Carbon Monoxide Measurements with Turnable Diode Laser Absorption Spectroscopy (TDLAS) in the Ethylene Manufacturing Process

Most of the 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 the purification via fractionation to form the desired product streams. The main products of steam cracking are ethylene and propylene.

Acetylene, carbon monoxide and carbon dioxide are byproducts of the cracking reactions. These byproducts destroy the catalysts used for production of polyethylene and need to be removed from the process. Depending on the hydrocarbon feedstock for pyrolysis and also on cracking furnace design and operating conditions, the amount of acetylene byproduct can be increased several percent.

In modern ethylene production, the most common method for acetylene removal is through selective hydrogenation in vapor phase. It is should be noted that during the hydrogenation process other chemical reactions could occur in the hydrogenation unit and as a result ethylene could be converted to ethane. Acetylene hydrogenates much faster than ethylene over the same catalyst when both acetylene and ethylene are present. This preferential adsorption of acetylene over ethylene assumes a sufficient amount of acetylene molecules to cover all active sites to minimize ethylene hydrogenation to ethane.

However, under conditions of industrial operations at the location near the bottom of the final bed where most of the acetylene molecules are already hydrogenated there is an insufficient number of the acetylene molecules to maintain total active site coverage. Carbon monoxide is used as a reaction modifier in front-end acetylene converters. Carbon monoxide and acetylene adsorb on the metal reaction sites on the catalyst. Carbon monoxide competes with acetylene for the reaction sites and thus controls the activity of the catalyst. At the same time, the presence of carbon monoxide prevents adsorption of ethylene on the reaction sites in the course of selective hydrogenation reaction and prevents the loss of the final product.

Typically, the concentration of carbon monoxide stays at 200 – 1000 ppmv concentration range for 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 carbon monoxide can be limited by the addition of thiochemical compounds to the cracking feedstock. Moreover, carbon monoxide could be measured as furnace effluent. In this situation the presence of carbon monoxide, 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 because adsorption rate for carbon monoxide is higher than of ethylene. These facts are 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 acetylene and carbon monoxide concentrations. Traditionally gas chromatography is used to provide acetylene monitoring in the process of ethylene production. Gas chromatology has the advantage of high sensitivity resulting in the ability to measure sub ppm levels of acetylene. The major disadvantage of gas cromatology is low speed. Standard gas chromatograph needs several minutes for propagation of the acetylene through the chromatograph column, as a result it can take several minutes to detect a change in acetylene concentrations limiting process optimization actions. TDLAS based measurements provide real time monitoring and can be used as a tool for process control.

Real time monitoring of the acetylene and carbon monoxide concentrations is critical to optimize the process and to minimize the impurities in the final product. Potential measurement points for carbon monoxide measurements is the inlet of the acetylene converter or outlet of the first bed of the converter and also effluent of the furnace.

The front-end acetylene converter can be located on the overhead stream of the deethanizer process sequence, or the converter can be located on the overhead stream of the depropanizer process sequence. The front-end deethanizer is shown 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 applications where the reactor precedes the caustic tower, the feed could contain significant amounts of sulfur, and wet C5 and lighter hydrocarbons. These differences in the gas stream need to be taken into account for the calibration of the acetylene and carbon monoxide analyzers. Feed composition as a function of acetylene reactor location is summarized on Table 1.

Feed Component	Back-end Acetylene Hydrogenation	Front–end Deethanizer Acetylene Hydrogenation	Front-end Depropanizer 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

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 carbon monoxide levels at the inlet of the acetylene converter or furnace effluent analysis, the above mentioned attributes help meet the optimal requirements of the plant operation better.

AMETEK model 5100 HD is an extractive type carbon monoxide analyzer. 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 carbon monoxide in ethylene manufacturing process. It is should be noted that significant spectral interference associated with methane, ethane and ethylene presence in a process gas stream prevents measurements of carbon monoxide in near infrared range. As a result, measurements of carbon monoxide were arranged in infrared range.

The data shown in Figure 2 represent the response of the instrument to a series of acetylene challenges in the concentration range of 0 -1000ppmv. The duration of each of the challenges was from about 20 minutes. Zero base line, which was represented by 30% hydrogen, 10% of methane, 21% of ethane balanced 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 acetylene readings on each of the challenges was 5 ppmv of the carbon monoxide concentration. The value of the accuracy evaluated at the levels of acetylene from 0 to 1000 ppmv was 10 ppmv.

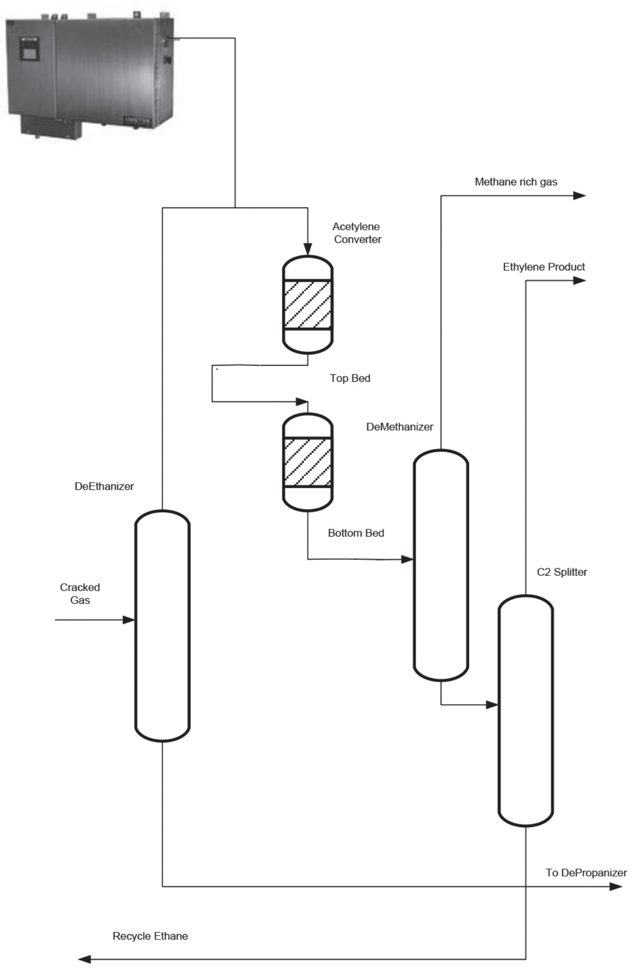

Figure 1: Front-End DeEthanizer Acetylene Hydrogenation.

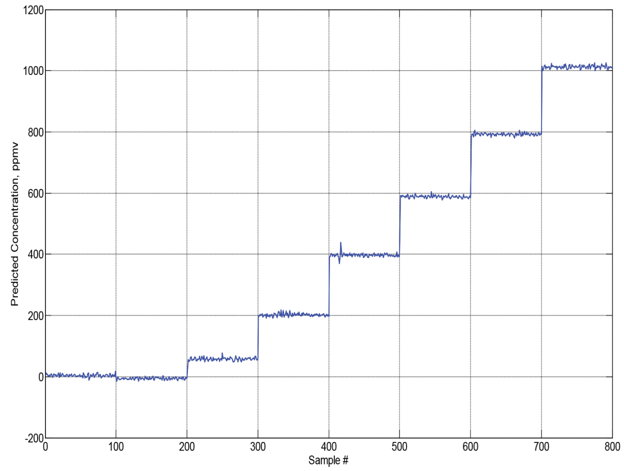

Figure 2: Carbon Monoxide Measurements in Front-End De-Ethanizer Process Gas.

The AMETEK 5100 HD TDLAS Analyzer

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