

Hydrogen Sulfide and Carbon Dioxide Measurements with Tunable Diode Laser Absorption Spectroscopy (TDLAS) in the Ethylene Manufacturing Process

Most ethylene is produced by thermal cracking of hydrocarbons in the presence of steam. Steam cracking is a thermal process where saturated hydrocarbons are broken down into smaller hydrocarbons by heating in the presence of steam. The main products of steam cracking are ethylene, propylene but also methane and hydrogen. Steam cracking is accompanied by a secondary process of coke formation. Coke deposits on the inner surface of the cracking pipes. This coke formation can reduce the yield of the cracking unit and is considered a negative effect causing reduction of the heat transfer in the reactor and could even shutdown the process.

To reduce formation of coke during thermal cracking, sulfur -based additives are usually added to the feedstock. The most common additives are thiochemical compounds. Thiochemical compounds provide passivation of the reactor coil and provide inhibition of metal-hydrocarbon complexes formation. Most of the sulfur based additives are decomposed even before entering the pyrolysis reactor, producing mainly hydrogen sulfide. It should be noted that influence of thiochemical compounds on coke formation is a complicated process and depends on many factors including type and mass of compounds that have been used and the composition of the reactor surface. It is known that by pre-sulfiding with about 200ppmv of hydrogen sulfide for 20 minutes prior to feeding the ethane to the reactor can significantly reduce the rate of coke formation on all metal surfaces of

the reactor. This effect is related to the formation of the metal sulfide on the surface which reduces the catalytic effect of the metal surface in coking.

At the same time hydrogen sulfide acts as a poison to the catalysts used for production of polyethylene. Removal of the hydrogen sulfide takes place in the caustic wash tower of the ethylene plant. In the scrubbing process, sodium hydroxide reacts with H_2S dissolved in aqueous solution to form sodium bisulfide and sodium sulfide. The extent of these reactions is dependent upon the amount of sodium hydroxide that is available relative to the amount of H_2S that is scrubbed into the solution. It should be noted that carbon dioxide may also be present in the feed gas used in ethylene production. CO_2 complicates the use of caustic for H_2S scrubbing because CO_2 is also scrubbed into caustic which causes additional caustic usage, contamination of the solution with carbonate salts and even potential plugging and fouling of process equipment with carbonate salts solids. Careful evaluation of the amount of CO_2 relative to the amount of H_2S is necessary. To provide optimal removal of the hydrogen sulfide and carbon dioxide, control of the amount of H_2S and CO_2 at the inlet of the caustic scrubber system is recommended.

After cracking section pyrolysis gas enters quenching section to stop the continuously cracking reactions. In quench section the gas cools down to some controlled temperatures by direct oil quenching and direct water quenching.

After several stages of compression included in quench section pyrolysis gas reaches partial condensation. Acid gases are removed after the compression stage by scrubbing them with a dilute caustic soda solution in caustic wash tower.

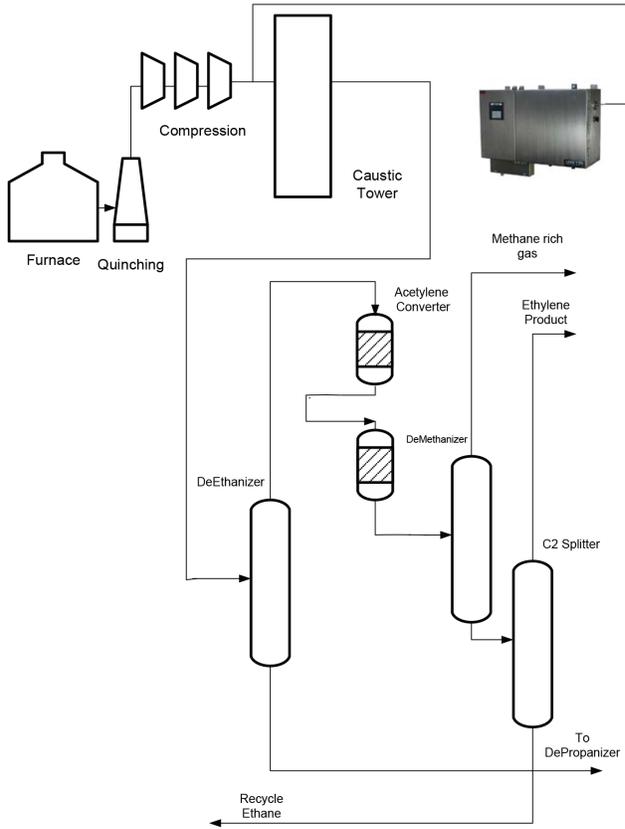


Figure 1. Measurements of H₂S and CO₂ at the Inlet of the Caustic Wash Tower with Front-End DeEthane Acetylene Hydrogenation.

