Carbon Monoxide and Carbon Dioxide Measurements with Tunable Diode Laser Absorption Spectroscopy (TDLAS) in the Furnace Decoking Process

In ethylene production a hydrocarbon feed stream mixed with steam enters a tubular reactor where under controlled conditions the feedstock is cracked at 800 – 850°C into smaller molecules within time of 0.1 – 0.5 seconds. This process takes place in the radiant coils of the furnace. After leaving the radiant coils of the furnace, the gas cools down instantaneously in the transfer line exchanger to preserve its composition. Cracking of the feedstock in the pyrolysis reactor causes carbon build up on the radiant coils and tube walls of quench exchangers. As coke builds up, the efficiency of heat transfer from flue gases to hydrocarbons in the tubes of the furnace goes down. In addition, coke deposition causes a pressure drop in the tubes of radiant coils and transfer line exchangers.

Cracking furnaces need to be decoked once the furnace coils get coated with carbon and lose efficiency. The furnace is taken off-line, the residual hydrocarbons are purged downstream with steam and the process flow is rerouted to a special decoking system. The time between the start of the ethylene production to shutdown of production due to coking is known as 'furnace run length'. The furnace run length can vary from 5 to 60 days. The process of decoking involves burning off the coke with air in the steam atmosphere which converts carbon to carbon dioxide and carbon monoxide. Due to the use of air in the decoking process, metal sites on the radiant coils become very active and cause a high coke and carbon monoxide release. Usually combustion of coke is controlled by the amount of air mixed with steam. The progress in decoking can be controlled by the monitoring of carbon dioxide and carbon monoxide in the furnace effluent. It rises as the carbon is burned off and then decreases to zero when the furnaces are clean again and the plant can be returned to normal operation. The decoking process is terminated when effluent of CO_2 content falls below the level of 0.1% on a dry basis. The process can be optimized by monitoring the carbon dioxide and carbon monoxide concentrations during the decoking process. Monitoring the decoking process in an ethylene furnace is a good application for our 5100 HD Tunable Diode Laser Absorption Spectroscopy analyzer.

Typically, decoked stream includes percent levels of carbon dioxide, carbon monoxide, water and oxygen balanced nitrogen.

Figure 1 shows a flow diagram of the ethylene furnace with control line exchanger and measurement control point monitored by the 5100 HD.

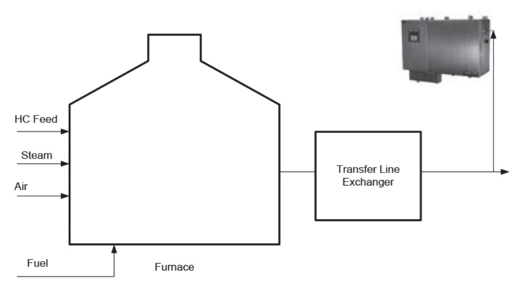

Figure 1: Monitoring of the Decoking Process in Ethylene Furnace.

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 dioxide and carbon monoxide levels at the inlet of the caustic wash tower the 5100 HD can optimize plant operations by increasing the 'furnace run length'.

AMETEK model 5100 HD is an extractive type analyzer designed for hot and wet sample analysis which is required for this application. 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 dioxide and carbon monoxide in ethylene manufacturing process. Model 5100 analyzer can be built with two lasers – two sample cells configurations in one enclosure to provide two distinct and simultaneous measurements.

The data shown in Figure 2 represent the response of the instrument to a series of carbon dioxide and carbon monoxide challenges in the concentration range of 0 -10%. Zero base line, which was represented by air saturated with water was also evaluated in this test. The data acquisition rate was 2 seconds/measurement.

Validation test for the analyzer resulted in maximal error value of 0.1volume percent evaluated as for carbon dioxide as for carbon monoxide measurements. This error was calculated as a difference between set value and averaged over the measurement time reading for each selected concentration level. 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 carbon dioxide readings on each (with except of 10%) of the selected concentration challenges was less than 600 ppmv. Repeatability of carbon dioxide readings at 10% level was 1200 ppmv. Repeatability of carbon monoxide readings was less than 300 ppmv.

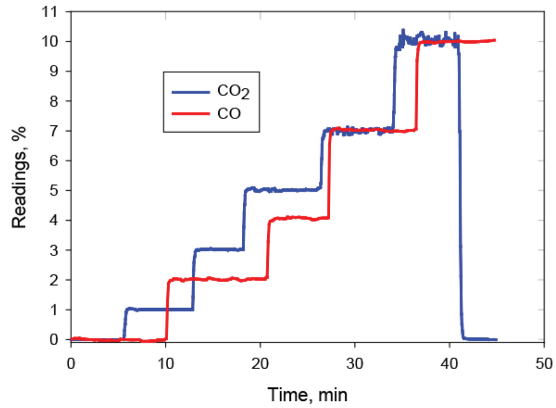

Figure 2: Response of the analyzer to a series of CO_2 and CO concentration challenges.

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150 Freeport Road, Pittsburgh, PA 15238
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www.ametekpi.com

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