Use of TDLAS for Carbon Dioxide Measurements in LNG Processing

The liquefied natural gas (LNG) plant is a large and complex industrial facility. The liquefaction process, which is the transformation of natural gas to liquid, involves operating at very low temperature. At these conditions CO_2 can freeze on the exchanger surface, plugging lines and reducing plant efficiency. The natural gas entering the liquefaction plant will often contain several contaminants that must be reduced to ensure satisfactory LNG plant performance and also to meet LNG sales specifications. The liquefaction process involves removal of components such as acid gases, helium, water, and heavy hydrocarbons. Acid gas removal is the next important step reducing carbon dioxide levels to about 50 ppm to meet normal sales gas specification. There are many acid gas treating processes available for the removal of CO_2 from natural gas. The selection of these processes is based not only on economic feasibility but also the effective removal of CO_2 .

These processes include chemical solvents, physical solvents, hybrid solvents, adsorption processes and physical separation based on membrane systems. Each of these technologies has advantages and limitations. The nature and amount of contaminants in the feed gas as well as the targeted removal capacity, the amount of hydrocarbons in the gas, the amount of gas to be processed, and the desired selectivity should all be considered.

Despite of the nature of the process used to purify the natural gas, optimization of the process requires measurement of the carbon dioxide before and after purification.

Amine gas treating refers to a group of processes that use aqueous solution of various amines to remove H_2S and CO_2. Today it is a common process used in refineries, petrochemical plants, natural gas processing plants. The use of blended amines in gas treatment provides significant improvement in the absorption capacity, absorption rate and in meeting solvent regeneration energy requirements. In most cases the amine mixtures contain methyldiethanolamine (MDEA) as the base amine with add either one or two more reactive amines such as monoethanolamine (MEA) or diethanolamine (DEA).

The typical amine treatment unit involves two stages. The first stage is amine contactor where natural gas is brought into contact with amine. In the absorber down flowing amine solution absorbs H_2S and CO_2 from the up flowing sour gas to produce sweetened gas stream with significantly reduced acid components. Sweet gas leaves the top of the absorber and flows to a dehydration unit before liquefaction. Resultant rich amine from the absorber with absorbed CO_2 and H_2S then follows to regenerator which is stripper with reboiler. In the second stage H_2S and CO_2 are stripped from the liquid phase to regenerate the lean amine solution which is returned to the amine contactor column. The general process flow diagram for amine CO_2 removal is shown in Figure 1.

Acid gas and steam pass through a condenser where the steam is condensed and cooled and returned to the top of the stripper as a reflux. Acid gas is separated and sent to the flare or compressed for the sequestration process. The acid gas leaves through the top of the stripper

