TDLAS analyzers for refinery gases

Accurate and reliable measurement of H_2S and H_2O

Endress+Hauser
People for Process Automation

Laser-based analyzers for refinery gases

Laser spectroscopy – a better solution for challenging process conditions

The Endress+Hauser advantage Tunable diode laser absorption spectroscopy (TDLAS) analyzers from Endress+Hauser perform on-line, real-time measurements of impurities in process gas streams from sub-ppm levels to low percentage levels. The unique design of our TDLAS analyzers, powered by SpectraSensors TDLAS technology, provide significant advantages over other technologies for monitoring H_2O and H_2S in refinery gas 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 the fouling and corrosion problems associated with Al_2O_3 and quartz crystal microbalance moisture analyzers, ensuring reliable long-term operation.

Fast response and analysis time TDLAS analyzers detect changes in analyte concentration much faster than other techniques. The wet-up and dry-down times associated with quartz crystal microbalance moisture analyzers result in a delayed response to concentration changes. Gas chromatography results can be delayed several minutes awaiting completion of a chromatographic run.

Low cost of ownership Unlike gas chromatographs (GCs) and lead acetate tape analyzers, TDLAS analyzers have virtually no consumable components resulting in a lower cost of ownership and a lower service and maintenance burden on technicians.

TDLAS analyzers for refinery area safety classifications

Monitoring contaminants in refinery gas streams for operational efficiency

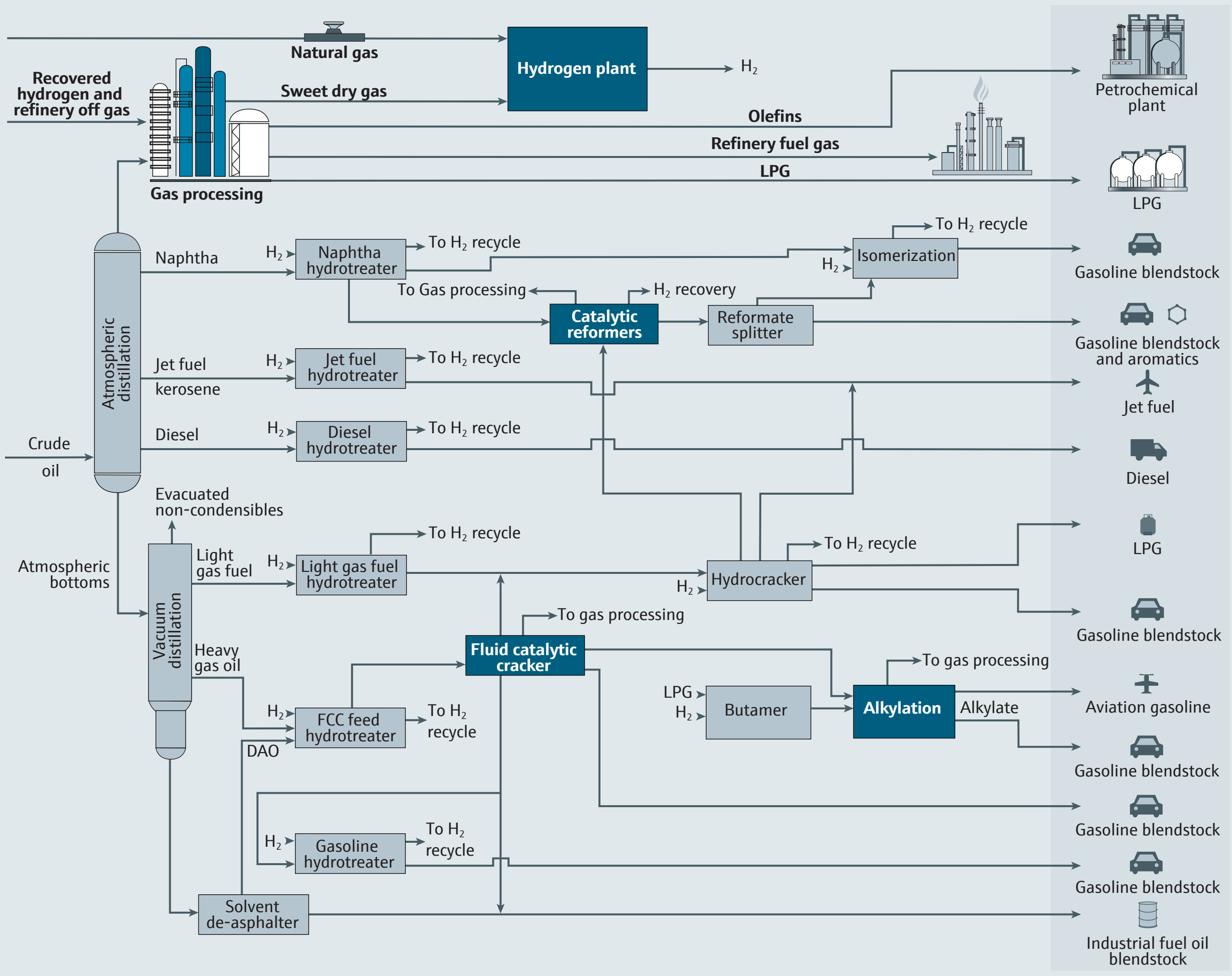
Selective and specific measurement of critical process contaminants

