

How One Analyzer Technology Can Improve a Semi-Regenerative Catalytic Reforming Process

Critical monitoring of water and sulfur in the hydrogen recycle line can reduce maintenance and extend catalyst service life.

By Alan Garza, Endress+Hauser

Oil refiners, going back to the earliest days of the industry, have found that breaking down crude oil into marketable fractions does not always result in high volumes of the most profitable products. For example, conventional thermal cracking may create far more naphtha and high-molecular weight fractions than can be sold, while leaving demand for more profitable high-octane gasoline blending components unfilled. As a result, petroleum chemists and process designers have created numerous catalyst-based methods for producing more desirable fractions initially, combined with converting low-value products into higher-value reformates, by using techniques such as:

- Fluid-catalytic cracking
- Alkylation
- Continuous-catalyst regenerative reformers
- Semi-regenerative catalytic reforming

Each process produces some share of high-value products, but also creates a stream of byproducts, some more desirable than others. The catalysts themselves tend to be sensitive to feedstock contaminants, which in the worst cases, can render the process fully ineffective. Sulfur plays a role here, as it does throughout the whole hydrocarbon chain, as a primary problem for the catalysts and final products, so it must be monitored in all its forms.

For purposes of this article, we will concentrate on one process, semi-regenerative catalytic reforming (SRR), which accounts for 60% of reforming capacity worldwide. More specifically, we'll focus on the instrumentation necessary to protect the catalytic action, and to optimize the process for production of high-value reformate and desirable byproducts.

Catalytic reforming process

SRR is a costly process, but when it is working well it produces three product streams made from surplus naphtha, increasing overall value well beyond the processing costs.

An SRR unit (Figure 1) converts deparaffinized naphtha into high-octane aromatic reformates (benzene, toluene, and xylenes) used in gasoline blending, plus a second stream consisting of hydrogen that can be used in other processes. The off-gas produced in the fractionation column will then be sent for further processing where LPG is separated from light hydrocarbons.

An SRR unit has three fixed-bed catalytic reactors, each employing a platinum/rhenium (Pt/Re) catalyst on a chloride alumina support. Fresh naphtha feedstock is mixed with hydrogen and then fed into the reactor train.

Each reactor works at a different stage in the process, breaking and rearranging specific types of molecules in a sequence.

- Reactor 1 handles dehydrogenation and conversion of naphthenes to aromatics
- Reactor 2 isomerizes normal paraffins to isoparaffins
- Reactor 3 facilitates hydrocracking of paraffins

After passing through the reactors, the stream is cooled to condense the reformate and separate it from the hydrogen. A portion of the hydrogen is recycled and mixed with fresh naphtha feedstock, but much of it is surplus at this point and can be drained off as its own product stream. Raw liquid reformate goes through one more separation step to remove the off gas before use in gasoline blending.

Over time, catalyst efficiency declines as coke builds up in the reactors, so the process must be shut down periodically to burn coke off and restore efficiency. Operational periods between this regeneration processes can be six to 24 months. After three to four regenerations, the Pt/Re catalyst must be replaced. A full regeneration cycle takes one to two weeks, which represents a major loss of production capacity. Consequently, careful process control and feedstock

