantages:

- Drop in yield in line with flow speed as a result of mixing processes and bypass
- The mechanical stress on the catalyst leads to abrasion. The resulting residue has to be removed from the flue gas. The catalyst losses have to be compensated for by adding more catalyst.

There are typical characteristics that make this type of reactor suitable for oxygen enrichment:

- Oxygen is thoroughly distributed in the fluidised bed. Hotspots caused by localised overconcentration of oxygen do not generally occur or can be prevented.
- The thorough mixing almost entirely eliminates the risk of overheating when the oxygen-enriched air is fed in.
- The fluidised bed also helps lower safety risks as the particles act as an anti-flammable barrier.

Figure 77: Fluidised bed reactor for roasting pyrite with oxygen-enriched air
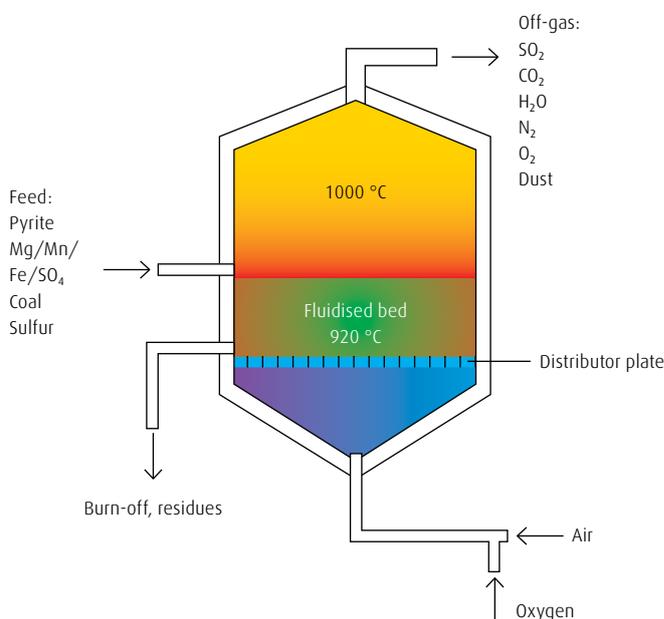
4.3 Examples of oxidation processes in the gas phase over solid catalyst

Many important oxidation processes are performed over solid catalyst either in a fixed bed or in a fluidised bed oxidation reactor. Table 24 shows an overview of respective products gained from hydrocarbons by the industrially applied process types and the optional gaseous oxidation media containing molecular oxygen.

Table 24: Organic base chemicals by gas phase oxidation (A = Air oxidation, E = O_2 enriched air, O = Oxygen only)

Product (raw material)	Global demand [kt/a]	Catalyst bed type "fixed"	"fluidised"
Acrylonitrile (Propylene & NH_3)	5,400	–	A & E
Acrylic acid (Propylene)	4,700	A	–
Ethylene oxide (Ethylene)	21,000	O	–
Vinyl acetate (Ethylene & acetic acid)	5,200	O	–
Ethylene dichloride (Ethylene & HCl)	34,600	A & E & O	A & E & O
Maleic anhydride (n-Butane or benzene)	1,900	A & O	A*
Phthalic anhydride (o-Xylene or naphthalene)	4,300	A	–
Formaldehyde (Methanol)	42,000	A	–
Methyl methacrylate (Methane & NH_3 via HCN)	3,800	A & E	–

*) Realisation of O_2 enrichment in the technical scale is on its way

With respect to the applied oxidation gas typically it is possible to apply air-only as well as O_2 enriched operation at the same process unit. Such flexibility normally can not be extended to oxygen only operation. The latter processes have to be based on process units especially designed for this purpose, typically allowing for considerably decreased plant dimensions and minimised off-gas volumes.

Above Table 24 confirms that air oxidation processes performed in the fluidised bed are prone to apply O_2 enrichment as a means for process intensification, typically in order to increase the production capacity of an existing unit.

4.4 Roasting pyrite using oxygen-enriched air

The process of roasting sulfide ores in a fluidised bed to produce sulfur dioxide is one example of an inorganic fluidised bed. The sulfur dioxide is used to produce sulfuric acid, which in turn is used, for example, to produce titanium dioxide.

In this case, pyrite, sulfate and sulfur are converted to sulfur dioxide in the presence of carbon.

The main reaction (56) is as follows:

$$4 \text{ FeS}_2 + 11 \text{ O}_2 \rightarrow 2 \text{ Fe}_2\text{O}_3 + 8 \text{ SO}_2$$
Pyrite   iron(III) oxide + sulfur dioxide   (56)

As a rule, the capacity of a fluidised bed reactor cannot be increased by raising air throughput due to the risk of solid entrainment if the fluidisation set point velocity is exceeded. However, oxygen enrichment can be used to boost capacity. In most cases, the oxygen is added to the

Figure 78: Results of a simulation showing the distribution of oxygen in an industrial reactor, where the oxygen is injected above the distributor plate via eight lateral nozzles
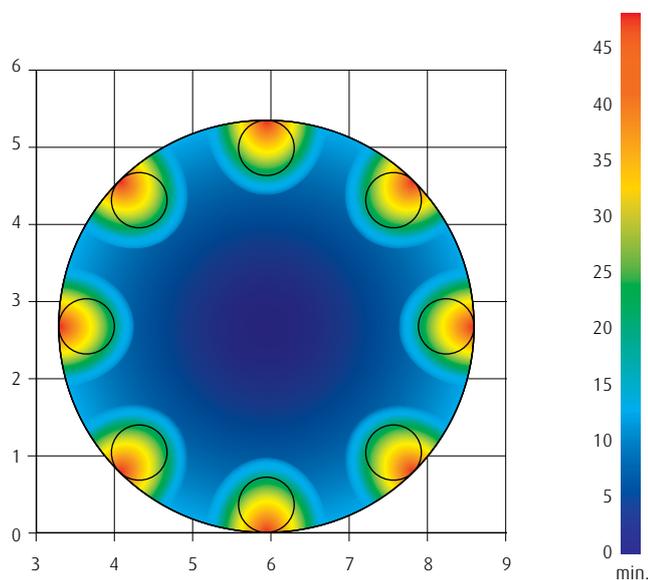
air, as shown in Figure 77. A common target is 28 vol% oxygen content, which is easily achievable. This level of oxygen enrichment increases capacity by around 15 percent.

