Application Note

Improving Process Control During Ammonia Production Using the Thermo Scientific Prima PRO Process Mass Spectrometer

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Key Words

- Steam-to-carbon ratio
- Air requirement
- Methane slippage
- Shift reaction
- H/N ratio
- Rapid multi-stream sampler (RMS)
- Magnetic sector analyzer

Introduction

Ammonia is one of the most important industrial chemicals in the world, with demand forecasted to grow 3% annually over the next five years. Close to 80% of the ammonia produced globally is used for the production of fertilizers. Ammonia is also an important component of explosives, fibers, plastics, and intermediates for dyes and pharmaceuticals.

The first step in ammonia production is the conversion of natural gas, liquefied petroleum gas or naphtha into hydrogen. Because these raw materials are in high demand for many other applications including use as heating fuels, prices tend to be very volatile. This price volatility means plants must maximize the efficiency of the ammonia production unit to maintain a strong bottom line.

The Ammonia Process

The manufacture of ammonia can be described simply by the classic Haber process formula:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

However, the production of the two reactants from raw materials (i.e. fuel, steam and air) requires a number of process steps. All of these steps occur during the gas phase and require fast, accurate gas analysis to optimize the process.

Figure 1 is a schematic of a typical ammonia plant based on natural gas feedstock. The streams that require analysis are:

- Natural gas
- Primary reformer feed
- Primary reformer effluent
- Secondary reformer effluent
- High temperature shift outlet
- Low temperature shift outlet
- CO_2 absorber outlet
- Raw synthesis gas
- Converter inlet
- Converter outlet
- High pressure purge
- Hydrogen recovery.

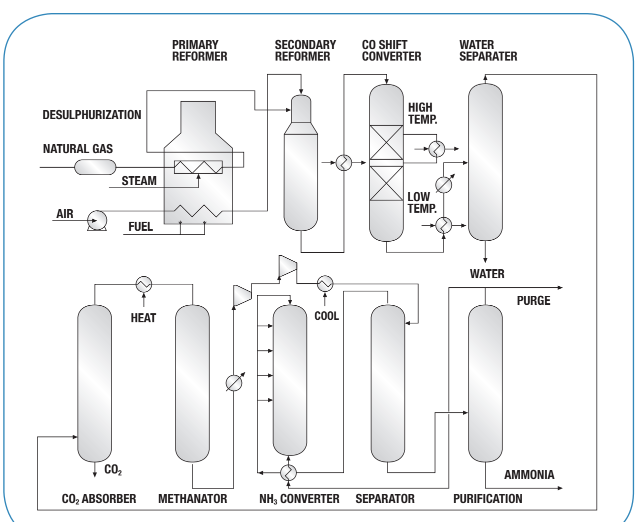

Figure 1.
Typical ammonia process based on natural gas feedstock.

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Process Analytical Requirements

The analysis of these 12 streams requires a wide range of compounds to be analyzed, including:

- Organics: C_1 to C_5
- Inorganics: N_2, H_2, NH_3, CO, CO_2, O_2, Ar, H_2S.

Concentrations range from tens of percent down to parts per million (ppm). In theory, a set of discrete analyzers can be used to measure some of the required components. However, installation and maintenance costs will be extremely high and vital analysis information will be missing. Alternatively, a process gas chromatograph (GC) can be used, but long analysis cycle times and frequent calibration and maintenance intervals limit the usefulness of this technique. This application note will discuss the advantages gained by using a multi-point, multi-component solution: the Thermo Scientific™ Prima™ PRO Process Mass Spectrometer. This field-proven analyzer provides fast, accurate and reliable data that can be used as part of a dynamic process control model.

Thermo Scientific Prima PRO Process Mass Spectrometer

Advantages of Mass Spectrometry

The Prima PRO process mass spectrometer offers analysis times measured in seconds rather than minutes and the ability to measure both inorganic and organic species over a wide dynamic range. One Prima PRO mass spectrometer can therefore monitor all sample points, from feedstock to final product, in the ammonia process.

