

SpectraSensors TDLAS Analyzers for Olefins Production

Accurate and reliable measurement
of C₂H₂, NH₃, H₂O, H₂S, and CO₂



SpectraSensors®
An Endress+Hauser Company

SpectraSensors: A leading global provider of laser-based process instrumentation

SpectraSensors' mission SpectraSensors specializes in the design and manufacture of tunable diode laser absorption spectroscopy (TDLAS) analyzers for on-line, real-time measurement of contaminants in process gas streams. Bringing together individuals from diverse scientific and engineering disciplines has enabled us to solve real-world problems and become the recognized leader in TDLAS technology with an unmatched portfolio of patents. Our commitment to providing accurate and reliable solutions for measuring contaminants in process gas streams is evidenced by an installed base of 7,500+ TDLAS analyzers around the world.

Industries served SpectraSensors' TDLAS analyzers are used in the natural gas, gas processing, liquefied natural gas (LNG), petrochemical, refining, and atmospheric testing industries.

SpectraSensors' organization SpectraSensors, Inc. was formed in 1999 as a technology spin-off of the NASA / Caltech Jet Propulsion Laboratory (JPL) in Pasadena, California. Technology development and analyzer manufacturing are based in Rancho Cucamonga, California, and the company headquarters is in Houston, Texas. A regional Center-of-Competence (CoC) is located in Compiegne, France to provide technical support to European customers.

SpectraSensors was acquired by Endress+Hauser in 2012. Endress+Hauser is a global leader in instrumentation for process automation based in Switzerland which has built an unsurpassed reputation for producing high quality instruments for measurement and control of liquid phase processes. Acquisition of SpectraSensors extends Endress+Hauser's presence into gas phase measurements and strengthens SpectraSensors' ability to support customers globally. In late 2013, Kaiser Optical Systems, Inc, the company which developed the Raman-based Optograf spectrometer, was also acquired by Endress+Hauser, further solidifying the company's position in gas analytics.



Natural Gas



Gas Processing



Liquefied Natural Gas (LNG)



Petrochemical



Refining



Atmospheric Testing



Laser-based analyzers for olefins production

Laser spectroscopy – a better solution for challenging process conditions

The SpectraSensors advantage Tunable diode laser absorption spectroscopy (TDLAS) analyzers from SpectraSensors perform on-line, real-time measurements of impurities in olefins from sub-ppm levels to low percentage levels. The unique design of SpectraSensors' TDLAS analyzers provide significant advantages over other technologies for monitoring C₂H₂, NH₃, H₂O, H₂S, and CO₂ in olefin process streams.

Non-contact measurement The laser and solid state detector components of TDLAS analyzers are isolated and protected from the process gas and entrained contaminants flowing through the sample cell. This design avoids fouling and corrosion damage that impairs the analytical performance of other techniques, ensuring reliable long-term operation.

Fast response and analysis time TDLAS analyzers detect changes in analyte concentration much faster than gas chromatography, quartz crystal microbalances (QCMs) and other techniques, an important performance characteristic for control of key process units in olefins plants.

Selective and specific analyte measurement TDLAS analyzers selectively measure the molecular absorptivity of C₂H₂, NH₃, H₂O, H₂S, and CO₂ in olefin process gas streams.

Low cost of ownership Unlike gas chromatographs (GCs), TDLAS analyzers do not require carrier and combustion gases and have virtually no consumable components resulting in lower OPEX and maintenance costs and service requirements.



