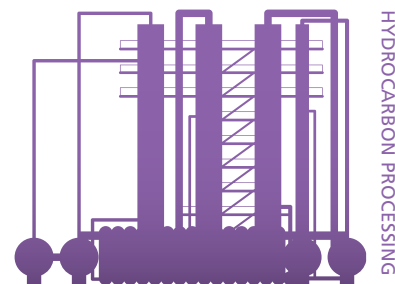


EXPERTS IN POLYETHYLENE SOLUTIONS



EXPERT PAPER

THE APPLICATION OF IMPROVED SENSING TECHNOLOGIES TO PROTECT PRODUCT QUALITY IN POLYETHYLENE

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Polyethylenes are thermoplastic resins obtained by polymerizing the gas ethylene [C₂H₄]. Because of its exceptional application flexibility, polyethylene's rise in popularity for both consumer and industrial uses means that today it is the largest volume plastic in the world.

Low density polyethylenes (LDPE) are polymerized at very high pressures and temperatures, and the high density types (HDPE) at relatively low temperatures and pressures. Another type called linear low density polyethylene (LLDPE) is manufactured through a variety of processes, of which gas phase is the most common. This most widely used Polyethylene process yields both HDPE and LLDPE with a wide range of copolymers. The simplicity of the process accounts for its popularity: A high efficiency catalyst system aids in the polymerization of ethylene and allows for lower temperatures and pressures than those required in making conventional

low density polyethylene. In addition, it accommodates a broad range of interesting property combinations used in both HDPE and LLDPE markets.

The gas phase process requires the production of a high quality product while maintaining high standards of process safety. Traditionally production has depended on the use of gas chromatograph technologies to measure for hydrocarbon impurities in the process, and electrochemical fuel cell technologies to measure for ppm levels of performance. While able to make the requisite measurements, GC technologies have long been criticized

for their relative expense to run and slow rate of response – problematic when protecting yield quality; while electrochemical oxygen sensors by their nature deplete and require regular calibration and replacement, resulting in ongoing cost and unnecessary system downtime.

In both cases, Servomex have adapted the latest advances in light hydrocarbon and O₂ analysis technologies to provide measurable performance advantages over traditional techniques. Combined, Servomex offers a next-generation analyzer solution for polyethylene improves yield, ensures product purity and guarantees safety.

RECYCLE GAS ANALYSIS: A NEW ALTERNATIVE TO GC MEASUREMENTS

As product quality is paramount throughout the process, the ethylene feed requires measurement for any residual light hydrocarbon present from the fractionation process. This type of measurement is also required later in the process, as any residual ethylene recovered in the degassing tower and recycled together with the ethylene from the top of the reactor. In this recycle loop a hydrocarbon measurement is required to control the recycle process more efficiently.

The analysis of light hydrocarbons in polyethylene production has traditionally been carried out using gas chromatographs (GC), in particular process gas chromatographs (PGC). It 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 by a detector. Measurement time for a C1-C5 analysis varies between 90 seconds to

5 minutes, depending on the type of instrumentation and configuration used. A continuous flow of dry, high-purity carrier gas, generally helium, is needed.



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A MEASUREABLE ADVANTAGE

THE APPLICATION OF IMPROVED SENSING TECHNOLOGIES TO PROTECT PRODUCT QUALITY IN POLYETHYLENE

An optical hydrocarbon gas analyzer based on infrared absorption techniques has long been envisioned to enable a far quicker speciation and quantification of the individual hydrocarbon components in multi-component matrices of alkanes, alkynes and alkenes. Servomex's SERVOTOUGH SpectraScan 2400 light hydrocarbon analyzer utilizes revolutionary new Tunable Filter Spectroscopy optical sensor technology for on-line hydrocarbon gas composition analysis – a measurement uniquely developed for applications where a real-time analysis is necessary for optimal process control. Faster and less complex to use than existing Gas Chromatograph (GC) analysis techniques, breakthrough real-time readings for light hydrocarbons C1-C6 are available almost instantly – taking seconds rather than minutes. In addition, an optical analyzer does not need a carrier gas, which reduces the infrastructure requirements and operating costs.

