Use of industrial gases in petrochemistry.

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Published in Hydrocarbon Processing 87 (2008) No.12
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The most important gases for petrochemistry, apart from light hydrocarbons, are oxygen ($O_2$) and nitrogen ($N_2$), hydrogen ($H_2$), carbon monoxide ($CO$), synthesis gas or syngas, a mixture of $H_2$ and $CO$, specialty gases such as gas mixtures used for such functions as process or quality control.

The quantities of gas required range widely, from less than 1 to over 100,000 Nm³/h. Specified purities also vary greatly from application to application, with values from 90 to 99.9999 vol. %.

The requisite quantity and purity govern both the production process selected and the form in which gases are delivered (cylinders, cylinder bundles, liquefied-gas tank trailers, near-by production plants such as on-site plants when dedicated to the corresponding process). The gas industry offers diverse manufacturing processes and a wide spectrum of delivery forms to the petrochemical industry [4].

**Abstract**

Industrial gases are widely applied in petrochemistry, where they are used as reactants, to ensure safety, to mitigate environmental impacts, for industrial services, and in analytical procedures.

The most important gas application areas in petrochemistry are identified and illustrated with examples. Requirements on gas production are set forth in terms of quantity, quality and reliability of supply. Finally, gas supply systems are discussed and an outlook for the years to come is offered.
By a big margin, the dominant oxidising agent in petrochemicals manufacturing is molecular oxygen. Compressed process air still figures as oxidant for many oxidations, but as a rule the advantage belongs to processes using pure gaseous oxygen (GOX) as oxidising agent because the candidate technologies are far more effective. For example, eliminating the large amount of inert gases that must be transported through the system with air oxidation results in a number of benefits: savings in investment costs and resources – leading to reduced environmental impact – can be achieved because of the possibility of using significantly smaller apparatus, highly positive effects on selectivity in many cases and a substantially smaller exit-gas stream. The last point alone often yields a considerable saving in fuel and an associated reduction in CO₂ emissions.

The use of supplemental oxygen frequently results in a substantial boost in the productivity of an existing plant that employs air oxidation. In many cases, corresponding oxygen enrichment of the process air, which commonly can be realised with only minor effort, represents a very promising way to intensify the process. Gains in capacity typically range between 10 and 15 percent. Such an increase in productivity can often be achieved by simply injecting GOX into the process air ducting. The added equipment cost for this mode of oxygen enrichment is comparatively slight, as fig. 1 indicates.

All three options for oxygen supply – dedicated on-site generation, liquefied gas supply and pipeline network – are used in petrochemistry.
As diagram 1 implies, even a moderate increase in the oxygen content of the process air allows a substantial reduction in the total gas flow rate while maintaining the original quantity of oxygen delivered. The possibility of cutting back the exit-gas stream is often a significant motivation for implementing oxygen enrichment.

**Catalytic oxidation processes**

Oxidation steps in petrochemical processes very often involve catalysis. Most such oxidations take place either in the heterogeneous gas phase on a solid catalyst surface, or in the (most often homogeneous) gas/liquid phase through the admission of a gas stream containing oxygen. Table 1 presents selected gas/liquid oxidations of industrial importance in which a variety of oxygen-containing gases – depending on the technology chosen – are used for oxidation.

**Table 1: Gas/liquid oxidations of industrial importance**

<table>
<thead>
<tr>
<th>Oxidation product (starting product)</th>
<th>Oxidising agent in gas/liquid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air</td>
</tr>
<tr>
<td>Terephthalic acid (p-xylene)</td>
<td>x</td>
</tr>
<tr>
<td>Dimethyl terephthalate (p-xylene/methanol)</td>
<td>x</td>
</tr>
<tr>
<td>Cyclohexanone (cyclohexane)</td>
<td>x</td>
</tr>
<tr>
<td>Cumene hydroperoxide (cumene)</td>
<td>x</td>
</tr>
<tr>
<td>t-Butyl hydroperoxide (isobutane)</td>
<td>–</td>
</tr>
</tbody>
</table>

**Diagram 1: Effect of O₂ enrichment on process air flow rate to oxidation reactor**

- **Process air flow rate**
- **N₂ in process air**
- **Air only**

![Diagram 1](image-url)
The oxidation of liquid p-xylene to terephthalic acid, a key feedstock for many polyesters, plays a major role in the petrochemical industry. In this air oxidation process, oxygen enrichment is increasingly employed to boost capacity. Most production units have capacities between 100,000 and 1,000,000 tonnes per year. Enriching the inlet air to 25 vol. % oxygen thus calls for several million Nm³/year of oxygen capacity. Among the salient effects that come with additional use of GOX is a capacity increase of more than 20%.

