Bonnie Crossland, Emerson Automation Solutions, USA, considers how gas chromatograph technology can be used to optimise fluid catalytic cracking.

n a refinery, the fluid catalytic cracking unit (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. Consequently, efficient operation of the FCCU directly impacts the refinery's profitability. The valuable light gases produced by the catalytic process are sent to a vapour recovery unit (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. To ensure optimum operation of the FCC and the VRU, real time compositional data to process control systems is required and the process gas chromatograph (GC) is the analytical workhorse for online compositional measurement in refineries. While other technologies, such as mass spectrometry or process gas analysers, can be considered in most refineries, GCs offer a balance of accuracy, process appropriate speed, ease of use, reliability and cost-effectiveness. While most refinery personnel accept GC technology as an excellent measurement solution for the FCCU and VRU, it bears an explanation of how GC measurement points provide essential information for efficient refinery operation.

FCCU

As a review, it is important to know that the feed to the FCCU in a refinery is 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



This fractionator acts like a miniature crude tower by separating the 'cracked' petroleum stream into various petroleum cuts, such as naphtha/gasoline, kerosene, etc. The heaviest fraction leaving the bottom of the main fractionator is typically recycled back to the feed stream for reprocessing. Exiting the overhead of the main fractionator is a gas vapour stream that is rich in olefin compounds. This stream is often sent to the VRU where the olefins are recovered for use in processes such as the alkylation unit.





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

petroleum streams, such as the coker or deasphalter. The feed stream is mixed with hot, freshly regenerated catalyst and heated to almost 1000°F before it enters the main FCC reactor. The chemical reactions start occurring immediately when there is contact between the catalyst and the oil in the pipe leading to the reactor. When 'cracking' the large molecules in the oil into smaller ones, carbon forms on the surface of the catalyst, quickly de-activating it.

Once inside the reactor, steam is injected to strip off any oil that is clinging to the catalyst. This causes the catalyst in the reactor to move in a fluid-like manner, hence the name 'fluid catalytic cracking'. The cracked oil vapours flow out of the top of the reactor, with the spent catalyst flowing out of the bottom. As the catalyst leaves the bottom of the reactor, it mixes with air and enters the regenerator vessel where the carbon on the surface of the catalyst is burned off. The regenerated catalyst mixes with the feed, completing the catalyst flow path.

Exiting the top of the regenerator is a hot flue gas stream that is then used to heat other boilers in the plant. While the catalyst is being regenerated, the hot petroleum vapours leaving the top of the reactor enter the main fractionator.

VRU

The feed to the VRU is the light gas stream leaving the overhead of the main fractionator. This stream is cooled enough to turn some of the components to a liquid before entering a vapour-liquid separator.

In a common VRU arrangement, the vapour and liquid enter a primary absorber at different points to create a counter-flow of liquid over the rising vapour. This is also to strip propane and heavier compounds out of the vapour before it leaves the overhead of the absorber and enters the secondary absorber. The secondary absorber provides another opportunity to strip these from the vapour 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.

Process GC for FCC optimisation

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. The GC measures the carbon dioxide/carbon (CO_2/CO) ratio in the hot flue gas stream. This ratio is critical to regulating the temperature in the regenerator since high temperatures can 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.

In some plants, to maintain lower regenerator temperatures, the regenerator can be operated in a partial combustion stage with a flue gas CO_2/CO ratio of less than six. Partial burning of the coke to carbon rather than completing burning the coke to carbon dioxide releases one-third less heat. Decreasing the CO_2/CO ratio results in reduced regenerator temperature. Hence, the GC's role at this point is to precisely measure the CO_2/CO ratio to protect the equipment and optimise the process.