The design of a refinery gas distribution network and management of gas streams directly affect production capacity. Refineries must produce, recover, treat, and recycle hydrogen and other gases in order to produce low-sulfur clean fuels.

Refinery gas streams contain contaminants that can adversely affect operational efficiency, process yields, and refinery operating margins. Endress+Hauser TDLAS analyzers perform on-line measurements of H_2S and H_2O in process gas streams to help refineries control these contaminants and optimize unit operations.

On-line monitoring of H_2S and H_2O provides refineries the data needed to improve process control, meet product specifications, mitigate corrosion and catalyst poisoning, comply with environmental regulations, and treat hydrogen and off gas streams for use in downstream refinery and petrochemical processes.

Refinery unit operations, products and gas streams



Fluid catalytic cracker unit (FCCU) C_3 gases

H_2S and H_2O measurement in propylene and propane

Fluid catalytic cracking units (FCCUs) are a major source of the propylene feedstock used in petrochemical plants. The yield of propylene from an FCCU varies with feedstock and operating conditions. Refineries operate FCCUs to achieve a balance of gasoline and propylene production.

The gas plant associated with an FCCU separates fuel gas from C_3 and C_4 gases and gasoline, and contains treatment equipment to remove H_2S, H_2O and other contaminants from these products.

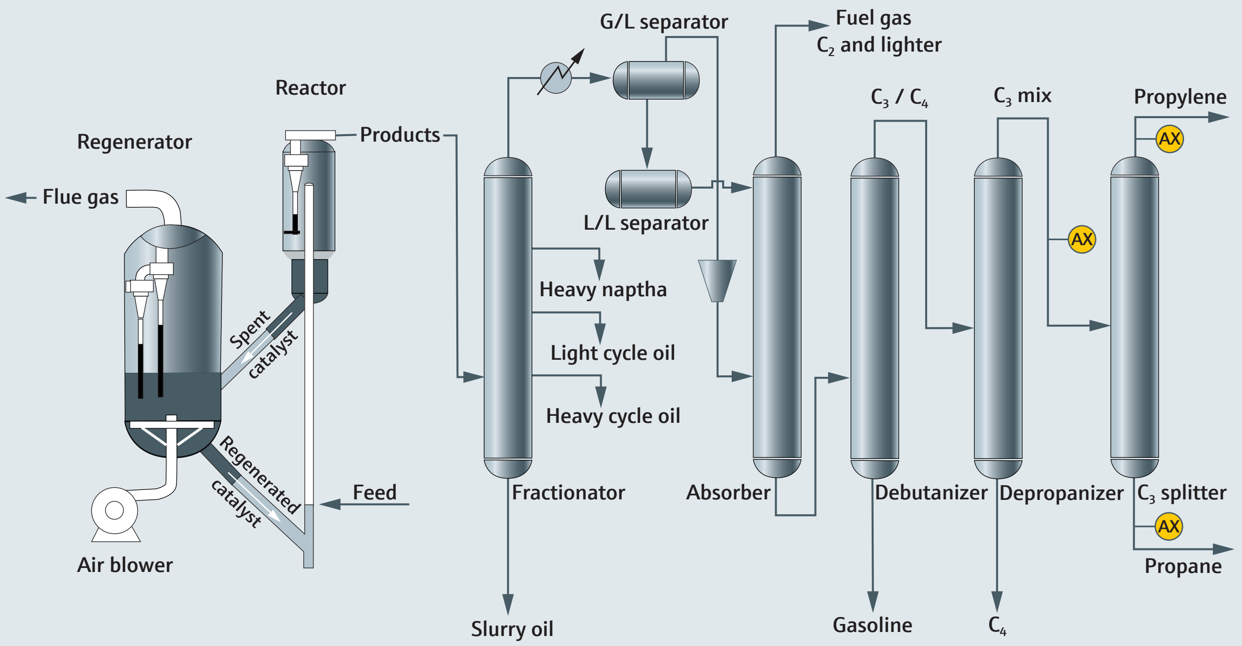
Many downstream petrochemical processes employ catalysts that are highly sensitive to H_2S and H_2O.

