White Paper

Effective, Reliable and Easy
TDLs in Refinery FCCs

Gas measurements in FCC unit catalytic regeneration and flue gases are essential for efficient and safe operation. But most gas analysis technologies are unreliable due to the extreme process conditions. A series of tunable diode laser analyzers that operate in situ deliver dependable measurements, long analyzer lifetime, and are simple to install and maintain.

Introduction

Fluidized Catalytic Cracking (FCC) is an essential operation in most modern refineries. FCC units break (crack) the long chain hydrocarbons in heavy gas oils into short chain hydrocarbons to produce gasoline and fuel oils.

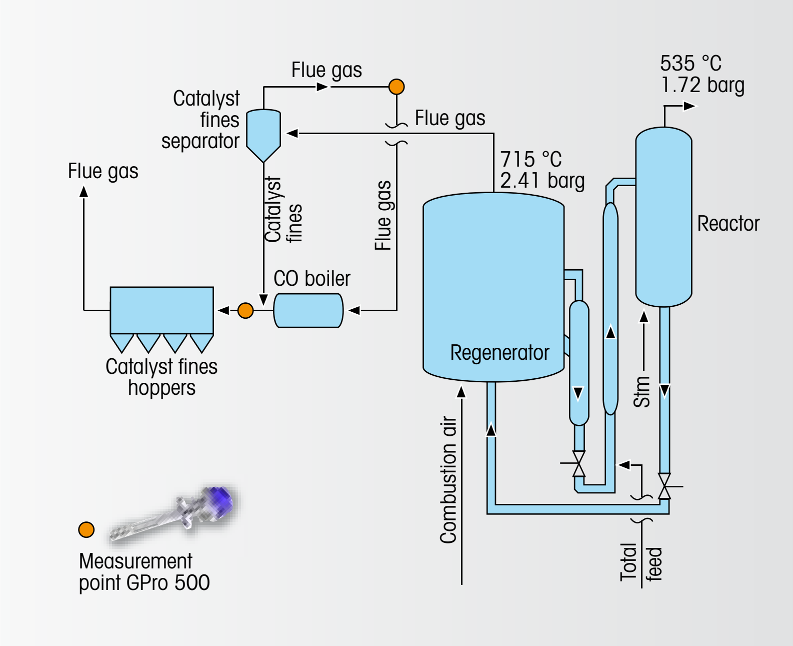
Flue gases produced in the catalyst regeneration process must be analyzed to prevent the risk of explosion and the venting of non-regulatory-compliant exhausts. Conditions in FCC units are challenging for many gas analysis technologies. Probe-type, in situ, tunable diode laser (TDL) gas analyzers offer measurement solutions that are not only dependable in FCC unit applications, but are also easy to install and are low in maintenance.

FCC unit process

The cracking of long chain hydrocarbons in FCC units is achieved by mixing vaporized feedstock with catalyst beads at a very high temperature. This mixture behaves like a fluid (hence "fluidized") and can be pumped around the FCC unit.

When in the FCC unit's reactor, the catalyst beads become coated with carbon (catalyst coke) from the cracking activity. This build-up reduces the catalyst's effectiveness and so must be removed. The removal process, catalytic regeneration, comprises burning off the coke using very hot air. This is an exothermic reaction and the heat produced is absorbed by the regenerated catalyst and is also used to vaporize the feedstock.

As well as heat, catalytic regeneration produces large amounts of CO and CO_2. It is critical to measure the levels of these gases in



Gas analysis measurement points in FCC unit

the regenerator flue gas as well as the residual oxygen level, as all of these are indicative of the rate and temperature of regeneration. If the regeneration rate is too fast and the temperature too high, the catalyst will become overheated and unwanted sintering may occur, with consequent reduction in efficiency and potential catalyst destruction. If the rate of regeneration is too low, then there will be insufficient oxidation of the carbon, leading to poor catalyst activity and inefficient cracking.

The CO-rich flue gas from the regeneration step is routed through a steam-generating boiler (CO furnace) where the CO is burned as a fuel to generate steam for use in the refinery and also to comply with environmental regulations on flue gas exhaust. Fuel (e.g., natural gas) may be added to the flue gas prior to the boiler to increase combustion efficiency.

Before it is vented to atmosphere, the flue gas may pass through an electrostatic precipitator (ESP) which removes particulates through the use of high voltage static electric fields between a series of metal pipes and plates that charge and then strip the entrained particles from the gas.

Gas and organic compounds measurement is important in FCC units to monitor catalytic regeneration, and in the flue gas from the CO boiler to the ESP, both for environmental reasons and to prevent explosions in the ESP caused by the CO and the high voltages across the ESP's plates.

CO furnace

Since there are a variety of complex chemicals in the petroleum feed, often including organic sulfur and nitrogen compounds, the flue gas from an FCC unit usually contains a wide range of contaminants. These can include not only CO but also trace levels of aldehydes, cyanides, ammonia, sulfur dioxide (SO_2), plus oxides of nitrogen (NO_X), metals and other particulates. Typical legislation therefore usually specifies a wide range of emissions measurements for these flue gases, often including oxygen, CO and possibly CO_2.

The exhaust gas from the regenerator unit (before the CO furnace) has the following typical composition:

Carbon dioxide	10–20 %
Carbon monoxide	10–25 %
Oxygen	< 1 %
Water vapor	1 %
Sulfur dioxide	< 0.5 %
Nitrogen oxides	< 0.1 %
Nitrogen	balance

The sample is very hot (circa 600 °C) and has a dust loading which is very high and includes many fine particles (typically down to 70 µm). Due to the sample conditions, careful thought must be given to the process adaptor type and materials of construction used.

