Oxygen enrichment in the petrochemicals industry

Adding oxygen enrichment to oxidation reactions in the petrochemicals industry offers a reduced carbon footprint, productivity benefits, and cost efficiencies

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Growing climate change pressures are focusing the spotlight on the need to decarbonise many sectors of industry, particularly those that are energy intensive and/or rely on fossil fuels. The petrochemical industry is a case in point. All petrochemical value chains rely on crude oil. In addition, energy-intensive oxidation processes are often required.

Many operators would thus welcome an opportunity to improve their carbon footprint overall, especially if this came with the added bonus of greater capacity, improved hydrocarbon conversion efficiency, and a lower energy bill. In many instances, this can be achieved without heavy investments in new equipment. The answer often lies in something as simple as oxygen enrichment. Adding oxygen can also give operators the flexibility they need to respond to fluctuations in demand and overcome seasonal bottlenecks, resulting, for instance, from diminished air blower performance and greater off-gas abatement needs in warmer months.

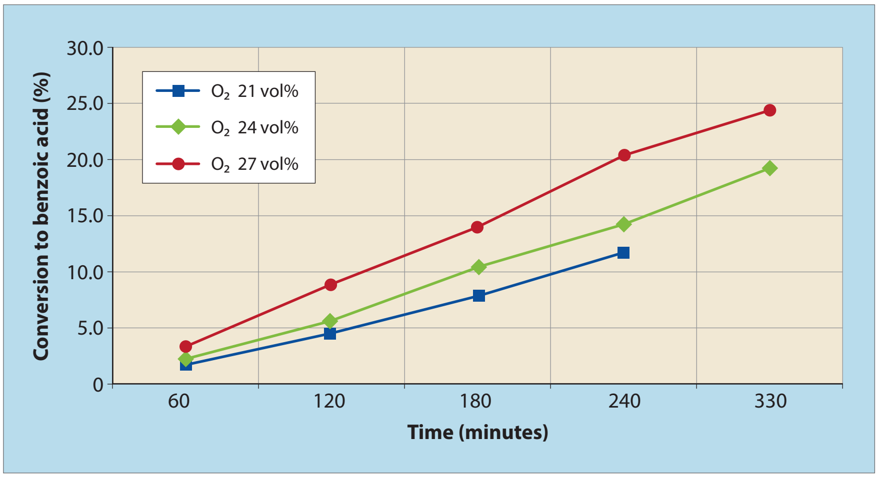

Figure 1 Conversion to benzoic acid in toluene oxidation (160°C, 9 bar)

Oxygen enrichment

Oxidation processes in refining and petrochemistry typically rely on the oxygen in ambient air. However, this is not particularly efficient as ambient air contains 78.8% nitrogen. This inert nitrogen 'ballast' has to be routed through the various process steps, thus increasing the compressing, heating, cooling, and blowing effort.

Replacing or enriching this air with oxygen increases the partial pressure of oxygen and reduces the process gas flow. This has multiple knock-on effects including gains in capacity and energy efficiency. This technology is widely established and successfully deployed for sulphur processing in Claus units, for instance, and for regenerating in fluid catalytic crackers (FCC). However, the benefits of oxygen enrichment are not restricted to refining and base chemicals. Increasingly, it is also being seen as a way for petrochemical companies to safely decarbonise their operations while boosting throughput.

Intensifying petrochemical processes with oxygen

In the petrochemical industry, catalytic air oxidation in the gas/liquid phase is used in the manufacture of intermediates and commodities such as terephthalic acid (PTA), acetaldehyde, phenol/acetone, cyclohexanone, and benzoic acid. They are also used in the production of fine and specialty chemicals and to heat feed streams, condition catalysts, and treat waste streams.

Experience in industrial scale plants has shown that the ambient air used for these processes can be enriched with oxygen – generally up to a maximum oxygen concentration (MOC) of 28 vol% – at minimal expense and without compromising on safety. This has the effect of intensifying the oxidation process and reducing unnecessary ballast in the process air.

