Industrial gases integration with petrochemicals processing

The roles of oxygen and CO_2 in ethylene oxide production

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Ethylene oxide (EO) production is one of the best examples of deep integration between the petrochemical and industrial gases sectors. In the presence of a catalyst, oxygen reacts with ethylene to produce ethylene oxide and yields carbon dioxide (CO_2) as a co-product.

CO_2 capture is essential in ethylene oxide production to avoid an accumulation of CO_2 in the reactor gas recycle loop. This CO_2 can be liquefied and sold to commercial applications.

The oxygen for EO production can be drawn in from the air, in which case four times the volume of nitrogen is brought into the process. This nitrogen is an inert ballast gas that plays no valuable role in the chemistry. To accommodate this volume of nitrogen, the equipment and piping must be very large.

On the other hand, if pure oxygen is used instead of air, the equipment for ethylene oxide production can be right-sized. The savings in the ethylene oxide plant are greater than the cost building an air separation plant. An

Steam cracker to produce ethylene

PET bottles

analogy is the difference between pre- and post-combustion capture of CO_2. In the case of pre-combustion CO_2 capture, nitrogen from combustion air is avoided and the equipment can be smaller.

Ethylene oxide applications and markets

Around 20 million tonnes of EO are produced each year. The EO molecule (CH_2OCH_2) is a cyclic ether and reacts easily to form other hydrocarbons. The majority of this EO is converted to monoethylene glycol (MEG) and polyethylene glycol (PEG) which is an antifreeze and is sprayed onto aircraft prior to take off to prevent ice build-up on the wings and fuselage.

MEG is the precursor for the plastic PET, which is commonly used to make drinks bottles and polyester fibres for textiles. EO can also be converted to ethanolamines, which are used as solvents for post-combustion CO_2 capture.

EO is an important product in the packaged chemicals gases sector. The US company Balchem, and their Belgian subsidiary Chemogas are leaders in the repackaging of ethylene oxide into drum tanks. These are used by manufacturing companies to sterilise products such as syringes and bandages for delivery to hospitals and the pharmaceutical sector.

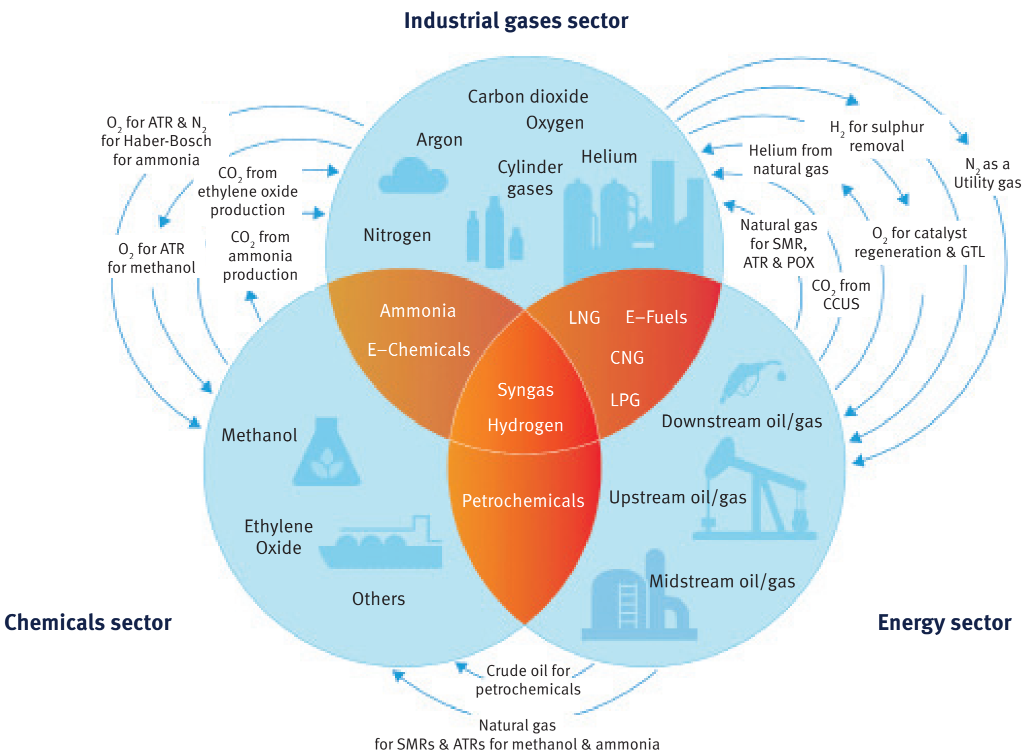
Smaller users, such as hospitals that wish to sterilise surgical instruments for reuse would typically purchase cylinders of 10% EO blended with nitrogen. These can be coupled directly to sterilising units. EO sterilisation takes place at around 50 °C and is more suitable for sensitive instruments that could be damaged by the heat or moisture of high temperature sterilisation with pressurised steam which takes place at 120 °C.

