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INTRODUCTION

Scope

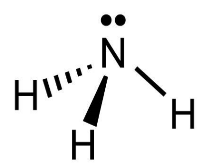
Ammonia is produced basically from water, air, and energy. The energy source is usually hydrocarbons, thus providing hydrogen as well, but may also be coal or electricity. Steam reforming of light hydrocarbons is the most efficient route, with about 77% of world ammonia capacity being based on natural gas.

The total energy consumption for the production of ammonia in a modern steam reforming plant is 40-50% above the thermodynamic minimum. More than half of the excess consumption is due to compression losses. The practical minimum consumption is assumed to be 130% of the theoretical minimum.

This guideline covers items in making an ammonia plant. Starting from the raw material, equipment, manufacturing process and the economics of ammonia plant.

General Design Consideration

Ammonia is an intermediate product in the manufacture of nitrogenous fertilizers. It is also used for direct application to the soil and in aqua condition with solutions of other nitrogenous fertilizers like ammonium nitrate and/or urea. Besides these, ammonia finds applications in the production of nitric acid, soda ash, cleaning agents, leather tanning, petroleum refining, pulp & paper industry, textiles, refrigeration, rubber & synthetic resin industries, explosives and food & beverages.



The history of ammonia cannot be detached from the large subject of nitrogen supply to the fertilizer and chemical industry. In the early days of chemical industry dependence was placed on natural and waste products of various kinds. Ammonia is the most stable form of “fixed nitrogen” which is used as an essential part of almost all types of fertilizers.

Before 1800, the principle sources of nitrogen were by product, organic material of various types which include manure, seed, meals, fish scraps, leather scraps and slaughter wastage. First of all‘Priestly’ produced ammonia in 1754 by heating “sub-ammonia (ammonium chloride) with lime. The new compound was named for Egyptian god arm mow, because ammonium chloride was first made fourth century (B.C) from camel dung near the temple of arm mow.

In 1875, Hildebraud tried to synthesize ammonia from nitrogen and hydrogen at atmospheric pressure. Dobernier realized that a catalyst would be needed for practical method. Between 1850 &1900, the general development of physical chemistry, the new concept of mass action chemical equilibrium did much to pave the way for ammonia synthesis.

First full plant scale was placed on stream in Badishe Aniline – und soda Fabric A.G. (BASF) by Fritz Haber and Carl Bosch at Oppau. Germany. The process became commercial Haber-Bosch process. Although several processes have developed since 1913. The main differences were the methods for the preparation of synthesis gas, the purification of synthesis gas, the design of ammonia convertor and method of receiving ammonia from converted flue gas.

Prior to 1945, coat and coke oven gas was the major raw material used for the production of hydrogen required for ammonia synthesis. During the past 35 years, there has been a trend towards the use of petroleum products. Most of the plants built during the past 25 years, throughout the world designed for the use of a natural gas, heavy oil as feed material. During last 15 years, Naphtha has become the most popular feed material in the areas where natural gas is not present. At present almost all of the ammonia plants in USA are based on natural gas.

Chemically combined nitrogen is essential for the growth of all living organisms. Neither animals nor (with one or two exceptions) plants can assimilate free nitrogen from the air; they depend upon nitrates, ammonium salts or other compounds found in the soil. The natural supplies of fixed nitrogen were adequate for many centuries to satisfy the normal processes of nature. However, by the beginning of the nineteenth century, the increase in world population and the growth of big cities created a demand from the more industrialized countries for other supplemental sources of fixed nitrogen. This supplement was first found in imported guano and sodium nitrate and later in ammoniacal solutions and ammonium sulphate by product from the carbonization of coal in gas works and coke ovens.

By the start of this century, with the demand for fertilizer nitrogen again having outstripped supply, necessity had once again become the mother of invention and three different processes for the fixation of nitrogen were in commercial operation and adequate supplies of fertilizer nitrogen were assured. One of those three was the direct synthesis of ammonia from nitrogen and hydrogen by the Haber-Bosch process. This was developed in Germany between 1905 and 1913 and virtually all fixed nitrogen is now produced by this process. The total world production in 1990 was over 100 million tons of fixed nitrogen and is increasing at the rate of over 4% per annum. More than 90% of this is produced as ammonia and about 80% of the total fixed nitrogen production is used in fertilizers.

