Acetylene Measurements in Ethylene Production using Tunable Diode Laser Absorption Spectroscopy (TDLAS)

Ethylene Production

Acetylene is a byproduct of the ethylene production process and considered an impurity in the final product. Even at a concentration of 10 ppmv acetylene acts as a poison to the catalysts used in the production of polyethylene from ethylene. Moreover, acetylene can form metal acetylides which are explosive contaminants. Typically the maximum concentration of acetylene in the ethylene final product should be less than 5 ppmv.

Acetylene Removal

Most of the 150 million tons of ethylene produced yearly are produced by the thermal cracking of hydrocarbons in the presence of steam. Ethylene plants can use a wide range of hydrocarbon feed stocks. One of the most common of them is naphtha, a mixture of hydrocarbons in the boiling range of 30°C to 200°C. In some regions including the United States and the Middle East, ethane is the most commonly used feedstock in ethylene production.

The ethylene production process involves the thermal cracking of the feedstock with steam to minimize the formation of coke and maximize the production of olefins. The second step in the process is fractionation to separate the desired products. In Figure 1 is shown a diagram of the main process units in a typical ethylene production plant. Depending on the hydrocarbon feedstock used, the cracking furnace design and operating conditions, the amount of acetylene byproduct can vary from 0.2 to 0.9% by weight. The most common method for acetylene removal is through selective vapor phase hydrogenation.

$$C_2H_2 + H_2 \rightarrow C_2H_4$$

It is should be noted that during hydrogenation process other chemical reactions can occur and as a result ethylene could be converted to ethane if the reaction is goes too far.

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

An acetylene hydrogenation unit can be located at one of several locations within the ethylene plant. Depending on the location, acetylene converters are called front-end and tail-end or back-end converters. The acetylene hydrogenation system is a catalytic reactor with several beds of catalyst (usually palladium based but could be also nickel or platinum based) which promotes the reaction of acetylene and hydrogen to form ethylene and correspondingly to reduce acetylene content. The number of beds can vary from one to four. Each bed reduces the amount of acetylene which results in the reduction from percent level on the inlet to a few ppmv at the outlet of the last converter.

Acetylene hydrogenates much faster than ethylene over the same catalyst when both acetylene and ethylene are present. The reason for the reaction rate difference is preferential active site adsorption by acetylene. This preferential adsorption of acetylene over ethylene assumes that there are sufficient amount of acetylene molecules to cover all of the active sites. However, near the bottom of the final bed where the acetylene concentration is low there are an insufficient number of the acetylene molecules to maintain total active site coverage and an increased potential for ethylene conversion to ethane. In this situation carbon monoxide injection provides a means for blocking and inhibiting the adsorption of ethylene because adsorption rate for carbon monoxide is higher than that of ethylene. Also during plant startup and other unusual upsets, the concentration of acetylene can suddenly reach very high levels and the process parameters must be adjusted quickly to bring the process back into balance. Therefore real time monitoring of the acetylene concentration in the hydrogenation process is critical to minimize the impurities in the final product.

Potential measurements points for acetylene measurements are inlet and outlet of the first bed, mid bed and at the outlet of the acetylene converter (Figure 1). The benefits of the measurements of acetylene in two streams at the same time are the optimization of hydrogen and carbon monoxide injection and reaction time to achieve the best conversion ratio for acetylene.

The levels of the acetylene at the inlet of the first converter are around one percent. The levels of acetylene at the mid bed of the converter are between hundreds and a few thousand ppmv; but for the outlet of the final converter bed, the acetylene concentration should be in the range of 0 – 5 ppmv.

Monitoring Acetylene Concentrations

To insure a near complete conversion of the acetylene and minimize the ethylene to ethane reaction, the optimum conditions for the hydrogenation process should be determined by real time monitoring of the acetylene concentration at a number of locations in the plant.

Traditionally gas chromatography (GC) has been used to monitor acetylene in ethylene production. However, despite of the high GC sensitivity allowing the measurement of sub ppm levels of acetylene, gas chromatography's disadvantages are slow response and high maintenance costs. Standard process gas chromatographs need several minutes for the chromatographic separation. As a result the acetylene concentration reading is only updated every 2-3 minutes, limiting the process optimization actions.

TDLAS is a non-contact analysis technique with long-term stability, high specificity and low cost of ownership. Laser based acetylene analysis offers the advantage of short response time (readings updated every 2 seconds), large dynamic range and low drift in comparison with gas chromatography. In applications such as monitoring the acetylene levels on the mid bed and outlet of the acetylene converter, the above mentioned attributes provide the real-time data needed to optimize the ethylene production process.