“EO is an important product in the packaged chemicals gases sector”

Air separation units for EO production

The modern process to produce ethylene oxide (EO) combines pure oxygen from an air separation unit (ASU) with ethylene. The ethylene is generally produced on a steam cracker unit from crude oil or ethane, which is a component of many natural gas streams. The reaction takes place at around 20 bar pressure and 250 °C.

Product overlaps and gas flows in the energy, chemicals & industrial gases sectors



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Handling ethylene oxide

The ethylene concentration in the reactor ranges from 35% by volume at the inlet to 25% at the exit. Ethylene is an extremely flammable gas and to prevent an explosive condition, the oxygen concentration must be limited to less than 10% by volume. To increase the safe amount of oxygen that can be used in the reactor, dilutant gases such as nitrogen, argon, methane, or ethane are added to the reactor feed gas.

In 2019, Linde started up two ASUs to supply oxygen and nitrogen to Taixing Jinyan Chemical Technology Co Ltd to support the production of ethylene oxide. The plants have a total combined production capacity of 29,000 Nm3/h and also supply air gases to other customers in the Taixing Economic Development Zone, one of China's largest chemical parks.

Dow's second largest chemicals complex worldwide is at Terneuzen in the Netherlands. 195,000 tonnes per year of EO can be produced at this chemicals park, which is shared with Trinseo who focus on aromatics. Air Liquide operates an ASU there to provide 350 tonnes per day of oxygen to the EO plant. The ASU was originally built and operated by BOC Gases in the last century. The EO plant emits around 130 tonnes per day of CO_2.

Catalysts – the silver bullet

In addition to being the world's second largest producer of EO, The Dow Chemical Company produces the METEOR™ EO-RETRO 2000 (MR2000) catalyst for EO production. MR2000 was selected by MEGlobal Oyster Creek for their EO production facility that started up in 2020. Linde operates an ASU to supply oxygen to the MEGlobal EO plant and also recovers, purifies and liquefies CO_2 captured from the EO process for distribution into the local market.

Shell is also a major EO producer. More than 50% of the EO produced worldwide uses Shell catalysts. Shell Catalysts & Technologies has been innovating and producing EO catalysts for more than 80 years.

The catalyst used for EO production is based on silver oxide catalyst mounted on an alumina support. EO catalysts are characterised by several performance factors, including conversion, selectivity, activity, productivity, and stability.

Selectivity represents the amount of ethylene converted to EO compared to the total amount of ethylene reacted to EO, CO_2 and other hydrocarbons.

Conversion refers to the amount of ethylene that reacts during each pass over the catalyst. Since the conversion is not complete, gases leaving the reactor are recycled back through the reactor to ensure the valuable feedstock is fully utilised.

Whist the role of the catalyst is to selectively produce EO, some CO_2 formation during the reaction is inevitable. Since the some of the reactor outlet gases are recycled to the reactor inlet maximise the conversion of ethylene, CO_2 must be removed from the process to avoid accumulation. This is achieved with a CO_2 capture loop using hot potassium carbonate (HPC) as the solvent.

Integrated CO_2 capture

Gases leaving the EO reactor are generally at around 20 bar and contain around 4% of oxygen and 8% CO_2. Luigi Tomasi, General Manager at Giammarco-Vetrocoke in Venice says that "HPC is ideal for selectively removing CO_2 from high pressure gas mixtures such as this. Unlike amine-based CCS solvents, HPC is not degraded by the oxygen present in this stream."

The equipment to capture CO_2 is generally a twin tower system. In the first tower, which operates at high pressure, CO_2 is absorbed into the HPC solvent. The high pressure helps to drive the gas into the liquid. Prior to entering the second tower, the pressure of liquid containing the gas is reduced, or flashed. This releases much of the CO_2 without the need to apply heat energy.

The solvent loaded with CO_2 is boiled at the base of the second tower to drive out the CO_2. This is where the energy to the CO_2 capture process must be applied. The regenerated solvent from the base of the second tower is pumped up to the pressure where it can enter the first tower to absorb more CO_2.

Tomasi adds that "Giammarco-Vetrocoke has implemented a three tower HPC-EcoEnergi™ configuration on multiple reference plants, achieving improvements in energy efficiency of more than 30%. As a further innovation, our HPC-NovaFlash™ configuration to achieve an extra efficiency improvement of up to 10%".

