

MEASURING CARBON MONOXIDE 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. Ethylene plants use different feedstocks. The most common feedstock is a mixture of hydrocarbons in the boiling range of 30°C to 200°C, including ethane and propane. The process is the same for all feedstocks: thermal cracking of the feedstock with steam to minimize the side reaction of forming coke followed by purification via fractionation to form the desired product streams. The main products of steam cracking are ethylene and propylene.



IMPORTANCE OF MONITORING CARBON MONOXIDE IN ETHYLENE PRODUCTION

Carbon monoxide (CO) is used as a reaction modifier in front-end acetylene converters. CO and acetylene adsorb on the metal reaction sites on the catalyst. CO competes with acetylene for the reaction sites and thus controls the activity of the catalyst. At the same time, the presence of CO prevents adsorption of ethylene on the reaction sites during selective hydrogenation and prevents the loss of the final product.

Typically, the concentration of CO stays at the 200 to 1000 parts-per-million-by-volume (ppmv) concentration range for the front-end acetylene converters and can be measured at the reactor feed or at the interstage, between the top and the bottom beds of the reactor. Concentration of the CO

can be limited by the addition of thiochemical compounds to the cracking feedstock. CO could also be measured as furnace effluent. In this situation CO, which is one of the cracking process components, can be added into the stream, providing a means for blocking and inhibiting the adsorption of ethylene. This is because the adsorption rate for CO is higher than that of ethylene. This is the basis for selective hydrogenation of acetylene to ethylene.

To avoid an incomplete conversion of the acetylene or an undesired continuing conversion of the ethylene to ethane, the optimum conditions for the hydrogenation process may be determined by real-time monitoring of CO concentrations.

PROCESS MONITORING WITH TDLAS

Traditionally gas chromatography is used to provide CO monitoring in the process of ethylene production. The major disadvantage of gas chromatology is low speed. Standard gas chromatographs need several minutes for propagation of the CO through the chromatograph column. As a result it can

take several minutes to detect a change in CO concentrations limiting process optimization actions. Tunable diode laser absorption spectroscopy (TDLAS) based measurements provide real-time monitoring and can be used as a tool for process control.

TDLAS is a non-contact analysis technique with long-term stability, high specificity and selectivity. A laser-based CO sensor offers the advantages of faster response time, a large dynamic range, and low drift in comparison with conventional techniques. In applications like monitoring CO levels at the inlet of the acetylene converter, or furnace effluent analysis, these attributes help meet the optimal requirements of the plant operation.

The AMETEK 5100HD is an extractive laser-based analyzer designed for hot/wet sample analysis. There is no complex sample conditioning required for the analyzer system, reducing complexity, cost and maintenance requirements. The 5100HD uses a sealed reference cell, providing real-time confirmation that the laser is locked on the desired absorption line. This continuous verification ensures high specificity and sensitivity. The dual-cell, dual-laser 5100HD is the choice of many customers to replace gas chromatographs for monitoring of CO concentrations at multiple sample points in ethylene production, without cycle time delays, or consumables such as carrier gas.

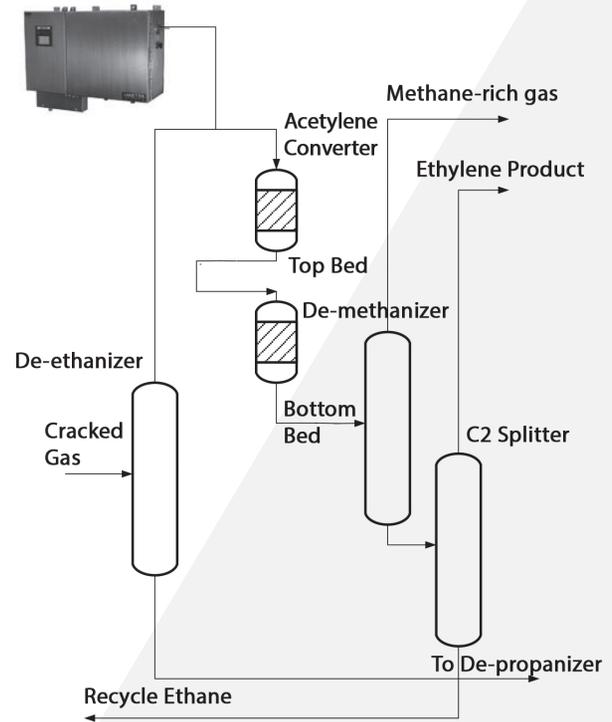


Figure 1. Front-end de-ethanizer acetylene hydrogenation

PROCEDURE

Real-time monitoring of the CO concentrations is critical to optimize the process and to minimize the impurities in the final product. Potential measurement points for CO are the inlet of the acetylene converter, the outlet of the first bed of the converter, and the effluent of the furnace.