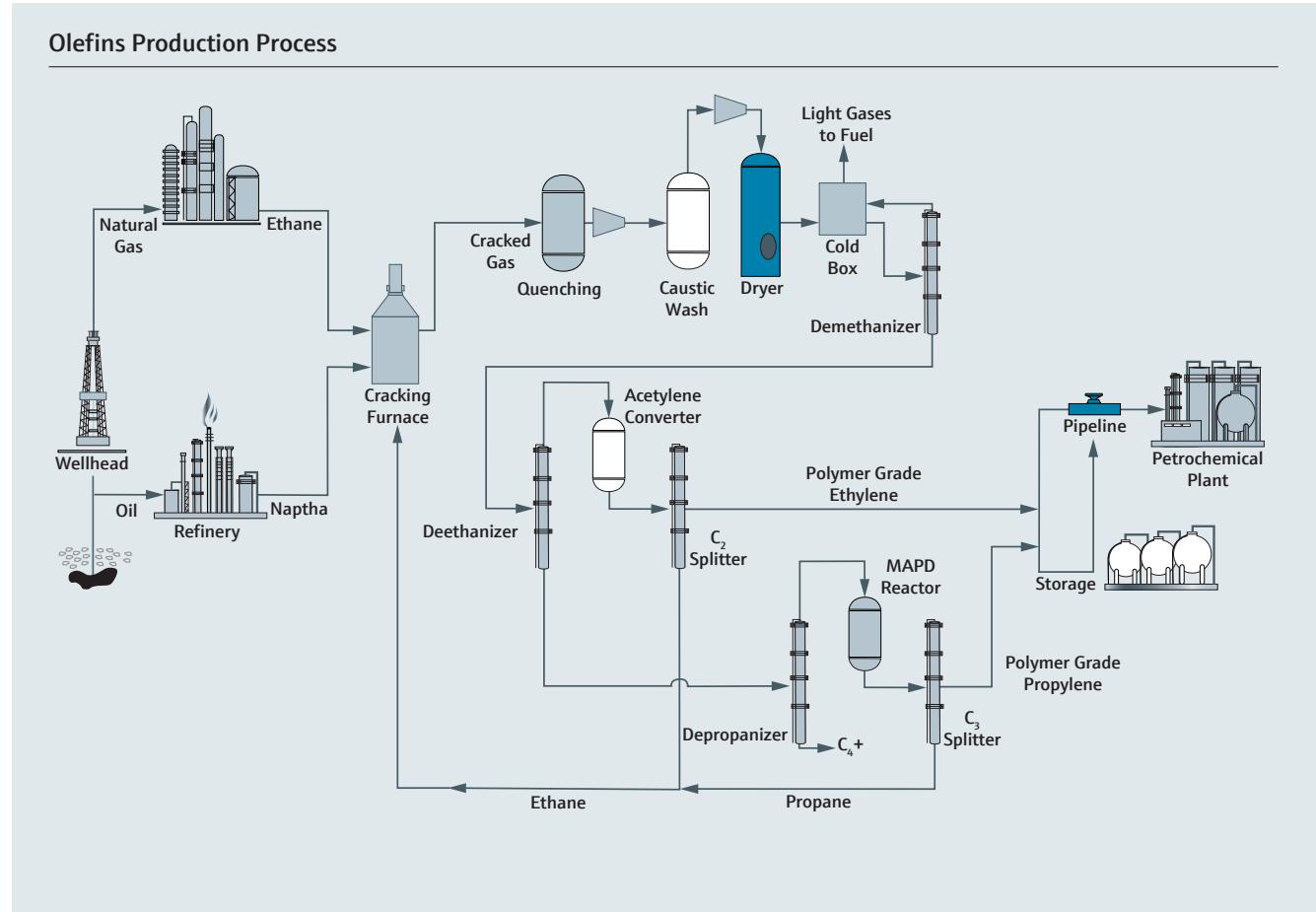
Monitoring contaminants throughout olefins production

Selective and specific measurement of critical contaminants

Crude oil and natural gas contain very small amounts of olefins because they are highly reactive. Consequently, olefins must be manufactured. Production of high purity olefins, ethylene (C_2H_4) and propylene (C_3H_6), involves steam cracking of hydrocarbon feed stocks such as naphtha or ethane followed by a series of unit operations to remove or convert contaminants in the resulting cracked gas stream. The final olefin gas streams serve as feed stocks for production of polymers and other petrochemicals requiring tight control of contaminants to meet purity specifications for these downstream processes.

SpectraSensors' tunable diode laser absorption spectroscopy (TDLAS) analyzers perform on-line measurements of contaminants (C_2H_2 , NH_3 , H_2O , H_2S , and CO_2) at critical points in olefins production plants to support continuous uninterrupted operation.

These measurements help plant operators improve process control, meet stringent product purity specifications, mitigate corrosion and catalyst poisoning, reduce flaring incidents and process shutdowns, and improve plant operating margins.