Typical petrochemical reactions

In the following, we will take a closer look at how oxygen enrichment can benefit two gas/liquid oxidation reactions, namely toluene to benzoic acid and p-xylene to PTA. Benzoic acid is a commercial as well as an intermediate product used in the food and pharmaceutical industries. The oxidation of toluene with air in the liquid phase is the most important step in the benzoic acid manufacturing process. It typically takes place at temperatures between 120°C and 180°C, at pressures of up to 10 bar and with a catalyst such as cobalt naphthenate.

Field trials have shown that by enriching the oxygen concentration

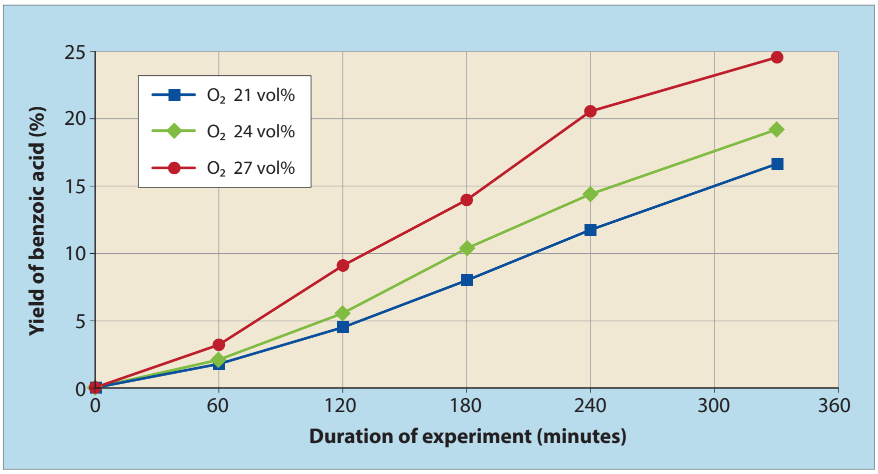

Figure 2 Measured impact on benzoic acid yield of oxygen content in oxidation gas (160°C, 9 bar)

in the process air from 21 vol% to 24 vol% or 27 vol%, the reaction speed and rate of conversion can be significantly accelerated at temperatures between 140°C and 160°C and a pressure of 9 bar. Selectivity can be increased and the oxygen content in the off-gas quickly drops to a very low level (see **Figures 1** and **2**).

PTA is a PET (polyethylene terephthalate) intermediate in huge demand worldwide. Here, oxygen enrichment is widely used to increase the oxygen concentration in the process air to between 23 vol% and 28 vol%. Experience has shown that this can boost capacity by anything from 12% to 30% while also reducing flue gas volumes considerably (see **Figure 3**).

Similar benefits have been observed with oxidations in fluidised beds, typically for reactions such as converting propylene and ammonia to acrylonitrile, ethylene dichloride (EDC) to vinyl chloride monomer (VCM)/polyvinyl chloride (PVC), and butane to maleic anhydride (MA).

Advantages of oxygen enrichment

Oxygen enrichment in petrochemistry offers a number of advantages beyond mere process intensification. These can typically be divided into decarbonisation, capacity, and cost gains.

Smaller carbon footprint

- Reduction in carbon emissions and in off-gas streams thanks to lower process gas flow
- Lower energy bill for heating and cooling steps, resulting in a better carbon balance for emissions trading
- Option of using off-gas – often with a higher energy content – as a fuel for waste abatement

Productivity benefits

- Fast, flexible way to increase plant throughput, also enabling seasonal debottlenecking during hot weather periods where air density is lower and air blowers/compressors may be struggling to provide sufficient process air
- Higher plant availability due to reduced strain on process equipment
- Increased conversion and selectivity, so more product can be extracted from the feed, thus also reducing waste and low value products

Cost efficiencies

- Cost savings for feedstock thanks to higher hydrocarbon yield and lower losses
- Energy savings for heating as the accelerated reaction speed means a lower temperature is required
- Reduced waste stream abatement effort with less fuel needed for off-gas incineration
- Flexible way to circumvent the need for capex-heavy investments in new equipment such as air blowers to increase capacity
- Low capex, easy retrofit option for existing plants
- Reduction in capex for new plants due to smaller equipment footprint

Safety matters

Despite the compelling advantages of oxygen enrichment, many petrochemical players are reticent to choose this avenue due to perceptions and reservations around oxygen safety. Like all oxidation reactions, safety is of course paramount in oxygen-enriched reactions.