Development work aiming at complete conversion from air to oxygen for the oxidation step is currently in progress. As diagram 2 indicates, significant effects can also be obtained with oxygen enrichment in other gas/liquid oxidations, such as the oxidation of cumene [5] and toluene [6].

Diagram 2: Conversion to benzoic acid in toluene oxidation (160 °C, 9 bar abs) at various O₂ contents in the oxidation air

Results gained in trials using O₂ enrichment in gas/liquid oxidation of toluene
High purity, typically over 99%, is required in most cases when using GOX in recycle processes, in order to prevent inert gases such as argon building up in the recycle stream.

When, on the other hand, GOX is employed for O₂ enrichment in air-based “once through” processes (for a typical example see fig. 2b) – no matter if the oxidation is carried out in the gas/liquid or the gas phase – its purity is generally only a secondary question. An oxygen content of around 90 vol. % normally suffices and can even be attained with non-cryogenic oxygen generators such as those using the PSA (pressure swing adsorption) principle [4].

A variety of heterogeneous gas-phase oxidations are candidates for the use of technologies with gas recycle (see fig. 2a) where only GOX is employed as oxidising agent. The highly advantageous setting here – in comparison to processes without gas recycle, which normally involve the use of process air (see fig. 2b) – means in particular a much-increased product selectivity and substantially less off-gas. Today, with hardly an exception anywhere in the world, the processes employed for oxidation of ethylene to produce ethylene oxide and vinyl acetate make exclusive use of GOX. Processes with gas recycle also hold great interest for the oxidative chemical treatment of light saturated hydrocarbons or “fuel-grade” feedstocks. Such processes have already been implemented on an industrial scale, as for example in the oxidation of ethane to acetic acid.

**Fig. 2a: Catalytic gas-phase oxidation with recycle**

**Fig. 2b: Catalytic gas-phase oxidation with air (“once through process”)**
Thermal oxidation processes

The key to industrial production of carbon black, sulphur and, in part, synthesis gas (H₂/CO; see chapter 3) is the use of molecular O₂ in sub-stoichiometric quantity for purely thermal oxidation. Complete oxidation is effectively suppressed in this way, which in turn ensures selectivity for the product in question. Such non-catalytic partial oxidation processes, characterised by oxidation conditions typically at over 800 °C, are in fact the exception in chemicals manufacturing, in part because the high temperature presupposes extraordinarily high thermal stability of the desired oxidation products.

The exclusive use of GOX as oxidising agent has been the state of the art for many decades in the gasification of carbon-containing feedstock to obtain H₂/CO mixtures. Quite a different situation prevails in the production of industrial carbon black and elemental sulphur by oxidative processes. Here, new plants continue to be designed largely for the use of process air, and the supplemental use of GOX, essentially as shown in fig. 2b, is mainly retrofitted to existing plants to intensify processes. This holds in particular for desulphurisation of gases with high H₂S content by the Claus process, nowadays by far the main source of industrially produced sulphur. Here, more than 100 plants all over the world have been retrofitted for O₂ enrichment. Among other beneficial effects, the main driver for GOX use here is often a considerable gain in capacity at existing air-based plants [7]. The same applies to the furnace black process, the dominant process for carbon black production in terms of volume (see fig. 3). In this process, even a moderate elevation of the O₂ content, from almost 21 to 23 vol.% in the process air, yields a 10-% increase in output.

Safety in use of O₂ for industrial oxidation processes

Safety concerns are of course central whenever fuels and an oxidising agent are present together, all the more so when not just air but also pure oxygen is in question.

In general, the presence of air containing an elevated O₂ level allows oxidation reactions to proceed more rapidly and intensively than in the air-only operating mode. Accordingly, the potential danger of working with such gas mixtures or with pure GOX must be addressed through:

- Appropriate process and apparatus design; see e.g. [8]
- Proper selection of materials and media for equipment that can come into contact with this gas phase

In particular, the following problems merit special attention when oxygen enrichment is practiced:

- Injection of oxygen into the air stream
- Startup and shutdown of the reaction stage
- Prevention of inhomogeneity in the reactor
- Compliance with concentration limits in the exit gas

Gas vendors often have appropriate solutions and tools available, such as oxygen injectors, instrumentation and control systems for retrofitting to existing plants, startup and shutdown strategies, safety analysis protocols and explosion limit calculation software.