Caustic wash treatment

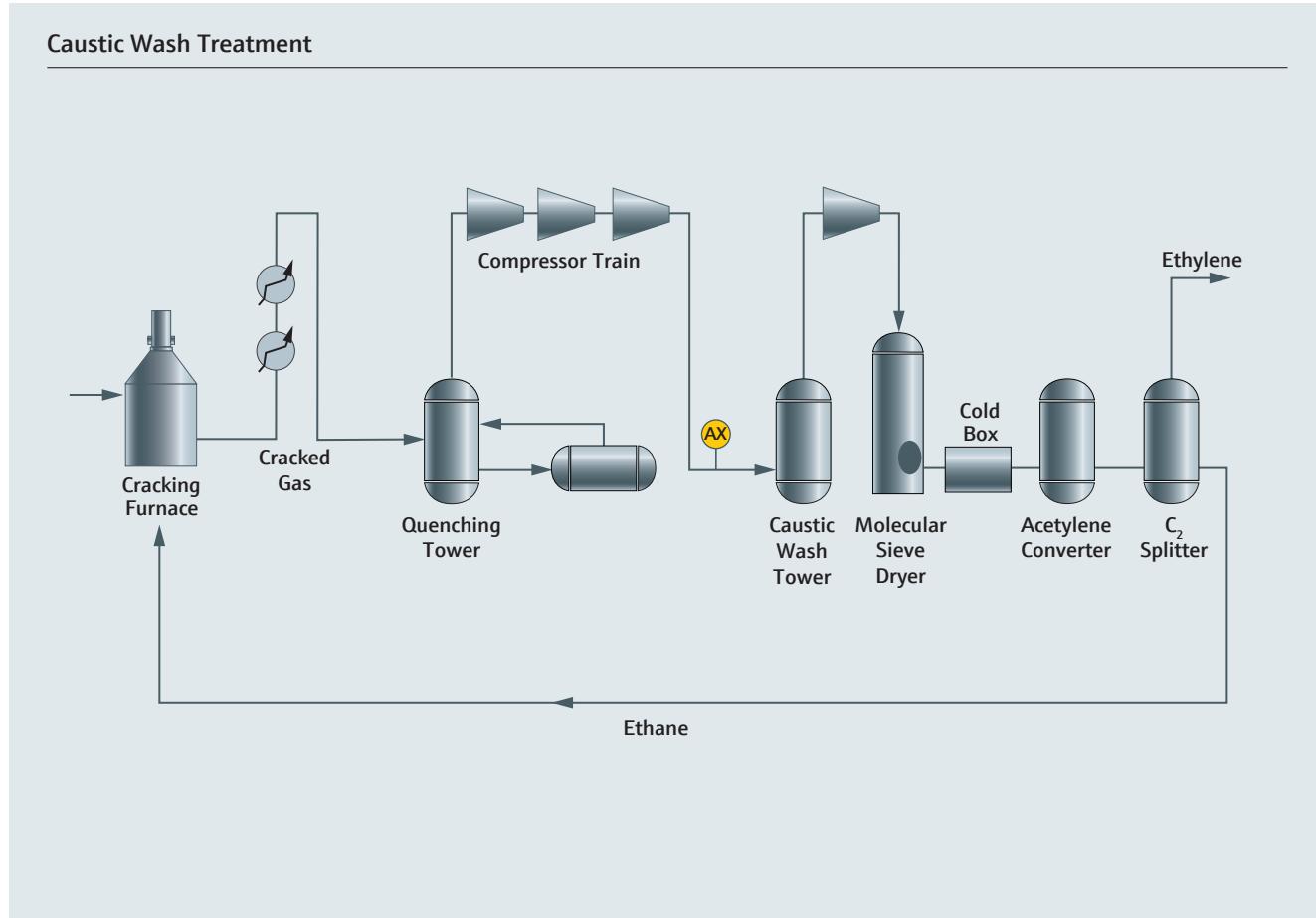
H₂S and CO₂ measurements in cracked gas

The acid gas produced by steam cracking of hydrocarbon feed stocks must be treated to remove CO₂ which can freeze and damage heat exchange and fractionation equipment and H₂S which is corrosive and a catalyst poison. Cracked gas exiting the quench tower is compressed by a multistage compressor. The gas is fed to a caustic wash tower located upstream of the final compression stage.

Inside the caustic wash tower, the gas is contacted with a countercurrent stream of aqueous sodium hydroxide (NaOH) which reacts with H₂S forming sodium sulfide

(Na₂S) and sodium hydrosulfate (NaHS) which are absorbed in the liquid phase. CO₂ reacts and forms sodium carbonate (Na₂CO₃) and sodium bicarbonate (NaHCO₃). Fresh NaOH solution must be added to maintain the efficiency of these scavenging reactions.

SpectraSensors' TDLAS analyzers monitor H₂S and CO₂ at the inlet of caustic wash towers to help control NaOH concentration and compensate for changes in H₂S and CO₂ loading and NaOH depletion.



