The precise and rapid analysis of process gases within an ethylene plant is vital to ensure safe and efficient operation, being used to optimize process efficiency while maintaining the highest levels of safety. These efficiencies can be achieved in a variety of ways, including shortening the residence time in the cracking furnace; rapid adaptation to changing feed-stocks; improving combustion control; optimizing fractionation; and improving process reliability. Safety can also be improved as a result of fast, reliable process analysis technologies with high measurement availabilities.

**PROCESS ANALYZER MEASUREMENTS**

The multiple processes involved in manufacturing ethylene require a range of gas analyzer measurements to help manage the efficient control and safety of the process, optimize combustion, maintain product quality and manage emissions to comply with environmental legislation; more than thirty different points of gas analysis are present in total. With considerable differences between the measurements required – for instance the type of measurement needed, the gas being measured or the relative concentration to be sensed - specific analyzer technologies are designed for and perform better at different points in the process. Traditionally these measurements have been predominantly made by infrared (IR) and gas chromatograph (GC) analysis techniques, supported by techniques for combustion and emissions analysis. However, recent advances in in-situ Tunable Diode Laser and in-line Tunable Filter infrared technologies have expanded the measurement technologies available for faster, safer or more accurate control of the process at certain points.

IR analysis techniques provide key measurements across the whole of the ethylene manufacturing process; for example, IR analysis is crucial to cracking an ethane or mixed light hydrocarbon feedstock. The majority of IR process analyzers employ a single beam, dual wavelength measurement technique that offers high performance, repeatability and long-term stability. In particular, the measurement is virtually unaffected by the build-up of sample cell contamination since it influences both wavelengths equally. A 50% loss of signal due to obscuration of the sample cell windows produces no more than 3% error in the reading. Analyzers using gas filter correlation (GFC) technology, such as the Servomex SERVOTOUGH SpectraExact 2500 infrared analyzer, can measure trace levels of carbon dioxide or carbon monoxide with exceptionally low cross-interferences from hydrocarbons.

Combustion control for the cracking furnace is provided through monitoring both oxygen ($O_2$) and carbon monoxide ($CO_e$). In these analyzers, sensors are housed in a sensor head mounted on the process wall, to which a sample is aspirated via a sample probe giving fast in-phase response of both $O_2$ and $CO_e$. The range of probes available enables a fast, dynamic and accurate analysis in high temperature combustion applications. However the advent of Tunable Diode Laser (TDL) technologies now allows a path-averaged combustion measurement of $O_2$, $CO$ and $CH_4$ to be made in-situ of the process.
Finally, emissions analyzers capable of measuring levels of flue gas emissions from the furnace processes, including O$_2$, CO, NOx and SOx, are usually required to meet legislative requirements.

The composition analysis of hydrocarbon gases is important in ethylene production as the raw product is refined and processed. The prevalent instrumentation technology used to-date for hydrocarbon gas speciation and composition measurement is Gas Chromatography (GC), in particular Process Gas Chromatography (PGC). This works by physically separating the hydrocarbon compounds through a long column as the stationary phase and a carrier gas as the mobile phase. The different hydrocarbon compounds exit the column at different times, which are then detected. Measurement time for a C1-C5 analysis varies between ninety seconds to five minutes, depending on the type of instrumentation and configuration used.

A continuous flow of dry, high-purity carrier gas, generally helium, is needed. An optical hydrocarbon gas analyzer based on infrared absorption has now been developed that enables the speciation and quantification of the individual hydrocarbon components in multi-component matrices of alkanes, alkenes, and alkynes. Comprising a real-time Tunable Filter infrared analyzer capable of accurately separating light hydrocarbon components, Servomex’s SERVOTOUGH SpectraScan 2400 uses a unique wavelength scanning tunable filter spectrometer to perform fast update rates for C1 through C5 analysis.

SpectraScan-specific applications in typical ethylene plants start at the point of gas feed, with the hydrocarbon feed gases initially cracked in a furnace and separated into desired products or fraction. This can be done in a variety of sequences, but monitoring of the feed gas composition typically includes C1 to C4 hydrocarbons. It performs such speciation without requiring physical separation of the compounds required by chromatography. The flow-through optical sensor provides unattended, real-time and consumable-free analysis suitable for on-line gas analysis. For the purposes of this article, a SpectraScan will be recommended for the speciation of light hydrocarbons, but GC remains an alternative for several areas where heavier hydrocarbons need measuring and response time is not so important.

SAMPLE CONDITIONING

The gas sample presented to the analyzer should be clean and dry. In a typical sample conditioning system, the pressure and flow of gas is controlled to suitable levels for the analyzer, and dried and filtered to remove any moisture or particulate matter. However, some streams on ethylene plants (particularly the cracked gas if sampled before the quenching system, and the decoking steam mixture) do require special sample conditioning before they can be analyzed. This would typically involve sampling components to remove heavy hydrocarbon contaminants, particulates, and moisture that would otherwise accumulate and block the analyzer sample lines.
FIRST STAGE: ETHYLENE CRACKING FURNACE

The quality of the raw ethane feedstock, particularly if obtained from natural gas, is critical and the feed gas quality is monitored for high levels of carbon monoxide (CO) and to maintain a consistent feed to the cracking unit (1). As carbon dioxide (CO2) can freeze out on the process equipment at the ‘cold end’ of the operation, it is removed to levels of less than 100ppm (typically 10ppm) in the treatment plants. An IR analyzer measuring in the range of 0-1000ppm CO2 is used to monitor the outlet stream (2) and show the performance of the treatment plant. The plant can also be used to remove hydrogen sulphide traces from heavier feedstocks such as Naphtha.