Fig. 3: Oxygen supply system installed at a carbon black plant
Synthesis gas (syngas), a mixture of hydrogen and carbon monoxide (CO), is not only the most important source for the production of pure gases, but it is also quite important as a building block for chemical syntheses [9].

For example, synthesis gas is the main feedstock for the production of methanol, which in turn is or can be the starting material for the manufacture of the following products, e.g.:

- Formic acid
- Acetic acid
- Formaldehyde
- Dimethyl ether or methyl tert-butyl ether
- Hydrocarbons such as olefins
- Hydrocarbon mixtures for fuels (such as FAME, i.e. fatty acid methyl ester)

Because of the wide range of possible applications for methanol, its potential in terms of a methanol-based economy beyond oil and gas is now under discussion [10].

In addition, the following process classes involving syngas are industrially important or becoming so:

- Oxosynthesis or hydroformylation of alkenes to make aldehydes, from which products such as alcohols and carboxylic acids are easily obtained
- Fischer-Tropsch synthesis of higher hydrocarbons, such as transport fuels

In this field, presently the conversion of biomass to liquid (BTL) is of high interest, e.g. in Germany, a pilot installation for gasification of biomass is being installed where various feed options can be tested.

In essence, there are two ways to produce syngas as a bulk product [1]. In the first, carbon-containing feedstock – which can be liquid (e.g. heavy residues from oil refineries), gaseous (natural gas) or solid (coal or biomass) – is partially oxidised by sub-stoichiometric addition of molecular oxygen in a non-catalytic operation. These thermally induced partial oxidations involve light cracking fragments of carbon-containing feed, so the production of syngas can be described in somewhat simplified form:

"CH" + ½ O₂ → ½ H₂ + CO

A first commercial-scale plant for production of ethanol – based on syngas produced from wood chips – is currently scheduled for completion in 2008 [11].

Besides the gasification route, the second method of major importance is steam reforming of hydrocarbons such as natural gas (most common), but also naphtha or methanol. The corresponding catalytic pathway is often employed for hydrogen production; the procedure can be divided into four steps:

- Feed pretreatment (such as desulphurisation)
- Steam reforming (this endothermic step can be accomplished, for example, by allothermic processing, i.e. heating of the catalyst as well as the feed/steam mixture by an external heat source), in this example starting with methane:
  \[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow 3 \text{H}_2 + \text{CO} \] (2)
- CO conversion (this exothermic catalytic process is also called “water-gas shift reaction”):
  \[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \] (3)
- Hydrogen purification, for example by pressure swing adsorption; see fig. 13

Generally, the H₂/CO ratio depends to a high degree on the starting products. The highest values, typically up to 6:1, can be achieved by steam reforming of light hydrocarbons, especially natural gas, where methane predominates as a gas component. Normally, the ratio must be adjusted to suit the application in question, for example by conversion of CO – according to equation (3) – in favour of a higher H₂ content or by separation of hydrogen and carbon monoxide.

In contrast to refinery operation, especially in the petrochemical field, a low H₂/CO ratio is often of interest. In such cases, a step such as the "reverse water-gas shift reaction" (i.e. the back-reaction of equation (3)) is an option if large amounts of CO₂ and H₂ are available at low cost [12]:

\[ \text{H}_2 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \] (4)

Reference [12] also offers a typical example based on a large-scale petrochemical complex with a variety of syngas-consuming processes.
Hydrogen.

In many cases, hydrogen (H₂) applications in petrochemical processing call for large quantities of hydrogen which normally are sourced from syngas production [13, 14]. Alternatively, H₂ can be supplied by electrolysis of aqueous solutions or by treatment of hydrogen-rich off-gases, such as those arising, for example, in petroleum refineries or in plants producing styrene monomer. Complex production clusters built recently tend to consume more H₂ than some of their various processes, such as platformers, are producing. This situation is mainly due to regulations calling for the production of “clean fuels”, especially originating from desulphurisation requirements. Present H₂ sourcing options rank considerably lower than syngas in terms of the quantity of H₂ produced or recovered.

A key requirement for H₂ generation is reliably steady product quality, which depends mainly on two factors:

- Catalyst performance in steam reforming, the predominating technology for H₂ production (in particular, catalyst poisons, such as S-containing compounds, must be minimised in the feed).
- Minimisation of impurities and by-products in the H₂ product to meet the demands of the processes supplied with this gas. Accordingly, the content of CO has to be kept very low in some hydrogenation processes, e.g. below one ppmv.