Key Control Parameters

Steam-to-Carbon Ratio

Steam and natural gas (or another source of hydrocarbon) react together in the primary reformer to form hydrogen and carbon monoxide: $CH_4 + H_2O \rightarrow 3H_2 + CO$. Some of the CO will react with the steam to form even more hydrogen: $CO + H_2O \rightarrow CO_2 + H_2$. The steam-to-carbon gas ratio requires tight control because energy is wasted when excess steam is produced unnecessarily. In addition, excess methane requires more energy for compression and causes inefficient catalyst activity.

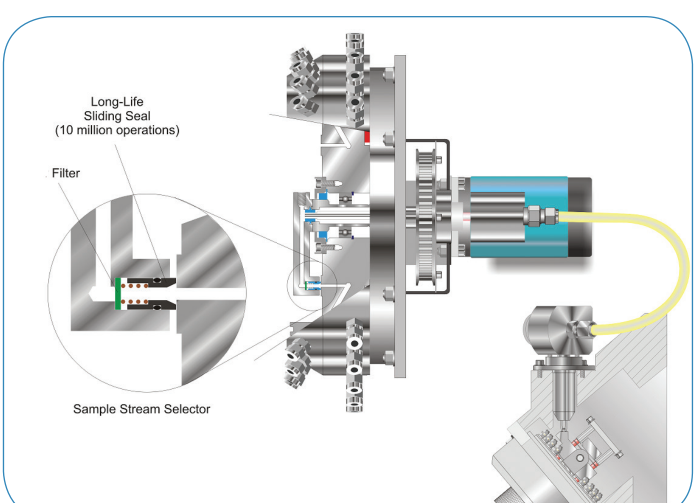

Figure 2. Rapid multi-stream sampler within the Prima PRO Process Mass Spectrometer.

Air Requirement

In addition to being the source of hydrocarbon for the process, natural gas is also used as fuel. The physical properties of the fuel gas must be measured accurately. Doing so ensures the air requirement for combustion control optimizes the energy consumption of the unit.

Methane Slippage

Only 30 to 40% of the hydrocarbon is converted in the primary reformer. The exhaust is therefore fed into a secondary reformer where the conversion to CO and H_2 continues. Air (the source of N_2) is introduced at this stage and combustion takes place at around 1250°C (2282°F).

It is important to minimize the amount of unreacted methane, or methane slippage, from the secondary reformer. If it is not minimized, this methane builds up in the ammonia converter loop. Because this process takes place at high pressure, the methane needs more compression energy which ultimately reduces ammonia yield.

Shift Reaction

It is important to remove all CO from the process before it enters the ammonia converter, or catalyst poisoning will occur. This removal takes place by ‘shifting’ the CO to CO_2 after which the CO_2 is absorbed. This shift occurs in two steps during high and low temperature shifts. If the CO is not properly removed, it can shift back to methane, creating a highly exothermic reaction that can damage the next process stage, the methanator.

H/N Ratio

The methanator is designed to remove any residual CO and CO_2. The syn-gas output from the methanator should be ideally comprised of 75% H_2 and 25% N_2. In practice, there will also be some residual CH_4 and argon from the air. The production of ammonia takes place over an iron oxide catalyst in the converter. During this process, it is vital to maintain the ratio of H_2 and N_2 as close as possible to the stoichiometric ratio of 3-to-1.

Analyzer Requirements

While the ammonia process presents a series of challenges to a typical process mass spectrometer, the Prima PRO mass spectrometer has been designed to overcome these challenges and offers a unique set of capabilities.

Rapid Multi-Stream Sampling

To effectively monitor all process streams, the mass spectrometer requires a fast, reliable means of switching between streams. Other technologies use solenoid valve manifolds that have too much dead volume or rotary valves that suffer from poor reliability. Figure 2 is a schematic of the rapid multi-stream sampler (RMS) of the Prima PRO mass spectrometer.

which offers an unmatched combination of sampling speed and reliability and allows sample selection from one of 32 or one of 64 streams. Stream settling times are application-dependent and completely user-configurable. The RMS includes digital sample flow recording for every selected stream which can be used to trigger an alarm if the sample flow drops or if a filter in the sample conditioning system becomes blocked.

