The Quantitative Analysis of Water in Hydrogen Recycle Gas Using Tunable Diode Laser Absorption Spectroscopy (TDLAS)

Introduction

Catalytic reforming is a chemical process used to convert petroleum refinery heavy naphthas, having relatively low octane value, into high-octane liquid products called reformates. The catalyst used in the reforming process can be deactivated by water. It is therefore very important to monitor the water concentration in the catalytic reforming process to minimize catalyst replacement costs. The AMETEK 5100 HD Tunable Diode Laser Absorption Spectroscopy (TDLAS) analyzer is a highly reliable and low maintenance solution for this application.

Catalytic Reforming

A petroleum refinery includes many unit operations processes. The first process in a refinery is the distillation of the feed stock crude oil. The light liquid distillate is called naphtha and will become a major component of the refinery's gasoline product after it is further processed through a catalytic hydrodesulfurization process to remove sulfur-containing hydrocarbons and a catalytic reformer to reform its hydrocarbon molecules into more highly branched molecules with a higher octane rating value. Naphtha contains paraffins, naphthenes (cyclic paraffins) and aromatic hydrocarbons ranging from those containing four carbon atoms to those containing up to ten carbon atoms. It has a lower boiling point of about 30°C and a final boiling point of about 200°C.

The naphtha from the crude oil distillation is further distilled to produce a light naphtha containing mostly hydrocarbons with six or fewer carbon atoms and a heavy naphtha containing mostly hydrocarbons containing six or more carbon atoms. The heavy naphtha has an initial boiling point of about 90°C and a final boiling point of about 200°C.

Catalytic reforming is a chemical process used to convert refinery heavy naphthas, typically having low octane value, into high-octane liquid products called reformates. The process rearranges the hydrocarbon molecules in the naphtha feed as well as breaking some of the larger molecules into smaller molecules. The overall effect is that the product reformate contains hydrocarbons with more branching and higher octane value than the hydrocarbons in the naphtha feedstock. The process breaks hydrogen atoms from the hydrocarbon molecules and produces significant amounts of hydrogen that can be used in a number of other refinery processes. Other byproducts are small amounts of methane, ethane, propane, and butanes.

The heavy naphtha rather than the light fraction is passed to the catalytic reformer. The light naphtha having molecules with six or fewer carbon atoms tends to crack into butane and lower molecular weight hydrocarbons in a catalytic reformer. These low molecular weight hydrocarbons are too volatile to be blended into gasoline at a significant level and are therefore not valuable as high-octane gasoline blending components. Also, the light naphtha six carbon atom molecules tend to form aromatics which is undesirable because governmental environmental regulations in a number of countries limit the amount of aromatics (most particularly benzene) that may be present in gasoline.

The most commonly used type of catalytic reforming unit has three reactors, each with a fixed bed of catalyst. All of the catalyst is regenerated in-situ during routine catalyst regeneration shutdowns which occur approximately once each 12 to 24 months. Such a unit is referred to as a semi-regenerative catalytic reformer (SRR). The most modern type of catalytic reformers are called Continuous Catalyst Regeneration (CCR) reformers. Such units are characterized by continuous in-situ regeneration of part of the catalyst in a special regenerator, and by continuous addition of the regenerated catalyst to the operating reactors.

A diagram of a typical catalytic reformer is shown in Figure 1. The liquid heavy naphtha feed is blended with a stream of hydrogen-rich recycle gas. Usually, three reactors are all that is required to provide the desired performance of the catalytic reforming unit. Most of the hydrogen-rich gas from the gas separator vessel returns to the recycle hydrogen gas compressor and the net hydrogen-rich gas is exported for use in the other refinery processes that consume hydrogen (such as hydrodesulfurization or a hydrocracker unit).

Analyzing Water in Hydrogen Recycle Gas

The catalyst used in the reforming process can be deactivated by water. Monitoring the water concentration in the catalytic reforming process is important to minimize catalyst replacement costs. Typically the maximum allowable water content is around 50 ppm although during the catalyst regeneration process the level can be much higher.

Historically, electrochemical detectors have been used to monitor the water level in the hydrogen recycle gas but this type of sensor degrades over time as it is exposed to heavy hydrocarbons and low levels of HCl present in the process. Exposed electrochemical cells can fail several times a year.

In the case of the AMETEK 5100 HD TDLAS system, the detector element does not come into contact with the process gas and, therefore, there is no change in the system response relative to the sensor contamination issues described above. The AMETEK TDLAS analyzer (Figure 2) is a highly reliable and low maintenance solution for this application. Typical validation results for the analyzer are shown in Figure 3. The AMETEK 5100 HD TDLAS analyzer provides an integrated heated sample compartment (up to 150°C) containing one or two stainless steel gas cells and the sample conditioning system (membrane filter). The analyzer is designed to be NEMA 4X and is available in configurations to meet North America, ATEX and IECEx safety requirements.

The AMETEK 5100 HD TDLAS analyzer can be used to determine the concentration of water in hydrogen recycle gas providing the real time results needed to maximize the catalyst used in the reforming process. Water concentrations down to 1 ppmv can be measured accurately.