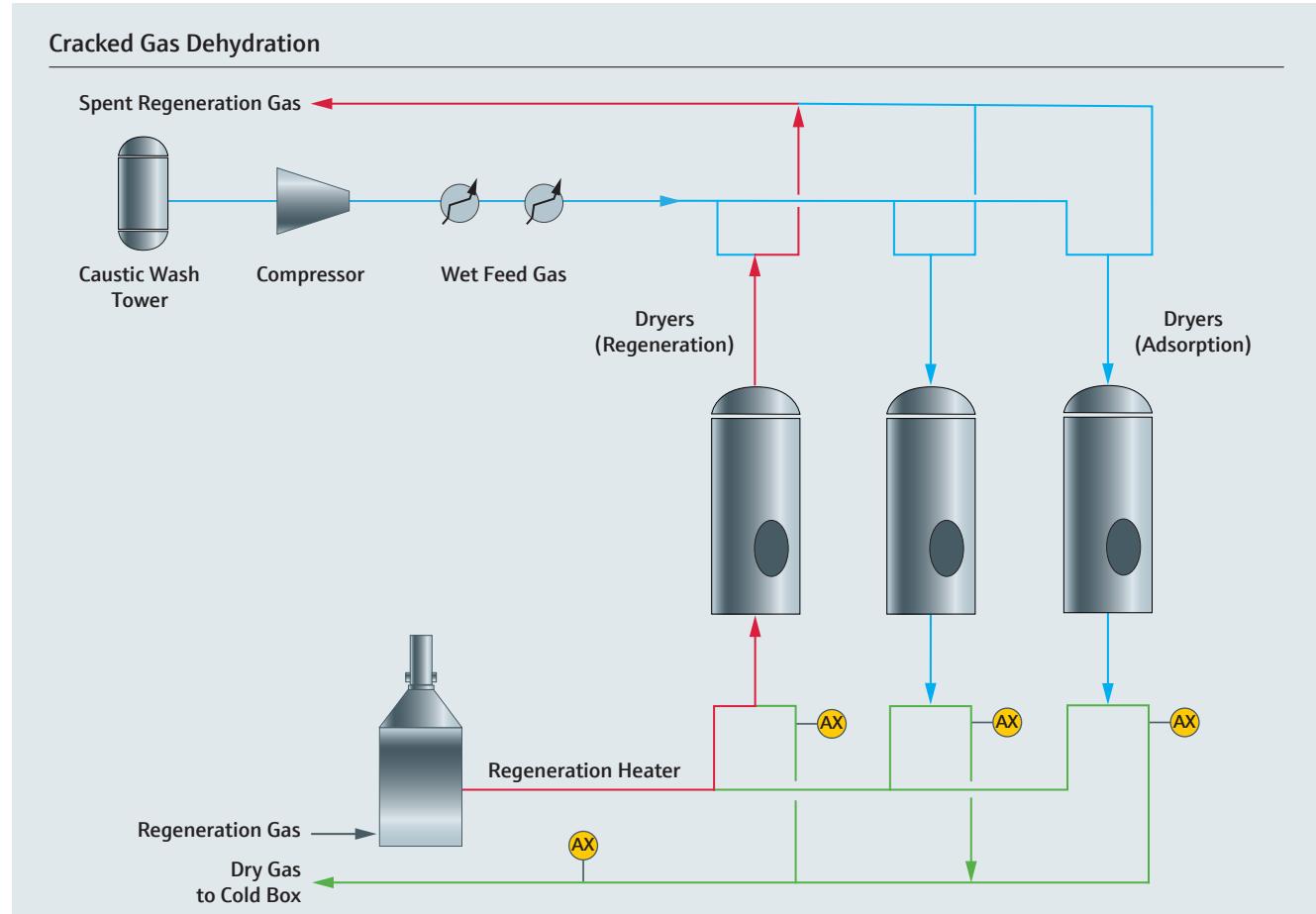
Molecular sieve dehydration

Trace level H₂O measurement in cracked gas

Cracked gas exiting a caustic wash tower is saturated with water vapor. Water must be removed before the gas undergoes cryogenic fractionation to avoid formation of hydrates and ice. Gas treated in the caustic wash tower is compressed and then cooled to remove as much entrained water as possible before it is sent to molecular sieve dryers. Compressing and cooling the gas reduces the water load on the molecular sieve adsorbent beds, lowering operating costs.

Molecular sieve dehydration is used to dry the cracked gas down to < 1 ppm_v before it is introduced into the cold box to remove hydrogen and sent on to the fractionation columns.

SpectraSensors' TDLAS analyzers monitor trace (sub-ppm) levels of H₂O at the outlet of molecular sieve dryer vessels to detect H₂O breakthrough and prevent gas with elevated levels of H₂O from entering downstream cryogenic separation equipment. TDLAS analyzers employ a non-contact, laser based measurement technique which responds much more rapidly to changes in H₂O concentration than quartz crystal microbalance (QCM) analyzers, providing a distinct advantage for this critical measurement.