The gas leaving the CO_2 stripper column is rich in CO_2, with water vapour being the main additional component. Much of the water vapour can be removed simply by cooling followed by and gas / liquid phase separation in knock-out drum. This stream is ideal to feed directly to a CO_2 liquefier.

Beyond its application in EO production, HPC is commonly used to capture CO_2 from steam methane reformer (SMR) syngas, which is at a similar pressure to the EO process. CO_2 must be removed in this application prior to the hydrogen being used for ammonia production. "There is no oxygen in the SMR syngas stream", injects Tomasi, "so we can

"The gas leaving the CO_2 stripper column is rich in CO_2, with water vapour being the main additional component"

add some organic promoters such as ethanolamine to the HPC solvent to increase the CO_2 capture rate in this application."

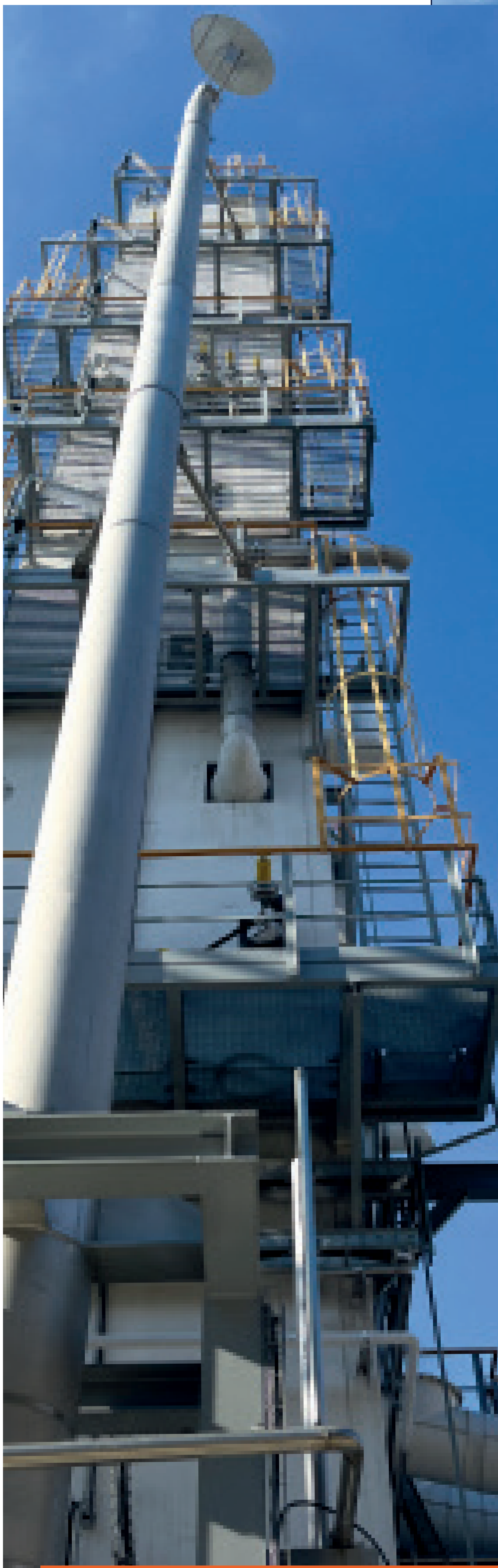
CO_2 capture from EO production in GCC countries

Gulf Cryo, a leading industrial gases company in the GCC region, obtains CO_2 from one of Equate Petrochemical Company's ethylene glycol (EG) plants in Kuwait's Shuaiba Industrial Area. Equate is owned by the Dow Chemical company and three Kuwaiti entities. A pipeline of several hundred metres transfers raw CO_2 from the stripper column on the EG plant to the Gulf Cryo site where it is dried, liquefied and purified using cryogenic distillation.

When the CO_2 capture and liquefaction process was commissioned in October of 2014, it became the first CO_2 Capture project in Kuwait. The facility has the capacity to liquefy 55,000 tonnes of CO_2 per year and cost USD16.5 million.

Gulf Cryo also operates a CO_2 capture and liquefaction facility at Petro Rabigh in Saudi Arabia. The plant was brought into operation in 2023 and was the first CO_2 capture plant in the Western Region of Saudi Arabia.

The plant captures CO_2 from a MEG plant which is located at Rabigh Petrochemical cluster in Saudi Arabia. The facility can capture 100,000 tonnes per year of CO_2. Some of this is supplied via pipelines to internal processes at the Petro Rabigh site, and the remainder is liquefied and supplied to industrial and commercial applications. gw



Air separation unit for oxygen production