On-line Gas Analysis in Urea Plants

Overview
In 2012, urea plants produced nearly 184 million tons worldwide. Over 90% of it is used as a nitrogen release fertilizer. More than 90% of world industrial production of urea is destined for use as a nitrogen release fertilizer. Urea has the highest nitrogen content of all solid nitrogenous fertilizers, therefore it has the lowest transportation costs per unit of nitrogen nutrient. Other uses can be found in the chemical industry with the manufacturing of urea-formaldehyde resins and urea-melamine-formaldehyde, for in explosives for making urea nitrate among other applications. Additionally, urea can also be used for SNCR and SCR reactions to reduce the NOx pollutants in exhaust gases made from Diesel combustion, dual fuel, and lean-burn natural gas engines.

Background
Urea is produced at an industrial scale from the reaction of synthetic ammonia (NH₃) with carbon dioxide (CO₂). As large quantities of carbon dioxide are produced during the ammonia manufacturing process as a byproduct from steam reforming of hydrocarbons, urea production plants are almost always located adjacent to the site where the ammonia is manufactured. For example:

1. Carbamate formation: fast exothermic reaction of liquid NH₃ with gaseous CO₂ at high temperature and pressure to form ammonium carbamate (H₂N–COONH₄)
2. Urea conversion: slower endothermic decomposition of ammonium carbamate into urea and water

The overall conversion of NH₃ and CO₂ to urea is exothermic. Ammonium carbamate solutions are notoriously corrosive towards metallic materials of construction, even the more resistant forms of stainless steel. Corrosion can be minimized by continuously injecting a minor amount of oxygen (as air) into the plant to establish and maintain a passive oxide layer on exposed stainless steel surfaces.

Applications
Carbon dioxide feed is recovered from ammonia synthesis gas and contains traces of hydrogen which can mingle with the passivation air to form an explosive mixture if allowed to accumulate in the plant. Therefore the H₂ content of the CO₂ feed need to be monitored.

In total recycle NH₃ stripping urea process, ammonia return gas from the urea reactor needs to be scrubbed of CO₂ before entering the ammonia compressor to avoid precipitant formation. Compressor fouling contributes heavily to significant and unplanned maintenance costs. Efficiency checks of the CO₂ scrubbers greatly minimize the ammonium carbamate and ammonium carbonate fouling potential.

Solutions
The H₂ concentration in CO₂ feedstock can go up to several thousand ppm with a normal value of 200 ppm. Normal values for N₂ are 2.9 %, 0.88 % O₂, 400 ppm Ar, 50 ppm CH₄ and 2000 ppm H₂O. All concentrations do not show much variation. Therefore a 0–1 % H₂ TCD measurement which is calibrated in a CO₂ background can be applied. The detection limit is < 100 ppm. For installation in hazardous area the TCD is packaged in a flame proofed housing of the X-STREAM series. For lower H₂ concentration with a lowest range of 0–1000 ppm H₂ measurements a special TCD solution in the MLT2 field housing is available.

A flowing reference with CO₂ is used to minimize drift effects. Sample gas flow and reference gas flow are controlled either with a pressure regulator and capillary or mass flow controllers. A purged system for installation in hazardous area can be configured. Both TCD solutions have to be calibrated in CO₂ background.
For the CO₂ measurement in the ammonia recycle gas a MLT analyzer can be provided with an internal heated compartment equipped with temperature controller to maintain cells and sample lines between 80 °C and 120 °C (176 °F and 248 °F). A heated sample handling system and the heated analyzer prevent formation of ammonium carbamate and ammonium carbonate.