A widely used optical gas analyzer technology used in process monitoring is non-dispersive infrared (NDIR), where one or a few discrete wavelength bands are used to measure the concentration of the sample gas through the absorption characteristics in those wavelength bands. In general, a single beam multi wavelength (SBMW) or the more conventional sample and reference beam units (multi-beam, single wavelength MBSW) represent the methodologies of most Process IR analyzers, giving fast component concentration updates (in seconds) outside the response time of sample conditioning systems. They are not however reliable in differentiating or speciating similar chemical entities, such as the different compounds of hydrocarbons.

The SpectraScan incorporates a powerful improvement of the SBMW method where, rather than using discrete optical filters with limited amount of wavelength bands selected to correspond to required measurements, a tunability element is introduced to enable a degree of continuous spectral coverage which leads to a capability to deconvolute complex spectra. Accordingly, Tunable Filter Spectroscopy (TFS) technology successfully and rapidly speciates light hydrocarbons and enables fast and reliable caloric value measurement.

Consisting of a light spectrometer, a flow-through sample cell, a single-element photo-detector and electronics, the SpectraScan's all-optical sensor platform

uses a unique tunable Fabry-Perot assembly that provides wavelength scanning with high etendue, enabling high-throughput and high-precision wavelength scanning in preselected region. The physical separation of the compounds as performed in chromatography is not required - instead the analyzer achieves speciation and quantification of the individual hydrocarbon components in multi-component matrices of alkanes, alkynes, alkenes and/or alcohols. The SpectraScan's measurements include Methane (50-100%, C1), Ethane (0-20% C2); Propane (0-10% C3); iso-Butane (0-5% iC4); n-butane (0-5% nC4); Pentanes (0-2% C5 lumped); and n-Hexane (0-2%, nC6), plus a measurement for Carbon Dioxide (0-20% CO₂).

Using the absorption of infrared light as it passes through the volume of gas, the absorption spectrum of each compound acts as unique "fingerprints" for identification or speciation analysis. In addition, the magnitude of the absorption is a function of the number of molecules of the gas, and in certain conditions a linear relationship according to Beer-Lambert law. With a known path length, pressure and temperature, the magnitude of the absorption spectra is used to compute volumetric concentrations. An advanced spectral processing and chemometric algorithm provides highly accurate and robust speciation performance, compensating for various spectral nonlinearities due to pressure, flow and temperature variations.

Unlike Fourier-Transform infrared spectrometers (FTIR), the TFS design is mechanically simple and does not require high-precision optical alignment, and thus insensitive to shock and vibration, while providing equal or better signal-to-noise performance. Compared to grating based spectrometers such as diode array based spectrographs, the TFS provides much greater optical throughput or Etendue which results in better quality spectra which are important for quantitative measurements. The TFS allows for a continuous wavelength scanning within a predetermined wavelength window or a set of wavelength windows, enabling "true" absorption spectra to be measured at very near spectral point spacing.

The stability of the analyzer is of great importance as it affects the maintenance requirements and operational costs.

The SpectraScan is specified to have a permanent span calibration/ accuracy and < 0.2% of full scale of baseline drift per month. The span accuracy is permanently maintained as it is based on "first principle" of direct absorption measurement where the measurement signal is solely dependent on the molar concentration, pressure and temperature. Pressure is continuously measured in real time and corrected, and sample temperature is maintained at 60°C through the use of a heated gas cell and an integrated pre-heat line. The spectral processing algorithm removes any baseline noise and drifts to the extent that light source drifts/degradation and contaminated windows, two common sources of drifts, are minimized or eliminated. TFS analyzers have run for months without the need for re-zeroing.

