TDLAS analyzers for olefins production

Accurate and reliable measurement of C_2H_2, NH_3, H_2O, H_2S, and CO_2

Endress+Hauser
People for Process Automation

Laser-based analyzers for olefins production

Laser spectroscopy – a better solution for challenging process conditions

The Endress+Hauser 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 our TDLAS analyzers, which are powered by SpectraSensors TDLAS technology, provide significant advantages over other technologies for monitoring C_2H_2, NH_3, H_2O, H_2S, and CO_2 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 C_2H_2, NH_3, H_2O, H_2S, and CO_2 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.

TDLAS analyzers for olefins production

Monitoring contaminants throughout olefins production

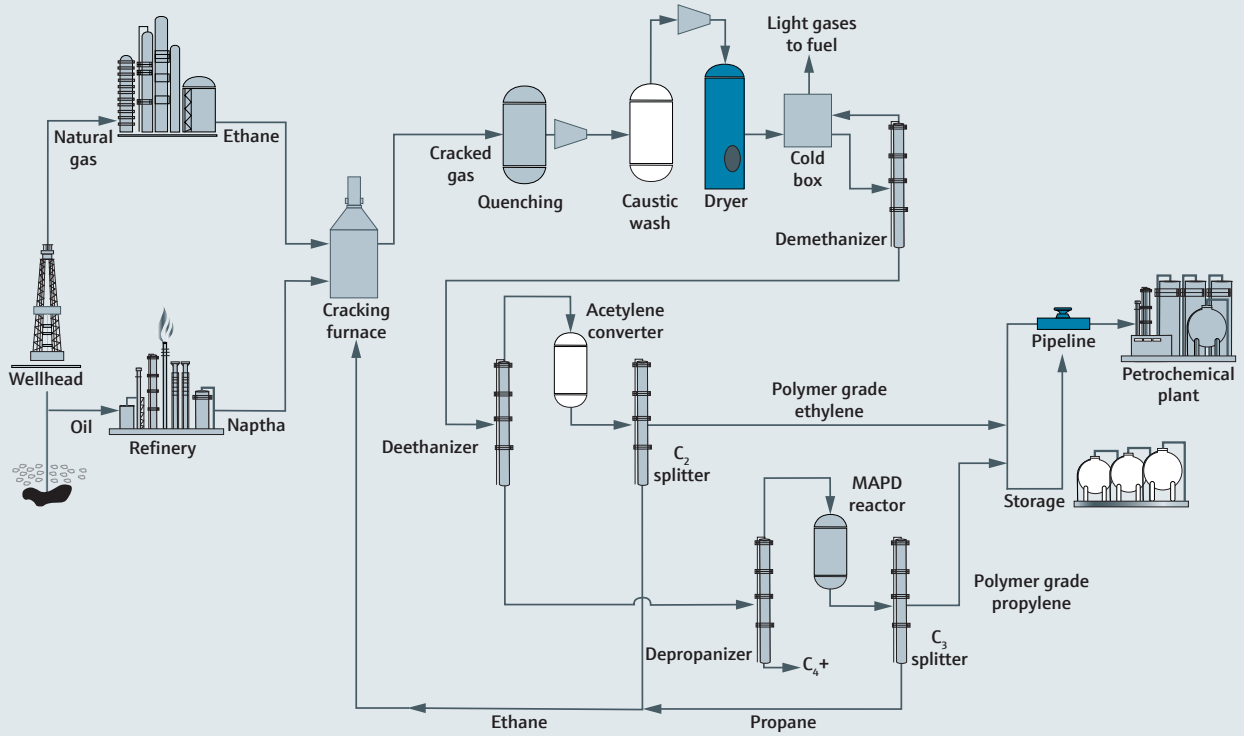
Selective and specific measurement of critical contaminants

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.

Endress+Hauser 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.