After any recycled ethane is blended with the treated feed, a SpectraScan measurement (3) maintains a consistent feed to the cracking unit. The SpectraScan (4) and a complementary hydrogen measurement, such as that provided by the H2Scan Hy-Optima 2700 (5) maintain constant fire and heating rates of the steam boiler and cracking unit, with a real time, low maintenance BTU analysis, especially when hydrogen (H2) and methane (CH4) rich tail gases are recycled to the burners.

Another important process measurement is the monitoring of the oxygen in cracking furnace combustion gases, where optimized combustion and reduced fuel consumption is achieved by both detailed fuel analysis and rapid flue gas analysis. A combustion monitor, such as SERVOTOUGH FluegasExact 2700 (6) and (8), provides analysis of both oxygen (O2) and combustibles (COe), while an in-situ TDL measurement (7), such as that provided by the SERVOTOUGH MiniLaser Oxy, offers an average path analysis of O2 across the furnace. Continuous Emissions Monitoring Systems (CEMS), such as the SERVOPRO 4900 and appropriate sample system (9)(10)(11)(12), are used to measure the stack emissions for legislative requirements of O2, CO, NOx and SOx. Emissions analyzers can also be installed either side of a Selective Catalytic Reduction (SCR) unit to monitor the SCR’s efficiency in reducing NOx emissions, while a cross-stack TDL analyzer (13), such as the SERVOTOUGH MiniLaser Ammonia monitors the NH3 level, which is allowed to “slip” through the catalysis during the NOx reduction reaction. On the outlet of the cracker unit a transfer line exchanger (TLE) rapidly cools the cracked gas to preserve the gas composition: a SpectraScan and H2Scan (14) monitor the gas quality after the cracking unit, ensuring the highest possible ethylene yield and to prevent under-cracking or over-cracking.

After every 20 days or so of operation, the cracking furnaces need to be decoked since they 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 CO2 (0-5%) in the effluent. It rises as the carbon is burnt off and then reduces to zero when the furnaces are clean again, and the plant can be returned to normal operation. During the decoking cycle a SpectraScan (14) with added CO2 channel can also be utilized to monitor CO2 levels, as well as to ensure the shortest decoking cycle with real time analysis, or a separate IR analyzer (15), such as the SERVOTOUGH SpectraExact can be utilized for this measurement.
SECOND STAGE: QUENCHING, SCRUBBING, COMPRESSION AND DRYING

After the cracking is complete, the gas feed needs to be cleaned and conditioned before fractionation. The gas is further cooled to remove any heavy hydrocarbons, while remaining CO<sub>2</sub> is also removed as this can freeze out in the liquefaction stages later in the process. An IR measurement for 5ppm CO<sub>2</sub> (1) provides rapid analysis of any CO<sub>2</sub> breakthrough.

The performance of the dryer / chiller stage is monitored by a combination of SpectraScan, H2Scan and SpectraExact measurement, (2) (3) (4), ensuring only minimal levels of C1 & C2 are separated with the hydrogen (H<sub>2</sub>). The H<sub>2</sub> can be further purified by a Pressure Swing Absorber (PSA), the output of which can be monitored for a range of impurities depending on the product requirement, which separates high purity hydrogen and hydrogen rich tail gas from the clean and dry cracked gas.
The clean and dry cracked gas is now ready for fractionation into its component parts. The deMethaniser separates the CH₄ and remaining H₂ from the cracked gas. The “tops” of the column can be monitored by a SpectraExact, SpectraScan and H2Scan (1) to ensure valuable hydrocarbons are not lost. A cold box or chiller is then used to split any H₂ from CH₄, producing H₂-rich and CH₄-rich tail gases that are monitored by the SpectraExact, SpectraScan and H2Scan (2) & (3). The “bottoms” of the deMethaniser are monitored by a SpectraScan (4) to ensure there are only low levels of CH₄ present. The SpectraScan’s unique light hydrocarbon analysis then delivers multiple measurement points across the C₁ to C₃ fractionation (5) (7) (8) (10) (11) (13) (14) (15). At each of these measurement points the SpectraScan is used to minimize hydrocarbon losses from the “tops” or “bottoms” of the fractionation columns. Due to the fast analysis of the SpectraScan, real time optimization of the columns is possible for the first time. The SpectraScan and H2Scan (6) (12) are used to optimize the hydrogenation units, which convert acetylene (C₂H₂) and C₃H₄ to ethylene (C₂H₄) and propylene (C₃H₆) by the addition of H₂. Adding too much H₂ is inefficient, risking over-conversion or the H₂ becoming a contaminant in the ethylene and propylene products. Before the ethylene is stored, trace O₂ as a contaminant can be measured using a ppm trace oxygen, such as the Servomex DF-300 analyzer series (9).