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HYDROCARBON PROCESSING®

Optimizing ethylene production with laser technology

Ethylene is one of the most valuable organic compound building blocks in the world. Global ethylene production is forecast to reach 200 MMtpy by 2020. Ethylene production is a highly competitive industry where purity is of utmost importance. Ethylene plants require highly responsive control technologies to keep the process stable. Traditionally, gas chromatographs (GCs) have been the measuring instrument of choice for all areas of ethylene production. From feed qualification, through the cracking furnaces and purification train, to the final product certification of ethylene delivered via ship or pipeline, a typical plant may have 40–50 GCs. In many of these areas, the GC remains the best analytic choice. However, in some critical segments of the plant, GC capabilities meet only basic requirements, specifically in ethylene fractionation, acetylene control and real-time product certification.

The GC role. GC performance is more than adequate in ethylene purity applications—unless the user has a better technology to choose, and that has been possible for only a relatively short period of time. Over the last few years, laser technology has quietly slipped into petrochemical manufacturing as an analytical option, and it has now advanced to a point where it provides a real improvement in terms of speed, precision, reliability and cost in critical areas of the purification train and product certification. Before plunging into the performance advantages of laser technology in the cold areas of ethylene production, it is important to emphasize the critical benefits of GCs in the "hot end," which is the real moneymaker in an ethylene plant. Increased throughput achieved by using GCs for furnace optimization and control can mean big profits. In a plant producing 1 MMtpy of ethylene, a 1% change in throughput can produce an enormous improvement in the bottom line. Although laser technology does not have any application in this part of ethylene production, new developments in laser technology could change its role in this section of the ethylene process.

Acetylene conversion. In the cracking process, some molecules are over-cracked into acetylene. An important step to maximize production is to convert acetylene back into ethylene. This process is done through the addition of hydrogen in catalytic beds called acetylene converters. Two acetylene converter units are used—one in service and one on standby. Analytical data are required for the inlet stream, mid-bed and outlet streams of acetylene converters to optimize conversion and avoid process excursions. Precise and rapid control of the catalyst activity is vital to maximize the ethylene produced. If the catalyst is not active enough, then not all of the acetylene will be converted into ethylene. Conversely, if the catalyst is too active, then some of the ethylene could be converted back to ethane. The ability to measure carbon monoxide (CO) is a key to controlling catalyst activity. In addition, monitoring the concentration of acetylene is required to initiate the switch from the in-service to the standby unit. It is essential to look for acetylene breakthrough at the outlet of the converters to avoid process excursions downstream. Most importantly, measurement of the outlet must be done quickly and with a very low limit of detection.

Ethylene fractionation. The goal of an ethylene plant is to produce 99.99% pure product. This purity is ensured during the final purification step, which takes place in an ethylene fractionation tower (**FIG. 1**). An analysis is required for process control of the fractionator to ensure on-spec production. Ethane and ethylene have similar physical properties, which makes them difficult to separate. Process control of product purity requires a fine balance to maintain ethane close to the specification limit without going off-spec or recycling ethylene. Operating the tower efficiently offers considerable economic advantages in re-

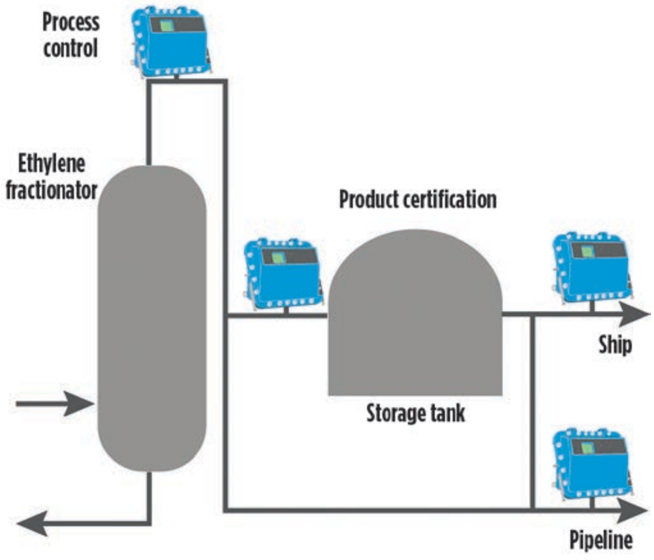

FIG. 1. Diagram of a typical ethylene fractionator.