These contaminants must be removed from C_3 propane/propylene mixtures to avoid carryover into the separated propane and propylene product streams.

On-line monitoring of H_2S and H_2O in C_3 mix, and the separated propane and propylene product streams ensures purity specifications are met for downstream refinery and petrochemical production processes.

Endress+Hauser's patented differential spectroscopy technique enables detection and quantitation of low ppm levels of H_2O and H_2S in propane/propylene mixtures.

Fluid catalytic cracker unit (FCCU) **C3 gas recovery**



Semi-regenerative catalytic reformer (SRR)

H_2O and H_2S measurement in hydrogen recycle gas

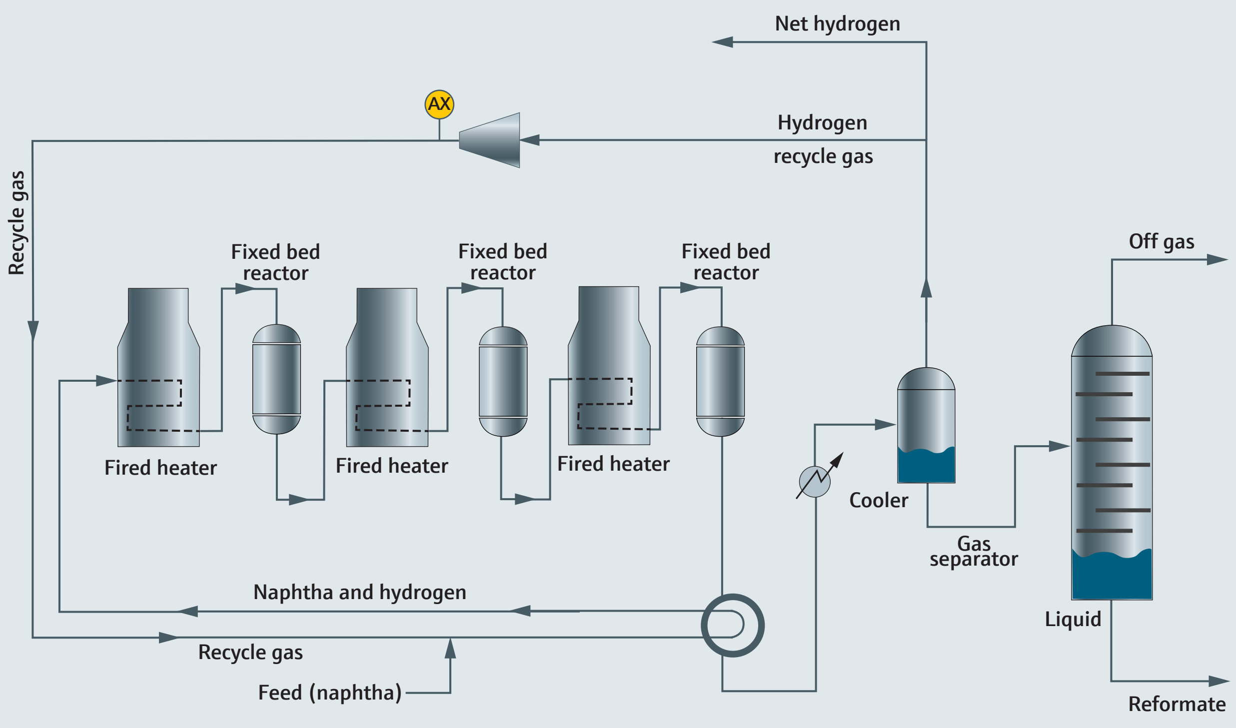
Catalytic reformers convert naphtha into high-octane aromatic compounds used in gasoline blending, and yield large quantities of hydrogen which is recycled and used in other refinery processes. A semi-regenerative catalytic reformer (SRR) unit has three fixed bed catalytic reactors employing a platinum/rhenium catalyst on a chloride alumina support. Water and an organic chloride compound are continuously injected to maintain acid sites needed to perform the conversion reactions.

