PROCESS INSTRUMENTS

APPLICATION NOTE

USE OF TDLAS BASED ANALYZERS FOR REAL-TIME PROCESS CONTROL IN ETHYLENE OXIDE PRODUCTION

Ethylene oxide (EO), which is derived from ethylene, is a high-volume chemical feedstock used to make a variety of other chemicals. The most important, in terms of volume, is the antifreeze agent ethylene glycol, which consumes more than 60% of EO produced.

THE PRODUCTION OF ETHYLENE OXIDE

For maximum yield and safe conditions, EO production requires a sophisticated process control system. Many constituents in the process must be analytically measured in real time. This application note will describe the use of Tunable Diode Laser Absorption Spectroscopy (TDLAS) for the measurement of oxygen (O_2), carbon dioxide (CO_2) and ethylene in the EO production process.

EO is produced by the carefully controlled oxidation of ethylene over a silver catalyst. Controlling the concentrations of the compounds in the reactor and the temperature/pressure is critical. If the conditions are too mild, little EO is produced but, if they are too severe, CO_2 and water are the only products. If silver oxide is used as a catalyst the dominant reaction is formation of EO.

$$C_2H_4 + {}^1/_2\, O_2 \xrightarrow{Ag_2O_2} C_2H_4O$$

Some ethylene still ends up being further oxidized (as much as 25% in some processes) resulting in the production of carbon dioxide and water as main by-products through this reaction.

$$C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O$$

The EO produced represents a small fraction of the total effluent stream leaving the reactor – the majority is unconverted ethylene, so EO manufacturing requires the recycling of ethylene back into the reactor. The limit of conversion to EO during each pass is determined by the oxygen concentration in the reactor. Normally, ethylene concentrations in the reactor are between 20 to 40% by volume. To prevent an explosive condition, O_2 must be limited to less than ~10%. To increase the flammable limit, diluents in the form of nitrogen, argon, methane, ethane or natural gas are added to the reactor mixture.

CO_2 formed in the reaction is mostly removed in the processing of the recycle stream, but can be partially left to act as a diluent. To optimize EO yield, catalyst selectivity can be increased by adding moderators such as 1,2-dichloroethane or vinyl chloride. Typical gas stream compositions for the inlet and outlet of the reactor are shown in Table 1.

Gas Component, mole% or ppm	Reactor Inlet	Reactor Outlet
Ethylene	35	33
Oxygen	8	6
Ethylene oxide	0.01	2.1
Carbon dioxide	2	3
Water	0.2	0.5
Argon	7	7
Nitrogen	3	3
Methane	44.8	44.8
Ethane	0.2	0.2
Ethylene dichloride	0.2 ppm	0.2 ppm
Vinyl chloride	1.2 ppm	1.2 ppm

Table 1. Typical stream composition for the reactor with methane ballast

In the EO production process (Figure 1), EO is recovered from the reactor effluent gases by absorption in aqueous absorbent. It is then stripped from the absorbent and separated from the residual water by fractionation. The aqueous absorbent from the EO stripper is recycled back to EO absorber. The overhead stream containing ethylene and CO_2 is sent to the CO_2 absorber, where CO_2 is partly removed from the recycling gas by absorption in a hot potassium carbonate solution. From the CO_2 absorber overhead the recycle ethylene gas is sent back to the reactor for a new cycle. The absorbent from the CO_2 absorber is sent to a CO_2 stripper where CO_2 is separated and then vented to atmosphere. The potassium carbonate is returned to the CO_2 absorber.

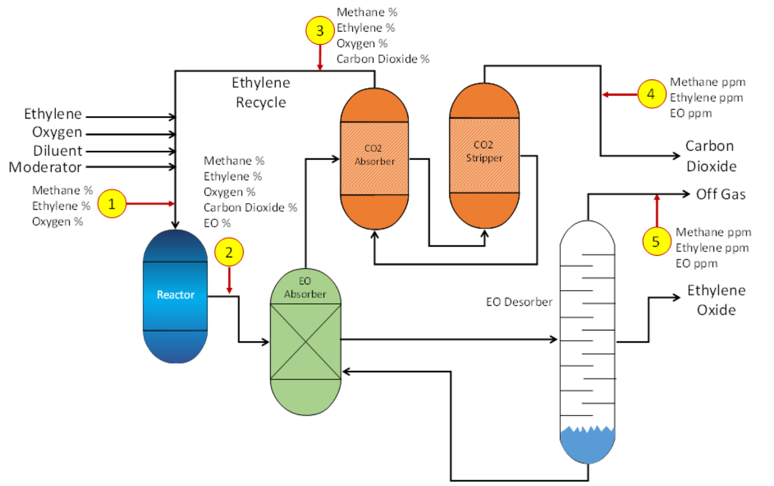


Figure 1. Typical ethylene oxide process with key analysis points

FAST, ACCURATE MEASUREMENT WITH TDLAS TECHNOLOGY

The recycled ethylene gas is sent back to the reactor for a new cycle. The absorbent from the carbon dioxide absorber is sent to the CO_2 stripper where CO_2 is separated and then vented to atmosphere or captured. The potassium carbonate is returned to the CO_2 absorber.