If capacity has to be increased further, additional oxygen can be fed directly into the fluidised bed above the distributor plate. Oxygen is injected laterally via nozzles attached horizontally to the container wall.

For this solution to be effective, the oxygen has to penetrate the fluidised bed sufficiently and be thoroughly mixed. A simulation of an industrial reactor using the finite element program FEMLAB produced the following results:

- The oxygen does not penetrate very deeply. As long as the reactor is not too narrow, there is no risk of the oxygen jet hitting the reactor wall.
- Under normal industrial conditions, however, the oxygen does not reach the middle of the reactor.

Jet length is primarily influenced by the following factors:

- Increasing gas velocity at the injection point: positive
- Increasing diameter of the injection nozzle: positive
- Increasing density of particles in the fluidised bed: negative
- Increasing diameter of particles: negative

A longer jet is preferred as this ensures good distribution across the width of the fluidised bed. In the worst case, it can just result in separation of gas bubbles. Figure 78 shows the simulated results for an industrial reactor. In this case, the oxygen does not penetrate far enough into the center of the reactor.

4.5 Oxidation of n-butane to maleic anhydride

4.5.1 Introduction
Global demand for maleic anhydride (MA) is expected to grow from 1.9 in 2012 to 2.8 million tonnes by 2018.

MA is used to manufacture the following products:

- Unsaturated polyester resins
- 1,4-Butanediol
- Copolymers
- Fumaric acid
- Lubricant additives
- Alkyd resins

This trend is primarily being driven by the rising need for unsaturated polyester resins. The global demand for MA is driven by Asia Pacific and Europe.

Over the last 30 years, n-butane has replaced benzene as the feed. In 1974, the first plant to use n-butane as feedstock went on stream in the US. However, benzene is still frequently used as a raw material. n-Butane remains an attractive option due to its relatively low price. Packed bed and fluidised bed technology are both used here. However, the packed bed system is currently the dominant technology.

There are two ways of manufacturing 1,4-butanediol (BDO). The more modern way, the Davy process (Davy Process Technology), uses a path from butane through maleic anhydride and methyl ester to produce butanediol. Licensed facilities have capacities ranging from 11,000 to 100,000 t/a. Plants are located in Lima (US), Al Jubail (Saudi Arabia), Kuatan (Malaysia), Ulsan (Korea) and Kaohsiung (Taiwan).

Figure 79: Packed bed technology for the production of MA from n-butane
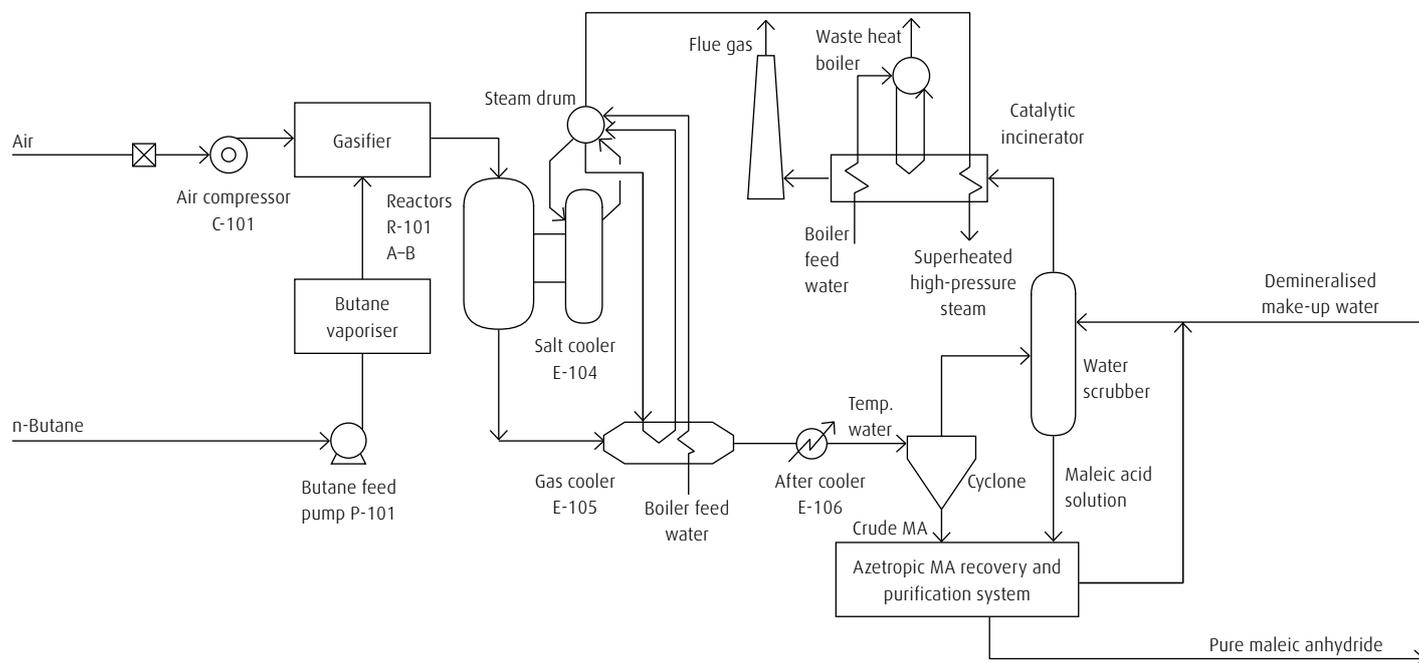
Global demand f or butanediol amounted to 1.1 million tons in 2005. The market is expected to grow by around 6 percent per year. This trend is primarily fuelled by demand for tetrahydrofuran, polybutylene terephthalate and gamma-butyrolactone.

Table 25 contains a list of European producers of MA.

