Ammonia Production Control

APPLICATION NOTE

Ammonia is one of the top 10 chemicals produced today. Most ammonia is produced by steam methane reforming of a natural gas feedstock. 85% of the ammonia produced is used for fertilizer in one form or another. Other industrial uses for ammonia include fibers, plastics, coatings and resins.

In looking to improve process efficiency and cut costs ammonia manufacturers have adopted a closed loop control strategy. The key to the success of this strategy is the Extrel® MAX300-RTG™ real-time gas analyzer. The MAX300-RTG is a rugged quadrupole mass spectrometer utilizing sophisticated electronics and offering fully automatic operation. The MAX300-RTG is a universal analyzer offering stable real time data acquisition and a dynamic range of 10 ppb to 100%. The exact concentrations of the stream components are immediately available for integration into the control scheme.

Due to its reliability, speed and accuracy the MAX300-RTG provides unsurpassed performance in ammonia production. The MAX300-RTG allows for tight control of four important process variables: the steam to carbon ratio, the H2:N2 ratio, methane slippage and process inert gases. Maintaining tight control of these variables results in three significant economic benefits to ammonia producers: lower fuel costs, higher yields and an overall optimized efficiency. Figure 1 is a simple diagram of the ammonia process indicating the typical streams analyzed by the MAX300-RTG.

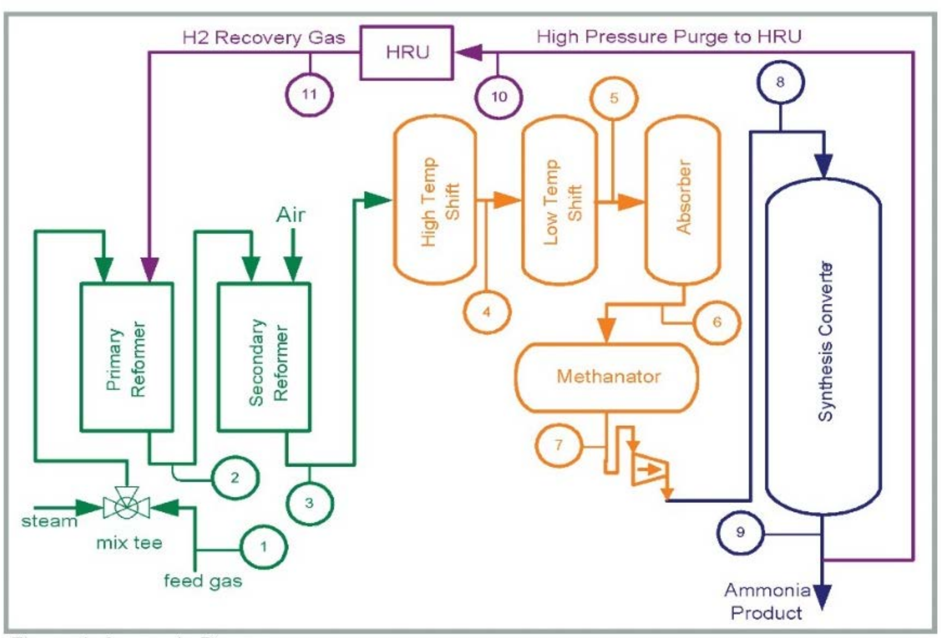


Figure 1: Ammonia Process

Feed Gas

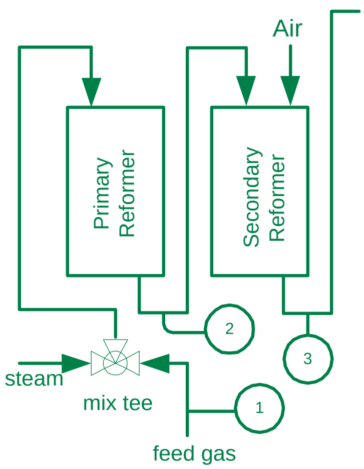
Control steam Generation Costs through Control of the Steam to Carbon Ratio to a tolerance of ± 0.02%.

