ADVANCES IN ON-LINE HYDROGEN MEASUREMENT

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ABSTRACT

Hydrogen is one of the most widely used reaction gases in the hydrocarbon processing industry. On-line compositional measurement is used to determine and control hydrogen concentrations in various process streams. An often applied gas measurement technology is continuous thermal conductivity which depends on the large thermal conductivity difference between Hydrogen and most other gases present. This measurement technology typically provides adequate precision under stable process conditions when impurities present are at low and stable concentrations. However, increased and changing concentrations of impurities can have an adverse impact on the hydrogen measurement precision and consequently have an impact on process control. This is especially evident during process changes. By utilizing an alternative analyzer technology to speciate and quantify hydrogen, high precision can be achieved under any process conditions without complicating the measurement configuration.

This paper discusses measurement requirements, variables impacting quantification at various process conditions as well as comparing alternative system configuration and economical aspects.

INTRODUCTION

Hydrogen is one of the most widely utilized gases in the hydrocarbon processing industry. It is generated and used for a wide variety of processes as reaction gas. Hydrogen is used for hydro-treating which is the process of converting groups of components such as olefins or aromatics in
the presence of hydrogen to more desirable paraffines. Another example is the reaction of sulfur and nitrogen with hydrogen to convert them to molecules that can be removed more easily. Hydro-cracking is utilized to reduce the boiling point range of hydrocarbon mixtures in order to manufacture various fuels with desired properties. High flow rates of hydrogen are needed to saturate the generated molecule fractions. Another process requiring hydrogen is the removal of carbonyl sulfide and carbon disulfide from petroleum fraction which is part of the tail gas clean up unit down stream of a Claus sulfur process.

Some of the hydrogen needed for many of those processes is partially produced during crude oil rafination. However the majority of the Hydrogen needed is generated by a dedicated process such as steam reforming of natural gas, methane or ethane or by oxidation of heavy hydrocarbons such as in fuel oil. Either process is followed by purification using cryogenic phase separation, adsorption or diffusion. The hydrogen purity, hydrogen generation and hydrogen consumption have to be measured and controlled in order to control those processes. On-line process analyzers are applied for the quantification of hydrogen.

Two on-line analytical measurement technologies utilized quantify hydrogen in a catalytic reforming process are compared.

**CATALYTIC REFORMING**

Catalytic reforming is used to convert undesirable groups of molecules to more desirable groups of components in the presence of catalyst. [1]. The objective of this process is to increase the knock-resistance or Octane number of motor gasoline [2] in order to utilize high efficient combustion engine, minimizing fuel consumption and emission. The process feed is straight-run gasoline and naphtha, consisting of paraffins, olefins, naphthenes and aromates. Part of the paraffins and naphthenes are converted to higher octane components by cyclization and isomerization. Part of the olefins are saturated to paraffins which in turn are partially converted to aromatics. Normal paraffins are partially converted to iso-paraffins. There are several reactions during this process. Dehydrogenation of naphthenes to aromatics and dehydrocyclization of paraffins to aromates generate excess hydrogen. Isomerization generates excess hydrogen as well. Hydro-cracking, such as the cracking and saturation of paraffins consumes hydrogen. The entire catalytic reforming process generates excessive hydrogen. The excessive hydrogen is separated from the effluent. Part of the hydrogen is removed from the process altogether and is used for hydro-treating the feedstock for the catalytic reformer to convert organic sulfur and nitrogen compounds to hydrogen sulfide and ammonia. These are then removed to protect the catalyst used for the reforming. Another part of the Hydrogen is returned and mixed with the feed to the catalytic reforming unit. The presence of Hydrogen in the feed provides a continuous means of regenerating the platinum catalyst used in the process. This is desirable for the continuous operation of the reformer in order to minimize coke buildup. Coke is generated during the reforming process and if not continuously removed covers the catalyst surface much more rapidly resulting in reduced catalyst activity and reduced efficiency. Consequently for maximum yield during reforming, long operating times between regeneration and stable process operation, the Hydrogen/Feed ratio has to be controlled.
There are two different analytical design technologies used to measure hydrogen on-line.

