UP REFINERY PROFITABILITY THROUGH ENHANCED ANALYTICAL MEASUREMENT

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Gas chromatographs are an important fixture in modern refineries (and petrochemical plants). Experienced plant operators depend on and fully understand the impact this analyzer system has on the profitability of the plant.

Refinery profits depend heavily on optimal operation in the critical fluid catalytic cracking unit (FCCU) and vapor recovery unit (VRU), and to achieve that operation, real-time compositional data to process control systems is required.

The FCCU is one of the most important processes for converting low-value heavy oils into valuable gasoline and lighter product. More than half of the refinery's heavy petroleum goes through the FCCU for processing, therefore optimal operation of the FCCU directly impacts the refinery's profitability. The valuable light gases produced by the catalytic process are sent to a VRU. VRUs are an important source of butane and pentane olefins, which are used as feed in refinery processes such as the alkylation unit. The alkylation unit then converts the olefins to high-octane products. The process gas chromatograph (GC) is the analytical workhorse for online compositional measurement in refineries and understanding the GCs function can aid in enhancing the refinery's operations.

FCCU Optimization

To improve the FCCU's performance, a process GC is used to measure the composition of the regenerator flue gas stream leaving the top of the regenerator. As a review, the feed to the FCCU in a refinery is composed of the heavy gas oils from the crude unit as well as vacuum gas oils from the vacuum crude unit. The feed can also come from other units that generate heavy petroleum streams, such as the coker or deasphalter. Before it enters the main FCC reactor, the feed stream is mixed with hot, freshly regenerated catalyst and heated to almost 1,000°F (538°C).

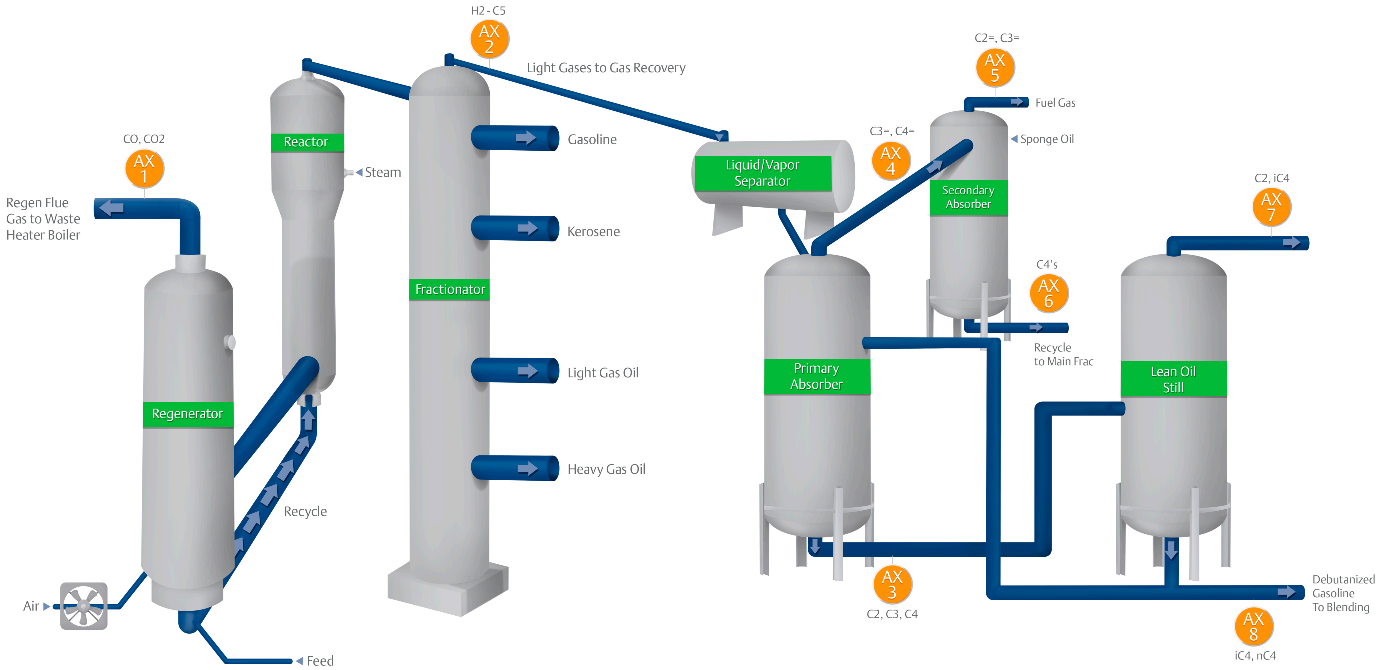

Figure 1. A typical FCCU

When the catalyst and the oil contact in the pipe leading the reactor, the chemical reactions happen immediately. Further reactions in the fluidized beds brings about the "cracking" of large molecules in the oil into smaller ones, carbon forms on the surface of the catalyst, quickly de-activating it.

Inside the reactor, steam is injected to strip off any oil or carbon that is clinging to the catalyst pellets. The cracked oil vapors flow out of the top of the reactor, with the spent catalyst flowing out of the bottom of the reactor to the regenerator. As the catalyst leaves the bottom of the reactor, it mixes with air as it enters the bottom of the regenerator vessel where the regeneration process starts with the carbon which gets burned off on the surface of the catalyst. The regenerated catalyst mixes with the feed, completing the catalyst flow path.

Hot flue gas stream exits the top of the regenerator and is then used to heat other boilers in the plant. While the catalyst is being regenerated, the hot petroleum vapors leaving the top of the reactor enter the main fractionator. The light gas stream leaving the overhead of the main fractionator composes the feed to the VRU. Cooling turns some of the components to a liquid before entering a vapor-liquid separator.