Both packed bed and fluidised bed technologies are used today. The packed bed process (Figure 79) was introduced in 1974 and fluidised beds (Figure 80) were introduced in 1981. The flow chart in Figure 80 shows the layout of the Alma process. The Alma process was developed by Alusuisse Italia and Lummus Crest in 1981. n-butane and air are fed into the fluidised bed reactor separately to prevent explosions during mixing. The mixing is done in the fluidised bed, where the moving vortex of packed bed particles prevents any explosions from occurring. As this is an exothermic reaction, built-in heat exchangers have to provide intensive cooling. This process generates steam. The fluidisation process causes attrition. The resulting fines have to be removed and disposed of, and regularly replaced with fresh catalyst. Once the gas leaving the reactor has been cooled and fines removed, the MA is separated and scrubbed.

The flue gas is thermally combusted and the resulting heat used to produce steam.

Table 25: European producers of maleic anhydride

Company	Location	Capacity [1,000 t/a]
BASF	Ludwigshafen, Germany	3
Compania Espanola de Petroleos	Algeciras, Spain	10
DSM Feinchemie	Linz, Austria	36, 42
Kemiplas	Koper, Slovania	2
GIKIDL	Lukavac, Bosnia	10
Polynt	Ravenna, Italy	65
Polynt	Bergamo, Italy	36
HOG	Szazhalombatta, Hungary	13
Sasol-Huntsman	Moers, Germany	105
Zaklady Azotowe Kedzierzyn	Kedzierzyn-Kozle, Poland	8

4.5.2 Reference material review

There is very little information available on the impact of oxygen on the oxidation of n-butane.

However, yields from industrial processes are low and so oxygen enrichment should, at least in theory, be of great interest to operators.

Figure 80: Alma fluidised bed technology for the production of MA from n-butane
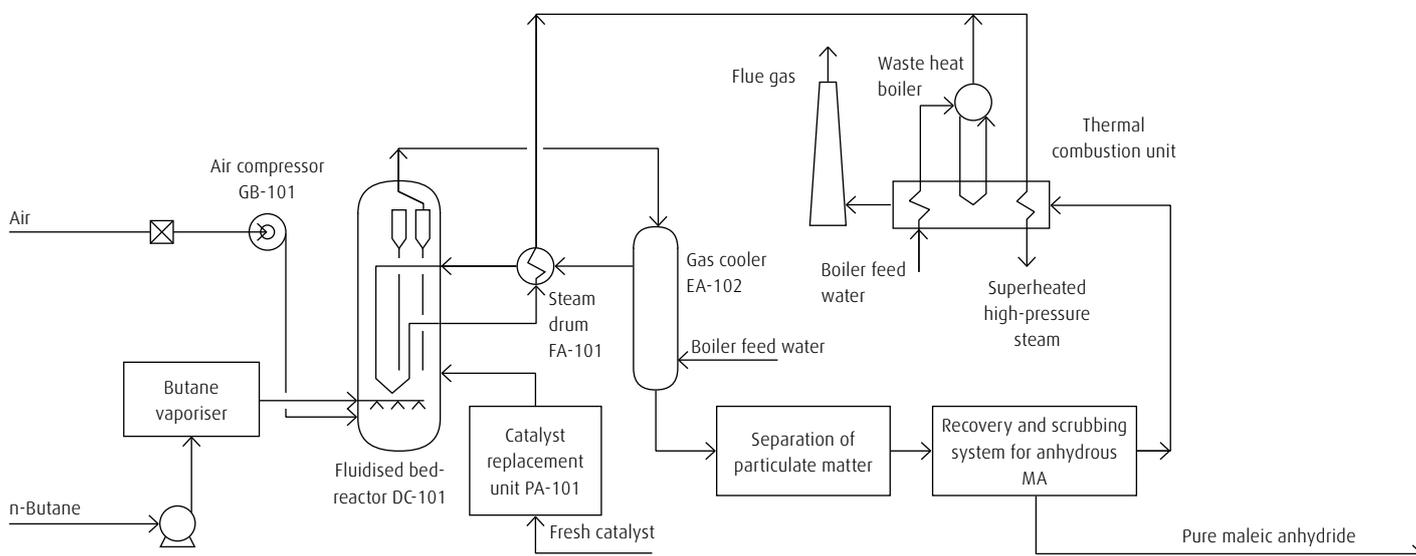
Oxygen enrichment delivers the following benefits:

- Increased capacity
- Increased production flexibility, ability to overcome bottlenecks linked, for example, to the air compressors
- Less flue gas
- Increased profit

Based on our own analyses, raising oxygen concentration from 21 to 23.7 vol% would increase capacity by around 8.5 percent.

A report published by SRI Consulting names the following two potential areas of improvement in the process:

1. Recycling butane
2. Using oxygen-enriched air for oxidation

The report lists oxygen enrichment as a way of debottlenecking. It shows that a mix of 5 vol% oxygen and 95 vol% air can increase reactor capacity by 21 percent.

K. Shima et al. focused on the catalyst and also compared packed bed with fluidised bed technology. Table 26 shows the results.

Table 26: Comparison of packed bed and fluidised bed processes

	Packed bed	Fluidised bed
Reactor	Tube bundle	Reactor tube
Productivity	Low	High
Butane concentration	Less than 2%	4–5%
Investment cost	High	Not so high
Temperature control	Difficult	Heating coils
Heat dissipation	Difficult	Relatively easy
Scale-up	Easy	Difficult
Catalyst degradation	Insignificant	Significant

They also compared the investment costs for both processes. Table 27 provides information on this. For a plant with capacity of 30,000 t/a, the fluidised process requires around 23 percent less investment, and the process becomes even more cost-effective as capacities increase. Catalyst performance has a significant impact on operating costs, however. And since catalyst attrition can be substantial in the fluidised bed process, the packed bed technology still plays an important role despite its other disadvantages.