The front-end acetylene converter can be located on the overhead stream of the de-ethanizer process sequence, or the converter can be located on the overhead stream of the de-propanizer process sequence. The front-end de-ethanizer is shown in Figure 1. In a front-end de-ethanizer design, the reactor feed contains a C2 and lighter stream. In a front-end de-propanizer design the feed to the reactors is composed of C3 and lighter hydrocarbons. In raw gas applications where the reactor precedes the caustic tower, the feed could contain significant amounts of sulfur, wet C5, and lighter hydrocarbons. These differences in the gas stream need to be considered for the calibration of CO analyzers. Feed composition as a function of acetylene reactor location is summarized on Table 1.

Feed component	Back-end acetylene hydrogenation	Front-end de-ethanizer acetylene hydrogenation	Front-end de-propanizer acetylene hydrogenation
	Mole %	Mole %	Mole %
Hydrogen		30	12
Carbon monoxide	0.0005	0.02	0.05
Methane		13.6	29.5
Acetylene	1	0.3	0.5
Ethylene	80	34	32.5
Ethane	19	22	5.5
Methyl acetylene			0.25
Propadiene			0.25
Propylene		0.08	19
Propane			0.45
Cracking feed	ethane	ethane	naphtha

Table 1. Feed composition as a function of acetylene reactor location

RESULT

Figure 2 represents the response of the instrument to a series of challenges in the concentration range of 0 to 1000 parts per million by volume (ppmv). The duration of each of the challenges was about 20 minutes. Zero base line, which was represented by 30% hydrogen, 10% of methane, 21% ethane, and a balance of ethylene was also evaluated in this test. 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 quality was expressed in terms of standard deviation of the measurement results. Standard deviation of the readings on each of the challenges was 5 ppmv of the CO concentration. The value of the accuracy evaluated at the levels of CO from 0 to 1000 ppmv was 10 ppmv.

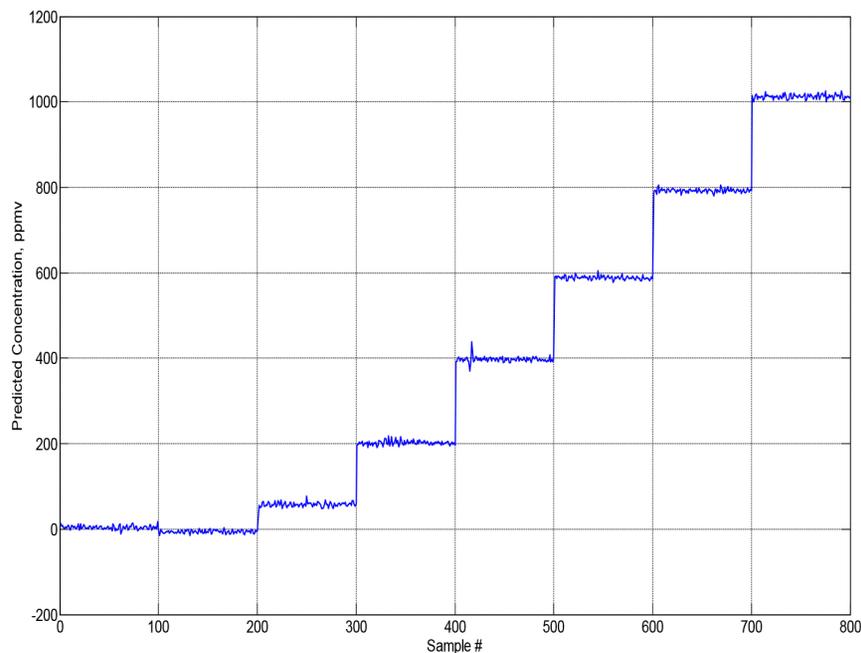


Figure 2. Carbon monoxide measurements in front-end de-ethanizer process gas

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