In the Primary and Secondary Reformers, a hydrocarbon feed stream and steam are mixed and passed over a reformer containing a nickel-based catalyst at 1500°F. This results in the formation of carbon monoxide and hydrogen according to the following equation.

$$CH4 + H2O \longrightarrow CO + 3H2$$

The formation of carbon, known as coking, is detrimental to the catalyst. To prevent coking, an excess amount of steam is mixed with the feed gas. A minimum ratio of 3.0 lb. moles of steam to 1.0 lb. moles of carbon, i.e., 3:1 should be maintained. However, to avoid dropping below this ratio and degrading the catalyst, plants normally operate with generously elevated steam to carbon ratios.

The generation of steam is one of the most expensive processes in ammonia production. Typically, steam is produced at a level 4 times that of the ammonia product. Tight control of the steam to carbon ratio can significantly decrease production costs.



The MAX300-RTG performs rapid analysis of the feed stream for hydrocarbon concentration and calculates the BTU value. This information is used to control the steam flow; allowing rapid adjustments and avoiding potential converter problems. The MAX300-RTG typically analyzes hydrocarbons up to and including hexane in a Natural Gas Feed Stream. The instrument has the ability to analyze the butane and pentane isomers separately. This results in better accuracy for the calculated BTU value. Using the MAX300-RTG as part of a closed loop strategy, Steam to Carbon ratio tolerances of ± 0.02% have been demonstrated.

Using the dual detector option, the MAX300-RTG can also analyze the Feed Gas stream for the presence of sulfur containing components such as hydrogen sulfide and mercaptans. Sulfur components are poisons and will de-activate the catalyst.

Feed Gas

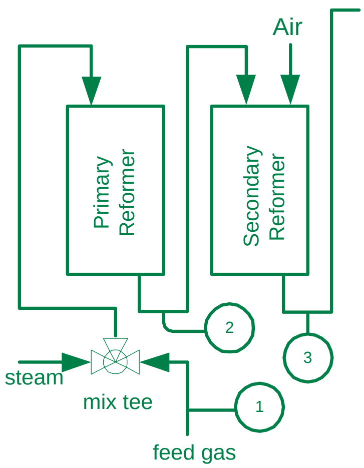
Component	% Conc.
Nitrogen	0.30
Carbon Dioxide	2.30
Methane	81.00
Ethane	9.60
Propane	4.10
n-Butane	1.10
i-Butane	0.40
n-Pentane	0.35
i-Pentane	0.15
Hexane	0.05
Hydrogen Sulfide	5 ppm

Primary Reformer Effluent and Secondary Reformer Effluent

Maximize Yield and Equipment Life through Unsurpassed Control of Methane Slippage

The amount of un-reacted methane in the Primary Reformer Effluent and Secondary Reformer Effluent is referred to as methane slippage. Methane slippage, also called leakage, is an indication of the reformer efficiency in the conversion of methane to hydrogen and carbon dioxide. The control objective is to maintain the methane slippage out of the secondary reformer at a very low and constant value, typically 0.3% methane or less.

The analysis of the Primary and Secondary Reformers requires both a highly sensitive and very stable sensor because of the complex chemical makeup. A wide dynamic range is also required as the methane conversion starts at 90% methane and ends at 0.3% methane. The sensitivity and the stability of the MAX300-RTG enables control tolerances of 0.05% to be achieved. These tight tolerances allow the operator to minimize the changes in methane slippage thereby maximizing yield and lengthening equipment life. Increases of up to 20% in run time, and equipment life have been observed in plants utilizing closed loop control with an Extrel CMS MAX300-RTG.