The ammonia plant is quite complicates petrochemical gas plant that foresee seven different chemical working on range of operative condition that spans from cryogenic -33^{o}C / -27^{o}F) up to elevated temperature (1000^{o}C / 1832^{O}F) as well as from low pressure (1 bar / 15 psi) to high pressure (150 bar / 2175 psig). The know how to manage all the wide range of operative condition and fluids to be handled is of the most importance.

Raw Material Used

Ammonia is produced by the reaction between nitrogen **(N_2)** and hydrogen **(H_2)**

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

Source of Nitrogen is atmospheric air and following hydrocarbons are generally used as the source of hydrogen.

- Natural gas
- Naphtha
- Heavy Oil

Other sources of hydrogen which were used earlier for manufacture of Ammonia are:
1) Semi-water gas made by gasification of coke/ coal with steam.
2) Hydrogen produced by electrolysis of water.
3) By product Hydrogen from chlorine production.

Anhydrous Ammonia Properties

Table 1. Physical Properties of Ammonia

Property	Value or Detail
Molecular Mass	17.03 g/mol
Colour	Colourless
Odour	Sharp, irritating
Physical State	Gas (at room temperature)
Melting Point	-77.7^{o}C
Boiling Point	-33.35^{o}C
Flash Point	11^{o}C
Decomposition Point	500^{o}C
Density (gas)	0.7710 g/L
Density (liquid)	0.6818 g/L
Vapour Density	0.5697
Critical Temperature	132.4^{o}C
Critical Pressure	111.3 atm
Heat of Fusion	58.1 kJ/mol
Heat of Vaporization	23.3 kJ/mol
Heat of Combustion	-316 kJ/mol

Chemical Properties

Table 2. Chemical Properties of Ammonia

Property	Value or Details
Chemical Formula	NH_3
Type of Base	Weak
Affinity (water)	High
Corrosiveness	Corrosive to Some Metals
Oxidation Power	Strong Reducing Agent
Reactivity	Quite Reactive
Volatility	Increase with increase in pH

Expansion in the Industry

Major expansion of the ammonia industry began in 1963. The demand for nitrogen based fertilizer throughout the world and the prospects for increased consumption in future years stimulate fertilizer producers to build many new ammonia plants. During the last few years, a trend has developed towards building large scale train plants with capacities of 600 to 1500 tons per day. During the last quarter century many improvements have been made in plant equipment, catalysts and instrumentation. These developments have contributed to substantiate reduction in the capital cost and operation costs of ammonia plants.

In 1960, the world production of ammonia was about 13 million ton. The use of ammonia can be apprehended by the fact that in 1967, 12 million of ammonia was manufactured in United States of America raised to 18 million tons the very next year.

Since 1954 the following sweeping changing in the technology of ammonia manufacture has taken place.

1. Feed ranging from natural gas to naphtha have been processed by steam hydrocarbon reforming at pressure up to 500lb/in^2 gauge.
2. Electric power consumption has been reduced to practically zero due primarily to the use of a highly efficient energy cycle which incorporates high pressure steam generation in conjunction with the maximum use of turbine drives to pumps and centrifugal compressors.
3. Enormous improvements in the gas purification processes .several low utility process are available for CO_2 removal including promoted MEA, promoted hot potassium carbonate process, sulfinol, the two stage Tri ethanol amine /Mon ethanolamine system and others. Moreover, removal of residual CO has been enormously simplified by the use of the methanation system. Space requirements for the purification system have been minimized.
4. Improved heat recovery, particularly in the reformer effluent system and the various catalyst reaction services.
5. Efficient use for steam
6. Use of higher activity catalyst for all the process services. The introduction of low temperature shift conversion catalyst has simplified the design of the raw

gas generation system and permitted substantial reduction in the quantity of feed processed in the reformer because of the associated reduction in purge in the synthesis loop.