Acetylene in ethylene

A critical measurement for process control and optimization

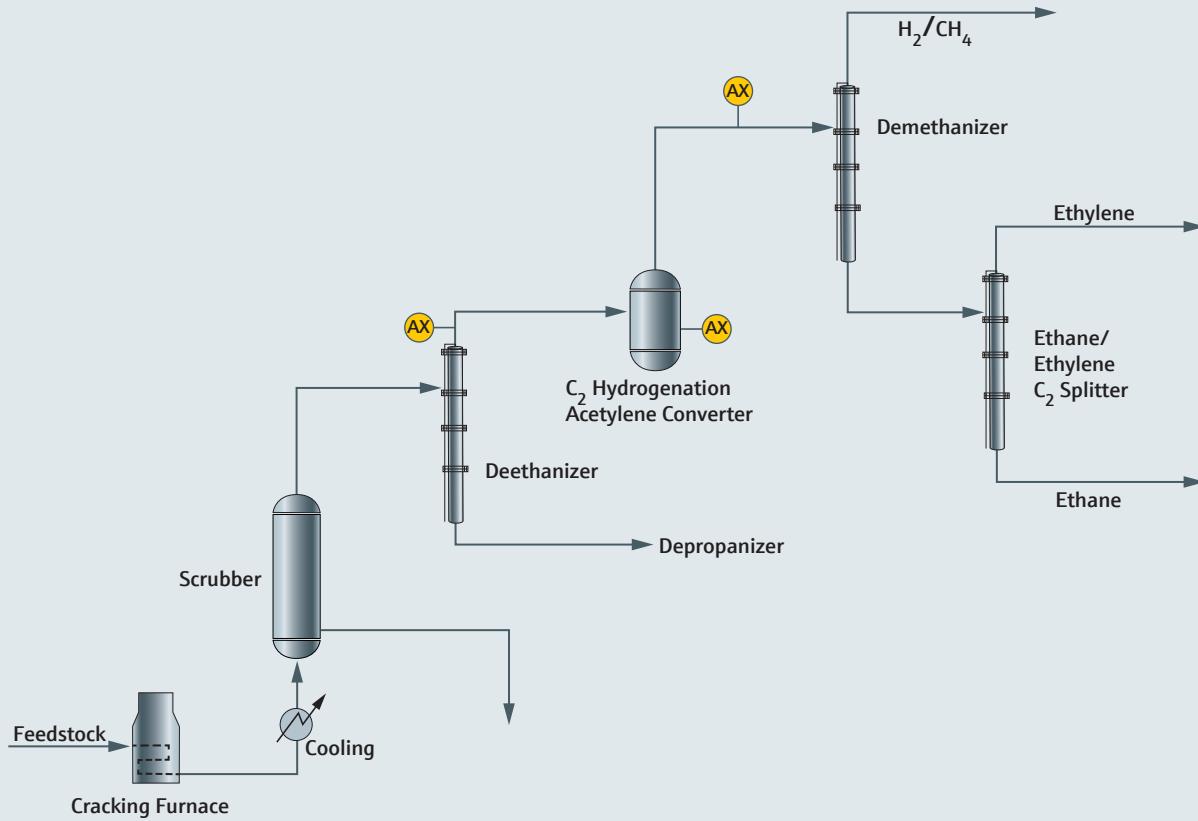
Acetylene is a byproduct of the cracking process that must be removed from ethylene because it poisons and deactivates catalysts used in polyethylene polymer production processes. The amount of acetylene present in cracked gas will vary based upon feedstock, plant design and operating conditions. Separating acetylene (C_2H_2) from ethylene (C_2H_4) is difficult due to the similar volatility of these gases. A catalytic hydrogenation reaction step is typically employed to convert acetylene into ethylene.

An acetylene converter unit consists of a series of reactors or a single vessel with multiple catalyst beds. The concentration of C_2H_2 is reduced from thousands

of ppm at the inlet of an acetylene converter to hundreds of ppm at the mid-bed down to low ppm or ppb levels at the outlet of the converter.

Ethylene plants are characterized by the type of separation column located before the acetylene converter. In a front-end plant the deethanizer is located upstream of the acetylene converter. In a back-end plant the demethanizer is positioned before the acetylene converter. A majority of ethylene plants use the back-end hydrogenation process. Back-end plants generally operate with naphtha and heavier feedstock. Front-end plants are more common for operation with ethane and lighter feedstock.