ducing product giveaway, thereby minimizing energy usage and avoiding ethylene recycle. Measuring the C_1 and C_2 molecules, as well as CO and carbon dioxide (CO_2), allows the tower operation to be fine-tuned for maximum efficiency and ensures that ethylene production is on-spec.

Hybrid QCL/TDL laser technologies can provide a measureable impact on plant operations and financial outcomes.

The purification demand.

In the ethylene purification steps, recent advances in laser gas analyzer technology can have substantial impacts. Historically, conducting high-sensitivity measurements of gas components, using laser absorption spectroscopy, has been compromised by the external path that the laser beam travels in the optical system. This external light path can make a significant contribution to the spectrum, particularly where strong absorption lines are being targeted for high-sensitivity measurements. A new approach is to completely eliminate the external light path by close-coupling the lasers and detector to the measurement cell using a novel zero-gap design.

How zero-gap design is achieved.

The external path spectral contribution is eliminated by reducing the portion of the laser beam exposed to the air to near zero. A typical analyzer layout, where the laser beam passes through an external path, is shown in **FIG. 2.** A layout with a zero-gap laser and detector is shown in **FIG. 3.**

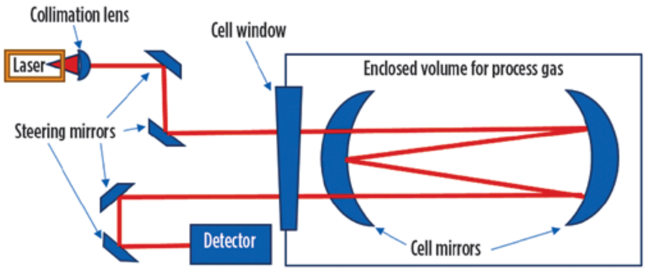

FIG. 2. Standard analyzer layout with laser beam exposed to the atmosphere.

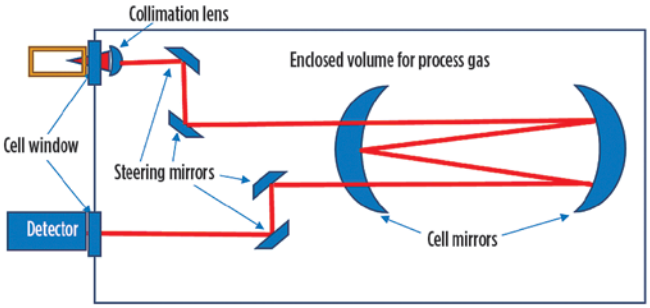

FIG. 3. Zero-gap analyzer layout wherein the path of light through the atmosphere is minimized.

The novel feature is mounting the steering mirrors inside the cell. This setup might seem strange at first, but it is no different from the normal practice of allowing the cell mirrors to be in contact with the sample. For clean streams, such as those in high-purity ethylene applications, no degradation of the optics is observed.

The analyzer can combine up to six quantum cascade lasers (QCLs) and tunable diode lasers (TDLs) in a single system for multiple gas measurements in a zero-gap configuration. The lasers are housed in modules that are identical for QCLs and TDLs. The laser module has a gas-tight window situated directly in front of the laser package window, and the laser light is divergent as it enters the cell assembly.