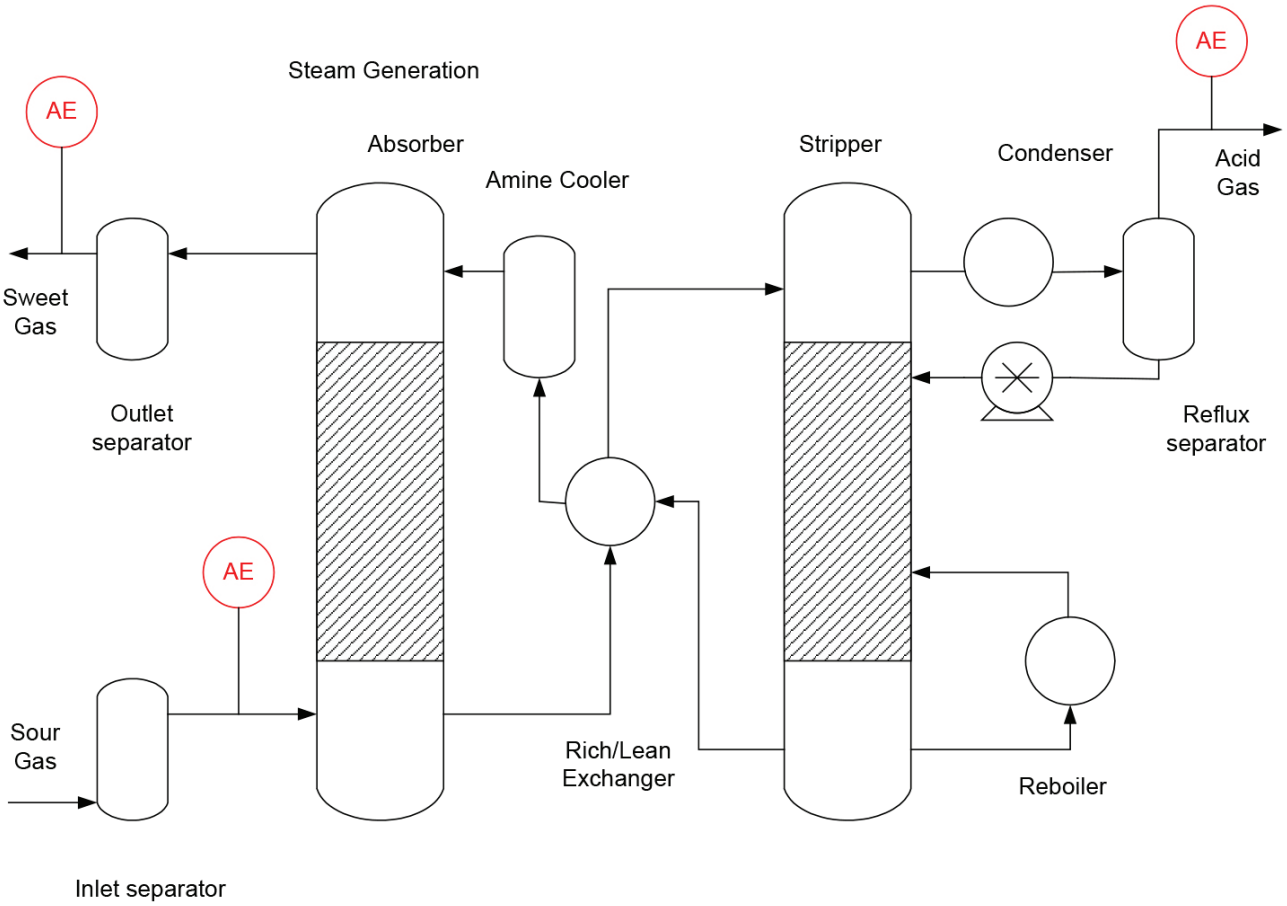

Figure 1: Amine CO2 Removal Process

column. The lean amine from the bottom of the stripper is returned to the absorber through heat exchanger and through the cooler. There are several control points where measurements of the carbon dioxide level will be for process optimization. These control points correspond to sour gas at the inlet of the absorber, sweet gas at the outlet of the absorber and to the level of carbon dioxide in acid gas. Usually the concentration range of carbon dioxide in sweet gas varies in the range of 0 – 50 ppm, the levels of CO_2 in sour gas correspond to 0 – 5% range and concentration of CO_2 in acid gas can vary in the range of 0 – 50%.

TDLAS is a non-contact analysis technique with long-term stability, high specificity and selectivity. Laser based carbon dioxide sensor offer 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 in LNG processing plant the above mentioned attributes help meet the optimal requirements of the plant operation better.

AMETEK model 5100 HD is an extractive type carbon dioxide 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. Ethane has spectral interference with carbon dioxide in the vicinity of carbon dioxide lines selected for measurements. Depending on the concentration of ethane in the natural gas measurements of CO_2, the concentration range 0 – 50 ppmv can be measured

in near infrared range (for concentration of ethane less than 7%) or in infrared range (for concentration of ethane higher than 7%).

Schematic diagram of the analyzers is shown on Figure 2 and Figure 3.

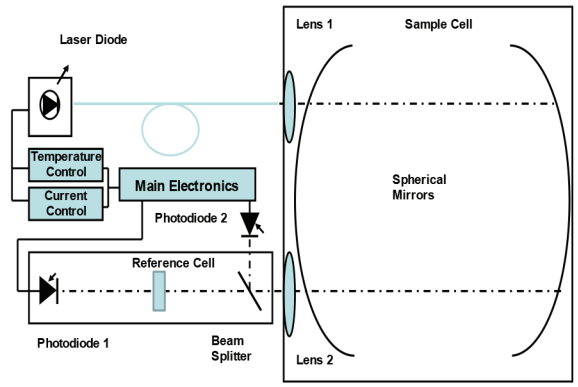

Figure 2:. 5100 HD Analyzer optical set up for low CO2 levels measurements in the NIR range.

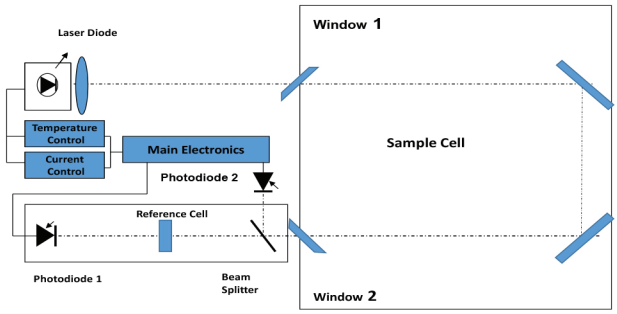

Figure 3:. 5100 HD Analyzer optical set up for low CO_2 levels measurements in the IR Range.

