Online analysis of peroxide in the HP-PO process

Propylene oxide (PO) is a colorless yet extremely flammable liquid derived from crude oil. PO is used in several industrial applications, but the majority is used to produce polyols which are the building blocks for polyether polyols (e.g., foams, coatings, adhesives) and propylene glycol (e.g., PET bottles, fibers, furniture).

There are several production processes currently available to manufacture PO. Some of these processes create co-products (e.g., chlorohydrin «CH-PO», styrene «SM-PO», and methyl *tert*-butyl ether «MTBE-PO») and others are derivative-free (e.g., hydrogen peroxide «HP-PO» and cumene «CU-PO»). Out of these processes, HP-PO is considered to have the smallest environmental footprint.

This Process Application Note is focused on HP-PO process monitoring of hydrogen peroxide (H_2O_2) online using an explosion proof process analyzer due to the hazardous production environment. Online analysis facilitates a high propylene oxide production yield while reducing costs with low feedstock consumption, as well as ensures a safe working environment for operators working in this highly hazardous process.

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INTRODUCTION

Propylene oxide (PO) is an important intermediate product for several markets because of its wide range of applications that are predominantly used in the polyurethane and solvent industries.

The global production of PO is more than 10 million tons per year [1]. This market is still growing and with it the need for a more cost efficient and environmentally friendly production process. PO production methods are available both with and without byproduct materials (Table 1). Depending on the market for these byproducts, one or more of these processes may be in major use globally at any time.

Table 1. List of propylene oxide production processes categorized by whether they produce co-products or not.

Processes with co-products	Derivative-free processes
Chlorohydrin «CH-PO»	Cumene «CU-PO»
Styrene «SM-PO»	Hydrogen Peroxide «HP-PO»
Methyl *tert*-butyl ether «MTBE-PO»	

The hydrogen peroxide to propylene oxide («HP-PO») process creates PO from propene (C_3H_6) and hydrogen peroxide (H_2O_2) using a titanium silicate catalyst (Reaction 1). This process is preferred over others since it has the smallest environmental footprint compared to all other existing technologies. Additionally, it has been proven to guarantee high yields of PO with only water as a byproduct.

Reaction 1. Overall reaction for the epoxidation of propylene with hydrogen peroxide (HP-PO).

H_2O_2 present in a methanol solvent is used as the *sole oxidizing agent* and is the critical feedstock and key parameter to measure the complete conversion rate to PO. Thus, there is a high demand for accurate and robust online process monitoring throughout the whole HP-PO reaction process.

Considering the dangerous nature of this process, online measurement techniques are key for safety reasons. H_2O_2 can be accurately monitored in the effluent of the **primary reactor** using an online analysis solution designed for extremely hazardous areas (Figure 1).
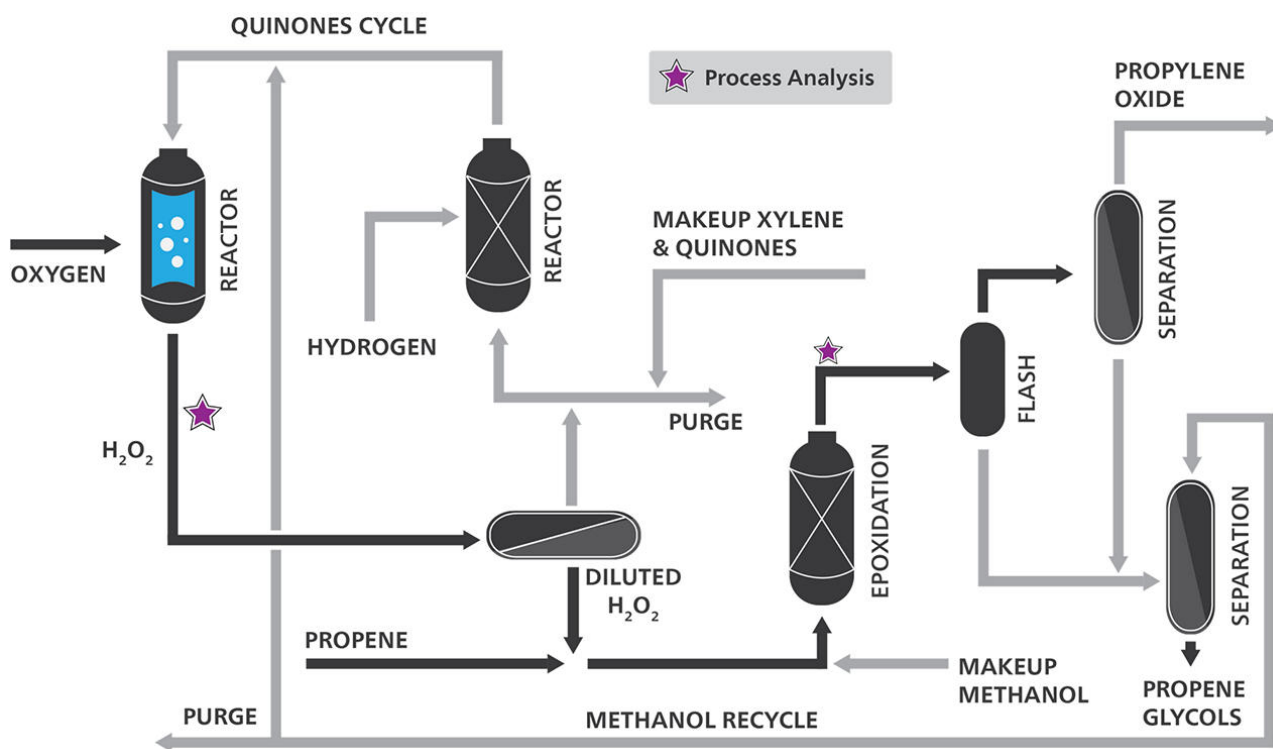
Figure 1. Schematic process diagram outlining the hydrogen peroxide-propylene oxide (HP-PO) method for byproduct-free PO production. Stars note where online process analysis can be integrated for safer, more efficient operations.