The additional benefits of the 5100 HD are numerous:

- The semiconductor laser used as the light source has a MTBF of more than eight years.
- Real-time verification algorithms combined with the internal reference cell provide a continuous indication that the analyzer is operating properly.
- The Wavelength Modulation Spectroscopy (WMS) data collection eliminates any concentration effects resulting from moderate cell contamination and any major fouling of the analysis cell results in an alarm output.
- The gas cell can be cleaned by plant technicians in less than an hour minimizing down time in case of a condensation related system upset.

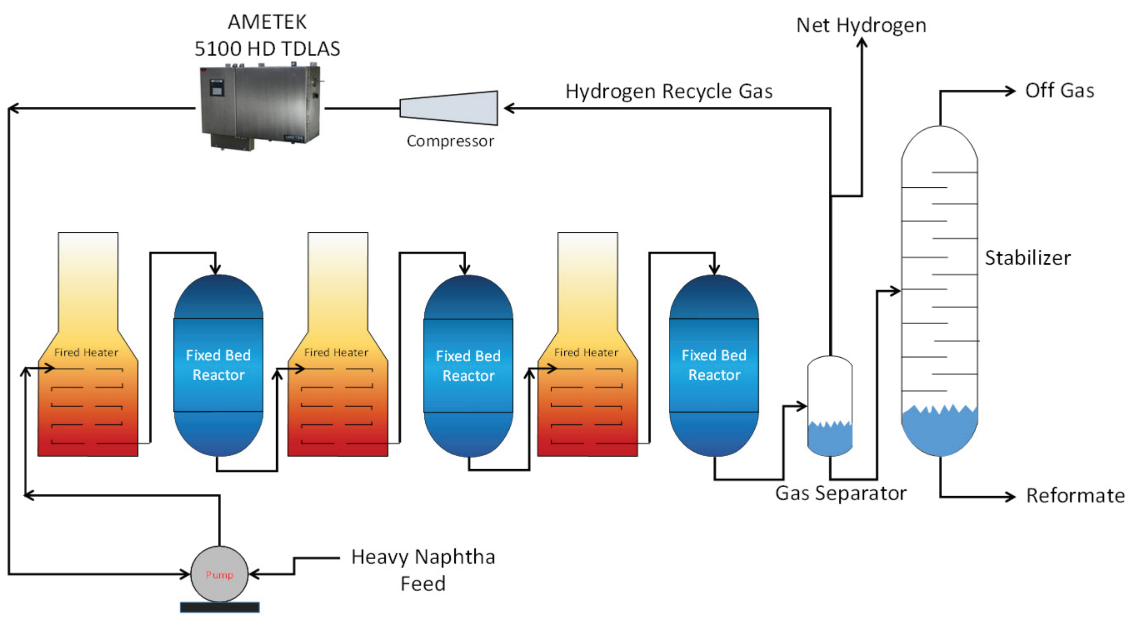

Figure 1: Diagram of a Three Bed Catalytic Reformer

Figure 2: The AMETEK 5100 HD TDLAS Water in Hydrogen Recycle Gas Analyzer

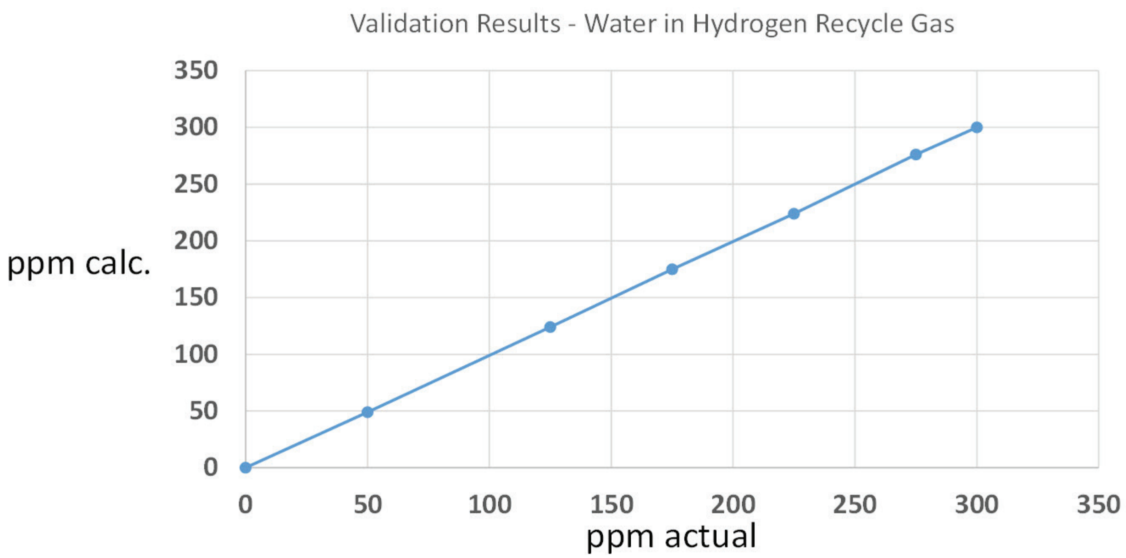

Figure 3: Validation Results for AMETEK TDLAS Measurements of Water in Hydrogen Recycle Gas

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