Normally, H₂ is delivered as a compressed gas by cylinders, trailers, on-site production plants or via pipeline (in the last case at 60 bar, for example); the purity routinely ranges up to 99.999 %. Which option is chosen depends heavily on the quantity and quality required and on the plant location [15]. Besides CO, the main impurities are nitrogen, oxygen and water. Appropriate purification treatments, such as catalytic combustion to eliminate oxygen, are employed.

In terms of safety, the following points must be taken into account:

- Weight: H₂ is the lightest of all gases
- Explosion hazard in enclosed spaces: H₂ is highly flammable and when escaping, the gas forms an explosive mixture with air within a wide composition range (4 to 77 % in air); in addition, the energy needed for ignition (0.019 millijoules) is very low
- Explosion hazard in process plants: H₂ also forms explosive mixtures with oxidising gases other than molecular oxygen, such as chlorine and dinitrogen monoxide

For back-up purposes or where quality requirements are very high, H₂ can be delivered as a cryogenic liquid at -253 °C via tank trailers. After vaporisation of the liquid H₂ coming from the storage tank, the gas typically has a purity of 99.9999 %. By far the most important application for H₂ is in hydrogenation. This term denotes a chemical reaction in which hydrogen is added to another chemical compound. Because the H₂ molecule is quite stable, hydrogenation calls for relatively drastic reaction conditions such as temperatures of up to 300 °C and pressures of up to 100 bar, as well as a catalyst to lower the activation energy. Transition metals, above all nickel, palladium and platinum, serve as catalysts inducing dissociative adsorption of H₂ molecules. This in turn allows for hydrogenation of a variety of functional groups such as shown in figure 4.

![Fig. 4: Synthetic applications of hydrogen](image-url)
Hydrogenation operations are conducted in both the gas and the liquid phase, as the following cases illustrate:

**Hydrogenation of benzene to cyclohexane in the liquid phase:**

- **Catalyst:** nickel or platinum metal
- **Conditions:** 20–40 bar and 170–230 °C
- **Reactor type:** multiphase stirred tank

Since recently, apart from the exemplary reaction conditions shown above, the total hydrogenation of benzene has gained interest in view of gas-related logistics. As the saturated reaction product has acquired an additional H₂ content of some 7 wt. %, the corresponding hydrogenation/dehydrogenation reaction system could become interesting in view of effective long-term storage and long-distance transportation of H₂ as a liquid [27]. The precondition for this is to find methods allowing for appropriate mild reaction conditions for H₂ addition, and its abstraction as well.

Selective hydrogenation procedures are often necessary when more than one functional group and/or a highly oxidised group is present in the feed.

**Selective hydrogenation of phenol to cyclohexanone in the heterogeneous gas phase:**

- **Catalyst:** supported palladium
- **Conditions:** 1–2 bar and 140–170 °C
- **Reactor type:** shell-and-tube

In sometimes only minor quantities, hydrogen is used as an auxiliary for a variety of purposes, as for example:

- Purification steps in process chains through reduction of by-products; for example, when oxidising p-xylene in the production of terephthalic acid, some 4-carboxybenzaldehyde occurs, spoiling product quality. By selective hydrogenation of the carbonyl group, the aldehyde content in the terephthalic acid product can be minimised to an acceptable level.
- The elimination of sulphur-containing contaminants – in many cases detrimental to catalytic processing – from feed streams is often initiated by conversion of these species (such as mercaptans or organic sulphides, resp. disulphides) to H₂S; an example is pretreatment of the natural gas feed for steam reformers, applying H₂ in a catalytic hydrogenation step.
- Matrix gas, for example in rearrangements in isomerisation reactions of hydrocarbons.
- As a tool for control of polymerisation reactions, as for example chain length regulation in the production of polypropylene.
- Heterogeneous hydrogenation to eliminate oxygen dissolved in boiler feed water.
- Auxiliary for analytical procedures, such as carrier or fuel gas in gas chromatography.

Rather surprisingly at first sight, the reducing agent hydrogen can serve in oxidations as well: as a very interesting alternative to the commonly used anthraquinone process, recent catalyst and process developments have paved the way for the long-sought-after direct combination of hydrogen and oxygen for production of hydrogen peroxide, successfully accomplished in alcoholic solution [17]. The great potential of H₂O₂ for selective epoxidation allows for subsequent catalytic oxidation of propylene under mild conditions in the liquid phase, yielding propylene oxide. This combined technology is not as much hampered by the occurrence of coupled products as competing state-of-the-art processes, and moreover, it is expected to be more economical. The first H₂O₂-based installation of an industrial-scale production plant is in progress [18].