**GAS ANALYSIS UTILIZING THERMAL CONDUCTIVITY**

Continuous gas analysis utilizing a Thermal Conductivity Detector (TCD) is a common technology applied to quantify Hydrogen continuously and on-line. The measurement is based on the difference in thermal conductivity of the measuring components. Ideally this technology is applied to a binary gas mixture in order to generate high measurement accuracy. However, hydrogen is one of the few gases with a much higher thermal conductivity compared to hydrocarbons (Figure 1). Therefore, this technology is commonly applied to measure high concentrations of hydrogen even in multi component mixtures as long as helium is only present in traces. This is acceptable as long as the concentration of interferences is low compared to hydrogen. The measurement is typically sufficiently accurate because the 8-9 fold higher thermal conductivity of hydrogen.

![Figure 1: Thermal Conductivity of Various Gases](image)

**FIGURE 1: THERMAL CONDUCTIVITY OF VARIOUS GASES [3]**

Continuous gas analysis utilizing thermal conductivity is simple. The sample stream continuously flows through the detector of the analyzer. The basic design of the detector is a heated filament which is subject to the sample flow. The detector configuration can be based on the classical design of exposed filaments as part of a Wheatstone-Bridge configuration or a more modern design utilizing a micro mechanical system (MEMS) design (Figure 2). The sample is not coming in contact with the actual filament with this modern design. Therefore this design permits the analysis of corrosive gases as well. Under stable flow conditions, a change in sample
conductivity generates a change in filament temperature. Independent of the various control designs such as constant temperature or constant current, the change of conductivity measured is proportional to the concentration change. The simplicity of the analytical configuration and the compact analyzer design provides a simple measurement system which is economical to install and has low operational cost.

**FIGURE 2: MODERN THERMAL CONDUCTIVITY DESIGN UTILIZING MEMS TECHNOLOGY** [4]

Although this technology is ideally suitable for binary mixtures, it can be applied to multi component mixtures. As long as the sample composition does not change significantly and the interferences are at low concentrations, relative high accuracy is provided. The impact of the interference components can be further minimized by using an external calibration standard reflecting the typical gas composition. However, as the concentration of the interferences deviate from the calibrated concentration, the higher measurement error. Figure 3 shows a number of different process conditions with their respective concentrations for hydrogen and other components present.

Conditions 1-4 are typical steady-state process conditions with high concentration of hydrogen and low concentration of other components. Conditions 5-11 show non-steady process conditions with progressively reduced hydrogen concentrations and increasing concentration of other components present. Therefore, despite the high thermal conductivity of hydrogen, the impact on the total sample conductivity is reduced with declining Hydrogen concentration. Furthermore, despite the significantly lower thermal conductivity of the other components in the sample, the impact on the total sample conductivity is more relevant with increasing concentration. Consequently, the more the hydrogen concentration declines and the more the concentration of the other components increase, an increase of measurement error occurs (Figure 4).

The error is rather small in the vicinity of the steady-state conditions and therefore permits control of the process in an optimum manner to maximize yield and quality. However, under
upset conditions the error can increase to such an extent that the measurement essentially becomes a liability. The progressively larger error can lead to process control issues such as over compensation resulting in longer periods of time to return the process back to steady-state condition and significant generation of coke in the catalytic reformer. Therefore, it is desirable to have an alternative measurement technology that provides high accuracy not only during steady-state process conditions but also under upset conditions, preferably with high data frequency for adequate process control and with similar advantageous life cycle cost.

FIGURE 3: SAMPLE COMPOSITION AT VARIOUS PROCESS CONDITIONS

FIGURE 4: CALCULATED RELATIVE ERROR OF H₂ QUANTIFICATION DUE TO A CHANGE IN SAMPLE COMPOSITION

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ON-LINE PROCESS GAS CHROMATOGRAPHY

On-line process gas chromatography has a wide range of analytical capabilities and is broadly applied. Process gas chromatographs need to have suitable packaging and necessary installation infrastructure in order to satisfy the task of analytical application versatility and the requirements of being utilized in industrial plants. The consequence is a certain analyzer size to accommodate such a wide variety of analytical configurations and detectors, the need for analyzer shelters to provide suitable environment for the analyzer, a system complexity and significant investment and operational cost.

