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Optimal gas analysis decisions improve ethylene plant operation

One of the most common and important building blocks in the petrochemical industry is ethylene, constituting a huge and fast-growing worldwide industry. Ethylene is an intermediate chemical used to manufacture many commercial products—approximately 200 MMt will be produced in 2020. Nearly half of global ethylene demand is for polyethylene (PE) production, but it is also used to make vinyl chloride, ethylbenzene and many other valuable intermediate products, such as ethylene oxide (EO), ethanol EO and ethanol.

Ethylene plant personnel strive to produce 99.99% pure product. These stringent purity requirements must be verified in production and at custody transfer points because the presence of impurities can poison catalysts and affect downstream processes, leading to costly repairs and downtime. Stringent environmental requirements relating to gas emissions also exist. Since purity is essential, the precision and reliability of the measurement is of key importance. Speed of response to any potential issues—along with cost reduction—are also critical to prevent potential process upsets and to ensure optimum throughput.

Many online compositional measurements can be used to improve operations and profitability. The measurement of purity and process optimization in ethylene plants is accomplished by gas analysis systems, principally gas chromatographs (GCs), laser spectroscopy analysis systems and conventional continuous gas analyzers. The latter use a variety of

measurement technologies such as photometric nondispersive infrared (NDIR) and nondispersive ultraviolet (NDUV), thermal conductivity, paramagnetic and electrochemical oxygen.

While virtually every ethylene plant uses some combination of these technologies, not all use them optimally. Applying the right specific gas analysis system in each process and unit will help

companies thrive in the competitive petrochemical industry.

The three main gas analysis technologies will be explained first, and where each should be applied to optimize operations is then discussed.

Gas chromatography. The composition analysis of hydrocarbon gases is important in ethylene production as the raw



FIG. 1. Gas chromatographs are used to make a wide variety of measurements in ethylene plants.

product is refined and processed, and gas chromatography is one of the most widely used techniques for hydrocarbon gas speciation and composition measurement (FIG. 1). Advantages include a wide range of measurement [from parts per million (ppm) levels up to 100%], a high degree of repeatability and detection of many different components in complex gas mixtures.

All GCs are composed of the same functional components: the sample handling system, the chromatograph oven and the controller electronics. A GC works by physically separating the hydrocarbon compounds in a column, with different hydrocarbon compounds exiting the column at different times, with each then detected.

In an ethylene plant, a key advantage of a GC is its ability to measure both heavy (beyond C_2) and light gases, which makes it the primary, if not only, choice in some

steps of ethylene production. In addition, the use of GCs in ethylene production is established and proven, so plant personnel are familiar with this technology.

Laser spectroscopy. Laser spectroscopy is the newest of the analysis technologies and has undergone significant development in the last decade. Today's semiconductor, laser-based systems incorporate both quantum cascade laser (QCL) and tunable diode laser (TDL) technology, allowing multiple component measurements to be made by a single device.

Advantages of laser spectroscopy in ethylene production include the ability to detect, analyze and monitor 6–12 different gases in one analyzer, eliminating the need for multiple analyzers, carrier gases and complex sample handling systems requiring coolers or chillers. Multi-component measurements using hybrid QCL/TDL technology (FIG. 2) are especially valuable in applications such as ethylene product certification, which would normally require multiple GCs.

In addition, the laser data spectroscopy collection methodology enables many thousands of spectra to be gathered. Each measurement is updated within one second with a good signal-to-noise ratio. Advanced signal processing enables real-time validation of measurements and greatly reduces the need for calibrations, minimizing ongoing operational costs. The response time is fast, typically less than 10 sec. to achieve 90% of step

change, so the measurement is effectively continuous and obtained in real time.

Conversely, GCs work on the principle of injection and separation followed by analysis, with cycle times ranging from 1 min to more than 15 min depending on the application. Therefore, the measurement data is periodic rather than continuous.

Conventional continuous analyzers.

