Propylene Oxide

The hydrogen peroxide to propylene oxide (HPPO) process using propene and hydrogen peroxide as the feedstocks is the result of co-operation between Evonik Industries and ThyssenKrupp Industrial Solutions. The Evonik-Uhde HPPO technology: Innovative · Profitable · Clean

Over 15 years of successful co-operations
Content

05  Overview
07  Fundamentals of propylene oxide
08  General process description
09  Process highlights
10  Process description of the new Evonik-Uhde HPPO technology
Engineering Excellence – Think globally, act locally

Having erected several thousand plants, ThyssenKrupp Industrial Solutions is one of the world’s leading engineering companies. Our Business Unit Process Technologies supplies chemical plants, refineries and coking plants on the basis of tried-and-tested technologies made by Uhde, while the portfolio of the Business Unit Resource Technologies comprises complete cement plants and grinding systems of the Polysius brand, as well as machines, plants and systems for mining, extraction, preparation, processing or transshipment of commodities.

With many years of experience in the EPC business, we offer our customers concepts, market studies, plant layouts, design engineering, supplies, manufacturing services, erection and commissioning – all from a single source. Our employees on all continents use their knowledge and engineering competence to create innovative solutions and to look for ways to conserve natural resources.

Over 40 locations in 25 countries – divided into six regions – form a close-meshed network that allows us to align our services to local conditions consistently. Thanks to this on-site expertise and global networking, we are able to set standards that offer our customers a true competitive edge.

Our comprehensive service concepts take the entire life cycle of a plant into account. We offer OEM spare parts service and complete maintenance management, as well as servicing, modernisation projects and conversions.
\[ \text{TS-1} \quad \text{MeOH} \quad \text{H}_2\text{O} \quad \text{>95%} \]
Overview

Evonik and ThyssenKrupp Industrial Solutions have jointly developed a co-product-free process for the production of propylene oxide (PO) via hydrogen peroxide. Apart from the economic benefits, it offers numerous further advantages compared with current state-of-the-art processes.

In 2001, Evonik and ThyssenKrupp Industrial Solutions announced an exclusive partnership for the development of the new process. Evonik investigated the process and developed a catalyst optimised for the particular purpose, while ThyssenKrupp Industrial Solutions contributed its expertise in process engineering and the design and construction of chemical and other industrial plants. At Evonik’s site in Hanau-Wolfgang (Germany), experts from the two companies further optimised the process parameters in a mini plant which included all recycle streams and reflected the complete production process. Since 2008 the Evonik-Uhde HPPO technology has been in successful commercial operation and has proven itself in the first plant of its kind at SKC in South Korea, which capacity has been expanded to 130,000 t/year in 2012. Evonik and ThyssenKrupp Industrial Solutions have been awarded by JiShen Chemical Industry Co, Ltd. to build a 300,00 t/year HPPO plant in Jilin City, Jilin Province in P.R.C., which has been started up in 2014.

The Evonik-Uhde process yields PO from propene and hydrogen peroxide ($\text{H}_2\text{O}_2$) using a special titanium silicalite (TS-1) catalyst. The advantages of the new process are clearly apparent. Operation will be more cost-efficient than the production processes currently used for PO, especially in view of significantly lower capital investment costs which allow the investor to be more flexible in his investment decisions. In addition, the new process is environment-friendly, it is highly efficient and the only co-product obtained is water. Moreover, feedstock consumption is low due to high specific yields (>95% of propene).

The advantages of the Evonik-Uhde HPPO technology:

- co-product-free
- efficient raw material consumption
- high-performance catalyst with long lifetime
- low investment costs

The new technology is licensed by Evonik and ThyssenKrupp Industrial Solutions and both plants, $\text{H}_2\text{O}_2$ and PO will be built by ThyssenKrupp Industrial Solutions as the contracting and engineering partner for both technologies. As the preferred supplier, Evonik will supply the $\text{H}_2\text{O}_2$ “over the fence” to the PO plant.
Figure 1: Main applications of PO/world consumption of PO in percent

Propylene oxide
Main applications

66% Polyether polyols
polyurethanes (PUR), flexible and rigid foam

17% Propylene glycols (PG)
polyester, pharmaceuticals, cosmetics

17% Others
Propylene oxide (PO), C₃H₆O, is a colourless, low-boiling liquid of high reactivity and is now one of the most important chemical intermediates, especially for the polyurethane and solvents industry. Its polarity and strained three-membered epoxide ring allows it to be opened easily by reaction with a wide variety of substances. Since the early 1950s it has become increasingly important for the chemical industry. As of 2013, around 8 million metric tons of PO is produced worldwide, with consumption rates outstripping GDP growth rates.

PO is a bulk chemical primarily used for the production of polyurethane precursors namely polyether polyols, as well as for propylene glycol and glycol ethers. Polyurethanes are used in a wide range of applications, including automobile components, furniture upholstery, thermal insulation, coating materials, sports shoes and sporting goods.

At present, two thirds of PO output is used for the production of polyether polyols, followed by about 17% for propylene glycols (PG) and about 17% for propylene glycol ether solvents and others.
The new Evonik-Uhde HPPO technology for the production of propylene oxide via $\text{H}_2\text{O}_2$ is shown in figure 2. The highly exothermic process takes place under relatively mild process conditions.