The RMS within the Prima PRO mass spectrometer can be heated to 120°C (248°F) and the stream selector position is optically encoded for reliable, software-controlled stream selection. Temperature and position control signals are communicated via the internal network. The RMS has a unique standard three year warranty. There are no other multi-stream sampling devices that offer the same level of guaranteed reliability.

Precision of Analysis

The mass spectrometer is required to monitor a wide range of component concentrations. To be used as part of a dynamic plant control strategy, the data must be reliable and available.

The heart of the Prima PRO mass spectrometer is a magnetic sector analyzer which offers unrivalled precision and accuracy compared with other mass spectrometers. Key advantages of magnetic sector analyzers include improved precision, accuracy, long intervals between calibrations, and resistance to contamination. Typically, analytical precision is between two and 10 times better than a quadrupole analyzer, depending on the gases analyzed and the complexity of the mixture. A unique feature of the Prima PRO mass spectrometer magnet is that it is laminated. It scans as fast as a quadrupole analyzer, offering the unique combination of rapid analysis and high stability. This capability allows for the rapid and extremely stable analysis of an unlimited number of user-defined gases. The scanning magnetic sector is controlled with 24-bit precision using a magnetic flux measuring device for extremely stable mass alignment.

The Prima PRO mass spectrometer features an enclosed ion source that provides high sensitivity, minimum background interference and maximum contamination resistance. The high-energy (1000 eV) analyzer offers extremely rugged performance in the presence of gases and vapors that have the potential for contaminating the analyzer.

A set of typical performance specifications for the Prima PRO mass spectrometer on ammonia process streams is shown in figure 3. It indicates an 8-hour analysis precision (single standard deviation) based on an analysis time of 15 seconds. Thermo Scientific™ GasWorks software permits analysis optimization on a per stream basis, enabling selection of the most appropriate ‘speed versus precision’ setting depending on process control requirements. Similarly, the most efficient peak measurements for each stream and the most appropriate display units (% or ppm) can also be selected.

	TYPICAL LEVEL %mol	PRECISION %mol
CH_4	80 - 95	0.02
C_2H_6	1 - 5	0.005
C_3H_8	1 - 3	0.005
$N\text{-}C_4H_{10}$	1 - 2	0.005
CO_2	1 - 3	0.003
N_2	2 - 5	0.01
Ar	0.5	0.001
H_2	0 - 1	0.002

Natural Gas Stream (Primary Reformer Feed)

	TYPICAL LEVEL %mol	PRECISION %mol
CH_4	0.5 - 2	0.002
CO	10 - 14	0.03
CO_2	8 - 10	0.01
N_2	23 - 24	0.02
Ar	0.1 - 0.5	0.001
H_2	55 - 65	0.03

Secondary Reformer Effluent

	TYPICAL LEVEL %mol	PRECISION %mol
CH_4	3 - 10	0.01
N_2	20 - 26	0.01
Ar	0.1 - 5	0.002
H_2	65 - 75	0.02
He	0.5 - 1	0.002

Synthesis Gas

	TYPICAL LEVEL %mol	PRECISION %mol
CH_4	5 - 10	0.01
N_2	15 - 22	0.01
Ar	1 - 5	0.002
H_2	55 - 60	0.02
NH_3	10 - 15	0.01

Convertor Outlet

Figure 3. Typical stream performance specifications for the Prima PRO Process Mass Spectrometer.

A guaranteed performance specification for the Prima PRO mass spectrometer is issued based on an individual customer’s specific stream details. This performance will be demonstrated during start-up by a trained Thermo Fisher Scientific service engineer.