The vapor and liquid enter a primary absorber at different points. This creates a counter-flow of liquid over the rising vapor and strips lighter hydrocarbons from propane and heavier hydrocarbon liquid out into upward flowing vapor before it leaves the overhead of the absorber and enters the secondary absorber. More heavy compounds and lighter hydrocarbons (see Table 1) are stripped from the vapor in the secondary absorber before it moves on to the fuel gas system.

The propane and heavier components from the primary absorber leave the bottom of the absorber and enter a lean oil still, which separates the olefin-rich butane components (that are needed for the alkylation unit) from the rest of the stream. The remaining components become a debutanised gasoline fraction that can be used in the blending of gasoline.

The ratio of carbon dioxide to carbon monoxide (CO2 to CO) in the hot flue gas stream is critical to regulating the temperature in the regenerator. Carbon monoxide represents partially converted carbon and hence results in high temperatures that damage the catalyst and can lead to extremely high expense for refiners. A high carbon level and contamination, such as metals on the catalyst, lead to a higher regenerator temperature. Higher temperatures diminish the lifespan of the regenerator equipment and accelerate catalyst deactivation. It is this ratio of CO2 to CO in the hot flue gas stream that a GC measures.

To maintain lower regenerator temperatures, some plants operate the regenerator in a partial combustion stage with a flue gas CO2 to CO ratio of less than six. Partial burning of the coke to carbon monoxide rather than completing burning the coke to carbon dioxide releases one-third less heat. Decreasing the CO2 to CO ratio results in reduced regenerator temperature. The GC precisely measures the CO2 to CO ratio to protect the equipment and optimize the process.

Table 1. Sampling points, measuring objectives and analyzers

Analyzer #	Stream	Components Measured	Measurement Objective
1	Regenerator Flue Gas	CO, CO_2	Used to calculate CO/CO_2 ratio to determine catalyst regeneration efficiency
2	Main Fractionator Overhead	H_2 – C5	Minimize loss of C5+ components as well as monitor C4–C5 olefins production
3	Primary Absorber Bottom	C2, C3, C4	Minimize light gases in feed to alkylation unit
4	Secondary Absorber Inlet	C3=, C4=	Minimize losses of olefins
5	Secondary Absorber Overhead	C2=, C3=	Minimize losses of olefins
6	Secondary Absorber Bottom	C4s	Minimize recycling of light gases
7	Lean Oil Still Overhead	C2, iC4	Reduce impurities in feed to alkylation unit
8	Lean Oil Still Bottom	iC4, nC4	Monitor Butane content to keep gasoline in RVP

A GC is also used to measure H2 – C5 in the overhead vapors of the main fractionator. The measurement helps keep the pentane concentration low, thus minimizing the loss of naphtha and gasoline components into the overhead stream. The GC also monitors the butane and pentane olefins generated in the reactor. These olefins are important feed components to other processes like alkylation, isomerization and other processes in the refinery. Clearly, every step of operation in the FCCU is "vetted" by the process gas chromatograph.

Optimizing the VRU

Primary Absorber

In the primary absorber of the VRU, a process GC is used to measure multiple components like ethane, propane, and butane in a single sample injection from the bottom stream, helping the control system minimize light gases entering the feed into the alkylation unit. The alkylation unit is an important secondary process that adds high-octane hydrocarbons to gasoline. High octanes, of course, are important to prevent engine knocking. The quality of the octane is negatively affected by ethane, propane, and n-butane that reduce the concentration of iso-butane and increase the likelihood of olefin-olefin polymerization. This results in reduced octane levels which, in turn, impacts the bottom line.

Secondary Absorber

Measuring for propylene and butylene in the stream with a GC prior to entering the secondary absorber helps reduce the loss of valuable olefins. An alkylate is formed when propylene and butylene are combined with iso-butane in the alkylation unit. This is the main component added to increase the octane of the gasoline. Minimizing the amount of propylene and butylene entering the secondary absorber allows more to go onto the lean oil still and the alkylation unit. To prevent the loss of olefins into the fuel gas stream, measurement of the overhead stream leaving the secondary absorber is assessed for ethylene and butylene.

Figure 2. Emerson's Rosemount 1500XA process GC.

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A GC is also used to measure the bottom stream of the secondary absorber. This feedback helps minimize the recycling of light gases back to the FCC main fractionator. This in turn helps reduce energy consumption and increases capacity since the recycled light gases need to be heated and cooled. This heating and cooling decreases throughput capacity of the fractionator, and, if it drops enough, can create a bottleneck in the plant's operation.

Lean Oil Still

As discussed, impurities in the feed to the alkylation unit reduce the quality of the octane and can cause undesirable olefin-olefin polymerization. Therefore, the overhead stream of the lean oil still is analyzed for ethane and iso-butane. Ethane is viewed as an impurity resulting from incomplete reaction. Iso-butane is a desirable component since it helps form the alkylate. The amount of butanes in the gasoline stream are controlled by analyzing the bottom stream for iso-butane and normal-butane. This, in turn, controls the gasoline's Reid Vapor Pressure (RVP), which is important for environmental compliance.

Conclusion

Optimizing the FCCU and VRU operations in a refinery directly impacts the profitability of the plant. Process gas chromatographs play a direct role in enhancing these functions. GC measurements help get longer life from regeneration equipment and expensive (or high valued) catalysts by providing feedback to better control temperature. They help minimize energy consumption for the FCCU main fractionator. They ensure the highest octane possible, and they reduce costs and improve product quality through optimization of operations.

Process GCs are a ubiquitous part of refinery operations, but recent enhancements in ease-of-use, the ability to run several streams at once (which reduces investment cost), and a low cost of ownership make this a workhorse of a very profitable colour.