Excess H_2O strips chloride from catalyst surfaces and forms corrosive HCl which is transported throughout the process piping of the SRR unit. On-line monitoring of the H_2O concentration enables refineries to control the chloride level for catalyst activity and minimize HCl formation.

Catalyst activity in an SRR gradually decreases as coke is deposited on the catalyst. The SRR must be shut down periodically to burn off coke deposits and regenerate the catalyst. Tracking the H_2O level in hydrogen gas recirculating through an SRR to dry down catalyst following regeneration helps determine when end point H_2O conditions have been reached to restart the SRR unit and resume production. Delays in restarting a SRR can cost a refinery hundreds of thousands of dollars per day in lost production.

Inside an SRR, sulfur compounds are converted into H_2S which is entrained in the recycle and net hydrogen streams. On-line monitoring of H_2S in the hydrogen recycle gas helps prevent poisoning of the platinum/rhenium catalyst.

Semi-regenerative catalytic reformer (SRR)



Continuous catalytic reformer (CCR)

H_2O and H_2S measurement in hydrogen recycle gas

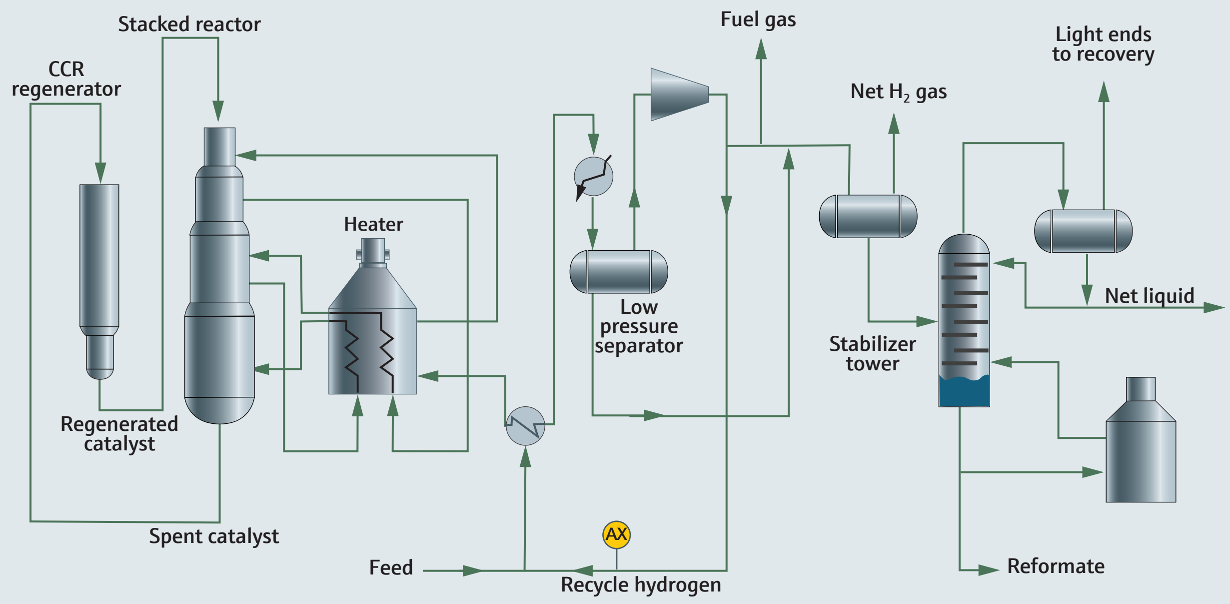
A continuous catalytic reactor (CCR) has a 3-stage stacked reactor employing platinum/rhenium catalyst on a spherical chloride alumina support. Gravity causes the catalyst to flow down through the reactor stack. The catalyst is continuously extracted from the bottom of the reactor stack and transferred to a separate, external catalyst regenerator.