For more examples see [14].
Carbon monoxide figures as a reactant in many industrial chemical syntheses [9], such as:

- Manufacture of phosgene
- Production of acetic acid by carbonylation of methanol
- Production of acetic anhydride by carbonylation of methyl acetate or dimethyl ether
- Oxidative carbonylation of methanol to dimethyl carbonate

Actually, CO also plays a role in complementing well-established technologies. For example, methyl methacrylate monomer is produced mainly from hydrogen cyanide and acetone, but a novel two-stage synthesis route involving ethylene, methanol and formaldehyde as starting materials along with CO is becoming competitive. One production plant of this type is now being erected in Singapore and expected to come on stream in 2008 [19].

The common way to obtain carbon monoxide is by cryogenic distillation of syngas. The gas is available in different purities:

- For bulk supply via pipeline from a nearby production plant up to 99.99 vol. % CO, this is adequate for most chemical syntheses (typical contaminants are H₂ and hydrocarbons along with air gases such as O₂, N₂ and argon, as well as water)
- Qualities up to “five nines” (quality grade 5.0, standing for a gas purity of 99.999%) for testing and calibration

Petrochemical processing normally uses large quantities of CO, generally produced by on-site plants (see fig. 6). A few chemical complexes have pipeline networks to supply the gas to various processes. Production capacities often range up to 30,000 Nm³/h. For minor demands, such as in laboratories, CO is normally delivered as a compressed gas.

The properties of carbon monoxide – it is highly toxic, combustible, colourless and odourless – mean that stringent safety requirements govern its shipping, storage and handling.
Carbon dioxide (CO₂) is a colourless, stable, noncombustible gas. Compared to N₂, the heavier CO₂ is not as chemically inactive and accordingly finds only limited use as an inerting gas in petrochemical applications. As CO₂ is an acid, it reacts with bases such as ammonia or carbanions. It can moreover be used for reaction or co-polymerisation with epoxides. But overall, CO₂ serves as a building block for only a few chemical reactions.

Including other purposes, however, such as product formulation or industrial services, CO₂ covers a wide variety of applications. The gas is used as:

- A component for chemical syntheses such as the production of urea, organic acids (e.g. hydroxybenzoic acids such as salicylic acid) and cyclic and polymeric carbonates [20]
- A feed for CO₂ production, especially if H₂ is available (see equation (4))
- A reagent for neutralisation of aqueous fluids with too high pH (often replacing sulphuric acid in this function)
- A solvent (in the supercritical state), as in the production of fluorinated polymers
- A foaming agent in production of voluminous polymers
- An inert gas mainly for blanketting, as it is heavier than air
- A fire extinguishing agent

As a solid – i.e. dry ice - CO₂ is used as:

- A coolant
- A surface cleaning agent (especially in dry ice blasting applications, where accelerated CO₂ pellets are used, for example, in maintaining heat exchangers or pipelines)

As CO₂ is a greenhouse gas (human activities account for the generation of more than 20 billion tons per year [20]), efforts are made not only to minimise output but also to discover new potential uses. Such novel applications have been found in the field of resource opening such as enhanced oil recovery (EOR), where CO₂ reduces the viscosity of in-situ oil deposits for facilitated recovery. In petrochemistry, however, bulk uses of CO₂ are not easy to find, even when the various options of reduction to carbon monoxide (including the Boudouard equilibrium and the Calcor process) are considered [21]. Many efforts to exploit the useful properties of CO₂ as a supercritical solvent have not yet led to a major breakthrough in the production of commodity chemicals. Another interesting approach for bulk use of this gas seems to be the dehydrogenation of saturated hydrocarbons where CO₂ could have potential as a supporting oxidant (see e.g. [22]). Such an application, however, does not appear to have been commercialised yet.

With a CO₂ content of 380 ppmv in air [28], the generation of this gas in air separation units is not economic, especially since high-volume gas mixtures with much higher CO₂ concentrations are available. It is accordingly obtained from natural sources, such as CO₂-rich natural gases, but also from a variety of production processes, where it is generally a by-product. Such processes include fermentation (mainly in bio-ethanol production), lime burning and reactions of carbonates with strong acids. Petrochemical CO₂ sources of industrial importance besides syngas production units are ethylene oxide plants. Here, the comparatively poor selectivity of the catalytic oxidation step is responsible for the high rate of CO₂ generation (see fig. 7). Thus, some 18,000 Nm³/h of CO₂ can be sourced from a large-scale plant producing 250,000 tons of ethylene oxide per year [12].