The process is controlled to optimize the conversion of ethylene to EO, but at the same time must assure that there are safe levels of O_2 in the reactor. CO_2 in the reactor outlet consumes valuable ethylene and needs to be minimized through process control. Optimizing the relative concentrations of O_2 and ethylene also requires real-time process analyzers. Historically, EO plant analyzers have included paramagnetic analyzers for O_2 measurements at the inlet and outlet of the reactor, infrared filter photometers for inlet ethylene feed control and Process Gas Chromatographs (PGCs) to measure all of the components of the gas at reactor outlet. Recent advances in TDLAS-based analyzers can provide measurements for closed loop process control for product yield optimization, plant monitoring and alarms, quality control and environmental safety. Obviously, control of the ethylene oxide plant performance cannot be solely limited to TDLAS analyzers. However, there are applications where they can be used very effectively, including measurements of ethylene, O_2 and CO_2.

AMETEK's 5100HD (Figure 2) is an extractive-type gas analyzer designed for hot/wet sample analysis with no requirement for complicated sample conditioning. The 5100HD offers high specificity and sensitivity and uses a sealed reference cell to line-lock the laser on a desired wavelength. Any minor shift in the observed spectrum is used as feedback to adjust the laser, ensuring the proper operating wavelength. Thus, there is a real-time confirmation that the laser is locked on the desired absorption line. It delivers significant advantages over prior analytical approaches for customers monitoring ethylene, O_2 and CO_2 in ethylene oxide manufacturing processes.

Figure 2. 5100HD TDLAS analyzer

OXYGEN MEASUREMENTS

The purpose of O_2 measurement in the EO reactor is to maximize O_2 concentration while controlling to a limit of around 8% to eliminate the possibility of an explosion. The typical measurement range for this application is 0 to 12% by volume. The primary locations for the measurement of O_2 in EO plants are the inlet and outlet of the EO reactor. TDLAS-based O_2 analyzers can be successfully used for this application without the level of redundancy required by paramagnetic analyzers.

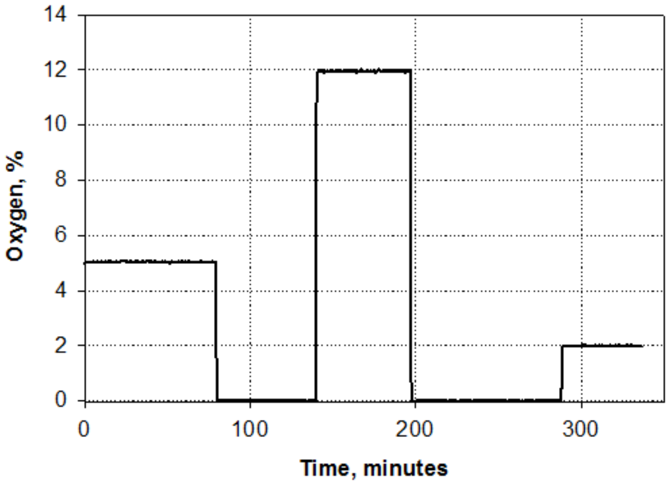
In an optical set-up for TDLAS, the beam from the laser diode is collimated with a plano-convex lens, used as the sample cell window. Since the absorption signal is weak, an extended path length sample cell is used. Multiple reflections of the laser light through the sample cell is achieved using a spherical mirror with a flat mirror at the focal point. Another long focus lens is used as an optical output window of the sample cell and operates as a condenser. On the output of the sample cell, the beam is divided in two by a beam splitter. Signals from sample and reference cell silicon photodiode detectors are input to separate channels of the main electronics unit.

The sample cell temperature is controlled within ±0.1°C and can be set in the range of 40 to 150°C (104 to 302°F).

The laser, reference cell and photo diodes are located in the main electronics compartment, isolated from the heated sample compartment.

Figure 3 represents the response of the AMETEK 5100HD TDLAS O_2 analyzer to a series of O_2 challenges in the concentration range of interest. Each challenges lasted 60 minutes or more, with return to the 0% gas baseline value between challenges. The speed of the T90 response time was 20 seconds and was determined using a flow rate of 2L/min. The data acquisition rate was 2 seconds/measurement.

A



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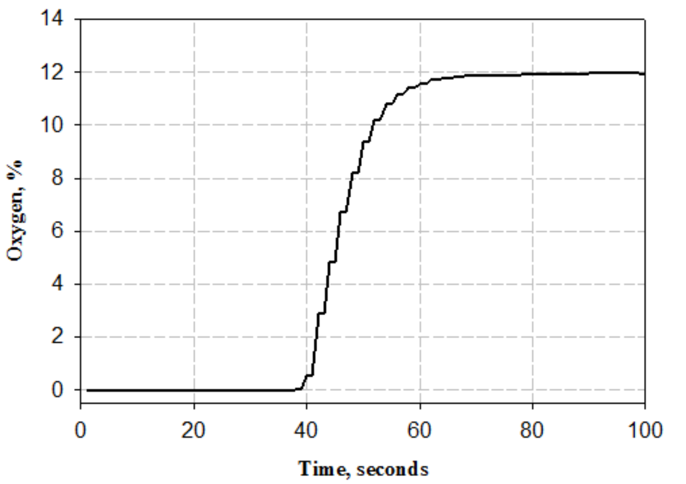

Figure 3. Oxygen in ethylene – Methane gas stream. Response to a series of concentration challenges (A), speed of the response (B)

During one year of field trials in a similar control application, the analyzer had zero failures, versus nine failures of the paramagnetic analyzer running in parallel.