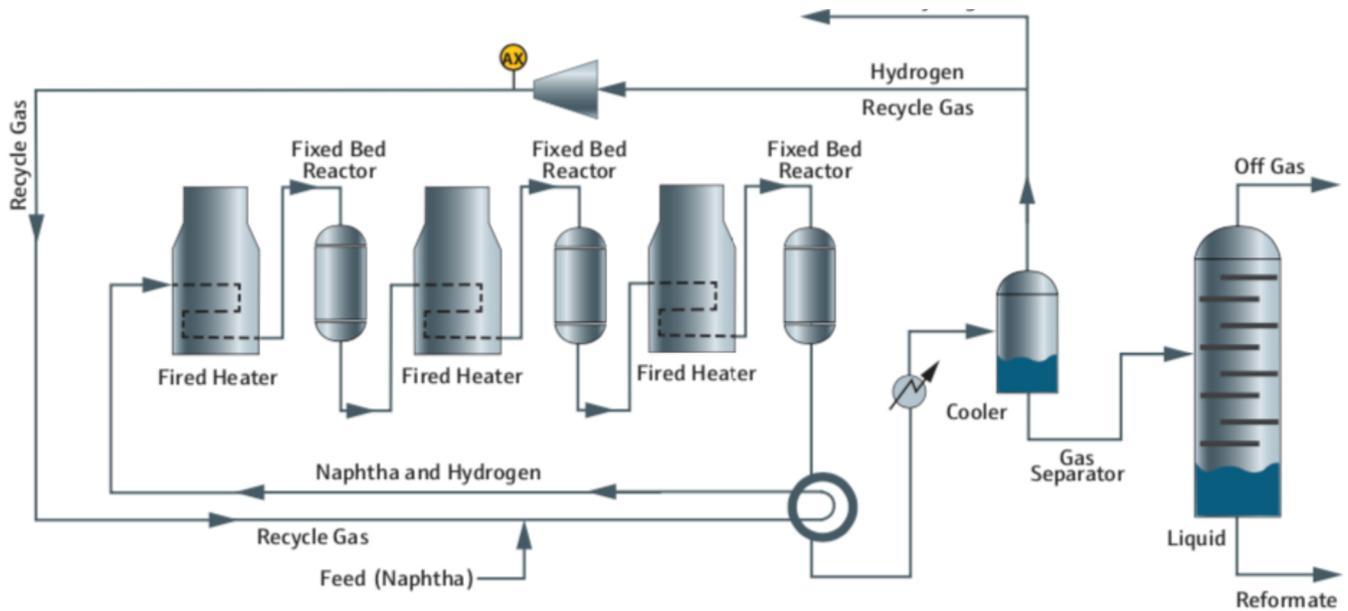


Figure 1: A typical SRR unit uses a three-stage reaction process. The critical analyzer (AX) is normally placed downstream from the hydrogen recycle gas compressor.

monitoring is necessary to minimize the need for maintenance and maximize uptime.

Improved operation begins with careful monitoring of H₂O and H₂S

Chemical composition of the hydrogen recycle gas is critical to equipment and process efficiency. There are two main areas of concern.

First, sulfur. H₂S and other sulfur compounds (including hydrogen sulfide, carbonyl sulfide, dimethyl sulfide, tetrahydrothiophene, and various mercaptans) poison the Pt/Re catalyst and increase coking, decreasing hydrogen production and reformat yield. Tolerable amounts can be as high as 1.0 ppm, but if the naphtha feedstock carries sulfur compounds more than this amount, it must pass through a hydrotreater unit to bring these contaminant levels down. Recycle hydrogen must be monitored for sulfur content to maintain process efficiency and minimize regeneration cycles.

Second, chloride. The process requires a small amount of H₂O and chloride so the catalyst can perform hydrocracking, isomerization, and cyclization conversion reactions efficiently. However, too much H₂O allows formation of corrosive hydrochloric acid (HCl) capable of reducing reformat yield and damaging the equipment. For example, HCl reacts with any traces of ammonia, creating ammonium chloride that can form deposits in the hydrogen recycle compressor. Entrained HCl can also cause corrosion farther downstream in the gas separator heat exchangers. If any equipment requires repairs, the entire SRR unit must be shut down, causing the loss of reformat production, with financial impact usually well beyond \$1 million per day, in addition to the repair costs.

Tracking the H₂O level in recycle hydrogen gas can determine when it is necessary to reduce the H₂O level and dry down the catalyst. The most effective and practical place to monitor and measure H₂S and H₂O is at the hydrogen recycle return line, downstream of the compressor (Figure 1). Finding the best way to measure these components has provided many challenges for SRR unit operators.

Methods for monitoring hydrogen sulfide

A traditional method for measuring H₂S is lead-acetate sensing tape, with a length of paper tape impregnated with lead acetate inserted into the recycle hydrogen stream. Over time, it reacts with H₂S to form lead sulfide, which appears as a black solid. The amount formed over a specific period of time can be measured by an analyzer to indicate the H₂S concentration. The analyzer automatically advances the tape mechanically to expose a fresh section to the gas stream for the prescribed interval. The tape itself is a consumable item, and the presence of lead acetate (CAS 6080-56-4) and lead sulfide on the spent tape makes it a hazardous waste according to U.S. and EU regulations under RCRA Code D002/D003, and EU 16 05 06, respectively, necessitating regulated disposal. This method of analysis can be accurate and require little or no calibration, but it is maintenance intensive and requires special disposal methods.