A GC is also used to measure the composition of gas vapour exiting the overhead of the main fractionator. This GC



Analyser	Stream	Components measured	Measurement objective
1	Regenerator flue gas	CO, CO ₂	Calculate CO/CO ₂ ratio to determine catalyst regeneration efficiency
2	Main fractionator overhead	H ₂ – C5	Minimise loss of C5+ components and monitor C4 – C5 olefin production
3	Primary absorber bottom	C2, C3, C4	Minimise light gases in the feed to the alkylation unit
4	Secondary absorber inlet	C3=, C4=	Minimise loss of olefins
5	Secondary absorber overhead	C2=, C3=	Minimise loss of olefins
6	Secondary absorber bottom	C4s	Minimise recycling of light gases
7	Lean oil still overhead	C2, iC4	Reduce impurities in the feed to the alkylation unit
8	Lean oil still bottom	iC4, nC4	Monitor butane content

Table 1. Sampling points, measuring objectives and analysers

measures $H_2 - C5$ in the overhead vapours of the main fractionator. The measurement serves as feedback on the stream to help minimise the loss of naphtha/gasoline components into the overhead stream by keeping the pentane concentration low. The measurement is also used to monitor the butane and pentane olefins generated in the reactor. These olefins are important feed components to other processes in the refinery.

Process GC for VRU optimisation

As with the FCCU, the VRU requires several process GCs to improve its performance. The primary absorber has one process GC on the bottom stream. The secondary absorber has three process GCs, one on the inlet, one on the overhead stream and one on the bottom stream. The lean oil still has two process GCs, one on the overhead stream and one on the bottom stream.

Primary absorber

A process GC is used to measure ethane, propane and butane in the bottom stream of the primary absorber. This measurement helps the control system minimise light gases entering the feed into the alkylation unit. The alkylation unit is an important secondary process that adds high octane hydrocarbons to gasoline. It is the high octanes in gasoline that prevent engine knocking. Ethane, propane and n-butane negatively impact the quality of the octane. They reduce the concentration of iso-butane and increase the likelihood of olefin-olefin polymerisation, resulting in reduced octane levels, which, in turn, impacts the bottom line.

Secondary absorber

Measurement of the stream prior to entering the secondary absorber for propylene and butylene helps reduce the loss of valuable olefins into the fuel gas stream. Propylene and butylene are combined with iso-butane in the alkylation unit to form an alkylate, which is the main component added to increase the octane of the gasoline. Minimising the amount of propylene and butylene entering the secondary absorber allows more to go onto the lean oil still and the alkylation unit. Measurement of the overhead stream leaving the secondary absorber is assessed for ethylene and propylene to prevent the loss of olefins into the fuel gas stream. GC measurement of the bottom stream of the secondary absorber provides feedback to help minimise the recycling of light gases back to the FCC main fractionator. Minimising the amount of light gases back to the fractionator helps reduce energy consumption and increase capacity. The energy consumption of the FCC main fractionator increases as the recycled light gases need to be heated and cooled. The throughput capacity of the fractionator is decreased as the amount of recycled light gases are increased. If enough light gases need reprocessing in the fractionator, the amount of actual throughput drops - possibly creating a bottleneck in the plant's operation.

Lean oil still

The overhead stream of the lean oil still is analysed for ethane and iso-butane. Ethane is viewed as an impurity. As stated above, impurities in the feed to the alkylation unit reduce the quality of the octane and can cause olefin-olefin polymerisation. Iso-butane is a desired component as it is used to form the alkylate. The bottom stream is analysed for iso-butane and normal-butane to help control the amount of butanes in the gasoline stream, which controls the gasoline's reid vapour pressure (RVP). This is important for environmental compliance.

Conclusion

Process GCs play a critical role in analysis to monitor and control the FCC and VRU processes. Their use aids in:

- Improving the lifespan of regeneration equipment and catalysts by providing feedback to better control temperature.
- Providing measurements from the secondary absorber bottom to help minimise energy consumption for the FCC main fractionator.
- Analysing the gas entering the alkylation unit to ensure the highest octane possible is formed.
- Ensuring optimal operation of the FCC and the VRU, thus leveraging the efficiency of the processes by reducing costs and improving product quality.

While GCs have optimised FCC operations since the 1950s, recent improvements in the technology, such as the ability to perform multiple analyses at once by running several streams at the same time on one GC and parallel chromatography, simplify the analysis process and reduce cycle time. Important advances in terms of ease of use and low cost of ownership have further solidified the GCs' position as a reliable gas measurement workhorse in refineries.