Olefins production process



Caustic wash treatment

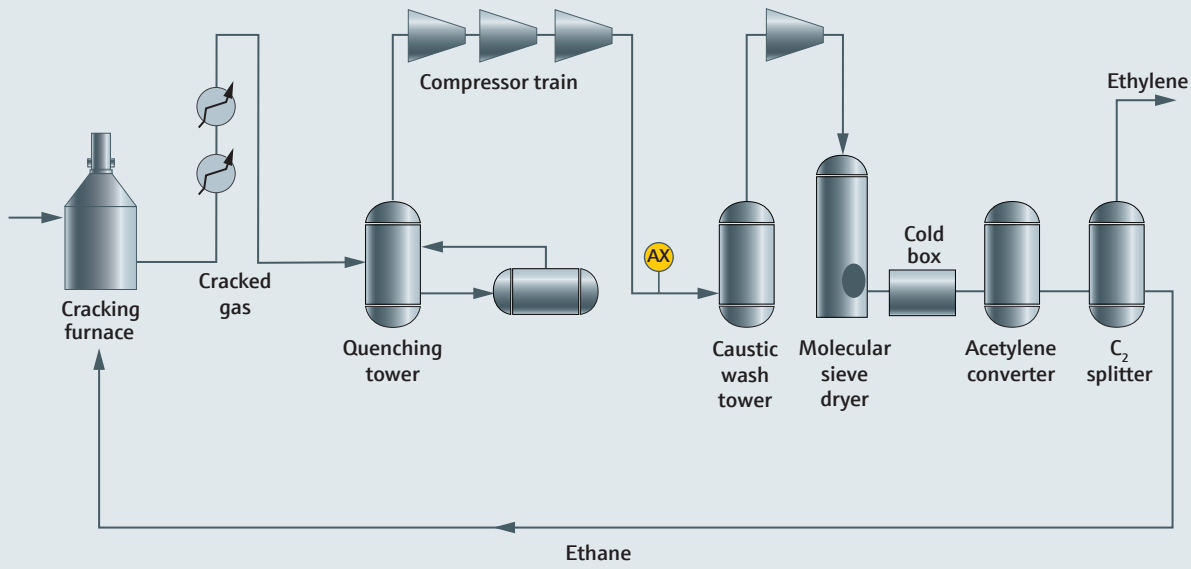
H_2S and CO_2 measurements in cracked gas

The acid gas produced by steam cracking of hydrocarbon feed stocks must be treated to remove CO_2 which can freeze and damage heat exchange and fractionation equipment, and H_2S 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 H_2S forming sodium sulfide (Na_2S) and sodium hydrosulfate (NaHS) which are absorbed in the liquid phase. CO_2 reacts and forms sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$). Fresh NaOH solution must be added to maintain the efficiency of these scavenging reactions.

Endress+Hauser TDLAS analyzers monitor H_2S and CO_2 at the inlet of caustic wash towers to help control NaOH concentration and compensate for changes in H_2S and CO_2 loading and NaOH depletion.