The analytical measurement of hydrogen in sample streams which is present in catalytic reformer is rather simple. The measurement system does not need the versatility of traditional process gas chromatographs if hydrogen is the only component of interest. A simpler on-line analyzer, compact and therefore suitable for mounting in the plant with minimum of protection is more than sufficient. Online process gas chromatographs have to satisfy certain requirements in order to install and operate an analyzer in the plant with similar economical advantages as a continuous gas analyzer. A significant percentage of the overall cost of installation of a measurement system is due to the infrastructure required. The engineering, shelter, installation as well as the wiring and plumbing to and from a suitable location can exceed half of the total installation cost of the measurement system. It is required to reduce the cost of engineering in order to reduce that portion. This is possible by reducing the infrastructure requirements by not requiring a centralized shelter but field mounting closer to the sampling point. However, this requires a compact field mountable analyzer package suitable to be installed in a simple weather protective enclosure, 3-sided shelter or just a sun/rain roof, at least in moderate climate regions. Furthermore it requires that the analyzer has little or no maintenance. Consequently repair on-site must be very simple which calls for analyzer modularity. This permits quick exchange of a few standardized parts and if fine tuning is required it should be done remotely.

MEASUREMENT

Improved process control on the catalytic reformer was desired as part of a refinery optimization. A continuous gas analyzer with a thermal conductivity detector has been used to quantify the Hydrogen purity. The accuracy of the quantitative measurement was considered inadequate. Instead of utilizing a traditional type of process gas chromatograph which have a wide variety of analytical capabilities but also have much higher installation costs, a simplified, miniaturized process gas chromatograph was applied due to the reasons outlined above. The initial hesitation to implement such a new design was low because the same analyzer for a different application was already installed a few months earlier in this particular plant. Therefore, the otherwise unknown engineering, installation and functionality uncertainties were predictable. The intention was to install the analyzer and sample system in small weather protective enclosures close to the sampling point (Figure 5). Ethernet was planned to be the basis of communication to a workstation for observation and from the Ethernet via a network access unit to the control system.
ANALYZER

In order to satisfy the requirements for field installation with minimum infrastructure requirements, an analyzer must be compact, modular, simple and tolerate potentially wide ambient temperature swings [5]. Consequently, the key to the design is not just the miniaturization of existing mechanical designs used today, but using Micro-Electro-Mechanical System (MEMS) technology. This technology can greatly reduce the analyzer size and consequently reduces installation requirements. It also permits standardized and exchangeable modular systems which reduces maintenance issues. Those requirements resulted in a design that consists of 3 standardized analyzer sections, the electronic module, the control module and the analytical module. The modules are integrated into a field mountable NEMA 4X [6] housing suitable for field installation. The analyzer is connected to a junction box providing power and communication links.

FIGURE 5: PROCESS GC INSTALLATION WITH WEATHER PROTECTIVE ENCLOSURES
The key design is in the analytical module, which contains all of the analytical hardware, from the injection system to the columns, column switching and detectors in one heated disk shaped enclosure. This analyzer is utilizing valveless switching based on “LIVE” technology [7-10] used for more than 25 years because the main failure source in a traditional gas chromatograph are the sample injection and switching valves. Although the injection system utilizes an injection loop and a diaphragm valve to separate sample and carrier gas flow, its importance is greatly reduced. Sample pressure variations are unimportant because the primary injection volume is equilibrated to the highly constant carrier gas pressure before injecting part of the volume into the separation columns [11]. Only a small slice of the primary injected sample is injected into the separation system after pressure equilibration. The sample volume injected is now proportional to the time duration of the diversion which can be controlled with high accuracy. Consequently, external sample pressure control is minimized and sample pressure variations are eliminated leading to significantly better repeatability. Furthermore, even if the primary diaphragm injection valves starts to develop functionality problems, it can be recognized early on. The analyzer remains functional as long as the valve injects the entire sample loop.

Column switching is based on pressure differential and permits switching by automatically changing pressure settings with the Electronic Pressure Controllers (EPC) in order to minimize possible maintenance and failures even more. By means of that technology, backflush and heart-cut operation can be achieved maintenance free without movable parts in the separation path.

The electrical and gas mating between the application and control module is achieved by a single torque nut. It has been demonstrated that exchanging an application module and injecting sample again can be achieved in as little as 30 minutes [12]. The same simplicity applies to the electronic board. Consequently, even in adverse weather conditions, replacing the entire analytical or electronic module can be achieved within minutes. Thus, field exchange of modules replaces field repair. The simplicity permits faster exchange, reduces analyzer technician training and ensures much shorter off-line time. Therefore, the simplicity of module exchange permits field installation of the analyzer with just a basic protective enclosure.