Conventional continuous gas analyzers utilize familiar sensing technologies such as NDIR, NDUV photometer and thermal conductivity detection, along with paramagnetic and electrochemical sensors. These analyzers are generally the choice whenever emissions must be monitored, and they can also be used to provide the required fast response times in measurements of light hydrocarbons (FIG. 3).

Conventional continuous gas analyzers measure extractive single or multiple molecules (analytes) in process gases, with the following technologies applied depending on the required measurement:

- NDIR for nitric oxide (NO), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), ethylene and propene (C_3H_6)
- NDUV for sulfur dioxide (SO_2) and nitrogen dioxide (NO_2)
- Chemiluminescence for nitrogen oxides (NO_x)
- Electrochemical and paramagnetic detectors for oxygen
- Thermal conductivity for percent hydrogen
- Flame ionization detectors for total hydrocarbon.

Up to five measurements using these different technologies can be combined in a single analyzer to provide continuous, multi-component gas analysis.

For photometer and oxygen measurements, conventional continuous gas analyzers and QCL gas analyzers can be used in similar applications, with technology selection dependent on the number of components to be measured, detection limits and gas composition. For example, when cross-interference gases are present, the response of traditional non-dispersive photometer technology can be influenced, and a GC or a QCL analyzer should be considered. However, when measuring hydrogen, conventional continuous gas analyzers or GCs are a better choice because QCL analyzers are not capable of

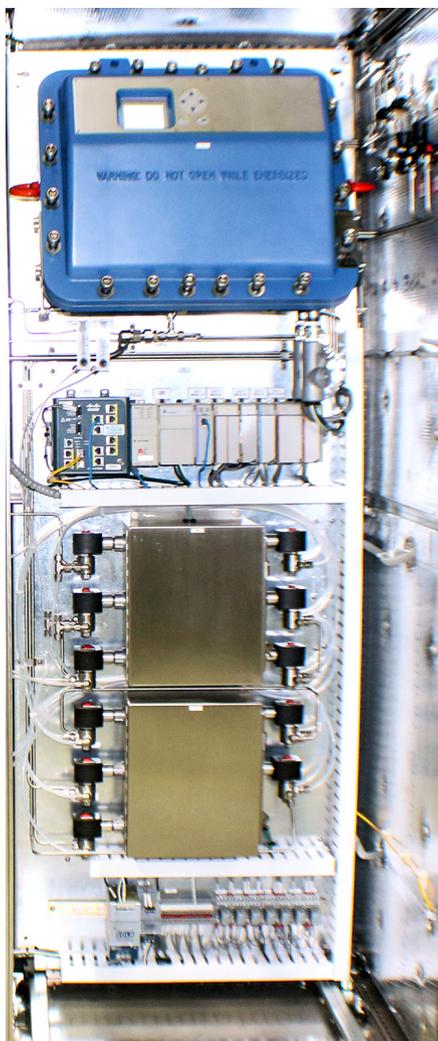


FIG. 2. Hybrid QCL/TDL technology provides speed, precision and reliability in critical areas of the purification train and product certification.



FIG. 3. Conventional continuous gas analyzers are often used for process control, product optimization and emissions monitoring.

providing hydrogen analysis. These traditional continuous gas analyzers are typically the most cost-effective technology of choice when monitoring one or two components in process gas streams.

Ethylene production. The typical ethylene plant is divided into two basic sections: the cracking furnaces (hot side) and the fractionation train (cold side). The fractionation train takes the effluent from the furnaces and separates it into a wide range of chemical products. Stack gases from the cracking furnaces and from steam generation are discharged to the environment and must be monitored.

The hot side—cracking furnaces. The hot side of ethylene production is the real moneymaker in an ethylene plant because increased throughput achieved by enhancing cracking furnace operation can greatly increase profitability. In a plant producing 1 MMtpy of ethylene, a 1% change in throughput can produce an enormous improvement in the bottom line. Energy represents about 25% of the cost of ethylene production, and approximately 18% of energy consumed is associated with heating and losses in the cracking furnaces, so furnace control has a substantial impact on overall plant efficiency. Over-cracking results in catalyst deactivation due to coke formation, while under-cracking reduces production.