The AMETEK 5100 HD TDLAS analyzer (Figure 2) 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). All that is required for installation is mounting the analyzer back pan and attaching a heated transfer line (need dependent on the dew point of the gas stream).

The benefits of the AMETEK 5100 HD are numerous in addition to the simple installation:

- The semiconductor laser used in the 5100 HD has a MTBF of more than eight years.
- The 5100 HD 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.

The Model 5100 HD is a new option for customers looking to replace gas chromatographs for monitoring acetylene in the ethylene manufacturing process. There are no consumables with a TDLAS analyzer and as a result the cost of ownership is very low. A comparison of the capital and operating costs for a TDLAS analyzer as compared with a process gas chromatograph are shown in Figures 3 and 4.

The data shown on Figure 5 represent the response of the instrument to a series of acetylene in ethylene challenges in the concentration range of 0-300 ppmv. The duration of each of the challenges was from 10 to 20 minutes with return to the 0% gas baseline. The zero gas was represented by a gas containing 60% ethylene and 40% of ethane, between challenges. The speed of the response T90 time was 20 seconds and was determined by the propagation of the gas in the sampling system with a flow rate of 2L/min. The data acquisition rate was 2 seconds/measurement.

Repeatability as a degree of agreement between replicate measurements of the same quantity was expressed in terms of standard deviation of the measurement results. Standard deviation of the acetylene readings on each of the challenges was between 0.4 ppmv and 1.8 ppmv of the acetylene concentration. The value of the accuracy evaluated at the levels of acetylene from 25 to 300 ppmv was in the range of 0.8 – 3 ppmv (Figure 5).

Measurements in the low ppmv range of acetylene concentrations corresponding to the outlet of the acetylene converter were achieved using a multi-pass gas cell integrated into analyzer. The data are shown in Figure 6. Measurements were carried out in an ethylene/ethane stream. The repeatability of the measurements was better than 30 ppbv and the value of the accuracy was about 100 ppbv. The instrumental drift of the analyzer over forty hours (Figure 7) had a standard deviation of 30 ppbv of acetylene.

Conclusion

AMETEK Process Instruments has a long history of providing highly reliable on-line instrumentation for the analysis of oxygen in flue gas (Thermox zirconium oxide) and moisture (Quartz Crystal Microbalance - QCM). The AMETEK 5100 HD TDLAS analyzer is a state-of-the-art laser based analyzer that can be used to determine the concentration of acetylene in an ethylene plant providing the real time results needed to optimize the production process. The 5100 HD can be configured with two sample cells to simultaneously monitor the inlet and outlet of the acetylene reduction reaction beds. Concentrations down to 100 ppbv can be measured reliability and the cost of ownership of the 5100 HD is very low as compared with a process gas chromatograph.