Table 27: Comparison of investment costs for a plant with a capacity of 30,000 t/a

	Packed bed [%]	Fluidised bed [%]
Reaction	100	37
Recovery	100	57
Scrubbing	100	102
Combustion	100	154
Overall	100	67

Figure 81: Petrox process
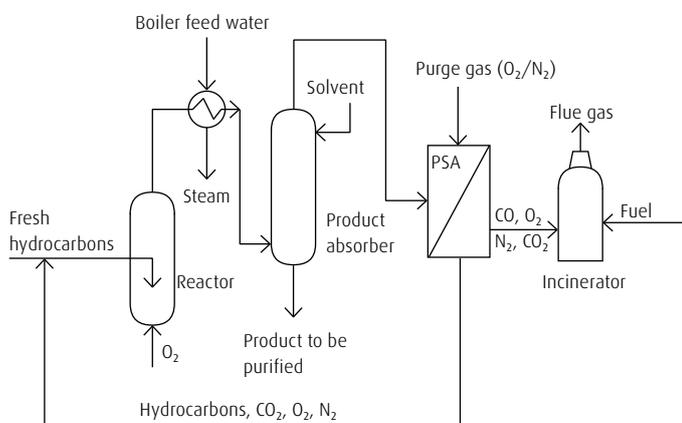
BOC Gases und Mitsubishi Chemical Corp. developed a recycling process for manufacturing MA. Known as the Petrox process, this technology aims to recover unconverted n-butane. It uses selective adsorption to separate the hydrocarbons from the inert gas and the carbon monoxides. Figure 81 shows this process in more detail.

Reports state that Petrox technology reduces investment costs by 10 percent and raw material costs by 20 percent. It is also said to substantially reduce the amount of CO_2 produced. The process is used in a major industrial plant in Japan.

Table 28: Licensors of technologies for the production of maleic anhydride

Company	Feed	Processes	Licenses
BP chemicals	n-Butane	Fluidised bed	3
Huntsmann Petrochem. Corp.	n-Butane	Packed bed	6
Lonza S.p.A.	Benzene n-Butane	Packed bed	3
Lonza S.p.A.	PSA waste gas	MA recovery	2
Lonza/ABB Lummus Global	n-Butane	Fluidised bed	9
Scientific Design, Clariant	n-Butane	Packed bed	9

Lonza AG developed a new generation of fluidised bed catalysts, known as X4, in Scanzoroscate, Italy, for their internal process flow. The catalyst builds on the traditional vanadium phosphorous oxide type catalyst, but has been modified with new promoters and synthesised in a new organic solvent system. It is reported to have 4-percent higher selectivity

and enables the reaction temperature to be brought down to 410 °C. The new catalyst also enables conversion rates of between 80 and 85 percent. Plant capacity has increased from 50,000 to 60,000 t/a, thanks to the increase in yield resulting from the new catalyst and the resolution of bottlenecks.

BP Chemicals developed and commercialised a new packed bed catalyst, known as BP-5. One of the main benefits of this new catalyst is its short start-up period. It can also be used with a gas feed flow that contains up to 2 mol% n-butane whereas conventional catalysts only work with concentrations of 1.5 to 1.7 percent. This enables operators to increase throughput by 15 to 20 percent. The catalyst can be used for over three years.

Emig, May and Scheidel carried out computer simulations on the behavior of a circulating downer regenerator fluidised bed during the partial oxidation of n-butane to maleic anhydride.

The yield from the partial oxidation of n-butane to maleic anhydride can be increased by adding carbon dioxide to the reactor feed. This effect is particularly strong when the reactor feed contains a high concentration of n-butane. The authors assume that the carbon dioxide causes partial re-oxidation at the surface of the catalyst and that this improves selectivity.

Bayer implemented its own program for developing its proprietary technology for maleic anhydride production. The company based its program at a pilot plant in Baytown, USA, which was constructed in the year 2000.

In a study by Linde, 192 citations were reviewed. The most important findings are summarised below:

- Conversion increases as the concentration of oxygen in the feed rises; it decreases as the concentration of butane in the feed rises.
- Selectivity follows the opposite pattern, although the drop in selectivity is low if the concentration of oxygen in the feed is increased. In some cases, selectivity remains unchanged.
- There are a number of sufficiently accurate kinetic models available for selected catalysts. Five different reactor models, primarily developed at the University of Erlangen, were included in the review.
- The review presented a new reaction regime in the fluidised bed reactor. Known as the two-zone fluidised bed reactor (TZBR), this concept has separate oxidising and reducing zones.

4.5.3 Kinetics

As part of his PhD, Mr. C. Becker carried out experiments at the University of Stuttgart using the catalyst developed at the University of Erlangen. Becker chose process conditions similar to those in the Alma process:

- Temperature: 380–440 °C
- Butane content: 0.6–4 vol%
- Oxygen content: 10–30 vol%.

The investigations were carried out in two reactor types – a packed bed reactor and a catalytic wall reactor. The results confirm that boosting

oxygen concentration increases conversion and has almost no impact on selectivity. Becker also ascertained that the kinetic model from Uihlein, which builds on an Eley-Rideal mechanism, shows the best test results.

The following kinetic model is thus recommended for further investigations:

Reaction diagram (57)

$$C_4H_{10} \xrightarrow{\;+\,O_2\;(1)\;} C_4H_2O_3 + H_2O$$

$$\xrightarrow[+\,O_2\,(3)]{} \xrightarrow[+\,O_2\,(2)]{}$$

$$CO + CO_2 + H_2O \qquad\qquad (57)$$
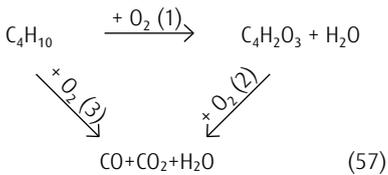
Stoichiometric relationships (58) to (60)
Synthesis reaction:

$$C_4H_{10} + 7/2\;O_2 \xrightarrow{\;\;r_1\;\;} C_4H_2O_3 + 4\;H_2O$$
Butane   Maleic anhydride   (58)

Consecutive reaction:

$$C_4H_2O_3 + p\;O_2 \xrightarrow{\;\;r_2\;\;} (6 - 2p)\;CO + (2p - 2)\;CO_2 + H_2O$$
$$p = 1 \text{ or } 2 \text{ or } 3 \qquad (59)$$