Issues to be avoided include uncontrolled and runaway reactions due to local temperature excursions, flammable gas phases of a sizeable volume, gas bubbles (which explode) with oxygen concentrations above the conversion threshold, potentially dangerous operating conditions when oxidation reactors are started up and powered down, and oxygen-enriched air temperatures above those of the reaction when the air enters the reactor.

However, the technology to overcome these risks and ensure smooth, safe operations is available and already proven in the field,

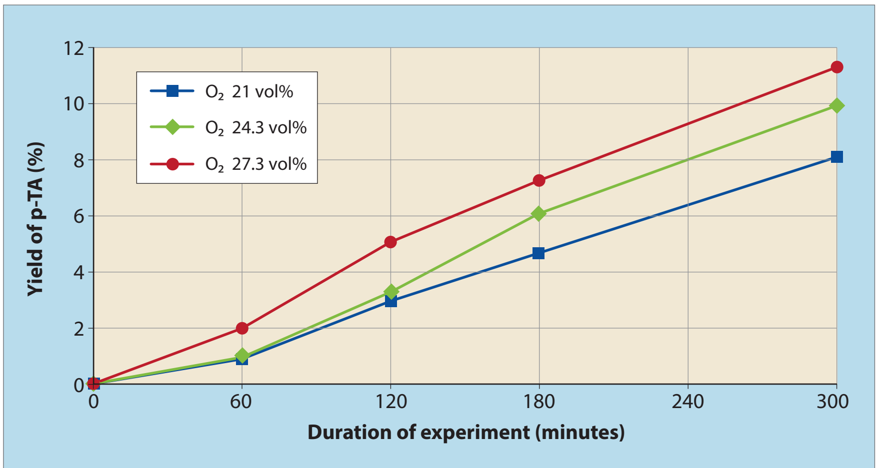

Figure 3 Relationship between yield of PTA and oxygen content in the oxidation gas

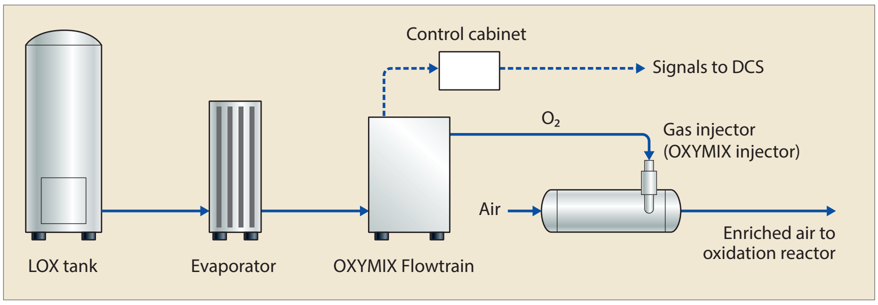

Figure 4 Arrangement for the installation of an Oxymix Injector

successfully deployed in various petrochemical plants, upstream petrochemical processes such as FCC, and in Claus units. Key safety requirements include a flow control valve enabling rapid, even mixing of the oxygen feed upstream of the reactor; a flow control cabinet ensuring the oxygen content remains under the MOC; various safety features such as block-and-bleed valves to cut off the gas supply in the event of an emergency; piping temperature control to make sure that cold oxygen does not enter the air duct; and complete disconnection of the gas supply from the processing plant during shutdowns (with gas creep safeguards).

Industrial gas specialists such as Linde Gas have developed robust safety concepts addressing all of these concerns and issues. With extensive experience in the design and delivery of oxygen enrichment applications and a proven track record in the safe handling and metering of oxygen across different supply modes, the company specialises in fail-safe oxygen injection technologies tailored to safety-critical applications, and in reliable measuring and control equipment. In addition to its Oxymix Injector and Oxymix Flowtrain gas control cabinet, both designed for precise, even and rapid metering and mixing of the oxygen within a short distance to avoid hotspots and runaway reactions, the company offers extensive feasibility assessments and field trials, project execution services, plus maintenance and gas supply services to ensure all-round peace of mind.