Coke formation is undesirable because the layer of coke acts as an insulator on the inside of the furnace tubes, reducing heat transfer from the furnace tubes into the cracked gases. The reduced heat transfer necessitates increased tube skin temperatures to maintain the cracking reactions. Although the furnace tubes are fabricated from high-temperature alloys, eventually the metallurgical limits of the metal are approached. At this point, the furnace tubes must be decoked. Failure of a furnace tube would allow flammable cracked gases to meet the hot furnace combustion gases, which could result in an explosion.

Feedstock and ethane recycle gases fed into the cracking furnaces require measurement of the various hydrocarbon concentrations for optimal blending. This can be done with GCs, while conventional continuous gas analyzers can also be used to monitor the recycle streams to maintain a consistent feed gas quality to the cracking unit.

The choice between the two depends upon the strengths and trade-offs inherent

in each technology. GCs eliminate interference issues by physically separating complex process gases before taking the measurement, but this separation takes time. Conversely, conventional continuous gas analyzers provide fast readings, but must make measurements without the benefit of chromatographic separation. These analyzers must also avoid potential interferences by other gases in the process stream using spectroscopic techniques.

One of the most impactful measurements performed in ethylene production is feedstock composition—used for optimization of furnace operation. Due to the presence of heavy gases in the stream, a GC is typically used to measure Btu (C_1-C_6+) value to ensure optimal temperatures and performance, with a thermal conductivity detector on each furnace fuel line. For Btu firing rate control, the fuel gas to the furnace is normally analyzed for Btu content. This requires complete analysis of the stream to obtain the most reliable Btu measurement.

Another key analysis point for hot side measurements is the exit from the transfer line exchangers. It is common to use two GC analyzers at this sample point for cracked gas control. For velocity (or residence time) control, the cracked gas is analyzed to determine the molecular weight. The sample point is located on the effluent of the secondary transfer line exchanger.

Since the speed of analysis is critical for proper control, two analyzers are recommended for each sample point. The first analyzer measures key compounds such as C_2 , $C_2=$, C_3 and $C_3=$ to provide the control system with the information required to calculate an estimated molecular weight for the velocity control. The second analyzer provides a slower but more complete analysis of the cracked gas. The analysis from the second analyzer is used to trim (or update) the estimated molecular weight obtained from the first analyzer.

Since it is not always practical to have two analyzers on every furnace, a dedicated analyzer can be used for each furnace to perform the short analysis, with one analyzer configured to provide complete analysis for several furnaces. This is done by routing the sample gases from the furnaces to the analyzer using a header system.

Furthermore, since the data from the short analysis is so critical for the proper control of the velocity rates, the analyzers providing fast readings are typically set up

to provide backup capability between each other in the event of an analyzer failure.

Conversion control requires the measurement of the feed to the furnaces. If the feed is a simple mix of ethane and propane, a GC is used. Complex feeds like naphtha require a density measurement to estimate the composition, typically performed not by an analyzer, but by a specialized instrument.

Cracking furnaces need to be decoked about once every 20 d of operation because the furnace coils acquire a coating of carbon over time and lose efficiency. This is done by burning off the coke with air in a steam atmosphere. The progress of the decoking phase is monitored by measuring the amount of CO_2 in the effluent. It rises as the carbon is burned off and then decreases to zero when the furnaces are clean. CO_2 measurement in the effluent is usually made by a conventional continuous gas analyzer, which measures CO_2 in conjunction with removing contaminants using an NDIR photometric detector.

After leaving the radiant coils of the furnace, the product mixtures are cooled instantaneously in transfer line exchangers to preserve the gas composition. This process is followed by oil quench, gasoline fractionation, water quench and gasoline stripping to deliver pyrolysis fuel oil and pyrolysis gasoline. The gas is then compressed in a multi-stage compressor train to separate it into various components. Acid gases are removed with caustic scrubber, drying and cooling.