**ANALYTICAL MEASUREMENT**

Hydrogen is the target component of the recycle stream from the catalytic reformer effluent. The measuring range is 0-40 %. Nitrogen is the carrier gas with a consumption of about 2 cylinders per year. The separation system consists of capillary columns. The pre column separates methane from carbon dioxide and ethane. Carbon dioxide and later eluting components are backflushed. Methane and the earlier components are transferred to the main column. The Molsieve main column separates hydrogen from nitrogen, oxygen, methane and carbon oxide. The analysis cycle time for hydrogen is 100 seconds. However, depending on the sample matrix it can be as short as 45 seconds. The relative standard deviation of the repeatability over an 8 hour period is 0.3%. The analyzers linear correlation over a concentration range of 40 % is 99.8%. (Figures 6 to 8).
FIGURE 6: SEPARATION OF HYDROGEN IN A SAMPLE MIXTURE OF METHANE AND ETHANE

Average 3.951 vol.%
StDev, abs 0.012 vol.%
StDev. Rel 0.304 %

FIGURE 7: REPEATABILITY OF HYDROGEN OVER 8 HOURS

y = 0.98x
R² = 0.9983

FIGURE 8: LINEARITY OF HYDROGEN OVER A RANGE OF 40%
PROCESS RESULTS

After installation of the Process GC, the continuous TCD Gas Analyzer and the new Process GC were analyzing the sample from the same sampling point simultaneously. Initially the continuous gas analyzer’s results were still used for process control. The results generated by the Process GC were used for comparison only. Under steady process conditions both analyzer track each other as expected. The off-set in Figure 9 is due to an intentional calibration off-set in order to keep both traces apart for better visibility. However, under changing process conditions, the analyzers perform differently. Although both analyzers provide the same qualitative profile, the quantitative results differ. The visible off-set between both analyzers vary based on the actual Hydrogen concentration. The measurement of the hydrogen on the Process GC is interference free, precise and linear over the measured range. The continuous TCD Gas Analyzer measures the hydrogen concentration too low. This is due to the previously discussed impact of the increased concentration of the impurities which have a lower thermal conductivity. Measuring the hydrogen concentration lower than it is has process control ramifications. The process control algorithm over-compensates which can be seen on the right side of the bottom graph in Figure 9 where the results from both analyzers almost converge. Consequently, the error in measurement leads to a longer period of time needed to bring the process back into steady-state conditions.

FIGURE 9: HYDROGEN PROCESS CONCENTRATION DETERMINED BY PROCESS GC AND CONTINUOUS TCD GAS ANALYZER, STEADY-STATE (A) AND CHANGING PROCESS CONDITIONS (B)
ECONOMICS

Compact process gas chromatographs applied to analytical suitable measurements are not significantly cheaper compared to traditional process gas chromatographs. The total cost of installation and therefore the cost of investment are significantly lower due to lower infrastructure requirements and the associated savings on engineering [13]. Consequently the measurement system can be installed closer to sampling points resulting in the need to extract much less sample volume. Depending on the proximity to the sample point and the sample composition, the extracted sample may be emitted to atmosphere or catalytically made harmless reducing the additional cost of sample recovery pipe installation. Simple new technology analyzers utilize fewer utilities such as gases and power. The costs of investment of a compact process gas chromatograph is significantly lower compared to a single traditional process gas chromatograph but still somewhat higher compared to that of a field mountable continuous gas analyzer.

The cost of operation is similar for a continuous gas analyzer and compact process gas chromatograph. There is additional cost associated with the carrier gas consumption for the process gas chromatograph. However, this is more than offset by the cost of purge air for the continuous gas analyzer in an electrical hazardous environment typically not needed by a process GC. Despite the simple design of the Process GC somewhat more training has to be considered.

CONCLUSION

A continuous thermal conductivity gas analyzer may be replaced by a compact on-line process gas chromatograph on some applications. The objective was measuring Hydrogen in a recycle stream of a catalytic reformer with higher precision using an on-line process gas chromatograph. This has proven to be correct especially during changing process conditions. Utilizing a compact on-line process gas chromatograph permitted to reduce the cost of investment significantly compared to a traditional process GC design. The somewhat increased cost of investment compared to a continuous gas analyzer are insignificant compared to the benefits of ensuring higher measurement precision and resulting in process yield and throughput.

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