Parallel reaction:

$$C_4H_{10} + n\;O_2 \xrightarrow{\;\;r_3\;\;} (13 - 2n)\;CO + (2n - 9)\;CO_2 + 5\;H_2O$$
$$n = 5 \text{ or } 6 \text{ or } 7 \qquad (60)$$
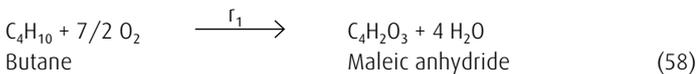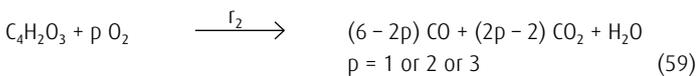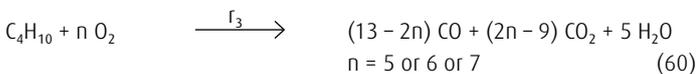
Kinetic model based on Eley-Rideal, see equations (61) and (62):

$$r_1 = \frac{k_1 \cdot p_{BU} \cdot \sqrt{p_{O2}}}{1 + K_{H2O} \cdot p_{H2O} + K_{BU} \cdot p_{BU}} \qquad (61)$$

$$r_2 = \frac{k_2 \cdot p_{MA} \cdot \sqrt[4]{p_{O2}}}{1 + K_{H2O} \cdot p_{H2O} + K_{BU} \cdot p_{BU}} \qquad (62)$$

Where:

k_i: Speed coefficient of reaction i
K_j: Adsorption coefficient of component j
p_j: Partial pressure of component j
Bu: Butane
H_2O: Water
MA: Maleic anhydride

This thus provides the foundations for using reactor simulations to analyse the impact of oxygen enrichment on industrial reactors.

4.5.4 Reactor simulation
A plug flow reactor and a fluidised bed were simulated under conditions similar to the Alma process.

The following parameters were used:

- Butane content in feed: 4–5 vol%
- Oxygen content in feed: 20–30 vol%
- Temperature in the reactor: 430–460 °C

The following reactor models were used:

- Plug flow model
- Two-phase fluidised bed model

The simulation shows that oxygen enrichment can increase yield by between 10 and 15 percent for both reactor types.

4.5.5 Safety factors
Safety is a critical issue for the following areas when introducing oxygen enrichment:

- Injecting oxygen into the reactor
- Using the right hardware to safely dose and inject oxygen into the air.
- To eliminate the risk of explosion, n-butane and oxygen-enriched air should be mixed in the fluidised bed reactor and not in the feed stream.
- The concentration of oxygen in the exhaust gas must be below the maximum permitted oxygen concentration. In this case, it is estimated to be below 6.9 vol%.

The properties of the fluidised bed reactor do not inherently present a risk of explosion. The particles in the bed act as a flame barrier.

4.5.6 Summary
The reference material review and the experiments underscore the benefits of oxygen enrichment in the oxidation of n-butane to maleic anhydride in a fluidised bed. Additional oxygen increases yield by up to 15 percent. The explosion hazard is manageable due to the properties of fluidised beds, and the maximum permissible levels of oxygen concentration in flue gas can be complied with.

5. Environmental protection.

Figure 82: Diagram of an oxidation process that uses air and additional oxygen as an oxidising agent
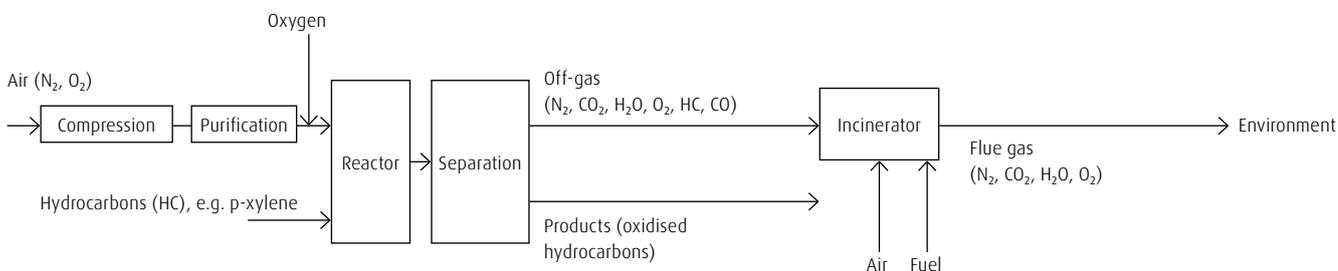
5.1 Reduction of flue gas

5.1.1 Introduction

To improve environmental performance, operators in the chemicals industry are looking to decrease the overall amount of flue gas produced as well as the amount of pollutants contained in flue gas streams. Previously, efforts in this area focused on scrubbing. In light of rising energy and raw material prices, however, the industry is increasingly looking to recover by-products, reduce the volume of exhaust gas produced and lower the effort required to combust it.

The chemicals industry has also committed to reducing greenhouse gas emissions, for example, within the framework of the Kyoto Protocol.

Industrial gases can be a useful tool here:

- Reduction of flue gas
  Air is used as an oxidising agent in many oxidation processes. Using oxygen-enriched air or converting processes to oxygen-only technology can reduce or eliminate nitrogen ballast and thus substantially reduce the amount of flue gas produced (see Figure 82). In many cases, valuable by-products can be recovered more easily from flue gas streams that do not contain nitrogen. Oxygen also reduces the amount of gas in the processing stages of a plant and subsequently the volumes that have to be transported, heated, cooled and processed in incinerators.
- Reduction of CO_2 emissions.

New developments aim to minimise the production of by-products and reduce total oxidation to carbon dioxide. However, these reductions can also be achieved at existing facilities by making a number of modifications:

- Reducing the temperature of a process to cut the amount of heating energy required. This can be done, for example, by using more effective catalysts, or, in some cases, oxygen enrichment.
- Reducing the amount of inert gas in reaction processes, for example, nitrogen content in air-only oxidation processes. This reduces the amount of energy required for heating, cooling, compressing and expansion throughout the course of a process, which in turn cuts CO_2 emissions.
- Increasing the selectivity of the oxidation process in order to produce less carbon dioxide and other by-products.
- Reducing pollutants in flue gas and recovering feedstocks from flue gas. Liquid nitrogen-based cryocondensation can be used to do this in plants with smaller capacities ($\leq 2,000$ Nm^3/h).