Inside the regenerator, coke deposits are burned off and the catalyst oxy-chlorinated and dried sequentially in separate zones. Following reactivation with hydrogen, the catalyst is returned to the top of the reactor stack.

On-line monitoring of the H_2O concentration enables refineries to control the chloride level required for catalyst activity and helps minimize HCl formation. Carryover of small amounts of HCl in the net hydrogen gas can cause serious operating problems in downstream processes using the hydrogen.

Sulfur compounds in the naphtha feed are converted to H_2S inside a CCR reactor. On-line monitoring of H_2S in the hydrogen recycle gas helps prevent poisoning of the platinum/rhenium catalyst.

Continuous catalytic reformer (CCR)



Refinery fuel and flare gas

H_2S measurement for environmental compliance

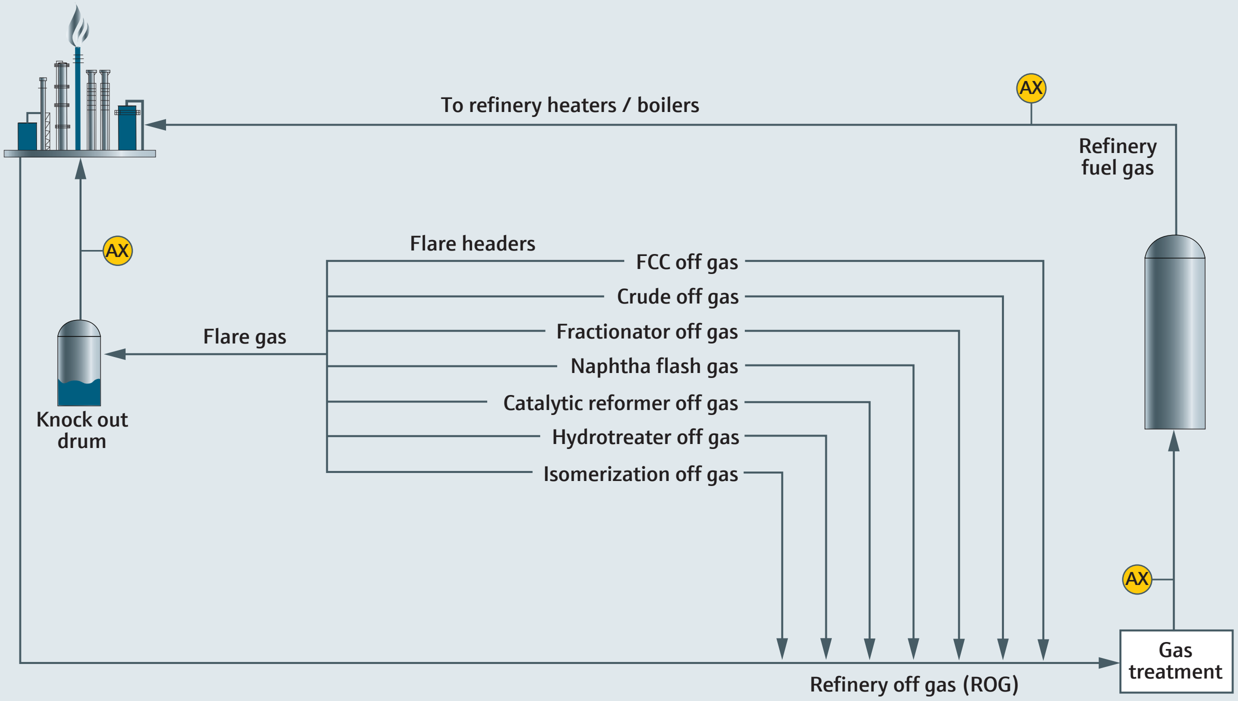
Refinery fuel gas is composed of a mixture of hydrogen and C_1 to C_5 hydrocarbons recovered from different unit operations within a refinery for use as fuel in fired heaters and boilers. In the U.S., sulfur emissions from combustion of fuel gas and refinery flare systems are regulated under the Clean Air Act & Amendments (CAAA).