In the reaction unit, the catalytic epoxidation of propene is carried out in the presence of a titanium silicalite catalyst using hydrogen peroxide ($\text{H}_2\text{O}_2$) in methanol as the solvent. The focal point of the development was the epoxidation reactor for the synthesis of PO using a fixed-bed reaction system which operates at elevated pressure and moderate temperature. The special design combines an intense heat transfer with an almost ideal plug-flow characteristic, resulting in a high PO selectivity.

The quality and characteristics of the hydrogen peroxide have a substantial influence on the process parameters. Evonik has developed a grade of hydrogen peroxide specifically designed for use as an oxidising agent in the epoxidation of propene.

Polymer-grade or chemical-grade propene can be used as feedstock. If chemical-grade propene is used, propane is separated from propene in an integrated propene rectifier.

The propene cycle of the PO plant is totally closed and the surplus propene recovered is returned to the reaction section.

The crude PO contains some impurities which are removed in the PO purification section by state-of-the-art rectification under moderate conditions.

Water and small amounts of by-products are removed in the methanol processing section and the purified solvent is recycled to the reactor.
Advantages of the new technology:

• Co-product-free process
• Epoxidation reactor specially designed for highly exo-thermic reaction conditions combines an efficient heat transfer with an almost ideal plug-flow characteristic
• High-performance catalyst with a long lifetime
• The process is free of chlorine
• Optional use of polymer-grade or chemical-grade propene feedstock

Economic benefits:

• Lower capital investment and energy consumption compared with state-of-the-art PO technologies
• High specific yields resulting in low feedstock consumption
• Stand-alone technology: no market dependency on co-products

Environment-friendly production:

• Totally closed solvent and feedstock cycles
• Valuable by-product are recovered from the waste water (approx. 37 kg propylene glycol per ton of PO)
• The energy balance of the entire plant is optimised by anaerobic waste water treatment (credit of approx. 220 kg steam at 20 barg per ton of PO)
• All off-gas streams from the PO plant can be treated using state-of-the-art technologies. If chemical-grade propene is used, the surplus propane can be used as an additional energy source.

Expected consumption figures:

• Propene (at 100%) < 0.77 kg/kg PO
• Hydrogen peroxide (at 100%) < 0.69 kg/kg PO
• Steam < 3.30 kg/kg PO
• Electricity 240 kwh / to PO

Propylene oxide product specification:

• PO purity by GC (dry basis) min. 99.97
• Water (wt.ppm) max. 100
• Aldehydes, total (wt.ppm) max. 50
• Colour, Pt-Co (APHA colour) max. 10
Process description of the new Evonik-Uhde HPPO technology

Reaction

In the PO reaction process, the reaction of propene (C₃H₆) and hydrogen peroxide (H₂O₂) takes place in a methanol/water mixture using a fixed-bed reactor with a special titanium silicalite catalyst (TS-1 type).

\[
\text{C}_3\text{H}_6 + \text{H}_2\text{O}_2 \rightarrow \text{C}_3\text{H}_6\text{O} + \text{H}_2\text{O}
\]

The process is characterised by mild process conditions with temperatures below 100°C leading to low formation of by-products. The pressure in the reaction unit is about 30 bar.

Due to the optimised process parameters, a high propene-based PO selectivity of more than 95% can be obtained.

The heat of the highly exothermic reaction is removed by an integrated cooling system. After reaction, the product mixture containing mainly methanol, water, propene and PO is withdrawn from the reactor and depressurised to a pressure slightly above atmospheric pressure.

Propene recycling

The product mixture leaving the reaction unit is decompressed and heated, resulting in a propene-rich gas phase which is compressed, condensed and returned to the reaction section.

The off-gas, which mainly contains inert compounds and a small quantity of oxygen from the decomposition of the hydrogen peroxide, is withdrawn and delivered to the battery limits.

PO purification

The depressurised liquid product mixture is then transferred to the pre-separation section where PO and dissolved propene are separated from methanol and water. A C₃ stripper removes the remaining C₃ hydrocarbons from the PO/methanol mixture.

The PO distillate is purified in the PO column and the remaining methanol and water as well as the small quantities of impurities are taken off in the bottom product. The PO distillate meets the highest quality standards.

Propene recycling section

Reaction section

Diagram showing the process flow from the reaction section to the propene recycling section, including the reaction of propene and hydrogen peroxide, the separation of PO and propene, and the recycling of propene.
**Methanol processing**

The methanol in the methanol/water mixture withdrawn from the bottom of the pre-separation column and from the bottom of the PO column is separated from the water in the methanol processing section. The emanating overhead methanol stream is returned to the PO reaction section.

The bottom product from the methanol column, which contains water and small amounts of high-boiling by-products, is delivered to the battery limits.

**Purification of chemical-grade propene**

If polymer-grade propene is used as the feedstock, the recycled propene is fed directly to the reaction section. Where chemical-grade propene is used, considerable amounts of propane are continuously introduced into the process with the fresh propene stream. Propane acts as an inert diluent in the reaction system. In order to keep the propane concentration at a constant level, the surplus propane is removed in the propene purification column.

The column increases the propene concentration in the overhead product while the bottom product accounts for the propane balance. The bottom product is sent to the battery limits while the propene stream is returned to the PO reaction section.