In the case of oxidation processes that use air as an oxidising agent, introducing oxygen enrichment based on reduced air flow or transitioning to pure oxygen can help reduce the amount of flue gas and greenhouse gases produced. Reducing the pressure drop and the amount of flue gas can also lower compression costs. Furthermore, flue gases, which often contain harmful and/or reusable hydrocarbons, are easier to clean if they are not diluted by nitrogen. And less nitrogen means that less energy has to be used to heat up streams in incinerators.

Figure 83: Reduction in fuel gas consumption during post-combustion due to oxygen enrichment (test results) (The oxygen shown was added to combustion air)
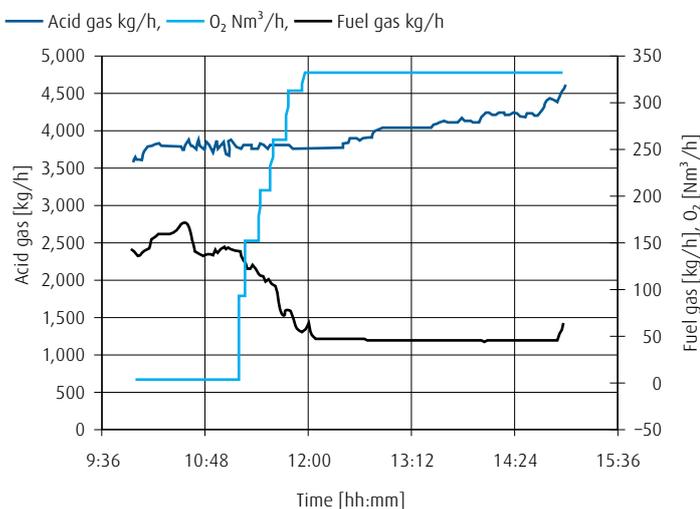
5.1.2 Oxygen enrichment in the Claus process

The Claus process converts hydrogen sulfide into elemental sulfur. It is one of the most important disposal processes in a refinery. Section 2.2 describes this process in detail. It also outlines the effects and problems of adding oxygen to the combustion air in a Claus furnace.

Oxygen enrichment also:

· Reduces the amount of flue gas produced
· Cuts the amount of energy required for heating
· Creates more hydrogen

Engineers were able to substantially cut the amount of heating gas required for post-combustion at a three-stage Claus plant primarily by increasing oxygen content in the combustion air of the Claus furnace to 28 vol% (measured results in Figure 83). The actual savings in fuel gas that can be achieved with oxygen enrichment depend very much on the operating conditions and design of individual Claus plants. In general, however, oxygen enrichment can cut consumption by between 20 and 30 percent.

5.1.3 Oxygen enrichment in the fluid catalytic cracking process (FCC)

FCC is a process step in crude oil refining that involves splitting a heavy vacuum distillate into gasoline components, liquid gases, gas oil fractions and a residue fraction in a fluidised bed reactor at 450 to 550 °C using a zeolite catalyst. Coke, a by-product of the reactions, builds up on the catalyst during this process. The catalyst is removed from the fluidised bed and fed into a regenerator, where air or oxygen-enriched air is used to burn off the coke deposits from the catalyst at 550 to 750 °C. The regenerated catalyst is then fed back into the reactor.

Section 2.3 contains a detailed description of the process, including information on oxygen enrichment.

Adding oxygen to the regeneration air can increase capacity and the flexibility in feed composition. It can also significantly reduce the amount of flue gas produced. Hundreds of thousands of cubic meters of air move through FCC plants every hour. Assuming a flue gas volume of around 200,000 Nm^3/h, increasing oxygen content to 25 vol% in the regeneration air reduces the volume of flue gas by around 33,000 Nm^3/h.

Experiments with oxygen enrichment in the regeneration process show that oxygen enrichment reduces the amount of CO in waste gas, increases the concentration of CO_2 and unfortunately can also raise NO_x content. If the amount of NO_x exceeds threshold values, there are a number of methods that can be used to bring NO_x content back down to permissible levels. These methods are described in section 2.1.

5.1.4 Ethylene oxide production with oxygen

Ethylene oxide can be produced by direct oxidation using air or pure oxygen. Oxygen reduces the equipment required and cuts operating costs, by lowering, for example, the amount of vapour, electrical energy and cooling water required. Oxygen also has environmental benefits and can, for example, substantially reduce the effort required to scrub the purge gas stream. As this stream does not contain any nitrogen, the ethylene and hydrocarbon content is high enough for it to be burnt in an incinerator without requiring any additional fuel gas. Oxygen also reduces ethylene losses. The drop in energy consumption subsequently lowers CO_2 emissions.

Due to all of the reasons above, today's new facilities are built to work exclusively with oxygen as an oxidising agent.

Figure 84: Drop in carbon dioxide emissions and fuel gas savings as a result of lower nitrogen content in flue gas

● CO_2, △ Natural gas
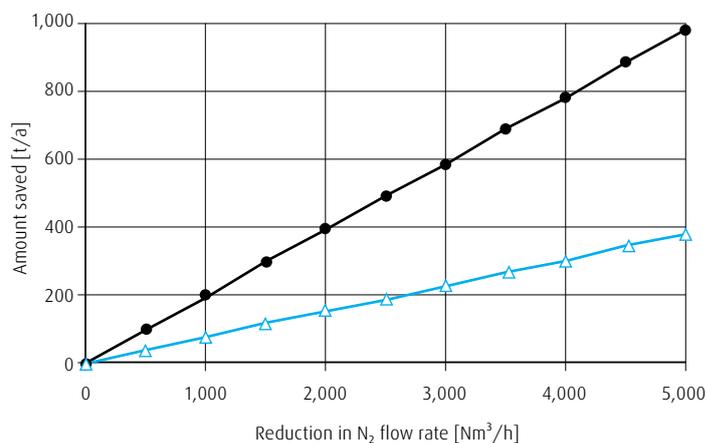
5.1.5 Using oxygen enrichment in the oxidation of cumene, toluene and p-xylene

These processes are oxidation reactions that take place in gas-liquid reactors. They are described in detail in chapter 3.