The U.S. EPA is responsible for issuing regulations and test methods for compliance enforcement. Regulations covering sulfur (SO_2) emissions from combustion of fuel gas and flare systems are defined in 40 CFR 60 Subpart Ja. Similar regulations aimed at reducing SO_2 emissions have been promulgated in Europe, the Middle East, and Asia.

The U.S. EPA recognizes that measurement of H_2S gives a good approximation of the total SO_2 that is generated from combustion of refinery fuel and flare gases. The required measurement range for H_2S in fuel gas is 0 – 320 ppm_v. The regulatory limit is 162 ppmv. One measurement every 15 minutes (96 times / day) is required to meet U.S. EPA requirements for continuous emissions monitoring.

For flare gas, H_2S levels must not exceed 162 ppm_v over a three-hour rolling average time period (approximately 500 lbs. of SO_2 in any 24-hour period).

Refinery fuel and flare gas systems



Refinery off gas (ROG)

Measuring contaminants in refinery off gas for olefins recovery

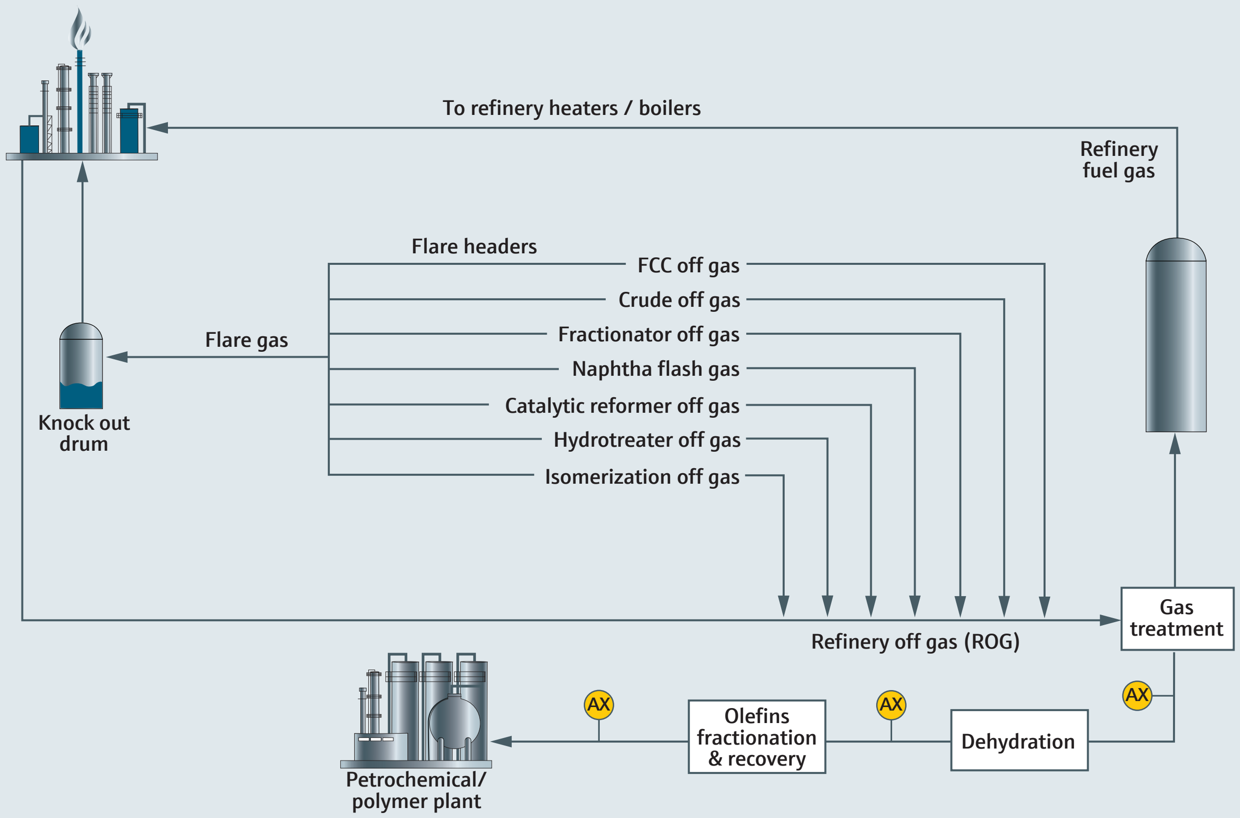
Refinery off gases recovered from unit operations are typically collected and sent to the refinery's fuel gas system. Large quantities of off gas from FCCU, coker, and catalytic reforming units can overload a refinery's fuel gas system with excess gas sent to flare.