To ensure process control, conventional continuous gas analyzers are used to measure CO and CO_2 after the caustic scrubber. The hydrogen-rich tail gas from the dryer/cooler stage is also analyzed for hydrogen purity using conventional continuous gas analyzers.

Ethylene plants also require special measures for emissions monitoring. NO_x , CO and SO_2 emissions from cracking furnaces and steam boilers need to be kept in compliance. NO_x limits are, in some global areas, less than 50 ppm, and there are often requirements for certified emissions monitoring to report values to the authorities.

Both QCL analyzers and traditional technologies can be used for emissions monitoring, depending on the components and ranges to be measured. NDIR or NDUV are typically used to measure CO, CO_2 and SO_2 . Chemiluminescence

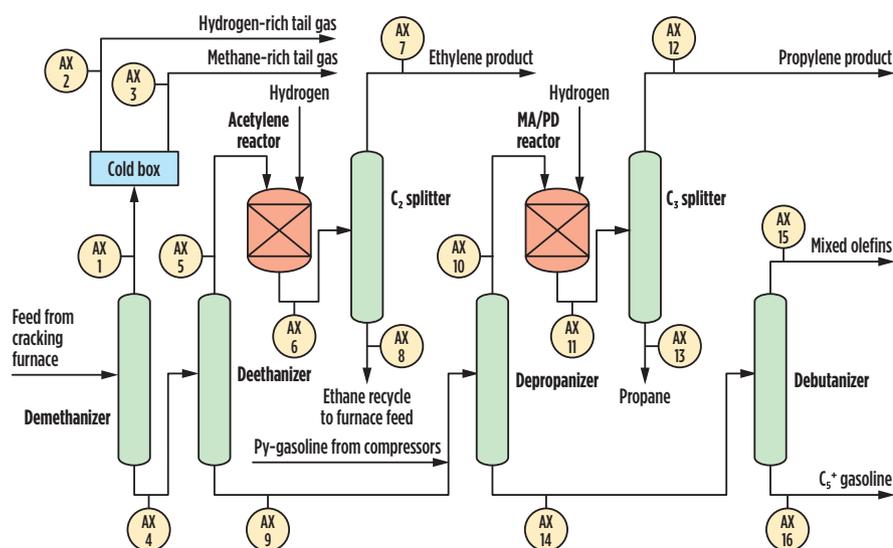


FIG. 4. Process flow diagram of a typical ethylene plant fractionation train.

is used for NO_x and paramagnetic is used for O₂. QCL analyzers can make all these emissions measurements in one analysis, in ranges from ppm to percent concentrations.

The cold side—fractionation train.

The separation of the furnace effluent into various products is performed through a series of fractionator towers that selectively separate one chemical group at a time. The effluent stream moves from one fractionator tower to the next, with the remainder after all tower processing sold as gasoline. The order in which the compounds are removed can be seen in FIG. 4.

After the furnace effluent has been cooled and compressed, it enters the first fractionator tower to remove methane and hydrogen. These light compounds leave the overhead of the demethanizer and enter a cold box, where they are further separated into a hydrogen-rich tail gas and a methane-rich tail gas.

Other processes needing hydrogen use the hydrogen-rich stream, and the methane-rich stream is often used as a fuel for burners and heaters. The remainder of the furnace effluent leaves the bottom of the demethanizer and enters the deethanizer. Components exit the overhead of the deethanizer and enter a reactor to remove any acetylene produced by hydrogenation. Once the acetylene has been removed, the reactor output is sent to a C₂ splitter fractionator that separates the ethylene from the ethane. The ethylene is sold as product, and the ethane is recycled back to the cracking furnaces as feed.

Simultaneously, the remainder of the furnace effluent leaves the bottom of the deethanizer and is fed into the depropanizer. Any pyrolysis gasoline condensed in the compression stage after the cracking furnaces is also fed to the depropanizer.