7. Plant capacities have been increased from 600 to 1700 tons/day as 100% single train operations throughout the unit including the ammonia convertor. In addition, there have been significant improvements in the fabrication of ammonia convertors. Full closure convertors can be offered in a wide range of capacities and operating pressures. Moreover, the internal layout of ammonia convertors have been modified in the direction of low pressure drop which still retaining efficient distribution of gas through the catalyst beds. The number of catalyst beds for the quench –type convertor has been optimized. Also, more use has been made of reduced size synthesis catalyst which has reduced both the volume of catalyst and the convertor size by 10-25% depending on the size of catalyst used and the available pressure drop of the loop.
8. Improvement in compressor design for all process service. Centrifugal compressors can be provided for the synthesis gas service for pressure up to 4700lb/in(g) for size in excess of 1700 tons /day operating over a wide range of speeds and horsepower.
9. Development of improved method for feed desulfurization including hydro desulphurization of naphtha feeds. Improvements in both cobalt molybdenum catalyst and zinc oxide sulfur absorbent catalyst have enabled all feeds to be desulfurized to levels of less than 0.25 ppm sulfur, thus ensuring protection of reforming catalyst against sulfur poisons with a resultant long catalyst life.

MINOR AND EMERGING USES

i. Fertilizer

Approximately 83% (as of 2004) of ammonia is used as fertilizers either as its salts or as solutions. Consuming more than 1% of all man-made power, the production of ammonia is a significant component of the world energy budget.

ii. Precursor to nitrogenous compounds

Ammonia is directly or indirectly the precursor to most nitrogen-containing compounds. Virtually all synthetic nitrogen compounds are derived from ammonia. An important derivative is nitric acid. This key material is generated via the Ostwald process by oxidation of ammonia with air over a platinum catalyst at 700–850 °C, ~9 atm. Nitric oxide is an intermediate in this conversion:

$$NH_3 + 2\ O_2 \rightarrow HNO_3 + H_2O$$

Nitric acid is used for the production of fertilizers, explosives, and many organic nitrogen compounds.

iii. Cleaner

Household ammonia is a solution of NH_3 in water (i.e., ammonium hydroxide) used as a general purpose cleaner for many surfaces. Because ammonia results in a relatively streak-free shine, one of its most common uses is to clean glass, porcelain and stainless steel. It is also frequently used for cleaning ovens and soaking items to loosen baked-on grime. Household ammonia ranges in concentration from 5 to 10 weight percent ammonia.

iv. Refrigeration

Because of its favorable vaporization properties, ammonia is an attractive refrigerant. It was commonly used prior to the popularization of chlorofluorocarbons (Freon's). Anhydrous ammonia is widely used in industrial refrigeration applications and hockey rinks because of its high energy and low cost. The Kalina cycle, which is of growing importance to geothermal power plants, depends on the wide boiling range of the ammonia-water mixture. Ammonia is used less frequently in commercial applications, such as in grocery store freezer cases and refrigerated displays due to its toxicity.

v. For remediation of gaseous emissions

Ammonia is used to scrub SO_2 from the burning of fossil fuels, and the resulting product is converted to ammonium sulfate for use as fertilizer. Ammonia neutralizes the nitrogen oxides (NO_x) pollutants emitted by diesel engines. This technology, called SCR (selective catalytic reduction), relies on a vanadium-based catalyst.

vi. As a fuel

Ammonia was used during World War II to power buses in Belgium, and in engine and solar energy applications prior to 1900. Liquid ammonia was used as the fuel of the rocket airplane, the X-15. Although not as powerful as other fuels, it left no soot in the reusable rocket engine and its density approximately matches the density of the oxidizer, liquid oxygen, which simplified the aircraft's design.

Ammonia has been proposed as a practical alternative to fossil fuel for internal combustion engines. The calorific value of ammonia is 22.5 MJ/kg (9690 BTU/lb) which is about half that of diesel. In a normal engine, in which the water vapor is not condensed, the calorific value of ammonia will be about 21% less than this figure. It can be used in existing engines with only minor modifications to carburetors/injectors.