The off gas streams from FCCU and coker units contain significant amounts of olefins that can be recovered, treated, and upgraded from low value fuel components into higher value ethylene and propylene.

Refineries with high crude oil processing capacities (> 250,000 bpd) may have integrated petrochemical complexes to take advantage of feedstocks recovered from refinery off gases. In these cases, the ROG must undergo more extensive gas treatment to remove contaminants (H_2S, CO_2, H_2O, NH_3, C_2H_2, Hg, and COS) than occurs in a fuel gas system prior to fractionation and olefins recovery.

ROG exiting an amine treatment unit is saturated with water. Water must be removed before the gas undergoes cryogenic fractionation. Molecular sieve dehydration is used to dry ROG streams down to < 1 ppmv H_2O to avoid formation of hydrates and ice during cryogenic fractionation. On-line monitoring of H_2O at the outlet of molecular sieve dryer vessels helps detect H_2O breakthrough and prevent gas with elevated levels of H_2O from entering cryogenic separation equipment.

Refinery off gas system for olefins recovery



HF alkylation

H_2O measurement in alkylation feedstock

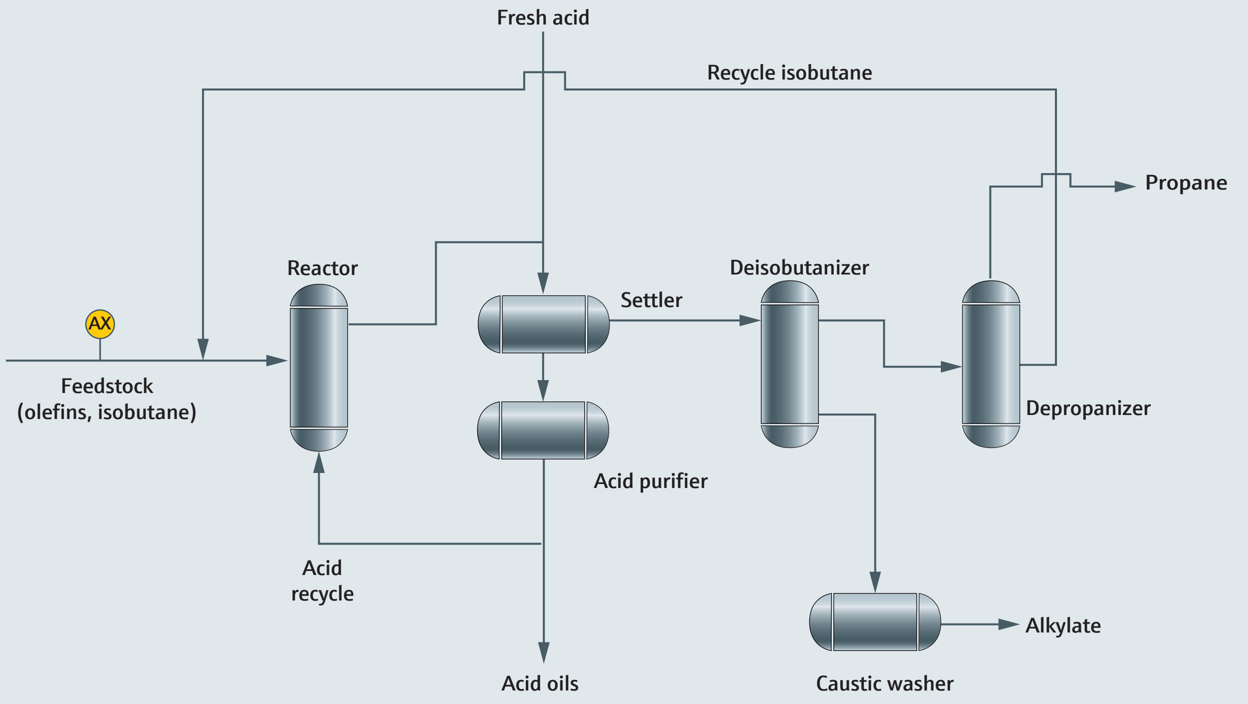
In HF alkylation, C_3 – C_5 olefins from a FCCU are reacted with isobutane to produce high octane fuel alkylate. Water must be removed from the olefin feedstock to minimize corrosion and formation of acid soluble oil (ASO) and fluorinated by-products. Process efficiency and properties of the alkylate end product (octane number, vapor pressure) are affected by HF acid purity and water content.

