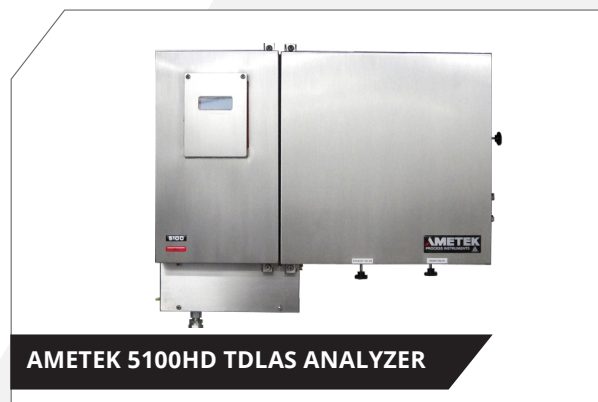


### MEASURING HYDROGEN SULFIDE AND CARBON DIOXIDE IN THE ETHYLENE MANUFACTURING PROCESS

## 5100HD Tunable Diode Laser Absorption Spectroscopy Analyzer

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 and propylene, but methane and hydrogen are also produced. Steam cracking is accompanied by an undesired 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.



### CONTROLLING HYDROGEN SULFIDE AND CARBON DIOXIDE

To reduce formation of coke during thermal cracking, sulfur-based additives are usually added to the feedstock. Most of the sulfur-based additives are decomposed even before entering the pyrolysis reactor, producing mainly hydrogen sulfide ( $H_2S$ ). It is known that pre-sulfiding – with about 200 parts per million by volume (ppmv) of  $H_2S$  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.

At the same time  $H_2S$  acts as a poison to the catalysts used to produce polyethylene. Removal of the  $H_2S$  takes place in the caustic wash tower of the ethylene plant. In the scrubbing process, sodium hydroxide ( $NaOH$ ) 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  $NaOH$  that is available relative to the amount of  $H_2S$  that is scrubbed into the solution. It should be noted that carbon dioxide ( $CO_2$ ) 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 by the 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.

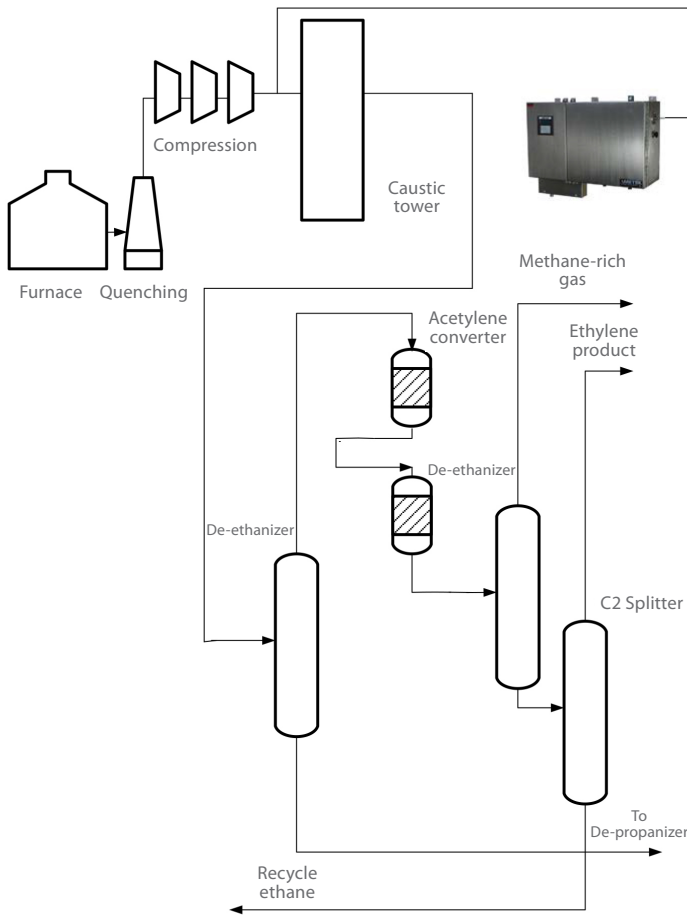
### EQUIPMENT

The 5100HD is an extractive laser-based analyzer designed for hot/wet sample analysis. There is no sample conditioning required for the analyzer system, reducing complexity, cost, and maintenance. The 5100HD uses a sealed reference cell to line-lock the laser on a desired wavelength. Any minor shift in the observed spectrum is used as feedback to adjust the laser ensuring the proper operating wavelength. The dual-cell, dual-laser 5100HD is the choice of many customers to replace gas chromatographs for monitoring of  $H_2S$  and  $CO_2$  in the ethylene manufacturing process because it provides continuous analysis of both components of interest, without cycle time delays or consumables such as carrier gas.

## PROCEDURE

After the cracking section, pyrolysis gas enters the quenching section to stop the continuously cracking reactions. In the quench section the gas cools down to a controlled temperature via direct oil and/or water quenching. After several stages of compression, the pyrolysis gas reaches partial condensation. Acid gases are removed after the compression stage by scrubbing them with a dilute caustic soda solution in the caustic wash tower. A front-end acetylene converter could be on the overhead stream of the de-ethanizer process sequence, or the acetylene converter could be on the overhead stream of the de-propanizer process sequence. One of these configurations is shown in Figure 1.