To meet these demands, significant capital would be required to increase present production levels. Although the second most produced chemical, the scale of ammonia production is a small fraction of world petroleum usage. It could be manufactured from renewable energy sources, as well as coal or nuclear power. It is however significantly less efficient than batteries. The 60 MW Rjukan dam in Telemark, Norway produced ammonia via electrolysis of water for many years from 1913 producing fertilizer for much of Europe. If produced from coal, the CO_2 can be readily sequestrated (the combustion products are nitrogen and water). In 1981 a Canadian company converted a 1981 Chevrolet Impala to operate using ammonia as fuel.

Ammonia engines or ammonia motors, using ammonia as a working fluid, have been proposed and occasionally used. The principle is similar to that used in a fireless locomotive, but with ammonia as the working fluid, instead of steam or compressed air. Ammonia engines were used experimentally in the 19th century by Goldsworthy Gurney in the UK and in streetcars in New Orleans in the USA.

vii.Antimicrobial agent for food products

As early as in 1895 it was known that ammonia was "strongly antiseptic. It requires 1.4 grams per liter to preserve beef tea. Anhydrous ammonia has been shown effective as an antimicrobial agent for animal feed and is currently used commercially to reduce or eliminate microbial contamination of beef. The New York Times reported in October, 2009 on an American company, Beef Products Inc., which turns fatty beef trimmings, averaging between 50 and 70 percent fat, into seven million pounds per week of lean finely textured beef by removing the fat using heat and centrifugation, then disinfecting the lean product with ammonia.

The process was rated by the US Department of Agriculture as effective and safe on the basis of a study (financed by Beef Products) which found that the treatment reduces E. coli to undetectable levels. Further investigation by The New York Times published in December, 2009 revealed safety concerns about the process as well as consumer complaints about the taste and smell of beef treated at optimal levels of ammonia.

viii. As a stimulant in sports

Ammonia has found significant use in various sports – particularly the strength sports of power lifting and Olympic weightlifting as a respiratory stimulant (psychoactive drugs).

ix. Textile

Liquid ammonia is used for treatment of cotton materials, give properties like Mercerization (It is a treatment for cotton fabric and thread that gives fabric or yarns a lustrous appearance and strengthens them using alkalies). In particular, it is used for pre-washing of wool.

x. Lifting gas

At standard temperature and pressure ammonia is lighter than air, and has approximately 60% of the lifting power of hydrogen or helium. Ammonia has sometimes been used to fill weather balloons as a lifting gas. Because of its relatively high boiling point (compared to helium and hydrogen), ammonia could potentially be refrigerated and liquefied aboard an airship to reduce lift and add ballast (and returned to a gas to add lift and reduce ballast).

xi. Woodworking

Ammonia was historically used to darken quarter sawn white oak in Arts & Crafts and Mission style furniture. Ammonia fumes react with the natural tannins in the wood and cause it to change colours.

DEFINITION

Absorber - A tower or column in which contact is caused between rising gases and falling liquid so that part of the gas may be taken up by the liquid. For example, a Gas Plant has a tower that absorbs butane and propane from the gases charged to it.

Absorption – is a physical or chemical phenomenon or a process in which atoms, molecules or ions enter some bulk phase – liquid or solid material.

Accumulator - A vessel for the temporary storage of a liquid or gas, usually used for collecting sufficient material for a continuous charge or reflux.

Boiling Point – is the temperature at which the vapour pressure of a liquid equals the pressure surrounding the liquid and the liquid changes into a vapour.

Catalytic Reforming – is a chemical process used to convert petroleum refinery naphtha distilled from crude oil (typically having low octane ratings) into high octane liquid products called reformates, which are premium blending stocks for high octane gasoline.

Catalyst - A material which will increase or decrease the speed of a chemical reaction without changing its own chemical identity.

Combustion - Chemical combination of the combustible that part which will burn) in a fuel with oxygen in the air supplied for the process. Temperatures may range form 1850 to over 3000ºF.

Compressor – is a mechanical device that increase the pressure of a gas by reducing its volume.

Commissioning - Preparatory work, servicing etc. usually on newly-installed equipment, and all testing prior to full production testing

Condensing – is the change of the physical state of matter from gas phase into liquid phase, and is the reverse of evaporation.