A collimation optic for each laser is situated within the gas path, and is mounted to the laser module to allow the laser to be aligned and collimated outside of the cell assembly. The collimated light from each of the six lasers is combined inside the gas path using beam steering optics into a single coaxial beam, which is then directed into a section of the cell that houses either spherical or astigmatic mirrors to extend the length of the path the light travels. Two detectors can be installed in the system to allow detection of the mid- and near-infrared (IR) light, depending on the types of laser installed. The light is distributed between the detectors using wavelength selective beam splitters that are also located inside the gas path. The laser light's total path length outside of the cell assembly is less than 1 mm in this configuration. This arrangement virtually eliminates any spectral absorption from the external light path, which enables parts-per-billion measurements of gases (such as H_2O and CO_2) for process gas streams.

Multicomponent detection.

QCL and TDL lasers are semiconductor devices that produce light in the IR region. They are fabricated to emit light at a desired wavelength, and are made to scan a spectrum using a laser chirp technique.

When the laser is pulsed with electrical energy to start the laser process, it heats up. As the temperature increases, the wavelength of the emitted light also increases. A laser chirp lasts about one microsecond. In this span, a spectrum of 1–3 wavenumbers is scanned. The raw detector signal is then pro-

	Components	Range[1]	Limit of detection (LOD)[2]	Units
Process control	Methane	0–1,000	5	ppmv
	Acetylene	0–20	0.2	ppmv
	Ethane	0–500	5	ppmv
	CO	0–5	0.05	ppmv
	CO_2	0–5	0.05	ppmv
Adders for product certification	Ammonia	0–20	0.2	ppmv
	H_2S	0–50	2	ppmv
	H_2O	0–10	0.1	ppmv
	Methanol	0–100	1	ppmv

[1] Components and ranges are indicative. Analyzer requirements will depend on complete gas list. Detailed specifications can be provided.

[2] Repeatability ±1% of reading or LOD, whichever is greater.

cessed to convert it into a spectrum from which the concentration of analytes can be calculated. QCL and TDL lasers can be chirped at a frequency of up to 100 kHz, enabling many thousands of spectra to be gathered in a few seconds and processed to provide a strong signal with a good signal-to-noise ratio.

The scanned wavelength region is selected to enable measurement of the desired analytes. By careful choice of lasers, compounds as diverse as hydrocarbons, sulfur species, solvents and nitrogen compounds can be measured. In addition, each laser might be able to detect more than one compound. For example, between six and 12 highly varied measurements can be made in a single analyzer. When GCs are used, multiple instruments are required; therefore, the use of lasers can save capital expenditure costs. An advanced signal processing procedure enables real-time validation of measurements and greatly reduces the need for calibrations, reducing ongoing operational costs.

Response time. Response time is a major issue in these applications, as well. In a QCL/TDL, the sample flows through a measurement cell where laser beams continuously analyze the gas. The response time is typically less than 10 sec to achieve 90% of a step change. The output is effectively continuous and in real time. Conversely, GCs work on the principle of injection followed by analysis. Cycle times for a GC vary from 1 min to more than 15 min, depending on the application; therefore, the concentration data is periodic rather than continuous.

This speed of the laser measurement is helpful in the process tower. However, it makes a huge difference in acetylene control, where it can quickly detect a process upset that might otherwise cost hundreds of thousands of dollars per hour to correct.

Product certification. Before exporting to customers, ethylene must be analyzed to ensure that it meets product specifications (**TABLE 1**). This step is critical to profitability. Traditionally, this analysis has been carried out using grab samples and laboratory analysis with GCs. However, components such as ammonia, methanol, nitrogen monoxide (NO), nitrogen dioxide (NO_2) and hydrogen sulfide (H_2S) can now be measured online in one analyzer using the hybrid laser technology. This multi-component measurement is valuable in product certification, which would normally take 3–6 GCs to measure. Speed is critical at this stage of the delivery process, but precision of measurement should not be compromised for rapidity. The laser technology allows for both, and online, real-time product certification can be achieved.

A significant leap. The use of GCs in ethylene production is established and proven. Plant personnel are knowledgeable on the use of the technology. It requires a significant boost in performance improvement to suggest the need for a change. Hybrid QCL/TDL laser technologies can provide a measureable impact on plant operations and financial outcomes. HP