Front-End Acetylene Hydrogenation



Acetylene in ethylene

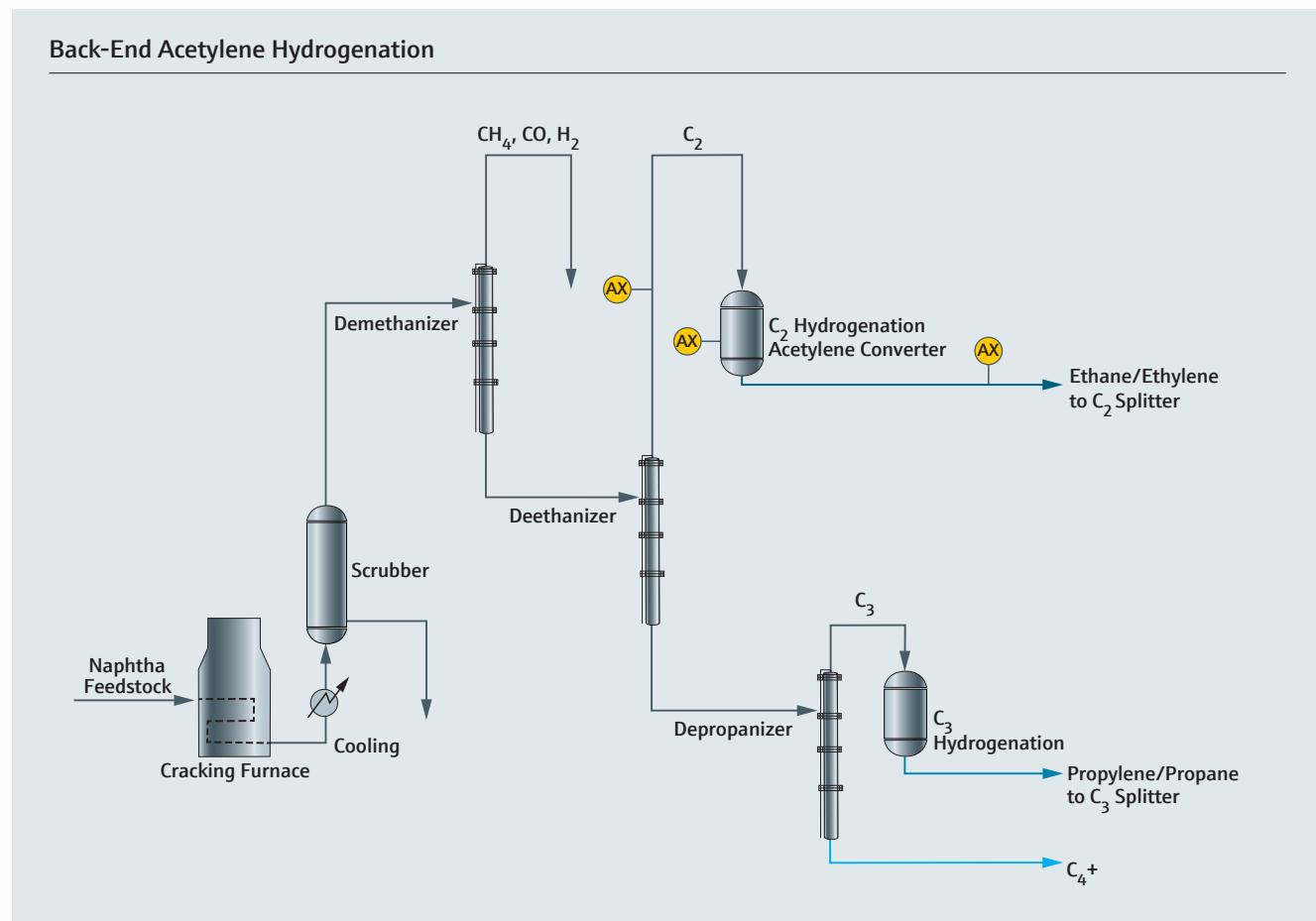
On-line monitoring to prevent off-spec product and flaring

Controlling the ratio of acetylene to hydrogen inside the converter is critical for optimization of ethylene production. Poor control of the hydrogen feed reduces conversion of acetylene into ethylene which can lead to acetylene slippage, off-spec product and flaring, or runaway exothermic reaction conditions inside the converter. On-line measurement of acetylene facilitates control of hydrogenation conditions.

Gas chromatography (GC) has been the traditional technique for acetylene measurements. Analysis time using a GC can extend to several minutes, during which time the C_2H_2 concentration and operating conditions inside the converter can change before chromatographic

results are available. The time interval required to complete a GC analysis may fail to detect an excursion of the C_2H_2 level in time to reestablish normal reaction conditions and avoid routing the gas to flare and taking the process off line.

The exceptionally fast response of TDLAS analyzers to changes in acetylene concentration (seconds versus minutes) is an important performance characteristic for control and optimization of hydrogenation conditions in acetylene converters. SpectraSensors' TDLAS analyzers are used to monitor C_2H_2 levels at the inlet, mid-bed, and outlet of acetylene converters. These on-line measurements help ensure efficient operation of the plant and the ethylene product meets specifications.