Air is the source of the nitrogen required for the ammonia reaction. Air is introduced into the process at the secondary reformer in an amount to yield an exit gas that has a 3:1 hydrogen to nitrogen ratio. The oxygen in the air reacts with the hydrocarbon feedstock in combustion and supplies the energy to reform the remainder of the gas. The secondary reformer reaction increases the hydrogen content and oxidizes most of the CO to CO2. CO2 is preferred over CO as it is much more soluble in water and can easily be removed further along in the process. The Secondary Reformer Outlet also contains a small amount of methane and argon which enter the synthesis loop as inert gases.

$$CH4 + H2O \longrightarrow CO + 3H2 + (CH4)$$

$$H2 + Air \longrightarrow 3H2 + N2 + (CO2 + CO)$$

Primary Reformer Effluent	
Component	% Conc.
Hydrogen	67.00
Nitrogen	1.50
Carbon Dioxide	11.50
Carbon Monoxide	8.00
Methane	12.00
Argon	0.10

Secondary Reformer Effluent	
Component	% Conc.
Hydrogen	57.50
Nitrogen	22.50
Carbon Dioxide	8.50
Carbon Monoxide	12.00
Methane	0.30
Argon	0.30

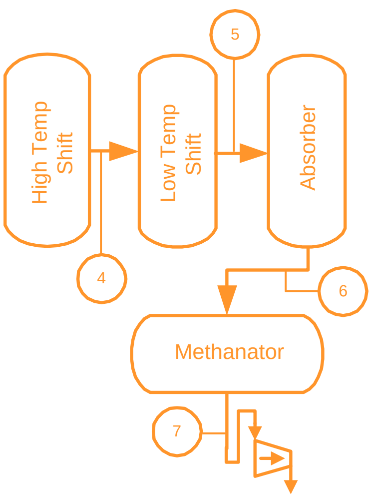
High Temperature Shift, Low Temperature Shift (CO Removal)

To maximize the amount of hydrogen produced, more steam is added to convert carbon monoxide to carbon dioxide and hydrogen. This reaction takes place in the shift converters at high temperatures over an iron-oxide based catalyst. The mass spectrometer normally measures both the High Temperature Shift and the Low Temperature Effluents.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

High Temperature Shift	
Component	% Conc.
Hydrogen	52.70
Nitrogen	27.27
Carbon Dioxide	14.53
Carbon Monoxide	3.60
Methane	1.55
Argon	0.35

Low Temperature Shift	
Component	% Conc.
Hydrogen	54.20
Nitrogen	26.40
Carbon Dioxide	17.19
Carbon Monoxide	0.40
Methane	1.50
Argon	0.35



CO2 Absorber and Methanator

The CO2 is generally removed by absorber-regenerator units containing many types of absorbent including monoethanolamine solution (MEA), sulfinol, propylene carbonate and others. After this process, CO in the product gas is reduced to less than 100 ppm.

CO2 and CO collectively known as carbon oxides, are poisons for many types of catalysts. The trace amounts of CO and CO2 remaining after the absorber must be removed from the synthesis gas. This is done by converting them to methane over a nickel or ruthenium catalyst in the presence of hydrogen in the Methanator. The amount of methane produced by this process is insignificant compared to the level of the un-reacted methane slip. After this process, the residual levels of the carbon oxides in the process gas will be less than 5 ppm.

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$
$$CO_2 + 4\,H_2 \longrightarrow CH_4 + 2H_2O$$

Absorber Outlet	
Component	% Conc.
Hydrogen	65.33
Nitrogen	31.80
Carbon Dioxide	0.08
Carbon Monoxide	0.48
Methane	1.81
Argon	0.41

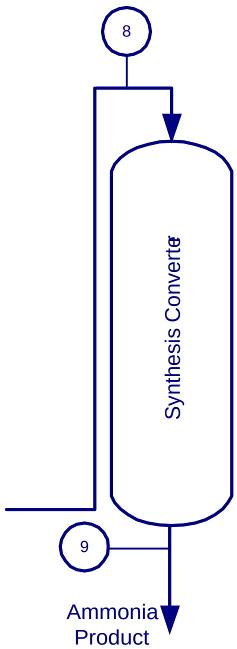
Methanator Outlet	
Component	% Conc.
Hydrogen	69.80
Nitrogen	28.00
Carbon Dioxide	< 5 ppm
Carbon Monoxide	< 5 ppm
Methane	1.70
Argon	0.30

Converter Inlet, Converter Outlet

Control the Feed to Air H2:N2 Ratio within ± 0.01%

Controlling the H2:N2 ratio at the Synthesis Converter Inlet is critical in the efficient production of ammonia. With the speed and stability of the MAX300-RTG and a closed loop strategy, the H2:N2 ratio at the Converter Inlet can be controlled within a tolerance of ± 0.01%. Using a gas chromatograph the tolerance is typically 0.10%.