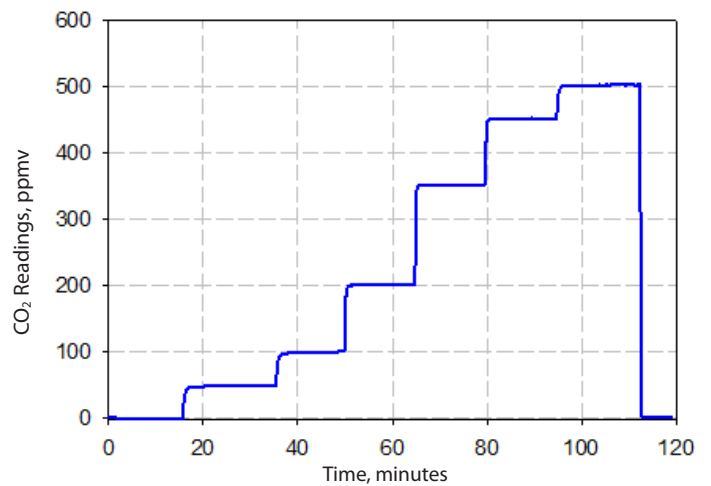
For front-end acetylene hydrogenation units, CO<sub>2</sub> and H<sub>2</sub>S will be in the inlet of the caustic wash tower reactor feed at a level of about 100 to 500 ppmv.



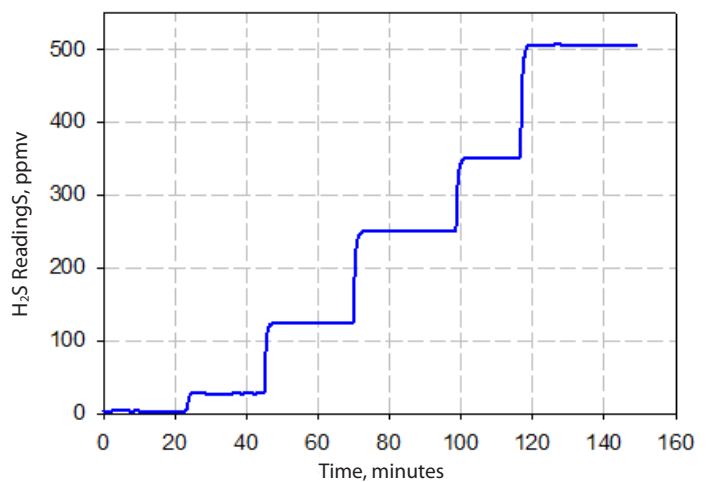
**Figure 1.** Measurements of H<sub>2</sub>S and CO<sub>2</sub> at the inlet of the caustic wash tower with front-end de-ethanizer acetylene hydrogenation

## RESULT

Figures 2 and 3 show the responses of the instrument to a series of carbon dioxide and hydrogen sulfide challenges over the concentration range 0 to 500 ppmv. The duration for each challenge was approximately 10 to 20 minutes, with the data acquired at a rate of 2 seconds per measurement. A return to the background gas baseline was also tested before, and after, the validation measurements. A background gas mixture of methane ethane and ethylene was used for these measurements. The response time (T<sub>90</sub>) was 20 seconds for carbon dioxide and 60 seconds for H<sub>2</sub>S measurements. T<sub>90</sub> time was limited by the larger purged volume of the Herriott sample cell (flow rate of 2L/min).



**Figure 2.** The response of the 5100HD to a series of CO<sub>2</sub> challenges



**Figure 3.** The response of the 5100HD to a series of H<sub>2</sub>S challenges

The results of the CO<sub>2</sub> and H<sub>2</sub>S validation test are summarized in Table 1. The accuracy for CO<sub>2</sub> measurements was evaluated as 5 ppmv and accuracy for H<sub>2</sub>S measurements was 7 ppmv. The accuracy was evaluated using the maximal deviation with respect to the target concentration for all levels.

CO <sub>2</sub> , ppmv	CO <sub>2</sub> Average, ppm	CO <sub>2</sub> , STD, ppm	CO <sub>2</sub> , Error, ppm	CO <sub>2</sub> Accuracy, ppm
0.0	-0.9	0.4	0.9	1.3
50.0	48.2	0.9	1.8	4.5
100.0	98.9	0.7	1.1	2.5
350.0	351.5	0.1	1.5	1.9
450.0	451.8	0.2	1.8	2.2
500.0	501.9	0.5	1.9	2.3
H <sub>2</sub> S, ppmv	H <sub>2</sub> S Average, ppm	H <sub>2</sub> S, STD ppm	H <sub>2</sub> S, Error, ppmv	H <sub>2</sub> S Accuracy, ppmv
0.0	-0.9	0.4	0.9	1.3
50.0	48.2	0.9	1.8	4.5
100.0	98.9	0.7	1.1	2.5
350.0	351.5	0.1	1.5	1.9
450.0	451.8	0.2	1.8	2.2
500.0	501.9	0.5	1.9	2.3

**Table 1.** Results of the CO<sub>2</sub> and H<sub>2</sub>S validation test.

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