Analysis of Low-Level Carbon Monoxide

The gas exiting the low temperature shift reactor contains minimal levels of carbon monoxide, typically between 0.1% and 0.5%. The analysis of trace levels of carbon monoxide in the presence of percentage levels of carbon dioxide and nitrogen presents a problem to all process mass spectrometers because these spectra overlap with one another. In all other process streams containing these three species, the CO levels are high enough to allow the use of fragment peaks. While it is possible in the low temperature shift, it is not measurable with the necessary precision. In this case, analysis of CO in the low temperature shift by NDIR is recommended. It is easy to integrate the NDIR CO analysis with the Prima PRO mass spectrometer data: a connector is fitted to the RMS to select the sample for the mass spectrometer to analyze and, at the same time, to divert the fast loop to the external NDIR analyzer. The Prima PRO mass spectrometer can also be used to provide a backup alarm for CO breakthrough.

Using Mass Spectrometry Data to Control the Process

The unique combination of magnetic sector stability, fast multi-stream switching and GasWorks quantitative software ensures the process data produced by the Prima PRO mass spectrometer is accurate and reliable. A range of industry standard communication protocols enable transfer of this data to process control systems to optimize the ammonia process.

Steam-to-Carbon Ratio

A detailed evaluation of the Prima PRO mass spectrometer was conducted by an accredited fuel gas calibration laboratory. The performance was benchmarked against a range of gas compositions in combination with an ISO 17025 accredited calibration cylinder. The Prima PRO mass spectrometer provided exceptional analytical performance, ensuring confidence in the data. In addition, GasWorks software easily calculates the steam-to-carbon ratio with just two analog inputs; one for the steam flow in weight per unit time and the other for natural gas flow in weight per unit time. Alternatively, the Prima PRO analyzer can simply transfer the composition data to the DCS using one of its industry standard communication protocols.

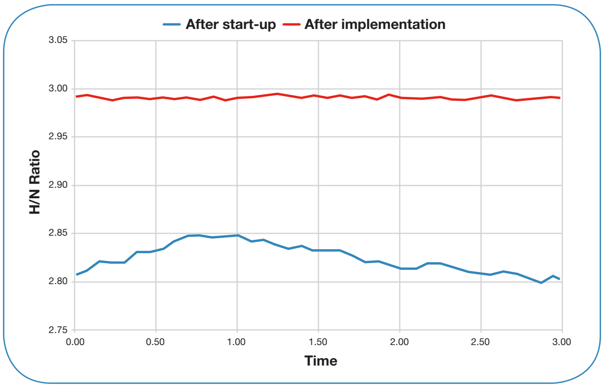

Figure 4. Improvements achieved in the H/N ratio using the Prima PRO Process Mass Spectrometer.

Improving H/N Ratio

The Prima PRO mass spectrometer measures the H/N ratio to a relative precision of 0.05% (i.e. precision of 0.0015 on a ratio of 3). In figure 4, the blue trend indicates the H/N ratio immediately after the mass spectrometer was installed while the red trend indicates the H/N ratio after implementing process control based on data provided by the mass spectrometer.

Figure 5.
Prima PRO Process Mass Spectrometer service kit.

Summary

The Prima PRO mass spectrometer offers the best available online measurement precision and stability for ammonia process monitoring and control. Its fault tolerant design combined with extended intervals between maintenance as well as simplified maintenance procedures ensure maximum availability of the analyzer. The plug-n-play standard service kit that is shipped with each analyzer is shown in figure 5. The reliability of the Prima PRO mass spectrometer is reflected in its industry-best three year parts and labor warranty.

Advantages of the Prima PRO Process Mass Spectrometer

- Optimizes processes, including:
  - Gas mixing and burner control in reformer
  - Steam/carbon ratio
  - Optimization of H/N ratio
  - 0.05% RSD
  - Methane slippage to ±20 ppm accuracy
- Facilitates monitoring of:
  - H_2S in natural gas
  - Inert gas build-up in synthesis loop
  - Catalyst activity to schedule plant outages

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