In industry, air is currently used as the oxidising agent in cumene and toluene oxidation processes. However, experiments have shown that adding oxygen to oxidation air requires little investment but can improve the throughput, conversion and environmental footprint of a process.

p-Xylene is oxidised on an industrial scale using air and oxygen-enriched air. Due to the large amounts of air involved, oxygen enrichment can deliver substantial savings when processing oxidation reactor off-gas. The effects of oxygen enrichment on the off-gas flow in gas-liquid oxidation processes are shown in Figure 44. Results were measured in a stirred tank reactor.

The amount of off-gas falls by between 15 and 18 percent when oxidation air comprises 24 vol% oxygen. Off-gas decreases by approximately 25 to 32 percent with 27 vol% oxygen content. Oxygen enrichment increases the energy content of off-gas, enabling it to be used as a fuel for burning other waste gas streams.

In summary, adding oxygen to oxidation air makes oxidation processes more cost effective. It also helps reduce the amount of flue gas produced and minimise hydrocarbon losses.

5.2 Reduction of CO_2 emissions

Adding oxygen to oxidation air or transitioning to oxygen-only oxidation reduces the amount of inert gas in the gas stream. This saves heating energy and subsequently CO_2 emissions. The following example demonstrates this. Figure 84 shows the reduction in fuel gas consumption and the subsequent drop in carbon dioxide emissions as a function of the reduced nitrogen content in a case where the nitrogen content is heated with natural gas from 20 °C to 200 °C. The example assumes that 0.35 kg of carbon dioxide is emitted during combustion for each kWh of calorific output.

Oxygen enrichment can, in some cases, increase the selectivity of oxidation processes, as experiments with p-xylene oxidation have shown. Oxygen enrichment of 27 vol% can increase selectivity by over 14 percent.

Improved selectivity simplifies off-gas treatment and improves environmental protection.

Figure 85: Diagram of a typical wastewater incineration process

1 Wastewater container, **2** Combustion chamber, **3** Gas cooler, **4** Molten salt, **5** Salt discharge, **6** Quencher, **7** Jet scrubber, **8** Wet-wall electrostatic precipitator, **9** fan, **10** Stack
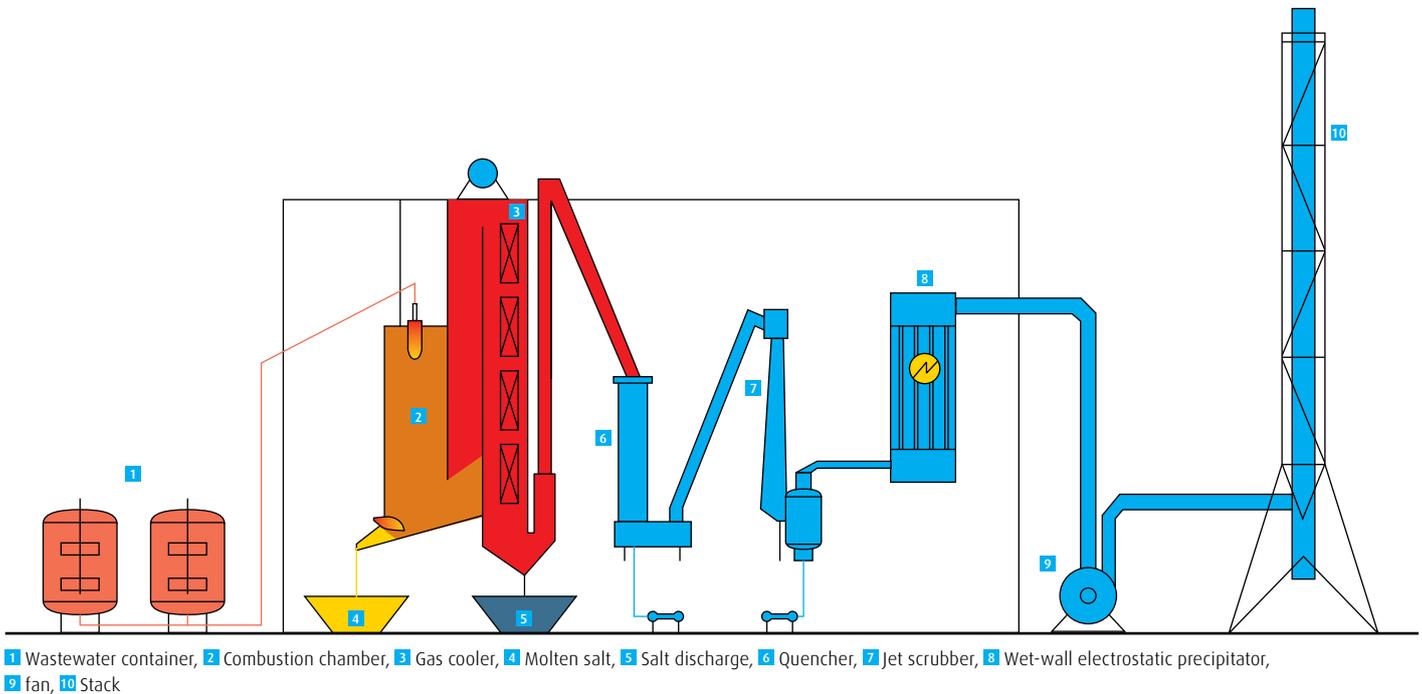
5.3 Waste gas combustion

Off-gases that contain hydrocarbons are burnt in dedicated combustion units. These gas streams can be produced by the combustion process, start-up or shut-down processes, disruptions or maintenance work. Most plants use combustion gas, air and, in the case of extreme contamination, water for soot-free combustion. Oxygen enrichment requires little investment yet it can increase plant capacity. Boosting oxygen content in combustion air can also reduce CO_2 emissions during waste gas combustion by reducing the amount of nitrogen that has to be processed by the plant. This, in turn, means that less fuel gas has to be used to aid the burning process. These effects were proven by experiments in an industrial plant operating with up to 28 vol% oxygen enrichment. Capacity at the plant increased by around 20 percent. Operators were also able to comply with residual oxygen content of 4.5 vol% and meet CO and NO_x thresholds.