Normally, CO₂ is delivered in cylinders but also in tanks as liquefied gas with a purity up to 99.999 vol. %. Special high-purity grades and mixtures with other gases are also available. It has to be appreciated that normally CO₂ cannot be detected by human senses and on the grounds of its properties – CO₂ is significantly heavier than air and human exposure at a concentration greater than 10 vol. % can be fatal – strict compliance with safety regulations is mandatory in all applications.

**Fig. 7:** Purified CO₂ from a petrochemical off-gas at the Marl chemical complex in Germany
Nitrogen is the gas most commonly used in the chemical industry. Because of the remarkable inertness of diatomic nitrogen, there are just a few instances in which it serves as a reactant, as in the production of ammonia. As a consequence, it serves to protect equipment, ensure product quality, perform cooling tasks and provide industrial services. Other applications include the conveyance of solid bulk material such as powders and the preparation of catalysts.

In the petrochemical industry, the main uses of nitrogen are in inerting procedures as well as industrial services. Sometimes, gaseous N₂ (GAN) is admixed with other gases as a diluent, for example with H₂ for hydrogenation purposes, as in the purification of crude terephthalic acid. H₂/N₂ gas mixtures are often used for activation of catalyst material, notably for hydrogenations.

Cryocondensation, where gases are cooled by cryogenic liquid nitrogen (LIN), may become more important in future. A typical cylinder-based N₂ application is its use as an inert gas for analytical procedures, for example as a carrier stream in gas chromatography.

**Inerting**
The purpose of inerting is to displace (atmospheric) oxygen, moisture or combustible gases with an inert gas. This task is most often performed with nitrogen, only occasionally with carbon dioxide, either to afford safety or to protect products.

**Nitrogen**

Safety-related uses of nitrogen include:
- Safe startup and shutdown of plants and apparatus
- Prevention of formation of an explosive atmosphere
- Reduction of explosion hazard when combustible liquids are being handled

Uses of nitrogen for product protection aim to prevent oxidation reactions with atmospheric oxygen and/or to block the admission of moisture.

There are three methods of inerting:
- Dilution purging
- Displacement purging
- Pressure swing purging

Besides the experimental determination of explosion limits, software tools are applied much more often in order to generate safety data; see fig. 8. Most of these programs apply only to systems at standard pressure, but more recent developments are under way to take into account the appreciable effect of pressure on the explosion limits.

Another class of software makes it possible to calculate in advance the inerting time and the quantity of nitrogen required for the several methods; for an example see [23].

The main advantages of nitrogen are that:
- It is inert, nontoxic, noncombustible and dry
- It can be delivered in a simple and flexible manner as cryogenic LIN stored in tank systems or sourced by the user as GAN from customised on-site plants or from pipeline systems

**Fig. 8: Safety system – flammability triangle**

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Lower flammability limit 1.2 vol. % fuel</td>
</tr>
<tr>
<td>(2)</td>
<td>Min. O₂ for flammability 10.9 vol. % oxygen (1.3 vol % fuel)</td>
</tr>
<tr>
<td>(3)</td>
<td>(C) Startup = 10.9 vol. % oxygen</td>
</tr>
<tr>
<td>(4)</td>
<td>At 25.0°C and 1.0 bar (a) for toluene (fuel)</td>
</tr>
<tr>
<td>(5)</td>
<td>Upper flammability limit 7.1 vol. % fuel</td>
</tr>
<tr>
<td>(6)</td>
<td>Shutdown = max. 2.7 vol. % fuel</td>
</tr>
</tbody>
</table>

Explosion triangle with toluene as a gaseous fuel in air, as calculated by Linde’s “Safety System”, a software tool.
Industrial services

The petrochemical industry makes use of a variety of service procedures and hardware items involving the use of gases. Most such processes have been, and continue to be, devised and employed through the collaboration of chemical companies, service firms and gas vendors.