Caustic wash treatment



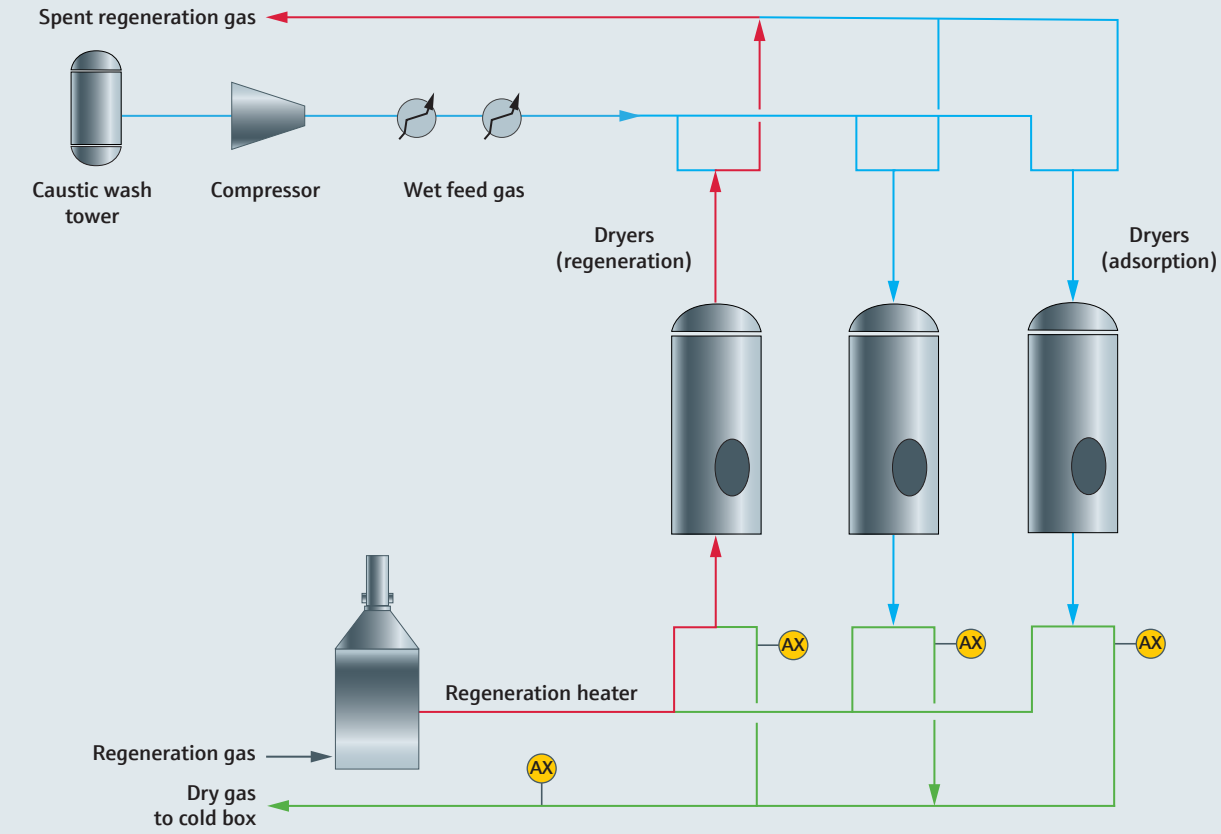
Molecular sieve dehydration

Trace level H_2O 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. Endress+Hauser TDLAS analyzers monitor trace (sub-ppm) levels of H_2O at the outlet of molecular sieve dryer vessels to detect H_2O breakthrough and prevent gas with elevated levels of H_2O from entering downstream cryogenic separation equipment. TDLAS analyzers employ a non-contact, laser based measurement technique which responds much more rapidly to changes in H_2O concentration than QCM analyzers, providing a distinct advantage for this critical measurement.

Cracked gas dehydration



Acetylene in ethylene

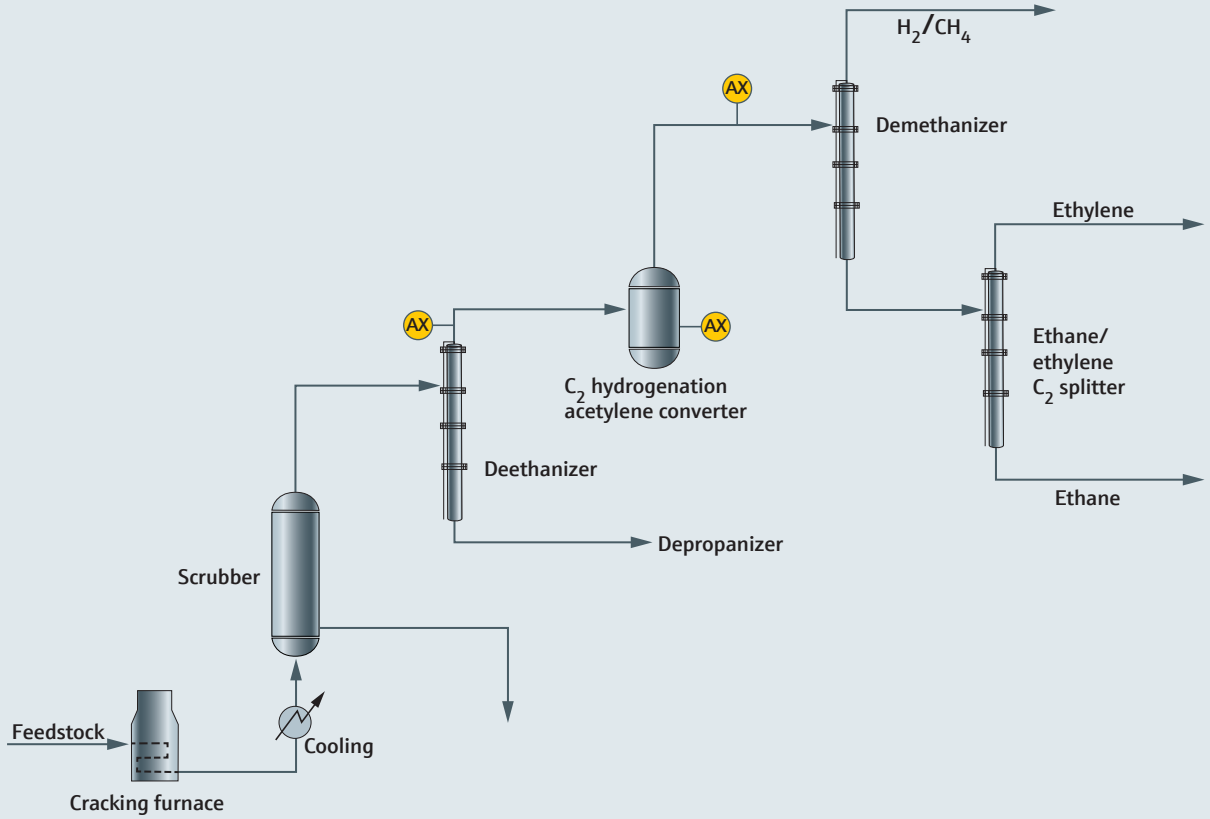
A critical measurement for process control and optimization