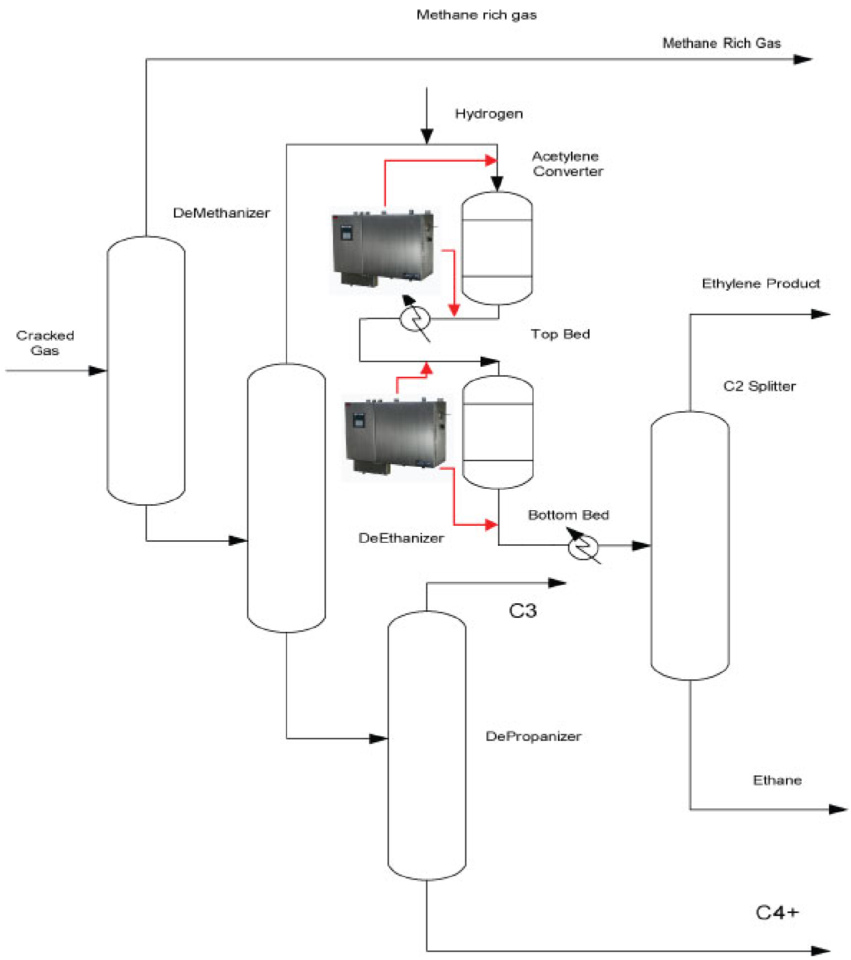

Figure 1. A diagram of a typical ethylene production plant and sampling points for a TDLAS analyzer.