Front-end acetylene converter could be on the overhead stream of the deethanizer process sequence, or the acetylene converter could be on the overhead stream of the depropanizer process sequence. One of these configurations is shown as flow diagrams in Figure 1. In a front-end deethanizer design the reactor feed contains a C₂ and lighter stream, whereas in a front-end depropanizer design the feed to the reactors is composed of C₃ and lighter hydrocarbons. In raw gas application where the reactor precedes the caustic tower the feed could contain significant amounts of sulfur, and wet C₅ and lighter hydrocarbons. For front-end acetylene hydrogenation units carbon dioxide and hydrogen sulfide will be in the inlet of the caustic wash tower

reactor feed at a level of about 100 – 500ppmv.

TDLAS is a non-contact analysis technique with long-term stability, high specificity and

selectivity. Laser based carbon monoxide sensor offers the advantage of faster response time, large dynamic range and low drift in comparison with conventional techniques such as gas chromatography. In applications such as monitoring the hydrogen sulfide and carbon dioxide levels at the inlet of the caustic wash tower, the above mentioned attributes help meet the optimal requirements of the plant operation better.

AMETEK model 5100 HD is an extractive type acetylene analyzer designed for hot/wet sample analysis. There is no sample conditioning for the analyzer system, just a fully integrated sample handling to transport the sample. The model 5100 HD uses a sealed reference cell for continuous on-line analyzer verification and offers high specificity, and sensitivity. The analyzer uses a digital implementation of the Wavelength Modulation Spectroscopy (WMS), so changing the experimental protocol is simply a matter of uploading a file. Model 5100 HD is the choice of many customers to replace gas chromatographs for monitoring of hydrogen sulfide and carbon dioxide in ethylene manufacturing process. It should be noted that significant spectral interference associated with methane, ethane and ethylene presence in a process gas stream prevents measurements of carbon dioxide in near infrared range. As a result, measurements of carbon dioxide were arranged in the infrared range.

The data shown in Figure 2 represent the response of the instrument to a series of hydrogen sulfide challenges in the concentration range of 0 -300ppmv. Zero base line, which was represented by 30% hydrogen, 10% of methane, 21% of ethane balanced ethylene was also evaluated in this test. The data acquisition rate was 2 seconds/measurement.

Repeatability as a degree of agreement between replicate measurements of the same quality was expressed in terms of standard deviation of the measurement results. Standard deviation of the hydrogen sulfide readings on each of the challenges is 3ppmv of the hydrogen sulfide concentration. The value of the accuracy evaluated at the levels of hydrogen sulfide from 0 to 300ppmv is 5ppmv.

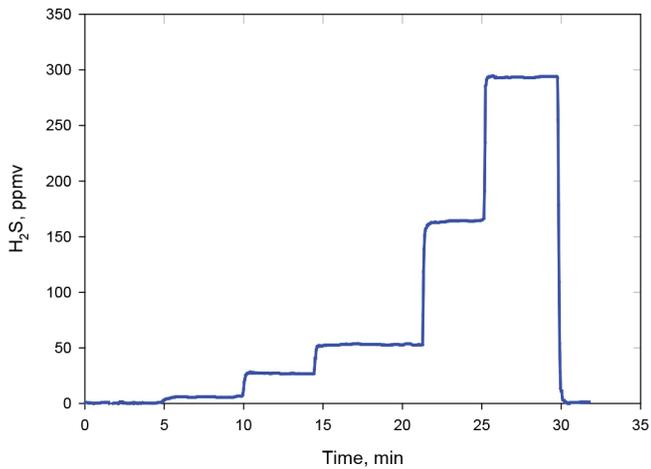


Figure 2: Response of the Analyzer to a series of H₂S challenges: 0, 5, 25, 50, 160 and 290 ppmv.



The AMETEK 5100 HD TDLAS Analyzer



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