It has been estimated that using the MAX300-RTG on the 4 critical streams for the H2:N2 ratio control and mass balance can produce an additional 10.3 tons of ammonia per day in a 1000 ton per day plant. This additional output is in comparison to the expected plant output when using a gas chromatograph with its typical 5-6 minute cycle time per stream.



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

Converter Inlet

Component	% Conc.
Hydrogen	65.00
Nitrogen	22.50
Argon	2.50
Helium	0.50
Methane	7.00
Ammonia	2.00

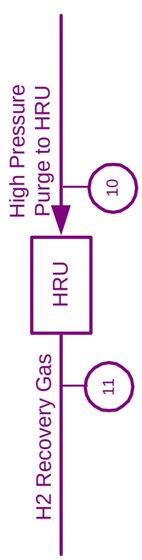
Converter Outlet

Component	% Conc.
Hydrogen	54.00
Nitrogen	19.50
Argon	3.50
Helium	0.50
Methane	7.50
Ammonia	15.00

High Pressure Purge and HRU

Maintain Constant Converter Feed Ratios through the Control of Process Inert Gases to ± 0.01%

The control of process inert gases such as argon, methane and helium is another important advantage provided by the MAX300-RTG mass spectrometer. The control of these inerts is important in maintaining constant converter feed ratios. Much of the converter feed make up is a result of recycled converter gases after ammonia production. Analyzing with the mass spectrometer, these inerts can be controlled within a tolerance of ± 0.01%. The streams typically analyzed to obtain this information are the Converter Inlet, Converter Recycle and High Pressure Purge Loop.



High Pressure Purge to HRU

Component	% Conc.
Hydrogen	62.00
Nitrogen	22.50
Argon	3.50
Helium	0.50
Methane	11.00
Ammonia	2.00

H2 Recovery Gas

Component	% Conc.
Hydrogen	50.00
Nitrogen	10.00
Argon	1.75
Helium	0.60
Methane	37.50

Conclusion

Ammonia manufacturers, in an attempt to improve process efficiency and reduce costs, have adopted closed loop control strategies. In the past few years, efficient process control has become even more important as the cost of raw materials have increased and the product price has decreased. Ammonia producers must take advantage of every available opportunity to improve their process. The key to a successful closed loop control strategy is the analyzers used to supply the Distributed Control System (DCS) with information. The analyzers must be fast, reliable, accurate, precise and rugged. Among ammonia producers, the Extrel CMS Process Mass Spectrometer has developed a reputation as the “must have” analyzer for the closed loop control of the ammonia process.

The Extrel CMS MAX300-RTG Process Mass Spectrometer has a proven record of performance and reliability. The mass spectrometer’s real time data acquisition, allows for 12 sample points to be reported in less than two minutes. In particular, the mass spectrometer provides information which allows tight control of four critical process variables:

1. The steam to carbon ratio can be controlled to a tolerance of ± 0.02% by an accurate and fast analysis of the feed gas stream. This significantly reduces steam generation costs.

2. Controlling the methane slippage at the reformer outlet leads to a maximum product yield and extends equipment life.

3. Production efficiency is increased by controlling the feed to air (H2:N2) ratio at the Synthesis Converter Inlet to within ± 0.01%.

4. Efficiency can also be improved by maintaining constant converter feed ratios through control of the process inert gases within 0.01%.

MAX300-RTG Real-time Gas Analyzer