Figure 2. The AMETEK 5100 HD TDLAS acetylene analyzer

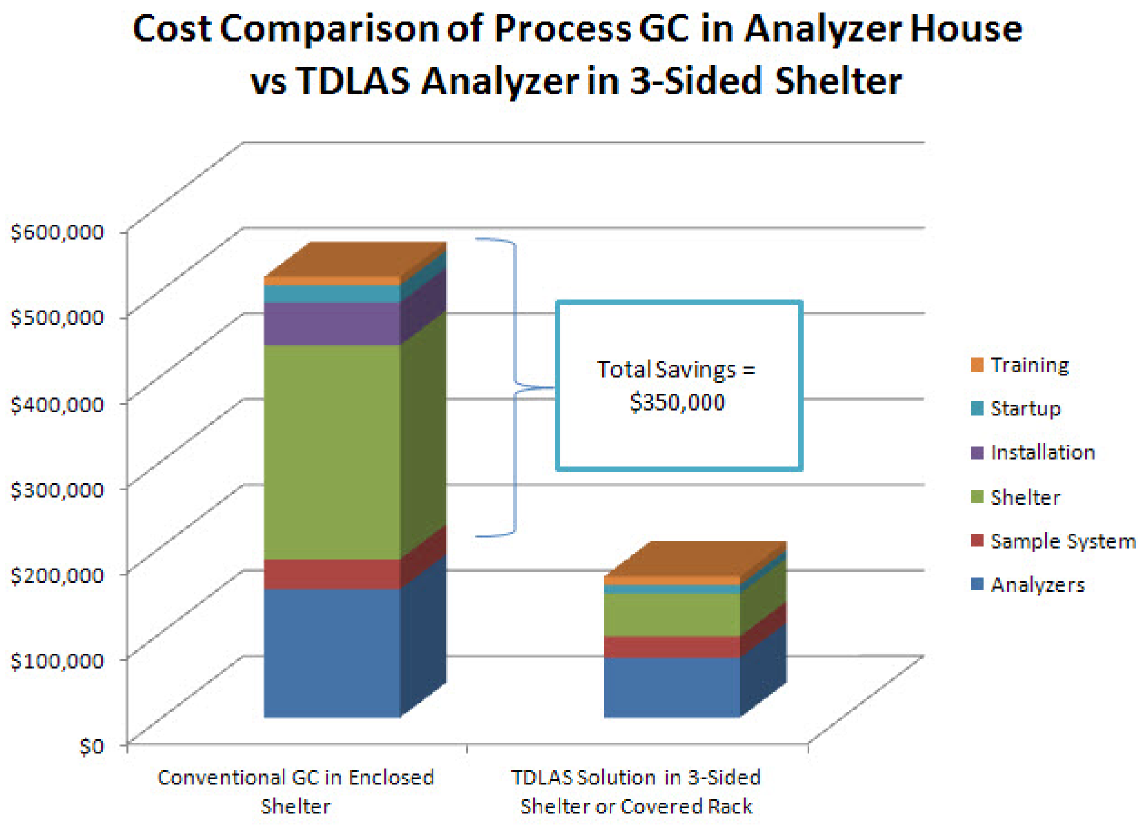

Figure 3. Capital cost of a TDLAS versus a process gas chromatograph

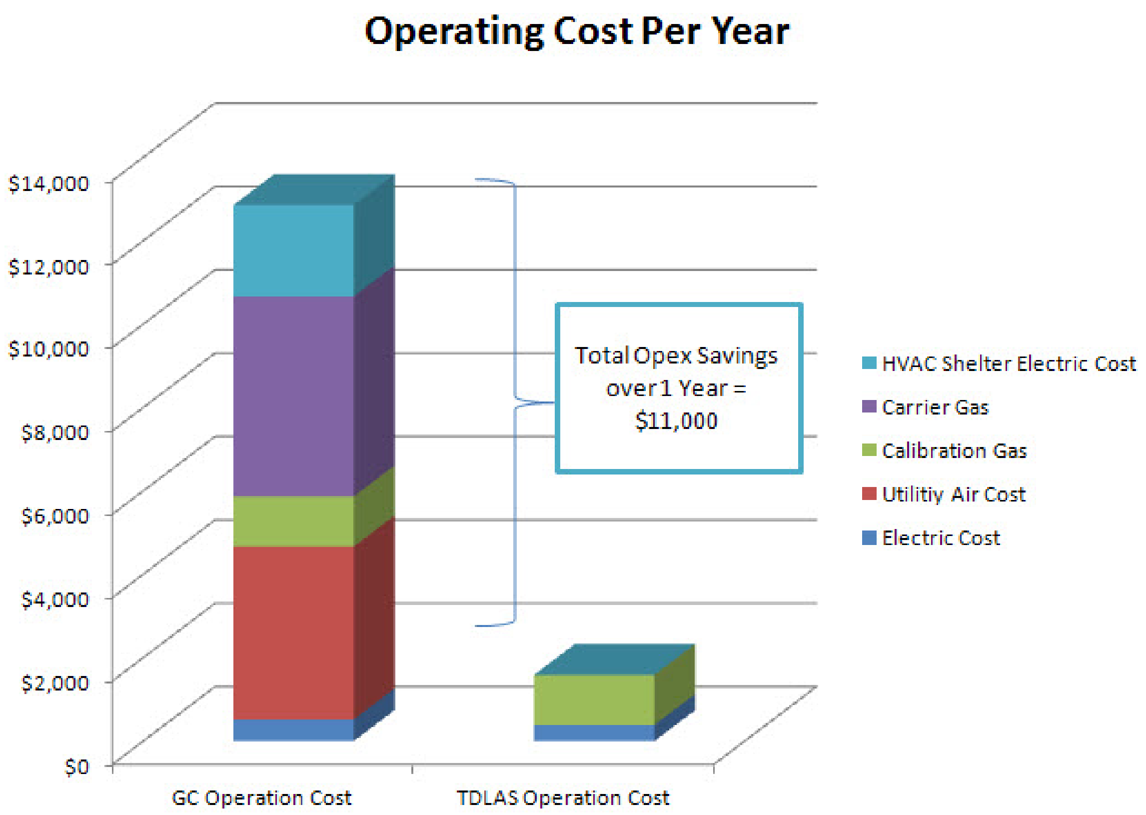

Figure 4. Operating cost of a TDLAS versus a process gas chromatograph

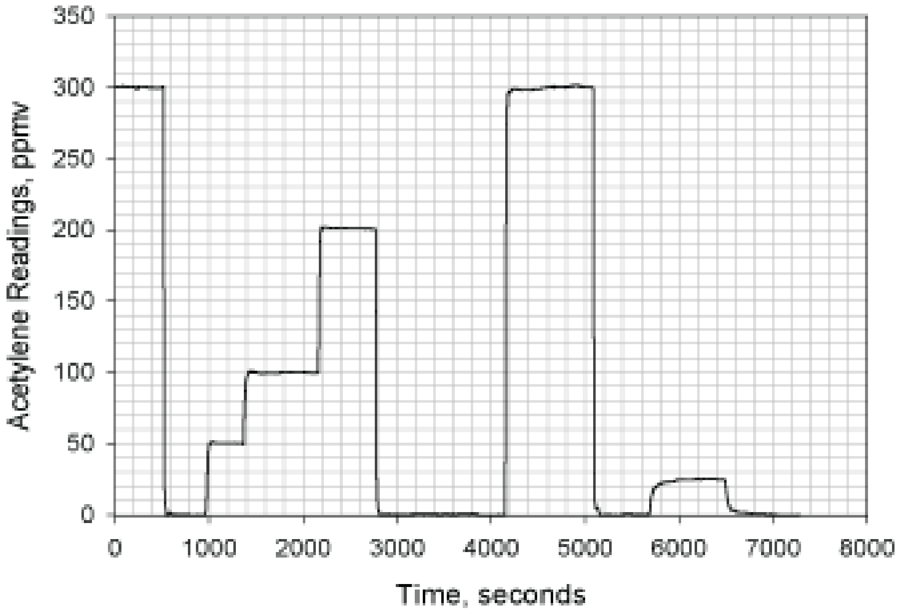