High purity ethylene

On-line monitoring of trace level contaminants

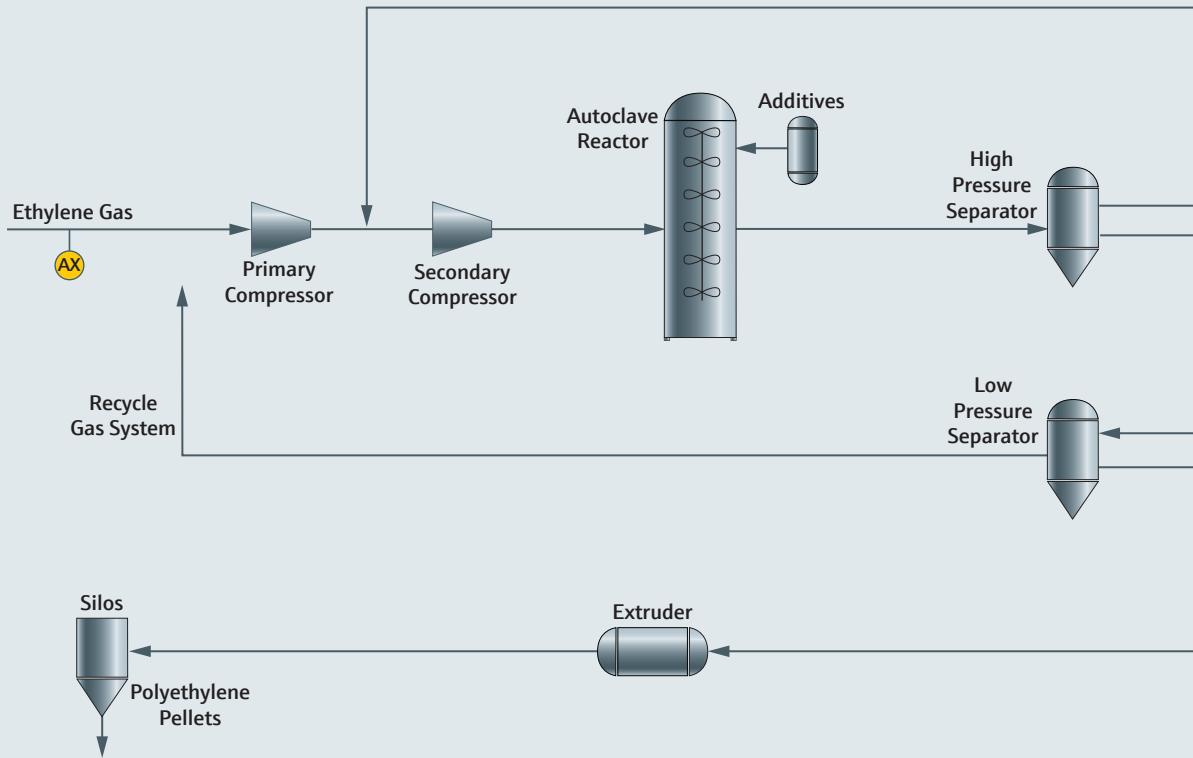
The catalysts used in LDPE, LLDPE, and HDPE polyethylene production processes are highly sensitive to H₂O, NH₃, C₂H₂, CO₂, and other contaminants that poison catalysts and reduce their activity. Purity specifications for polymer-grade ethylene are very stringent, requiring reliable high-sensitivity measurements.

The maximum allowable concentration of H₂O and C₂H₂ for some polymerization processes is 1 ppm. Pipeline specifications for high purity ethylene set the maximum NH₃ concentration at < 0.25 ppm. CO₂ can be absorbed in ethylene and must be removed to protect polymerization

catalysts. Ethylene plants use molecular sieves and adsorbents to remove polar contaminants (H₂O and NH₃) from ethylene to achieve polymer-grade specifications.

The exceptionally fast response of TDLAS analyzers to changes in H₂O, NH₃, C₂H₂, or CO₂ concentration is important for on-line monitoring of ethylene purity in production plants and at custody transfer points in feed streams to polyethylene polymer plants. SpectraSensors' patented differential* spectroscopy technique enables detection and quantitation of sub-ppm levels of H₂O and NH₃ in high purity ethylene.