The use of nitrogen – because it is non-toxic, non-combustible and mostly non-reactive – clearly dominates in terms of gas application for industrial services in the petrochemical industry. The principal operations involving this air gas are:

- Purging and drying of apparatus
- Reactor service (shutdown, cooling, catalyst replacement, startup; see fig. 9)
- Mechanical cleaning of furnaces, pipes and pipelines by jets of nitrogen mixed with abrasive particles
- Pipeline scraping, renovation and mothballing
- Leak testing with nitrogen/helium mixtures

The latter procedures, applied mainly during turn-around and maintenance activities, contribute to cutting time and costs, improving safety and reducing environmental impact.

The principal areas of gas application development in the field of industrial services are in optimisation of reactor service (nitrogen injection, speed-up of cooling processes) and inerting operations (reduction of inerting time, minimisation of nitrogen consumption).
Cryocondensation

The application of cryocondensation techniques in petrochemistry is not widespread at present. But rising prices for hydrocarbons and increasingly stringent environmental standards suggest that this gas purification process will find increasing use in the future.

In most applications, cryocondensation means passing exit gas streams through heat exchangers where they are cooled against a coolant to such an extent that valuable products or pollutants contained in them condense or freeze out onto the heat-transfer surfaces. This non-destructive procedure allows for recovery of the liquefied material.

Using liquid nitrogen (-196 °C at 1 bar) as coolant makes it easy to achieve and control temperatures below the dew point in order to comply with regulatory limits for exit gases. Condensation against liquid nitrogen makes low temperatures – down to -150 °C are needed in some cases – accessible. The operation is more reliable and economical than when conventional refrigeration equipment is used. Condensation capacity is easily and quickly adjusted over a broad range by controlling the inlet rate of liquid nitrogen.

Cryocondensation is an economical method for treating exit gases laden with hydrocarbons and lowering downstream levels to the ppm range. The ease with which the technique can be combined with other treatment or recovery methods, adsorption in particular, means an expanded range of potential applications. At present, throughputs of up to 2000 Nm³/h of exit gases can be handled economically by cryocondensation. An example is the recovery of ethylene from exit gas streams. Typical inlet values are:

- Temperature: 10–40 °C
- Pressure: 1.2–20 bar
- Volumetric flow rate: 1000–2000 m³/h

The raw gas contains high concentrations of hydrocarbons – such as 60–85 wt. % ethylene or hydrocarbon mixtures – that have to be separated. Multistage cryocondensation, where the stages are operated at different temperatures, is employed for such purposes. The temperatures in the heat exchangers are controlled through the rate of liquid nitrogen injection. Fig. 10 shows a simplified flow diagram for a three-stage cryocondensation operation to collect or freeze out vinyl acetate and water along with ethylene.

**Fig. 10: Simplified flow diagram for three-stage cryocondensation**

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1. Liquid nitrogen (LIN)
2. Emission source
3. Process gas
4. Clean gas
5. Gaseous nitrogen (GAN)
6. Condensate
7. Re-use
8. Inerting
9. Environment
In a typical application, ethylene is to be reduced to a few percent by weight in the exit gas and the recovered ethylene recycled to the production process. After its cooling energy has been utilised, the nitrogen can be used for inerting purposes, either directly or via an existing nitrogen network, thereby securing additional value. Retrofitting of fully assembled cryocondensation units into existing plants is generally a simple, quick operation. Pilot systems for such applications are available (see fig. 11), e.g. for trial operation on site.

The recovery of hydrocarbons from exit gases offers two benefits. Firstly, environmental impact is reduced because much less carbon dioxide is produced than when exit gases are oxidised by incineration according to the usual procedure, that is, in most cases using additional fuel gas. Secondly, there is a high potential for economic gain because, in an example of ethylene recovery, plant investment for cryocondensation equipment is amortised within 0.5-2 years.
Acetylene.

Acetylene, an endothermic compound which is energetically costly to produce, was long ago supplanted by ethylene as a C₂ source for basic chemistry. Steam crackers producing ethylene also generate acetylene as a by-product. As a rule, the acetylene is hydrogenated to ethylene as part of the process, but at a few crackers it is isolated by gas scrubbing and thereby recovered as a vendible pure gas fraction. Acetylene is also obtained by pyrolysis of a wide range of hydrocarbons such as methane or crude oil and, not least, by hydrolysis of coal-based calcium carbide.

In western countries, it is only in exceptional cases that ideal site conditions combined with other favourable factors justify acetylene-based production of commodity chemicals such as butanediol [24] or vinyl acetate monomer [25]. On the other hand, in regions that have abundant and cheap coal – which can serve both as the energy source and the carbon feedstock – acetylene can still be an interesting C₂ source. This is the case especially in China, where, for example, the carbide/acetylene route to vinyl chloride monomer is actually outshining the globally dominant production technologies based on ethylene [26].