At the depropanizer, the output is sent overhead to a reactor to remove any methyl acetylene (MA) and propadiene (PD) from the stream by hydrogenation. This reactor's output is then sent to the C₃ splitter fractionator to separate the propylene from the propane. The last of the furnace effluent enters the final fractionator tower to separate out the C₄ olefins, leaving the rest to become the pyrolysis gasoline that exits the bottom of the debutanizer.

Production stages. In the fractionation train, the first analyzer (AX1 in FIG. 4) monitors the overhead streams of the demethanizer. This measurement can be used to minimize the loss of ethylene into this stream, which mainly consists of methane and hydrogen. A laser-based or conventional continuous gas analyzer is used to perform the measurement.

Two more analyzers (AX2 and AX3 in FIG. 4) monitor separation into the hydrogen-rich tail gas stream and the methane-rich tail gas downstream of the cold box. Hydrogen purity can be measured with a thermal conductivity analyzer utilizing suppressed ranges. The hydrogen is sometimes further purified by a pressure swing adsorption (PSA) process. If impurities in hydrogen need to be measured downstream of the PSA process, either a QCL or a conventional continuous gas analyzer

can be used, depending on the impurities present and the ranges to be measured.

The methane-rich tail gas often needs to be blended to ensure constant heating values or gas concentrations. Depending on the accuracy needed for the measurement and the components to be analyzed, a GC or a conventional continuous gas analysis measurement can be made. GCs provide a much higher accuracy with the ability to measure many more components selectively, whereas a conventional continuous gas analyzer provides faster response.

An analyzer (AX4 in FIG. 4) monitors the bottom streams of the demethanizer to measure light gases, such as C₁ and CO₂. Any gases that get to this point ultimately end up in the final ethylene product stream as impurities and should be minimized. This is done by using measurements of the C₁/C₂ ratio, which are made using a GC.

The next series of analyzers are also GCs and are used to control the purity of the ethylene product. This starts with the measurement (AX5 in FIG. 4) of the deethanizer overhead, used to minimize the amount of C₃ in the stream while maximizing the recovery of the C₂.

To monitor the removal of the acetylene (AX6 in FIG. 4), an analysis is performed in the effluent from the acetylene converter to ensure acetylene levels will meet final ethylene product specifications. This is done through the addition of hydrogen in catalytic beds.

Two acetylene converter units are employed: one in service and one on standby. Analytical data are required for the inlet stream, mid-bed and outlet streams of the acetylene converters to optimize conversion and avoid process excursions. These acetylene converters are fixed-bed catalytic hydrogenation reactors, and the catalyst has a finite life. Inlet, mid-bed and outlet measurements indicate acetylene breakthrough. The standby converter should be brought online before the acetylene breaks through into the outlet.

While GCs are frequently used for this stage, laser spectroscopy should also be considered since it can provide all critical measurements in a single analyzer in seconds. Fast response is critical because acetylene can poison catalyst and cost millions of dollars in losses.

At the C₂ splitter, an analyzer (AX7 in FIG. 4) monitors the ethylene product stream for impurities, while another (AX8 in FIG. 4) measures the bottom streams to

minimize any loss of ethylene in the ethane that is being recycled. These measurements can be made using a GC, as well as a conventional continuous gas analyzer.

A series of GCs are used to control the purity of the propylene product, starting with the measurement (AX9 in FIG. 4) of the stream leaving the bottom of the deethanizer. Any C₂ components present would end up in the propylene product stream, an undesirable outcome, so these components need to be controlled by measuring and maintaining the optimum C₂/C₃= ratio.

The depropanizer overhead stream is monitored (AX10 in FIG. 4) for C₄s, and this measurement is used to minimize their presence in the propylene product. To monitor the removal of MA and PD, a GC is installed at the exit of the MA/PD reactor (AX11 in FIG. 4). C₃ splitter measurements can be made using conventional continuous gas analyzers, like the in-tray C₂ splitter measurements.