Continuous emissions monitoring

As mentioned, the flue gases from the CO boiler (or directly from the catalytic regenerator) are vented to the atmosphere after suitable scrubbing to remove dust and pollutants. The gas composition will be similar to that of a typical incinerator flue gas:

Carbon dioxide	10 – 20 %
Carbon monoxide	< 1000 ppm(v)
Oxygen	1 – 5 %
Water vapor	10 – 15 %
Sulfur dioxide	< 1000 ppm(v)
Nitrogen oxides	< 500 ppm(v)
Nitrogen	balance

The sample at this stage will have a moderate dust loading.

Emissions monitoring will be required which will typically include CO, oxygen and again possibly CO_2 measurements. The choice of analyzer technologies and types will depend on user or regulation preferences, and the required hazardous area rating (refineries are invariably Zone 1 or Zone 2 [Class 1 Division 1 and Division 2] areas).

Issues with gas analyzers

A number of analyzer technologies are in use on FCCs for gas measurement. Paramagnetic and non-dispersive infrared (NDIR) analyzers were initially employed but measurement response was slow due to sample conditioning and transportation times. Also, narrow tubing could easily become blocked with particulates and extractive sample cells fouled. This made these analyzer types high in maintenance if measurement reliability was to be preserved.

Many oxygen analyzers based on the paramagnetic principle have a measuring cell which is assembled using epoxy resins. These are susceptible to attack by traces of corrosives in the sample, eventually leading to premature failure of the cell.

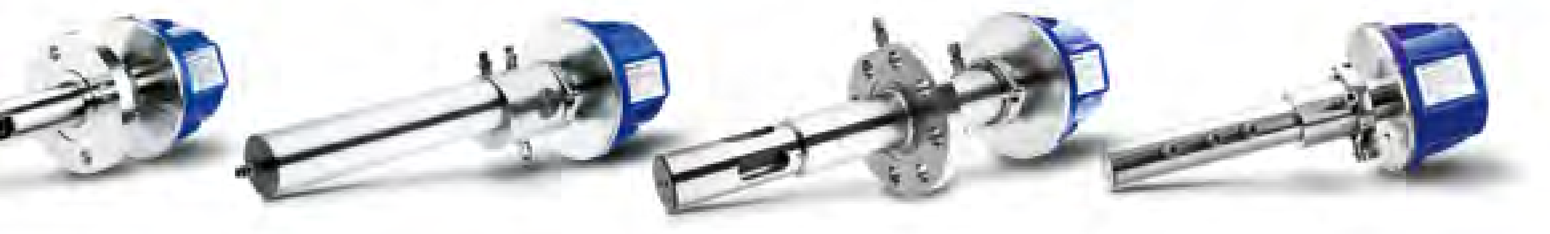
Oxygen analyzers using electrochemical cells should not be considered for these applications. The electrochemical cell uses an alkaline electrolyte which will be rapidly neutralized by the acidic contaminants in the sample gas, leading to cell exhaustion. If an electrochemical cell falls to zero output (i.e. 0% oxygen) this would constitute "failure to danger" on any safety application.

The majority of CO combustion sensors in common use are based on pellistor technology, but these are also not without their issues. They are prone to measurement errors due to the two pellistor beads not being perfectly matched, radiative heat loss from each bead being different, and dirt in the gas building up on the sample pellistor but not on the reference. But their biggest issue is poor selectivity to CO, which can make measurements from such sensors highly unreliable.

A gas analyzer technology that is fit for purpose

Tunable diode laser (TDL) analyzers offer a modern approach to gas measurement in FCCs that overcomes the drawbacks of the above sensors. TDL analyzers work on the principle of laser absorption spectroscopy. A focused and tunable laser beam is used to analyze absorption lines that are characteristic of the particular gas species to be measured. TDLs usually measure in situ or directly from the gas stream without any sampling or conditioning.

TDL analyzers for process applications have two basic design types, namely cross-stack and probe-type. In the cross-stack design, the laser source is placed on one side of the pipe or duct and the receiver on the other. The wider the pipe diameter, the more difficult it is to align the laser source and receiver. In



probe-type TDL analyzers, the defining feature is the sensor probe that protrudes into the process gas stream. The laser source and the detector are contained in a single unit, requiring a single flange connection.

Compact, reliable, accurate and low maintenance TDLs

METTLER TOLEDO's GPro 500 is a series of compact, probe-type TDL O_2, CO CO_2 and water vapor gas analyzers. They are highly suited to the conditions found in FCC units as they can be used with sample gases which contain corrosive traces and which are highly flammable. The range carries Optical Intrinsic Safety (OPIS) certification, meaning that the analyzers do not create optical energy of a sufficient magnitude to cause an explosion. The measurement performance offered on GPro 500s is also superior to other technologies, particularly in stability and rejection of measurement interferences.

The series is available with a variety of adaptions that enable a very wide range in both application use and point of insertion. These adaptions include a sintered metal filter and baffle for hot and dusty applications such as catalytic regeneration, and a wafer cell for use in pipes as narrow as DIN 50.

Where an extractive solution is preferred or required (due to more extreme process conditions) the GPro 500 can be configured with an extractive cell.

Unlike other gas analyzer technologies, GPro 500 analyzers have no moving parts, and other than annual verification, require no maintenance.

Conclusion

Fluidized Catalytic Cracking units are found in most modern refineries and effective FCC unit operations are reliant on dependable gas measurements from resilient analyzers. METTLER TOLEDO's GPro 500 range of robust, in situ gas analyzers deliver highly stable O_2, CO, and CO_2 measurements in regenerators and flue gas. Their compactness, modularity and extremely low maintenance make them the ideal choice for FCC unit applications.

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