Additionally, analyzing the residual H_2O_2 concentrations in **finishing reactor** overheads upstream of the propene recovery section ensures that unreacted hydrogen peroxide is closely monitored for control measures after the epoxidation reactor (**Figure 1**).

Due to the hazardous environment at these production plants, strict safety precautions have to be implemented with all production and process equipment. The **ADI 2045TI Ex proof (ATEX) Process Analyzer** from Metrohm Process Analytics (**Figure 2**) complies to all electrical safety requirements and is specifically designed for high throughput processing in hazardous locations.

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APPLICATION

Hydrogen peroxide is analyzed by using a complexing agent followed by a colorimetric measurement with dipping probe.

Figure 2. The Metrohm Process Analytics ADI 2045TI Ex proof (ATEX) Process Analyzer.

Table 2. Key parameters to monitor in HP-PO effluent streams.

Analyte	Effluent of the primary reactor (%)	Effluent of the finishing reactor (%)
H_2O_2	0–2	0–0.25

FURTHER READING

White Paper: Utilizing online chemical analysis to optimize propylene oxide production
Determination of sulfuric acid in acetone and phenol
Monitoring of 4-tert-butylcatechol in styrene in accordance with ASTM D4590
Inline process monitoring of moisture content in propylene oxide

BENEFITS FOR ONLINE ANALYSIS IN PROCESS

- Protection of company assets with built-in alarms at specified warning limits
- Accurate moisture analysis in hygroscopic sample matrix
- Safer working environment for employees (high temperature and pressures, autopolymerization, ATEX)
- Increased product yield with an optimized production process: more profitability

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REFERENCES

1. Kawabata, T.; Yamamoto, J.; Koike, H.; Yoshida, S. *Trends and Views in the Development of Technologies for Propylene Oxide Production*; Sumitomo Kagaku, 2019; pp 4–11.

CONTACT

Metrohm Brasil
Rua Minerva, 161
05007-030 São Paulo

metrohm@metrohm.com.br

CONFIGURATION

ADI 2045TI Ex proof Analyzer

The ADI 2045TI Ex proof Process Analyzer is used in hazardous environments where explosion proof protection is a critical safety requirement. The analyzer fulfills EU Directives 94/9/EC (ATEX95) and is certified for Zone-1 and Zone-2 areas. The analyzer design combines a purge/pressurization system with intrinsic safety electronic devices. The air purging phase and permanent overpressure prevents any potentially explosive atmosphere in the ambient air from entering the analyzer enclosure. The analyzer smart design avoids the need for purging large analyzer shelters and can be located at the production line in the hazardous zone.

Titration, Karl Fischer titration, photometry, measurements with ion selective electrodes, and direct measurements are all possible with this Ex-p version.

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