Implementing a cryocondensation process upstream of the waste gas combustion can also help reduce the respective overall effort, by treating smaller, separate sub-flows that contain chlorinated hydrocarbons. This cryocondensation step can also reduce contamination from unwanted chlorinated hydrocarbons, which can cause corrosion.

The measures described here help cut carbon dioxide emissions and eliminate capacity bottlenecks and corrosive damage at combustion facilities.

5.4 Using oxygen enrichment for wastewater incineration

Wastewater incineration plants are increasingly experiencing bottlenecks due to rising capacity demands. Figure 85 shows a diagram of a typical wastewater incineration plant.

These kinds of combustion plants are used, for example, when recovering organic components from wastewater or separating mixtures comprising several components is not economically and/or when wastewater contains substantial amounts of salts. Wastewater is incinerated at temperatures in excess of 1,000°C in dual fuel burners, for example. If the organic content in the wastewater is too low to evaporate the water and to superheat the steam, additional energy must be provided. This is usually done by burning natural gas.

The waste heat is used to produce steam, which is also used to evaporate the water.

Increasing oxygen content in the oxidation air for the combustion chamber to 28 vol%, for example, can increase throughput by up to 30 percent. This can be done without any major technical investments. This result has been confirmed by experiments in an industrial facility. Oxygen enrichment can also cut natural gas consumption by reducing the amount of nitrogen in the gas stream. If the gas stream contains less inert gas, less energy is required to heat it, and this translates into lower CO_2 emissions.

Appendix.
Important explosion protection terms.

Flammable liquids	Flammable liquids are liquids that have a flashpoint. They are neither solid nor unctuous at 35 °C and have a vapour pressure of 3 bar or less at 50 °C. They are divided into different risk categories.
Flammable gases	Flammable gases are gases that can form a flammable mixture with air at normal pressure.
Density ratio	Density of a gas or vapour relative to the density of air.
Explosion	An explosion is the exothermic chemical reaction of a flammable gas (or a finely dispersed solid) with another substance, including oxygen in air. The explosive velocity ranges from 1–1,000 m/s and the pressure increase from 3–10 bar.
Explosive atmosphere	An explosive atmosphere is an explosive mixture of gases, mist, vapour or dust with air. Other factors such as moisture and atmospheric conditions influence the explosiveness of an atmosphere.
Explosive mixture	An explosive mixture is a mixture of gases or vapours that may also include mist and dust. If ignited, these mixtures will result in a self-propagating reaction.
Explosive limit, lower (LEL) [vol%] EN 1839	The lowest concentration of flammable substance in air, at which there is no more flame propagation (explosion) after an ignition.
Explosive limit, upper (UEL) [vol%] EN 1839	The highest concentration of flammable substance in air, at which there is no more flame propagation (explosion) after an ignition. The upper explosive limit of mixtures with oxygen is significantly higher than with mixtures with air. Temperature and pressure influence explosive limits.
Flash point (T_{Fl})	The flash point of a flammable liquid is the lowest temperature at which it can vaporise in sufficient amounts so as to form an ignitable mixture in air at air pressure of 760 Torr (1,013 mbar) in an open or closed crucible.
Liquid gases	Liquid gases are gases that usually can be liquefied at low pressures and at room temperatures. These include propane, propene, butane and butene.
Hazard categories	In Germany, flammable liquids are classified as follows in line with the "Verordnung über brennbare Flüssigkeiten" (Directive governing flammable liquids (VbF): A: Water insoluble liquids with a flash point below 100 °C AI: With a flash point below 21 °C. AII: With a flashpoint between 21 °C and 55 °C. AIII: With a flash point between 55 °C and 100 °C. B: Liquids that are soluble in water in any ratio at 15°C and have a flash point below 21 °C.
Hazardous explosive atmosphere	A hazardous explosive atmosphere is an explosive atmosphere that occurs in a dangerous quantity. A mixture is deemed to be present in a dangerous quantity if ignition would result in an explosion that would cause direct or indirect injury to persons in the area.

The maximum experimental safe gap is a standardised process for individual flammable gas mixtures. MESG is the gap width at which a flashback will not occur for a given flammable gas mixture. Gases and vapours are allocated to the following explosive categories based on their MESG:

Maximum experimental safe gap (MESG) IEC 60079-1	Maximum experimental safe gap [mm]	Explosion group
	> 0.9	IIA
	0.5 ≥ 0.8	IIB
	< 0.5	IIC

Minimum ignition energy (MIE)	Minimum ignition energy is the minimum amount of energy required only to ignite a flammable gas or a vapour-air mixture by means of a discharge from a capacitor at atmospheric pressure and a temperature of 20 °C.
Limiting oxygen concentration (LOC)	The oxygen concentration limit (LOC) is the limiting concentration of oxygen in a mixture of combustible with air or inert gas below which an explosion is not possible.
Autoignition temperature	Autoignition is a process in which a flammable substance spontaneously ignites in air without an external source of ignition. It is an exothermic oxidation reaction that primarily occurs with solids that have large surfaces (e.g. dust). Low-volatile, organic liquids can also autoignite if they are distributed over a substrate with a large surface area. The autoignition temperature is the lowest temperature at which a flammable substance will spontaneously ignite in a normal atmosphere without an external source of ignition. Published values can only be used as a reference as they are strongly influenced by a range of other factors (e.g. the shape and size of the material or sample and the test methods used).

Flammable gases and liquids are divided into different temperature categories based on their individual autoignition temperatures.

Temp. classification	Ignition temp. [°C]	Max. surface temp. [°C]
T1	> 450	450
T2	> 300 ≥ 450	300
T3	> 200 ≥ 300	200
T4	> 135 ≥ 200	135
T5	> 100 ≥ 135	100
T6	> 85 ≥ 100	85

Temperature classification (T1 to T6)
IEC 60079-4

Evaporation number	Ratio of time needed to completely evaporate a given liquid relative to the time needed to completely evaporate a reference solvent, such as diethyl ether or n-butyl acetate, under the same conditions.

This table lists and defines important terms in the field of explosion protection. Directive 94/9/EC on equipment and protective systems intended for use in potentially explosive atmospheres (ATEX) was the main source of information here.

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