Oxygen enrichment in action

Drawing on its experience in low, mid and high level oxygen enrichment applications, Linde supplies a low risk, low investment and short payback solution for debottlenecking challenges in petrochemical plants. The Oxymix Injector has already been successfully deployed under various operational conditions in over 100 oxygen enrichment projects worldwide. Multiple reference projects also attest to the safety, efficiency and climate mitigation benefits of enrichment technology in the petrochemical industry.

Case study: toluene to benzoic acid

A leading global specialty chemicals company uses oxygen enrichment technology from Linde for the oxidation of toluene to benzoic acid. Linde's technology has helped to increase the throughput and improve the quality of the product by increasing selectivity (more of the feed is reacted to the desired product).

Linde initially presented lab results to the customer as proof-of-concept. Linde went on to offer a full-scale test at one of the two production lines to validate the lab results in an operating environment. Prior to testing, Linde supported a HAZOP study to demonstrate that the safety concept it presented was robust. During a regular shutdown of the plant, the Oxymix Injector was installed. The injector was connected to a mobile trailer with an evaporator and a test Oxymix Flowtrain oxygen control unit (see **Figure 4**).

The results of the one-week test in June 2019 were so promising that the chemicals company ordered a permanent installation for this first line a few weeks later. This went on stream the following December. The oxygen enrichment solution met all quality requirements due to higher selectivity and increased throughput, leading to an order for an oxygen enrichment installation for a second line in summer 2020. This started up in January 2021.

To accelerate rollout, Linde provided the customer with two test Oxymix Flowtrain units while they waited for the ordered equipment to arrive. The customer was thus able to start immediately with oxygen enrichment and produce more product at higher quality earlier than expected.

Case study: p-chlorotoluene oxidation as a fine chemistry intermediate

Another global specialty chemical company was looking to improve the efficiency of certain reactions, specifically the production of an intermediate chemical to manufacture a special red dye pigment. The reaction takes place in a fluidised bed reactor. These reactors are ideal for oxygen enrichment as the mixing action inside the reactor is intensive. This results in even temperature distribution and the avoidance of hotspots.

In May 2019, Linde performed oxygen enrichment tests on-site and these proved successful. After one month, the customer asked if it could borrow the test equipment to operate the reactor with oxygen enrichment until a permanent solution could be installed. Linde was able to provide mobile oxygen supply equipment and a test Oxymix Flowtrain enabling the company to switch over to oxygen enrichment almost immediately.

Case study: EDC as intermediate for PVC

The VCM oxyreactor installed at one of the sites of a global chemicals company was running close to design capacity without oxygen enrichment. The company was keen to increase throughput beyond design capacity. It turned to Linde for an oxygen enrichment solution to achieve this. The plant is now able to exceed design capacity using about 1 t/h of oxygen. The addition of oxygen enrichment to the VCM oxyreactor enables the company to react with speed and flexibility to changing market demands by adapting production on demand.

Case study: p-xylene to PTA as PET intermediate

For several years, Linde has been supplying one of the world's leading producers in the intermediate petrochemicals industry with oxygen to overcome productivity constraints in the manufacture of PTA. The company awarded the contract to Linde based on the ease of integration and robust safety concept for oxygen injection and control of the Oxymix injector concept and the Oxymix Flowtrain oxygen supply equipment.

OXYMIX is a mark of Linde Gas.

Heinz-Dieter Obermeyer is Senior Expert, Application Technology for Chemicals and Refining with Linde Gas. A chemical engineer, he has worked for Linde for 27 years and is responsible for developing hardware for oxygen enrichment, including Linde's Oxymix Flowtrain and Oxymix Injector which received a patent and has been installed in over 100 furnaces worldwide. He holds a diploma and a PhD from the Technical University of Munich.