A more sophisticated approach for measuring sulfur and its compounds is a flame photometric detector analyzer. A sample of the recycle hydrogen is mixed with air and a flammable carrier gas, and then burned as a reducing flame in an airless oven. This creates chemiluminescence caused by excited sulfur, which can be measured by a photomultiplier tube and flame photometric detector. This approach can be

very accurate, and it is capable of speciating a range of sulfur compounds. However, it requires specialized gas consumables and tends to be maintenance intensive. It is also overkill for this application where a simple H₂S measurement is sufficient for process control.

Technologies for monitoring water

Measuring H₂O in the stream calls for entirely different technologies than those mentioned for H₂S, usually necessitating a second analyzer. Traditional H₂O sensors pass a sample of the recycle hydrogen over a surface chilled to well below the dew point, causing water vapor to condense on the surface. This can be a mirror combined with optical evaluation of the deposit, a quartz crystal microbalance to weigh the deposit, or electrodes to capture changes in capacitance caused by the deposit.

A common element of these measurement approaches is that the sensing surface must be heated and dried after each reading to clear the deposit, and then re-chilled for the next measurement cycle. Aluminum oxide probes can measure moisture without being chilled but must still be heated to take a new reading. This slows down the cycle time, which may result in delayed detection of a changing situation. Additionally, some contaminants, if present in the gas stream, can also condense and leave traces on the sensor. These traces tend to build up over time, decreasing measurement accuracy.

TDLAS, one analyzer for both measurements

Tuned-diode laser absorption spectroscopy (TDLAS) takes an entirely different approach to gas analysis than the technologies just discussed. It applies the characteristics of gases and liquids to absorb specific wavelengths of light depending on their chemical composition. How this works has been summarized by the Beer-Lambert law, and it has been applied in numerous ways for industrial gas detection and analysis. TDLAS analyzers are particularly well suited to the components found in natural gas and refining applications, so they are seeing wider deployments within the larger hydrocarbon industry.

For this specific application, the characteristics of H₂S and H₂O are both well understood. Using wavelengths between 1.8 and 2.8 μm (micrometers), it is possible to identify absorption peaks in the recycle hydrogen stream caused by H₂S and H₂O, such that they can be quantified simultaneously but separately. For example, the peak caused by H₂O at 1877 μm is easy to measure, providing an accurate value of water content in the stream.

A TDLAS sensor (Figure 2) is very simple and has no moving parts outside of valves for the sample handling lines. The gas sample flows into a tube driven by line pressure. Placing the assembly in a heated enclosure ensures that the sample remains fully in a gaseous state, preventing condensation of any components. The sample's temperature and pressure are both monitored for the final measurement calculations.

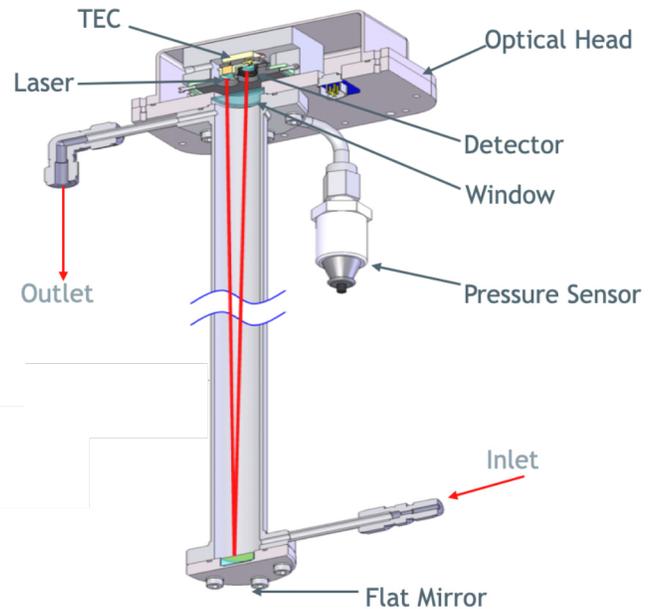


Figure 2: A TDLAS sensor measures absorption of specific wavelengths of light caused by the presence of specific chemical components.

At one end of the tube is a mirror, and at the other end is a sapphire glass window, behind which is a diode laser next to a detector. The laser puts out a brief flash, sending its beam into the tube, where it is reflected back to the detector by the mirror, effectively doubling the travel distance through the sample gas.