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

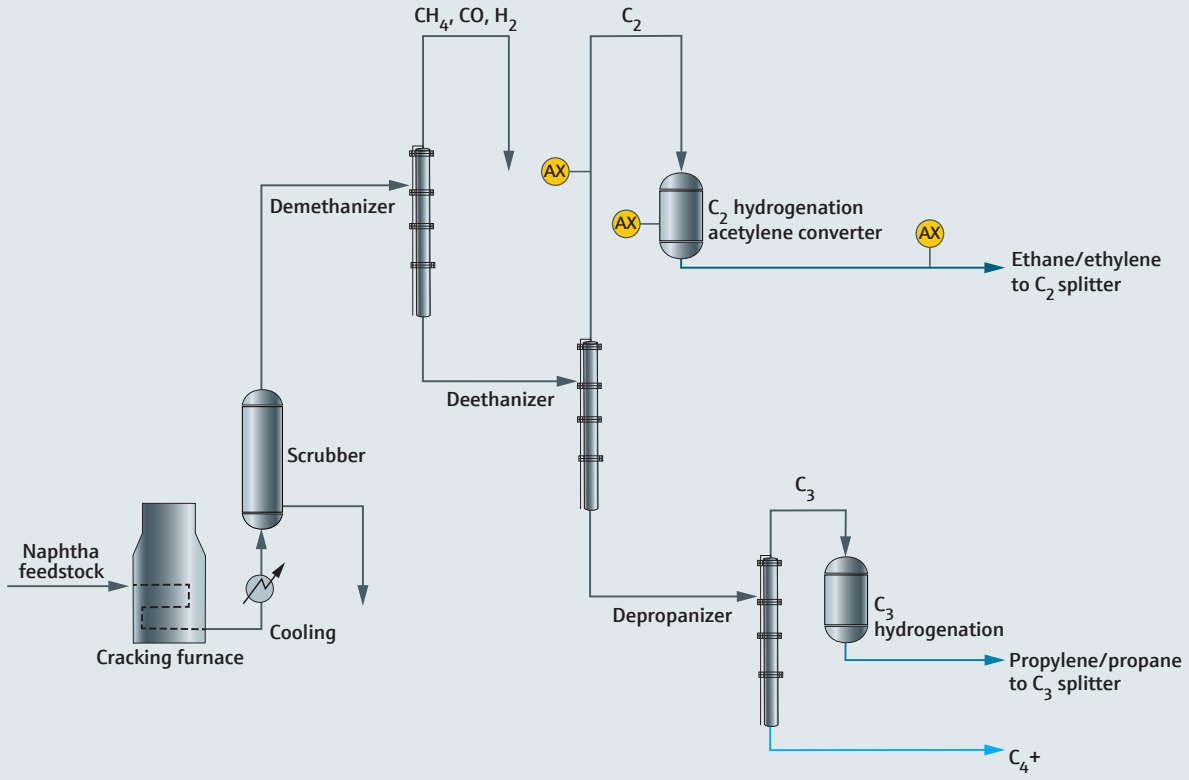
On-line monitoring to prevent off-spec product and flaring

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 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. Endress+Hauser 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.