Two analyzers monitor the propylene product for purity (AX12 in FIG. 4), and the propane stream (AX13 in FIG. 4) to minimize the loss of propylene. The final series of analyzers monitors the final separations of the furnace effluent, beginning with the measurement of the depropanizer bottom streams (AX14 in FIG. 4). This analyzer monitors the C₃/C₄= ratio, used to control C₃ impurity levels in the mixed olefins product stream.

Two more analyzers, typically GCs, monitor the purity of the mixed olefins (AX15 in FIG. 4), with this measurement used to minimize the loss of C₄ olefins in the gasoline stream (AX16 in FIG. 4). TABLE 1 summarizes the previous text, showing the components measured in each stream, along with the measurement objective.

After ethylene leaves the fractionator, its purity must be certified by measuring certain key contaminants using GC or laser spectroscopy. Ethylene plants produce product at 99.99% purity for use as feed to PE, PE glycol and polyvinyl chloride plants, among others.

Final product ethylene can be transported in pipelines as a supercritical fluid, or it can be cooled for transport by ship as a cryogenic liquid. Certification of ethylene purity can be performed by a GC or by laser spectroscopy when response time is critical.

Analysis rules of thumb. While every application is different, GCs are generally

TABLE 1. Ethylene plant fractionation train measurement

Analyzer no.	Stream	Component measured	Measurement objective
1	Demethanizer overhead	C ₂ =	Minimize the loss of ethylene
2	Hydrogen-rich tail gas	H ₂	Determine H ₂ purity
3	Methane-rich tail gas	Btu	Calculate Btu for use as fuel gas
4	Demethanizer bottom streams	C ₁ , C ₂ =	Control methane in the ethylene product stream
5	Deethanizer overhead	C ₃	Control ethylene purity product
6	Acetylene reactor effluent	Acetylene	Control acetylene impurity in ethylene product
7	Ethylene product	C ₁ , C ₂ , acetylene, CO ₂	Measure impurities in ethylene product
8	C ₂ splitter bottom stream	C ₂ =	Minimize the loss of ethylene in the ethane recycle stream
9	Deethanizer bottom stream	C ₂ , C ₃ =	Control ethane in the propylene product stream
10	Depropanizer overhead	nC ₄	Control propylene product purity
11	MA/PD reactor effluent	MA/PD	Control MA/PD impurity in propylene product
12	Propylene product	C ₂ , C ₃ , MA/PD	Measure impurities in propylene product
13	C ₃ splitter bottom stream	C ₃ =	Minimize the loss of propylene into the propane stream
14	Depropanizer bottom streams	C ₃ , C ₄ =	Control propane in the mixed olefins product stream
15	Debutanizer overhead stream	C ₃ , C ₄ , iC ₅ , nC ₅	Measure impurities in the mixed olefins product stream
16	Debutanizer bottom streams	C ₄ =	Minimize losses of C ₄ olefins into the C ₅ + gasoline stream

used whenever heavy gases above C₂ are present in a complex mixture of several hydrocarbons, and when speciation is more important than fast response. For fast, continuous measurements of smaller molecules in process control and emissions monitoring applications, laser spectroscopy, non-dispersive photometry, thermal conductivity and paramagnetic sensing technologies are commonly used.

Hybrid QCL/TDL analyzers are often preferred for multi-component measurements when cross-interference gases are present, which can affect the measurement accuracy of traditional non-dispersive photometer technology. However, the detection limits of QCL analyzers are slightly lower than non-dispersive photometer-based analyzers.

For applications requiring measurement of one or two components in process gas streams, the conventional continuous gas analyzers are more cost-effective. Individual applications will vary significantly depending on the specific process used for ethylene production, so these guidelines only suggest which tech-

nologies should be considered.

With the large number of chemical separations being performed in an ethylene plant, gas analysis plays a key role in process control by monitoring the various process streams in ethylene production. Process analytics performed using gas analysis measurement data can be used to maximize yields and ensure product quality, thereby increasing profits by improving efficiency. **HP**



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