Figure 5. Typical Performance in the Acetylene Medium Concentration Range

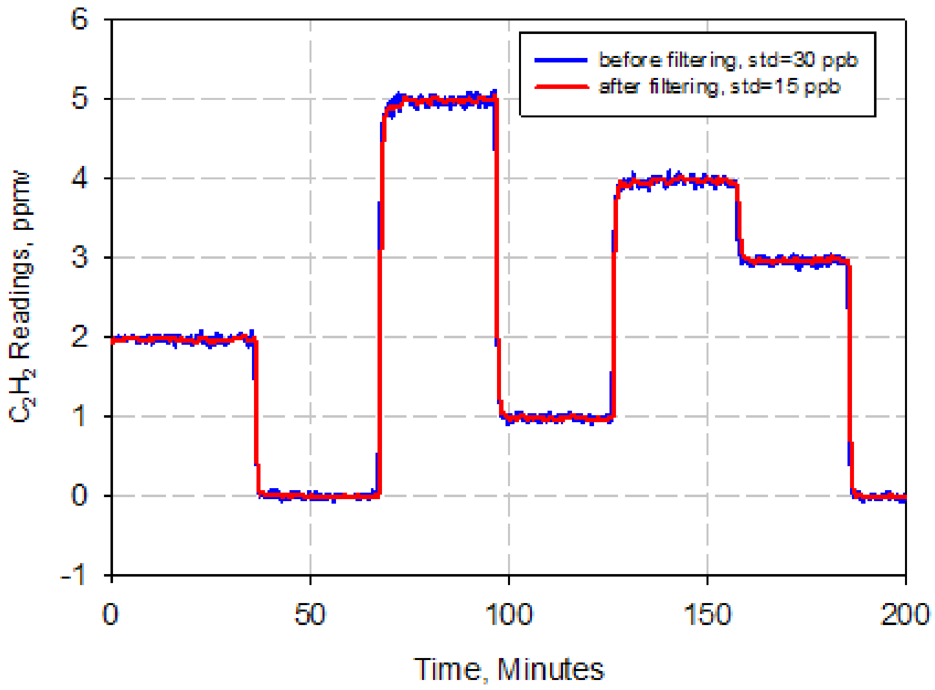

Figure 6. Typical Performance in the Acetylene Low Concentration Range

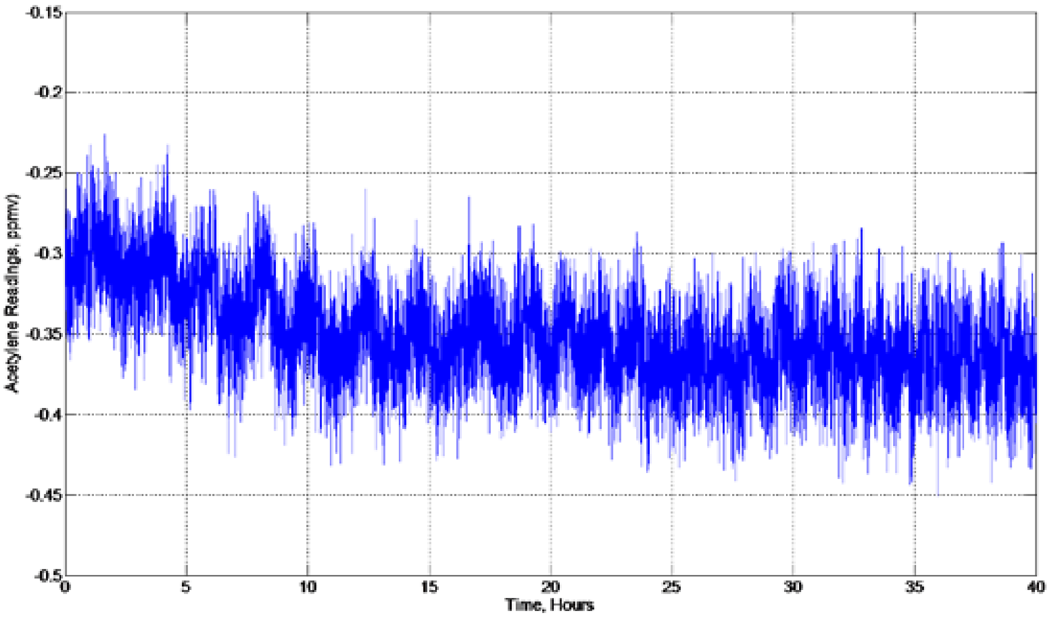

Figure 7. 40-hour Drift Measurements for Acetylene in Ethylene

TDLAS

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