CARBON DIOXIDE MEASUREMENTS

There are several process control applications for CO_2 measurements at ethylene oxide plants:

- Reactor inlet (0 to 5% CO_2 volume)
- Reactor outlet (0 to 5% CO_2 volume)
- Ethylene oxide stripper overhead (0 to 30% CO_2 volume)
- Carbon dioxide stripper overhead (0 to 30% CO_2 volume)

PGCs have a relatively long measurement time (2-3 minutes), but TDLAS-based measurements provide real-time monitoring with a data acquisition rate of typically 2 seconds. During regular plant startups with a new catalyst the CO_2 concentration can change suddenly, so real-time monitoring is important to maximize EO yield.

The instrument was subjected to a series of carbon dioxide challenges over the concentration ranges of interest. The duration for each challenge was several minutes. The response time (T90) was 30 seconds at a flow rate of 2L/min. The data acquisition rate was 2 seconds per measurement.

The standard deviation of the readings was 25ppmv for measurements in the 0 to 5% range. The accuracy in the range 0 to 5% was 100ppmv.

ETHYLENE MEASUREMENTS

Optimal conditions for EO production may be determined by real-time monitoring of ethylene concentrations at the different locations of the process. Historically, filter IR photometers have been used, but require frequent zero measurements, which is undesirable for real-time process control. TDLAS-based measurements provide real-time monitoring with a data acquisition and analysis rate of a few seconds.

Meeting the need to measure ethylene in the inlet and outlet of the reactor, AMETEK offers a TDLAS analyzer with dual sample cells. This allows simultaneous measurements of the ethylene concentration in two separate gas streams with results for each stream reported every two seconds.

The measurement of ethylene is performed with two Distributed Feedback (DFB) lasers (Figure 4). The outputs of both lasers are coupled into single-mode optical fibers, which in turn are connected to fiber-optic beam splitters.

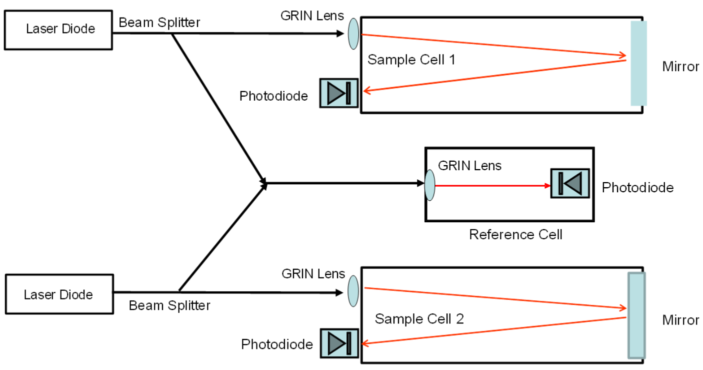

Figure 4. Schematic diagram of the dual cell 5100HD analyzer for the ethylene measurements

The splitters are used to divide the optical power in a 50/50 ratio for use in the sample and reference measurements, respectively. The reference cell contains a known concentration of ethylene in a non-absorbing matrix and is used to lock the output radiation wavelength of the laser for both sample channels.

The instrument faced a series of ethylene challenges in a concentration range of 0 to 50%. Each challenge was approximately 30 minutes with return to the 0% gas baseline, represented by methane. The T90 response time was 20 seconds at a flow rate of 2L/min. A measurement for each stream is completed every two seconds.

The standard deviation of the ethylene readings on each of the challenges was between 0.1 % and 0.3% of the ethylene concentration. The value of the accuracy evaluated at the levels of ethylene from 0 to 50% was in the range 0.3 to 0.5% ethylene.

During the drift test, a sample with 0.5% ethylene in nitrogen was run through the sample cell at a flow rate of 2L/min. No significant trends or correlations with the environmental temperature or sample pressure were observed. Over 24 hours, a mean value of 0.5% of ethylene, with a standard deviation of 0.01%, was recorded; the value of the drift was less than 0.03% ethylene.

CONCLUSION

The monitoring of O_2, CO_2 and ethylene in the EO production process are critical applications that demand an analyzer with a near-100% availability to maximize the production of EO and assure plant safety. The built-in verification feature of the 5100HD provides a real-time check on the analyzer's optical system performance. Fast response, no sample conditioning, and immunity to interference from moisture makes the laser-based AMETEK 5100HD a superior and dependable choice.

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