The water content of olefin feedstock is typically in the range of 1 – 5 ppmv. On-line monitoring of H_2O helps prevent build-up of ASO which consumes HF and reduces acid strength. HF consumption can cause an acid runaway condition requiring process shutdown for costly, specialized maintenance.

The exceptionally fast response of TDLAS analyzers to changes in H_2O concentration helps control the H_2O content of feedstock entering an HF alkylation unit. The non-contact, laser-based measurement technique of TDLAS analyzers avoids fouling and corrosion that leads to frequent replacement of devices using direct contact sensors.

The superior on-stream factor (analyzer availability) of TDLAS analyzers reduces the need for personnel to enter the HF alkylation unit area to undertake repair or replacement of H_2O analyzers.

HF alkylation process



Instrument air systems

H_2O measurement in instrument air

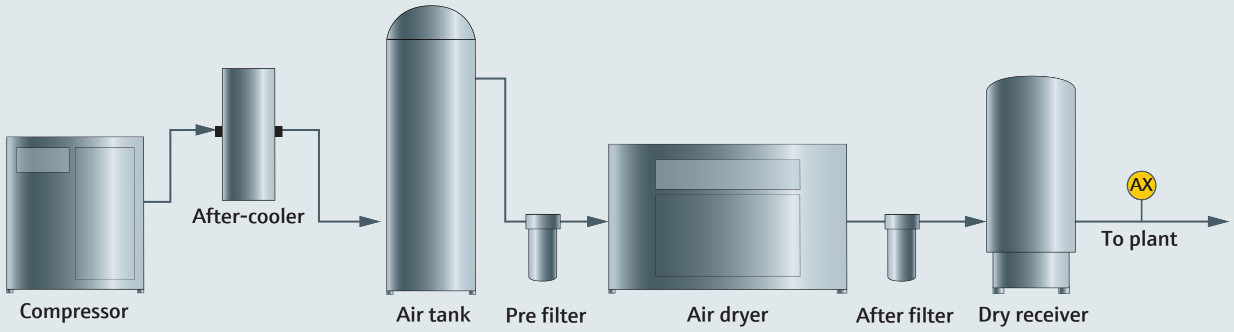
The air supplied to instruments, transmitters, solenoid valves, and pneumatic controllers must be clean and dry for efficient operation of control system components. Corrosion damage from moisture in an instrument air system can cause false readings and/or instrumentation malfunctions potentially leading to process upsets or shutdowns.

Refineries and petrochemical plants monitor moisture in instrument air to protect pneumatically controlled devices and ensure those devices are functioning properly and safely.

Moisture, particulate matter, lubricants, and hazardous or corrosive chemicals are the four major types of contaminants defined in ISA-S7.3: Quality Standard for Instrument Air.

TDLAS analyzers have proven to be effective means of monitoring moisture in refinery instrument air systems. The laser and detector components are isolated and protected from contaminants entrained in instrument air. This design avoids the fouling and corrosion problems experienced with analyzers using direct contact sensors (aluminum oxide capacitance sensors and quartz crystal microbalances).

Instrument air system



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