

DELTA F CORPORATION
APPLICATION NOTE NO.
108



Ultra High Purity Oxygen Measurements in Olefins

Modern olefin co-catalyst systems are providing higher yields of the final polyolefin product along with improvements in product quality and performance. However, in order to secure these benefits, the olefin feedstock stream must be oxygen free.

The Role of Oxygen Analyzers

Successful production of polyolefin products depends on the presence of catalysts to initiate and control the polymerization reaction. Contaminants in the feed stock, such as oxygen, can interfere with the catalytic action. The feed stocks must be monitored for oxygen content in order to maintain high product quality and maximum yields.

For years, the Ziegler-Natta catalyst has been widely used in the industry as the catalyst of choice. In recent years, experiments with metallocene done by Walter Kaminsky have lead polyolefin producers to try this new catalyst. While metallocene has existed as a catalyst since the late 1950's, it is only recently that it has been used as a co-catalyst with the Z-N catalyst to produce polyolefins with a narrower molecular weight distribution and other improved properties.

The new metallocene catalysts are more susceptible than the Z-N catalysts to oxygen. The level of oxygen, in most cases, must be kept below 50 parts per billion. With the presence of too much oxygen, premature polymerization and undesired branching or cross linking will occur. Cross linking causes processing problems during extrusion or molding, and branching of the polymer will lead to a lower density and a softer product. Oxygen can also lead to long polymerization induction periods by consuming the initiator. It can also cause the polymerization to terminate prematurely, leading to lower molecular weight, reduced viscosity, and reduced polymer strength. Oxygen can poison catalyst sites which decreases process efficiency and causes lower yields. Detection of oxygen contamination can also indicate potentially dangerous air leaks in reactors, pumps, valves, or interconnecting piping. An oxygen analyzer that can respond quickly is essential to meet the necessary process control and safety requirements demanded for today's high quality products.

Conventional Approach to Monitoring Oxygen

Conventional galvanic oxygen sensor technology uses two dissimilar metal electrodes, typically silver and lead, which are consumed in the process of measuring oxygen. The sensors have a relatively short life span of several months because the:

- Lead anode is consumed,
- Silver cathode is attacked by trace acid gases, and the
- Electrolyte is susceptible to contamination.

The galvanic sensors operate like a battery. As these sensors age, they begin to read lower than the actual oxygen concentration as electrode sites are depleted. False low readings lead operators to believe that the process is proceeding normally when higher oxygen levels are causing poor product quality.

Sparging, a technique where nitrogen is constantly flowed through an electrolyte to remove trace amounts of dissolved oxygen, is sometimes used with this type of sensor to reach ppb level measurements. The sparging of the sensor is disruptive to the precise readings that are required.

Analyzers with replaceable battery-type galvanic sensors that measure parts per billion must be recalibrated frequently because the silver cathode is poisoned by ppb level acid gases, typically halogens or sulfides that are common in even the most pure olefin feed stocks.

The slow speed of response and the inaccuracies that occur without constant maintenance can result in a loss of product.

The Delta F Difference

Delta F has solved the problems associated with the galvanic sensors with its NanoTrace Oxygen Analyzer. It provides unmatched capabilities, such as:

- Extremely Stable, Long-term, Drift-Free Operation
- Factory Calibration to NIST Traceable Standards
- Acid Gas Operation
- Quick Start-up and Rapid Response
- Excellent recovery from upsets

Unlike battery-type sensors, the Delta F sensor does not require periodic replacement and **does not produce false low readings**. The sensor operates on a coulometric process whereby oxygen is reduced at the cathode to hydroxyl ions. Assisted by the potassium hydroxide electrolyte, the ions migrate to the anode, where they are oxidized back to oxygen which vents out of the sensor. Where conventional electrochemical sensors use a consumable lead anode to drive the reaction, an analyzer voltage drives the reaction in the Delta F sensor.

As a result, much better measurement stability is achieved and periodic sensor replacement is eliminated. In contrast to galvanic sensors which require frequent (usually weekly) calibrations, the Delta F sensor may only require semi-annual span checks and addition of water, and monthly zero calibration "checks". The fast speed of response of the Delta F Sensor gives immediate indication of change in the oxygen level whether they are caused by an ambient air leak or by poor quality feed stock. Delta F's STAB-EL™ option is available to protect the analyzer from the harmful effects of trace acid gas contaminants, such as H₂S or halogens.

The Delta F sensor's sensitivity to oxygen concentrations of less than 0.2 ppb meets the stringent specifications required by the new catalysts. This detection level is unmatched in the industry.

All Delta F Sensors Carry a Five Year Conditional Warranty and they need to be replaced rarely, if ever.

The Delta F Platinum Series

Enclosures are available to meet hazardous location requirements. Easy menu setup, user scaleable outputs, networking capability via serial communications, hazardous area enclosures, and very low maintenance requirements make Delta F analyzers ideal for most olefin applications.

Recognized for Quality

Delta F's Quality Management System has been certified to ISO-9001 by Lloyd's Register Quality Assurance Ltd. This demonstrated compliance with an internationally accepted standard assures you of the highest quality in product design, manufacturing, and service.

Delta F Oxygen Analyzers can be ordered with a full scale range of 0-2 parts per billion (ppb) to as high as 0-25 percent. For specific product recommendations, contact Delta F Corporation, 4 Constitution Way, Woburn, MA 01801-1087, Tel. (781)935-4600, FAX (781)938-0531, e-mail marketing@delta-f.com.