Back-end acetylene hydrogenation



High purity ethylene

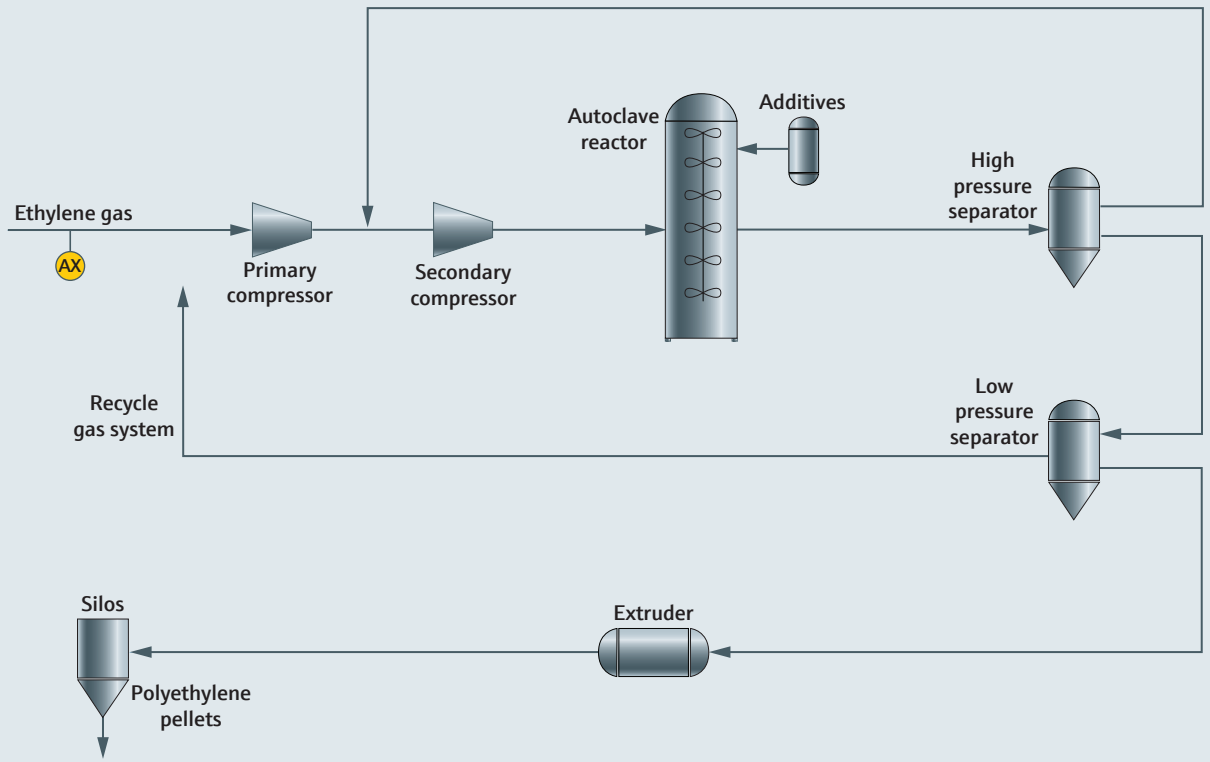
On-line monitoring of trace level contaminants

The catalysts used in LDPE, LLDPE, and HDPE polyethylene production processes are highly sensitive to H_2O, NH_3, C_2H_2, CO_2, 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 H_2O and C_2H_2 for some polymerization processes is 1 ppm_v. Pipeline specifications for high purity ethylene set the maximum NH_3 concentration at < 0.25 ppm_v. CO_2 can be absorbed in ethylene and must be removed to protect polymerization catalysts. Ethylene plants use molecular sieves and adsorbents to remove polar contaminants (H_2O and NH_3) from ethylene to achieve polymer-grade specifications.