Measurements of carbon dioxide in the NIR range was performed with a distributed feedback laser. The output of the laser was coupled into single-mode optical fiber which was connected to a fiber-optic beam splitter. The splitter was used to divide the optical power in a 50/50 ratio for use in the sample and reference measurements, respectively. Gradient refractive index (GRIN) lenses were used to collimate the output of the single-mode fibers and direct the resulting beams through the sample and reference cells. The sample and reference cells each contained InGaAs-photodiode detectors, which were connected to separate input channels of the electronics unit. With this configuration it was possible to make simultaneous measurements of unknown samples and known references, which were used to lock the output wavelengths for the laser. It is should be noted that configuration of the sample cell compartment included two cells for the measurements of carbon dioxide in two different streams (for example measurements of the inlet and outlet of the acid removal unit is also available). The optical path of the sample cell could be adjusted corresponding to concentration range of measured carbon dioxide including multi pass Herriott cells used for low concentration range measurements.

Measurements in the IR range were organized in a similar optical set up. An interband cascade laser was used as a radiation source. The beam was collimated and send to the sample cell with an optical path of 10 cm. Indium arsenide antimonide photo voltaic detectors were used in sample and reference channels. As in previous set up electronics was providing control of the injection current and temperature of the laser.

The data shown on Figure 4 represent the response of the instrument to a series of carbon dioxide challenges in the concentration range of 0 -50 ppmv. The duration of each of the challenges was from 10 to 20 minutes with return to the zero gas baseline, which was represented by methane between challenges. The speed of the response T90 time was 100 seconds and was determined by the propagation of the gas in the sampling system with a flow rate of 1L/min. The data acquisition rate was 2 seconds/measurement.

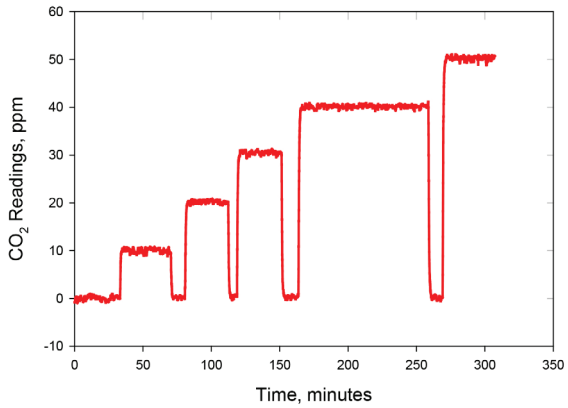

Figure 4:. Response of the Analyzer to a Series of Carbon Dioxide Challenges.

Repeatability of the carbon dioxide readings on each of the challenges was about 0.5 ppmv of the carbon dioxide concentration. The value of the accuracy evaluated at the levels of carbon dioxide from 0 to 50 ppmv was 1.5 ppmv.

To provide accurate measurements of carbon dioxide in natural gas it is important to account not only methane but also other components of natural gas stream, especially ethane and their effect on carbon dioxide readings. Account of these components was provided by including them in corresponding calibration model based on multivariate regression.

The advantage of using TDLAS based technology for carbon dioxide measurements in natural gas stream in comparison with gas chromatography in the speed of the response and low maintenance value. At the same time TDLAS provides higher accuracy and selectivity of the measurements in comparison with NIT and IR photometry.

The AMETEK 5100 HD TDLAS Analyzer

AMETEK®
PROCESS INSTRUMENTS

150 Freeport Road, Pittsburgh, PA 15238
Ph. +1-412-828-9040, Fax +1-422-826-0399
www.ametekpi.com

REGISTERED ISO 9001 MANAGEMENT SYSTEM

F-0525 Rev. 1 (0217)

SALES, SERVICE AND MANUFACTURING:

USA - Pennsylvania
150 Freeport Road, Pittsburgh PA 15238 • Tel: +1-412-828-9040, Fax: +1-412-826-0399

USA - Delaware
455 Corporate Blvd., Newark DE 19702 • Tel: +1-302-456-4400, Fax: +1-302-456-4444

Canada - Alberta
2876 Sunridge Way N.E., Calgary AB T1Y 7H2 • Tel: +1-403-235-8400, Fax: +1-403-248-3550

WORLDWIDE SALES AND SERVICE LOCATIONS:

USA - Houston, Texas
Tel: +1-713-466-4900, Fax: +1-713-849-1924

BRAZIL
Tel: +55 19 2107 4100

CHINA
Beijing / Tel: +86 10 8526 2111, Fax: +86 10 8526 2141
Chengdu / Tel: +86 28 8675 8111, Fax: +86 28-8675 8141
Shanghai / Tel: +86 21 6426 8111, Fax: +86 21 6426 7818

FRANCE
Tel: +33 1 30 68 89 20, Fax: +33 1 30 68 89 99

GERMANY
Tel: +49 21 59 91 36 0, Fax: +49 21 59 91 3639

INDIA
Tel: +91 80 6782 3200, Fax: +91 80 6782 3232

SINGAPORE
Tel: +65 6484 2388, Fax: +65 6481 6588