A very large amount of energy is stored in the acetylene molecule. This, along with other properties of the gas, calls for careful handling in accordance with regulations. For major demand, as common in petrochemistry, the gas can be delivered by pipeline from a nearby generation plant.

Gas supply systems.

In general, the opportunities in gas generation and supply are varied, and optimal economics depend on many conditions. Table 2 sums up the optimal choices among gas supply systems for most applications [4]:

Table 2: Gas supply systems

<table>
<thead>
<tr>
<th>Gas</th>
<th>Flow rate, Nm³/h</th>
<th>Purity, vol. %</th>
<th>Plant type</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>Up to 800</td>
<td>&gt; 99.9</td>
<td>Shipment by trailer</td>
<td>Gas or liquid, such as for hydrogenation at startup</td>
</tr>
<tr>
<td></td>
<td>100 to 100,000</td>
<td>&gt; 99.9</td>
<td>PSA, on-site plant</td>
<td>Recovery from (refinery) off-gases; load range typically 30–100%</td>
</tr>
<tr>
<td></td>
<td>300 to 200,000</td>
<td>&gt; 99.9</td>
<td>Steam reformer plus CO shift (see equ. (3)) plus PSA, on-site plant</td>
<td>Load range typically 50–100%</td>
</tr>
<tr>
<td>N₂</td>
<td>0 to 1,000</td>
<td>&gt; 99.99</td>
<td>Shipment by trailer/truck</td>
<td>Liquid supply from tank, esp. for widely fluctuating demand</td>
</tr>
<tr>
<td></td>
<td>50 to 1,000</td>
<td>&lt; 99</td>
<td>N₂ membrane, on-site plant</td>
<td>Load range typically 30–100%</td>
</tr>
<tr>
<td></td>
<td>100 to 5,000</td>
<td>&lt; 99.5</td>
<td>N₂ PSA, on-site plant</td>
<td>Load range typically 50–100%</td>
</tr>
<tr>
<td></td>
<td>200 to 300,000</td>
<td>&gt; 99.99</td>
<td>Cryogenic air separator, on-site plant</td>
<td>Liquid supply from tank, even for widely fluctuating demand</td>
</tr>
<tr>
<td>O₂</td>
<td>0 to 1,000</td>
<td>&gt; 99.5</td>
<td>Shipment by trailer/truck</td>
<td>Load range typically 50–100%</td>
</tr>
<tr>
<td></td>
<td>300 to 5,000</td>
<td>&lt; 94</td>
<td>O₂ PSA (VPSA), on-site plant</td>
<td>Load range typically 70–100%; largest GOX production volumes for gasification units</td>
</tr>
<tr>
<td></td>
<td>1,000 to 120,000</td>
<td>&gt; 99.5</td>
<td>Cryogenic air separator, on-site plant</td>
<td></td>
</tr>
</tbody>
</table>

The maximum gas flow rates listed above are not fundamental limits and may be exceeded in particular cases.
Fig. 12: Two steam reformer units producing H₂ from natural gas at Burghausen (Bavaria)
Fig. 13: PSA system for purification of hydrogen (in the background) and CO$_2$.

Fig. 14: Cryogenic air separation units with large capacities for gaseous oxygen and nitrogen production are often associated with big petrochemical clusters; here with tanks containing liquefied gas products at Stenungsund (Sweden).
In years to come, the petrochemical industry will see the effects of the following trends:

- Intensification of petrochemical processes including those in the industrialised countries, e.g. higher capacities, fewer production steps, enhanced product selectivities
- Construction of large new petrochemical complexes in the newly industrialising countries
- A shift of production sites from Europe and North America toward market areas and locations with sources of fossil feedstocks
- Increasing employment of renewable feedstocks and use of biotechnological production processes
- Increasing use of coal, oil sand resources and light hydrocarbons also as a chemical feedstock
- Optimisation of production units with respect to energy conservation and reduction of CO₂ footprint
- More and more stringent environmental protection standards also in developing countries

These changes will also affect the use of industrial gases. For example, larger and more energy-efficient gas generators will come into service. The demand for individual gases will also show differential growth, with the greatest anticipated potential in the demand for hydrogen and oxygen (by total replacement of air or oxygen enrichment). The world demand for gases in petrochemistry is expected to grow most of all in the newly industrialised and developing economies.
References.


[23] "PAM – Program", proprietary development of the Linde AG.


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