Low Density Polyethylene (LDPE) Production Process



High purity propylene

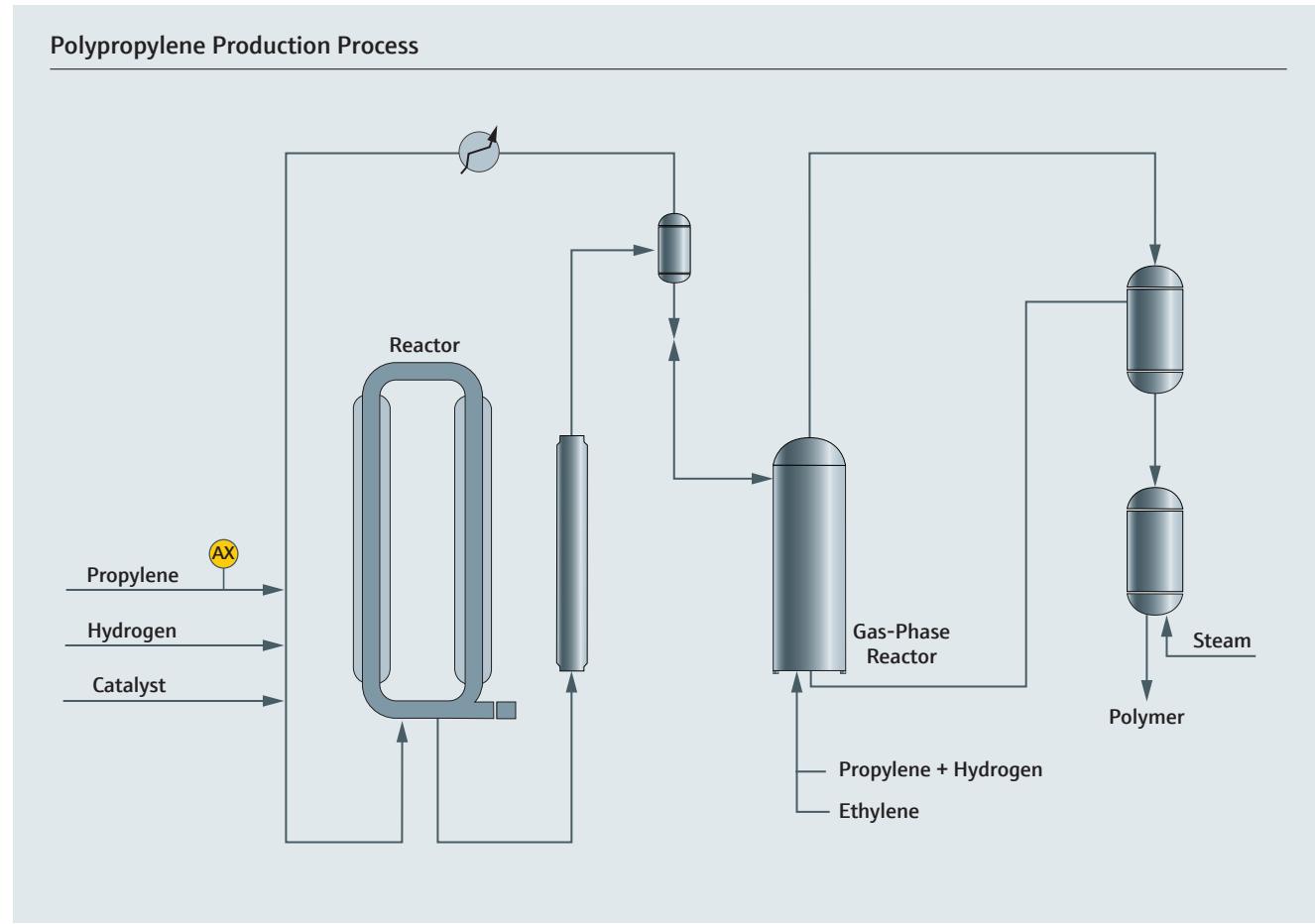
On-line monitoring of trace level contaminants

The catalysts used in polypropylene polymerization processes are highly sensitive to H₂O, NH₃, and other contaminants that poison and reduce catalyst activity. Purity specifications for polymer-grade propylene are very stringent. The maximum allowable concentration of H₂O, and NH₃ for some polymerization processes is 1 ppm_v.

Propylene comes from three major sources; ethylene cracking furnaces, refinery fluid catalytic cracking (FCC) units, and propane dehydrogenation. The propylene product stream from these sources can pick up traces of water during transportation in pipelines or storage in salt

caverns. On-line monitoring ensures the H₂O content of polymer-grade propylene is within specifications for its intended use. Out-of-spec propylene may be rejected by polymer plants, require additional treatment steps, or be sent to flare incurring high costs.

The exceptionally fast response of TDLAS analyzers to changes in H₂O concentration is important for on-line monitoring of propylene purity in production processes and at custody transfer points in feed streams to polymer plants. SpectraSensors' patented* differential spectroscopy technique enables detection and quantitation of sub-ppm levels of H₂O in high purity propylene.



Endress+Hauser is a global leader in measurement instrumentation, services and solutions for industrial process engineering. The company acquired SpectraSensors in 2012. Soon thereafter Kaiser Optical Systems was also acquired bringing the Raman-based Optograf analyzer into the product portfolio further solidifying Endress+Hauser's position in process gas analytics.

Contact

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