Improving ammonia plant performance with process gas chromatographs

Process gas chromatographs have been used since the 1950s to provide real-time compositional data to process control systems. Today, there are tens of thousands of process gas chromatographs in use throughout the process industry making the gas chromatograph the analytical workhorse for online compositional measurements. One example of how process gas chromatographs are used for improving process operations can be found in the ammonia plant.

Commercial production of ammonia is an important part of a number of industries such as in the manufacture of nitrogenous fertilizers. It is also commonly used as a base component for manufacturing a wide range of explosives. Ammonia is also a popular refrigerant since it is easily liquefied by compression.

The Ammonia Plant

The manufacture of ammonia entails a number of chemical reactions that convert a hydrocarbon stream into a hydrogen-rich stream that is then reacted with the nitrogen in air to form the ammonia (NH_3). The hydro-carbon feed stream is almost always a natural gas stream although some feed streams of naphtha or other heavy oils are also used.

The feed stream is first run through a desulfurization reactor to remove sulfur and other compounds that damage the catalyst of the other reactors. Steam is then added to this treated stream before it enters the two reformer reactors that convert the hydrocarbons and water into hydrogen and carbon monoxide. This can be seen in the following chemical reaction:

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

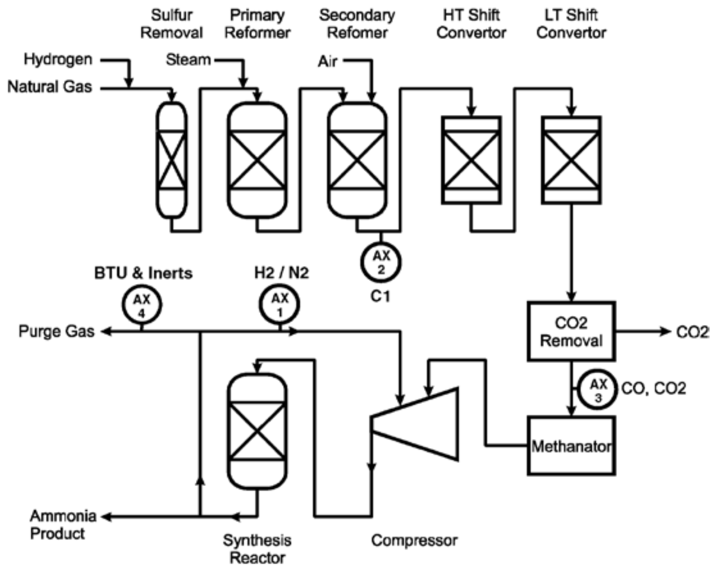

Figure 1 - Flow Diagram of a Typical Ammonia Plant

Some of the CO will react with the water (steam) to form even more H_2:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Two reformers are used since only 30-40% of the hydrocarbons are reformed in the first reactor. Air (N_2) that is needed for the final synthesis is added at the reformer stage so that any hydrocarbons and CO_2 in the air can be processed with the reformer effluent.

The gases exiting the reformers are primarily H_2, CO, CO_2 and any unreacted hydrocarbons (C_1) in addition to the N_2 and O_2 from the air.

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Before this stream can be converted to ammonia, the CO and CO_2 must be removed since they will ruin the catalyst in the ammonia reactors. The removal is done in three stages. The first is to "shift" the CO into CO_2 by the following reaction:

$CO + H_2O \rightarrow CO_2 + H_2$

For maximum conversion, the shift reaction is done in two stages, one at a high temperature and the other at a lower temperature.

With 99+% of the CO converted to CO_2, the next step is to run the stream through a CO_2 removal system that is often an amine absorber unit that selectively strips out the CO_2. Finally, any remaining CO_2 (and CO) is converted to methane in the methanator reactor.

With the removal of CO and CO_2, the stream is compressed to over 1500 psi. The stream then enters the final reactor where the conversion is made to ammonia by the following reaction:

$N_2 + 3H_2 \rightarrow NH_3$

Since only 30% is converted on each pass through the synthesis reactor, a large recycle stream returns much of the effluent back to the compressor for re-processing. There is also a small purge gas stream that is removed from this recycle to control the build-up of inert gases that accumulate in the process. The purge gas is often used as a fuel gas to heat burners and furnaces in the plant.

Improving Unit Performance With Process Gas Chromatographs

There are a couple of key measurements that must be made to keep the ammonia plant operating efficiently. The most critical measurement (AX #1 in Figure 1) is the H_2 to N_2 ratio between the synthesis reactor and the compressor in the recycle stream. The ratio must be keep at the proper levels to get the maximum formation of ammonia at each pass.

Another important measurement (AX #2 in Figure 1) tracks methane conversion on the exit stream of the secondary reformer by measuring the C_1 content.

The last two measurements (AX #3 and #4 in Figure 1) are occasionally seen when maximum operating efficiency is desired. Measuring the CO and CO_2 levels as they leave the CO_2 removal unit helps optimize that unit's performance. Finally, monitoring the purge gas helps keep the inert levels at an optimum level; typically 10-15%. This analyzer can also measure the BTU content if the purge gas is being used as a fuel for process heaters. A summary of these applications can be seen in Figure 2.

The Emerson Solution

Emerson has a long history of providing process gas chromatographs for the ammonia industry. Emerson's process gas chromatographs have set the standard for on-line process measurement by supplying analyzers that are both robust and capable of handling the analytical requirements.

Analyzer #	Stream	Components Measured	Measurment Objective
1	Synthesis gas recycle	H_2, N_2	Maintain H_2 to N_2 ratio for optimum synthesis conversion
2	Feed to CO_2 scrubber	C_1	Monitor for unconverted C_1
3	Exit of CO_2 scrubber	CO, CO_2 and CO_2	Monitor for complete removal of CO
4	Purge gas	Inerts and BTU	Optimize purge gas rates and track BTU for use as fuel gas

Figure 2 -Summary of Process Gas Chromatograph Applications in a Typical Ammonia Plant

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