Software scans the detector to check the most critical wavelengths absorbed by H₂O and H₂S. The algorithm performs its calculations, resulting in the final concentration values (Figure 3), and the sample can be exhausted from the tube. Everything happens in a matter of seconds, so measurement intervals can be performed often to suit the requirements of the application.

Since the characteristics of the diode laser and detector are very stable, and the absorption characteristics of the subject gases don't change, a TDLAS analyzer exhibits virtually no drift and generally needs no calibration. With no moving parts, gas bottles, or delicate mechanisms, TDLAS analyzers (Figure 4) are easy to deploy and maintain in the field.

Financial effects and considerations of an SRR unit

As mentioned earlier, an SRR unit is expensive to operate, but it yields high-value products. Therefore, it is incumbent on operators to fulfill three objectives:

- Optimize the process to produce the highest possible reformat yield and quality
- Extend the time between catalyst regeneration
- Maximize service life of the expensive catalyst

Application Data – hydrocarbon analysis of H ₂ S	
Target Component (Analyte)	H ₂ S in Semi-Regenerative Reformer Hydrogen Recycle Gas
Typical Measurement Ranges	0-50 through 0-300 ppm*
Typical Repeatability	±2% of Full Scale*
Measurement Response Time	1 to ~60 seconds*
Principle of Measurement	Differential Tunable Diode Laser Absorption Spectroscopy (H ₂ S scrubber included)
Validation	Certified blend of H ₂ S in Nitrogen balance

Application Data – hydrocarbon analysis of H ₂ O	
Target Component (Analyte)	Water in Semi-Regenerative Reformer Hydrogen Recycle Gas
Typical Measurement Ranges	0-50 ppm (control) and 50-500 ppm (trend)*
Typical Repeatability	±1 ppm (control) and ±10% of reading (trend)*
Measurement Response Time	1 to ~60 seconds*
Principle of Measurement	Non-Differential Tunable Diode Laser Absorption Spectroscopy
Validation	Certified blend of H ₂ O in pure N ₂ or integrated permeation system

Figure 3: A TDLAS analyzer, such as a SpectraSensors SS2100 from Endress+Hauser, is designed for hydrocarbon analysis of H₂S (upper table) and H₂O (lower table).



Figure 4: TDLAS analyzers are compact and can usually be field mounted, without the need for elaborate shelters.

Clearly, process availability is paramount, since having an SRR unit down for regeneration or worse, catalyst replacement, results in loss of revenue. Since control of both H₂O and H₂S has a major impact on yield, catalyst life, and overall efficiency, the analyzer on the hydrogen recycle line plays a critical role in ensuring the success of the SRR unit.

At the same time, the analyzer must deliver its value with minimum cost. A TDLAS analyzer is generally not the lowest cost option, at least based on initial purchase price, however its reduced operating costs quickly overcome the higher initial investment. There are no consumables, and these devices can run for years without requiring maintenance, recalibration, or replacement. Therefore, costs such as analyzer technicians, repair or replacement of probes, as well as an inventory of spare sensor heads are eliminated. The aggregate savings on such tangible costs can easily amount to tens of thousands of dollars per year for each analyzer.

There are also operational considerations. During an abnormal process event, a liquid slug in a sample line can render conventional moisture sensors inoperative for hours or days. For this reason, many refineries have resorted to redundant analyzers, with associated sample handling conditioning and stream switching, which can double or triple the installed costs. These installation complexity costs, combined with consumables and maintenance, quickly negate lower initial purchase costs. Moreover, the revenue gained from even a single additional day of production, or an improvement in reformat quality resulting from tighter process control, greatly exceeds the total cost of any analyzer deployment.

TDLAS analyzer technology for H₂S and H₂O measurements in this and other hydrocarbon processing applications has proven itself highly accurate and reliable over the long term, even in hostile operating environments. The results of higher unit availability with increased production revenues, combined with reduced operating and maintenance costs, should clarify the decision-making process when selecting an analyzer technology.

All figures courtesy of Endress+Hauser

About the Author



Alan Garza is the product marketing manager for the Advanced Analysis product lines at Endress+Hauser. He began his career at Endress+Hauser as a rotational engineer where he developed in multiple instrumentation technologies. Alan was also part of the Inside sales team where he championed gas analytics and developed as an applications engineer. His

background also includes business development and operations management. Alan holds a BS in Mechanical Engineering Technology from the University of Houston.

www.addresses.endress.com

WP01182CZ4EN01.22