The exceptionally fast response of TDLAS analyzers to changes in H_2O, NH_3, C_2H_2, or CO_2 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. Endress+Hauser patented differential spectroscopy technique enables detection and quantitation of sub-ppm levels of H_2O and NH_3 in high purity ethylene.

Low density polyethylene (LDPE) **production process**



High purity propylene

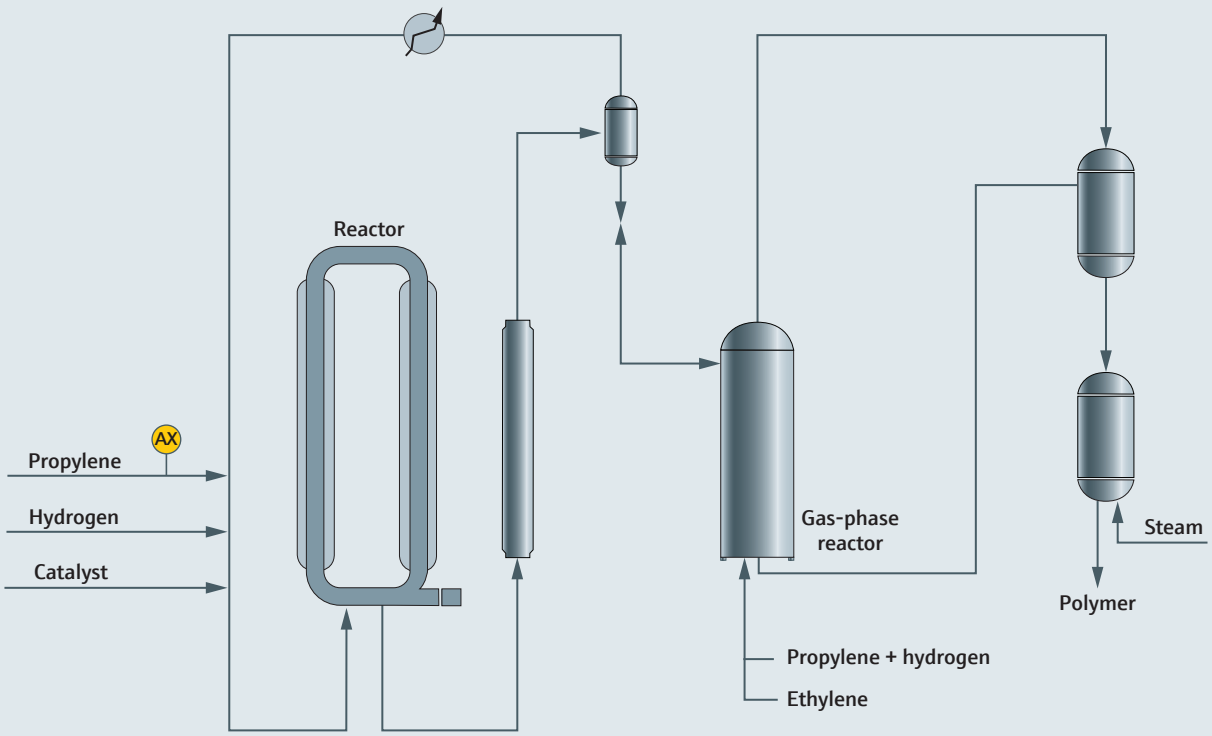
On-line monitoring of trace level contaminants

The catalysts used in polypropylene polymerization processes are highly sensitive to H_2O, NH_3, and other contaminants that poison and reduce catalyst activity. Purity specifications for polymer-grade propylene are very stringent. The maximum allowable concentration of H_2O, and NH_3 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 H_2O 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 H_2O concentration is important for on-line monitoring of propylene purity in production processes and at custody transfer points in feed streams to polymer plants. Endress+Hauser patented differential spectroscopy technique enables detection and quantitation of sub-ppm levels of H_2O in high purity propylene.

Polypropylene production process



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