The TFS based hydrocarbon composition analyzer's performance is characterized in a number of laboratory tests to demonstrate its accuracy, linearity, calibration robustness, selectivity and stability. The accuracy is defined in terms of root mean squared error of prediction (RMSEP), where measured concentrations are less than 0.2%. C1 to C4 saturated alkanes are measured with equal to or better than 0.05% accuracy; propene and ethene have slightly lower prediction accuracy (RMSEP 0.15% and 0.18% respectively) which is mainly due to concentration over ranging.

Robustness of the calibration model is proved by over-ranging ethane and ethene to 32% outside their calibration limits of 25% and 10% respectively, where accuracy is not affected in the presence of hydrogen, an un-modeled background. Overall repeatability of the measurements are within a highly acceptable 0.02%.

The result is a breakthrough measurement for light hydrocarbon analysis, which eliminate the slow performance and cost-of-ownership issues posed by GC technologies by providing unattended, real-time and consumable-free analysis ideally suited for the polyethylene manufacturing process.

A complementary measurement for hydrogen is provided by the H2Scan, an inline analyzer easily configurable alongside the SpectraScan.

THE APPLICATION OF IMPROVED SENSING TECHNOLOGIES TO PROTECT PRODUCT QUALITY IN POLYETHYLENE

ENSURING QUALITY: PREVENTING OXYGEN CONTAMINATION

The polyethylene manufacturing process requires polymer grade ethylene and any comonomers to be blown into the base of a liquidized bed reactor. To maximize yield, the ethylene and comonomer need to be as pure as possible, a process that requires the trace measurement of O₂.

When the final product stream is produced, additives are introduced before the polyethylene powder is transported to the finishing area where it is extruded, pelletized, dried and bagged. At both this additive stage and pelletization phase, a ppm O₂ impurity measurement is again required. This is needed because the air around the pelletizer is blanketed with an inert gas to prevent oxidation of the polymer.

The required ppm trace level O₂ measurement has traditionally been provided by analysis using electrochemical cells – which, although providing the requisite measurement, operates through

an electrochemical reaction that depletes over time. As a consequence, such cells require frequent calibration and/or replacement, with a performance that deteriorates over time. Ideally, a non-depleting technology is required that delivers a stable, reliable performance.

Servomex has solved the problems associated with traditional electrochemical cells by using carbon electrodes that never undergo a chemical change. The non-depleting Coulometric sensor technology enables the measurement of oxygen at ppm and ppb levels - without the requirement for periodic replacement or false low readings associated with electrochemical cell sensors.

The sensor operates on a simple coulometric process whereby oxygen in the sample gas is reduced in an electrochemical reaction. The sample gas is in direct contact with the sensor cathode. Oxygen in the sample gas is reduced

electrochemically at the cathode to hydroxyl ions (OH⁻). The electrolyte solution contains potassium hydroxide (KOH) which assists in the migration of hydroxyl ions (OH⁻) to the anode where they are converted back to oxygen to complete the reaction. The current flow resulting from the reaction is proportional to the oxygen content in the sample gas. The processed signal is then displayed on the front panel in ppm or ppb units of oxygen and transmitted either as a 4-20ma, DC volt or digital signal.



DF-340E

The Coulometric sensor responds very quickly to changing oxygen concentrations. In addition to fast response to changes in O₂ concentration, the performance of the sensor is unaffected by changes in flow rate. Because the non-depleting sensor is not consumed during the measurement it has a long lifespan and does not require a purge gas to protect it when not in use.

The Coulometric sensor is integrated into Servomex's DF-340E trace oxygen analyzer, optimized for measuring trace O₂ in pure gas streams and multi-gas backgrounds. Designed for hazardous area use and certified to CSA Class I, Div II and the latest ATEX

specifications, the DF-340E and DF-370E, making it ideal for potentially hazardous locations in the polyethylene production process.

Designed to optimize the performance of the Coulometric performance, the technology is factory-calibrated to simplify set-up and significantly reduce ongoing maintenance. Only an annual span adjustment is recommended for the DF-340E – a significant reduction in maintenance costs and downtime in comparison to analyzers using electrochemical technologies.

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