HOW GAS ANALYZERS CAN HELP TO OPTIMIZE PERFORMANCE IN HYDROGEN PRODUCTION

Gary Egerton of ABB Measurement & Analytics looks at the key role of gas analyzers in measuring the performance of steam methane reformers (SMRs) used in hydrogen production.

With hydrogen set to play an increasingly central role in the energy mix for both vehicles and home heating, ensuring that maximum quantities are produced at high purities is growing in importance. Even without these potential uses, hydrogen still has a major role to play in treating heavy feed stocks, and in the hydrogenation of biofuels.

The main method of producing hydrgoen is steam-methane reforming (SMR). Much of the installed base of SMR plants is linked to refinery operations, with the balance being associated with syngas, methanol and ammonia production in the chemicals and fertiliser sectors.

Steam reforming is endothermic - that is, heat must be supplied to the process for the reaction to proceed. This takes the form of high temperature steam, which is used to produce hydrogen from a methane source, typically natural gas. The methane reacts with the steam under a pressure of between 3 to 25 bar in the presence of a catalyst.

The products of this reaction are hydrogen and carbon monoxide, with a small amount of carbon dioxide. In a further stage, known as the water-gas shift reaction, the carbon monoxide and steam are reacted to produce carbon dioxide and more hydrogen. The carbon dioxide and other impurities are then removed to leave mostly pure hydrogen.

Steam reforming can also be used to produce hydrogen from other fuels, such as ethanol, propane, or even gasoline.

Improving the process

The SMR process consumes methane or other feedstocks in the reaction to produce hydrogen. The hydrocarbons are also used as fuel to generate heat for the SMR reactions. The aim of an economical SMR process is therefore to maximize hydrogen production while minimizing the consumption of feedstocks and hydrocarbons.

In addition to making the process more productive, this gives environmental benefits, producing fewer emissions of gases such as $CO_{2^{1}}$ NOx, SOx and particulate matter. There are several approaches that can be used but one of the best is to optimize the process parameters through the use of instrumentation to measure temperature and pressure and analyze gas compositions.

Some of the most fundamental gas analysis requirements on an SMR process are:

• Measurement of the reformer burner flue gas oxygen concentration.

Meeting these requirements demands a wide range of gas analyzers based on different technologies and having varied features and levels of precision to suit the application.

The first task is to decide what the most essential functionality is for each measurement stage in the process. For example, this could be continuous and instantaneous measurement of a specific type of molecule. Alternatively, a range of gases may need measuring, but for which an instantaneous reading is not required.

We can illustrate this with the requirements for the calculation of BTU for the feedstock. This is best achieved with a rapid response process gas chromatograph for SMR feed gas analysis. The instrument needs the ability to analyse the mixed composition of the natural gas stream. This can contain a variety of light hydrocarbons, including ethane and propane as well as methane. In some cases, the SMR can be fed with refinery gas which can contain a highly diverse mix of fuel gases.

Fitted with a thermal conductivity detector (TCD), such an instrument would be ideal for determining the BTU value of natural gas or naptha feed to SMRs. A good instrument should be able to analyse and characterise a gas mixture sample every two minutes. Analysis of the gas composition then allows the BTU to be calculated.

Direct read analyzers

Unlike the intermittent analysis that is adequate for calculating BTU value, Direct Reading Instruments are electronic devices that provide a rapid or continuous detection or measurement of the concentration of the compound in question.

Because they provide continuous information, every change in the process can be observed. This allows the control system to react within seconds to ensure that the process can be continuously optimised.

One of the major uses for a direct read instrument in an SMR process is methane slip. Methane should be reacted to $CO_{2'}$ carbon monoxide (CO) and hydrogen in the SMR. If excessive amounts of methane slip through the process, this can be a clear sign that something is wrong.

Because methane is infrared active, absorbing infrared light, it can be detected using a non-dispersive infra-red (NDIR) analyzer. These instruments are flexible enough to be used across a range of gases including carbon monoxide, carbon dioxide, methane and other light hydrocarbons. If the analyzer detects excessive amounts of methane slipping through the process, this could indicate that the catalyst needs replacement. An alternative cause is low temperatures in the SMR. This can be solved by increasing the amount of fuel gas supplied to the burners. Although some of these factors, such as the performance of the catalyst, are longer term, others such as temperature changes can occur rapidly. A direct read instrument will help to fix the issue with minimal delay.

Controlling carbon

The steam-to-carbon ratio is one of the most important measurement areas in an SMR process. Controlling this ratio correctly gives significant increases in the unit's efficiency. Typically, the ratio must be above 3:1 to prevent carbon deposition on the catalyst.

One of the recognized ways of controlling this ratio is through the use of a gas chromatograph analyzer and orifice plate. Alternative methods include using an NDIR analyzer.

NDIR analyzers are also ideal for measurement of the final hydrogen purity, even though hydrogen is not IR active and is not detectable on an NDIR. Although most of the gas coming off the SMR will be hydrogen, the most significant factor is the absence of CO and $CO_{2^{\prime}}$ which are detectable by NDIR instruments. These two gases are poisonous to the hydro-treating catalysts in the subsequent processes where the hydrogen is used in the refinery.

The final hydrogen product specification should ideally have a maximum total combined CO and $\rm CO_2$ content of 10 parts-permillion by volume (VPM).

The measurement of flue gas oxygen is usually based on a zirconium oxide cell. One instrument mounts this at the tip of the probe that is inserted into the flue duct. This gives a direct, in situ measurement, providing an accurate and rapid oxygen reading to help optimize combustion control.

The most modern instruments take advantage of digital communication to offer facilities such as remote operations, self-diagnosis and automatic calibration. Vendors may also offer condition monitoring services, allowing customers to check and keep track of the health of their measurement devices. The service will usually provide health check reports to both customers and the experts at the device vendors, allowing the vendor to recommend service interventions.

In this way, measurement instruments for SMR processes can be kept operational for as long as possible, ensuring continued accurate monitoring of the hydrogen production process.

- Calculation of the calorific (BTU) value of the incoming feedstock
- Monitoring methane slip through the SMR
- Controlling the steam-to-carbon ratio in the SMR
- Measurement of the final hydrogen product purity

For more information about ABB's process gas analysis technologies, visit https://new.abb.com/products/measurement-products/analytical.

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