Condensate - Volatile liquid consisting of the heavier hydrocarbon fractions that condense out of the gas as it leaves the well, a mixture of pentanes and higher hydrocarbons. See also gas condensate.

Corrosion - The wasting away of metals as a result of chemical action. In a boiler, usually cause by the presence of O2, CO2, or an acid

Cryogenics - In oil industry terms this refers to very low temperature handling processing or storage of hydrocarbon substances. See also Cavern storage.

Damper - A device for regulating the flow of flue gases in a chimney, thus controlling the amount of excess air to the furnace.

Downcomer - The conduit or overflow pipe in a distillation tower through which the liquid from one tray enters and is distributed to the tray below

Density – is the relationship between the mass of the substance and how much space it takes up (volume).

Desulfurization – is a chemical process for the removal of sulphur from a material.

Distillation - The process of heating and "flashing" or boiling off successive fractions (component hydrocarbon substances) from a crude oil feedstock, or a product of earlier distillation.

Downstream - "Downstream" is a relative term (the opposite of "Upstream") in oil industry operations. For instance, a refinery is "downstream" of a crude oil production unit, and a petrochemical unit, and a petrochemical plant usually downstream of a refinery. The term has also come to mean all operations occurring after the delivery or lifting of saleable quality crude or gas from the production unit or associated delivery terminal

Excess Air Air supplied for combustion in excess of that theoretically required for complete oxidation.

Flue Gas The gaseous products of combustion in the flue to the stack. Gases from the combustion of fuel. Their heating potential having been substantially spent, they are discarded to the flue or stack. They consist primarily of CO2-COO2-N2 and water vapor.

Heat Exchanger - A process vessel which typically uses the passage of one fluid through a set of internal tubes to heat up or cool down another fluid in which they are immersed. There are many different designs and uses

Hydrocarbons - Organic compounds of hydrogen and carbon, whose densities, boiling points and freezing points increase as their molecular weights increase. Although composed of only two elements, hydrocarbons exist in a variety of compounds because of the strong affinity of carbon atoms for other atoms and for itself. The smallest molecules of hydrocarbons are gaseous; the largest are solids. Petroleum is a mixture of many different hydrocarbons.

Inert Gas – Un reactive; will not support combustion. In refinery use is generally nitrogen or CO2 (carbon dioxide) (flue gas).

Methanation – is the reaction by which carbon oxides and hydrogen are converted to methane and water.

Naphtha - A collective name given to a range if distillate fractions covering heavy gasolines and some of the lighter kerosene distillates.

Natural Gas/NGL's - Natural Gas is primarily Methane and also some Ethane with small quantities of entrained heavier fractions, such as Propane, Butane, etc. These, and others, are readily condensed from the Natural Gas flow and are known as Natural Gas Liquids, or NGL's, as distinct from Liquid Natural Gas (L.N.G.) which is Methane/Ethane refrigerated to the liquid state. NGL may be produced from condensate reservoirs.

Purification – is the removal of impure elements from something.

Purge - To maintain gas flow in an over-rich or lean concentration in order to avoid the build-up of oxygen and an explosive mixture

Preheat - Heat added to a fluid prior to an operation performed on that fluid.

Pressure Drop - The decrease in pressure, due to friction, which occurs when a liquid or gas passes through a pipe, vessel, or other piece of equipment.

Pump - A machine for moving a liquid by taking energy from some other source and transferring it to the liquid.

Reactor - The vessel in which all or at least the major part of a reaction or conversion takes place. On most units this will be the vessel in which the catalyst is located.

Reboiler - A part of a fractionation tower designed to supply all or a portion of the heat to the tower. Liquid is withdrawn from the bottom of the tower and heated in the reboiler. The vapors formed are returned to the tower. The remaining liquid may or may not be returned to

Specific Gravity – is the ratio of the density of a substance to the mass of a reference substance for the same given volume.

Velocity – is the rate of change of the displacement, the difference between the final and initial position of an object. Velocity is an important concept in kinematics, the branch of classical mechanics which describes the motion of bodies.

NOMENCLATURE

$\Delta H°$	Entalphy
PSA	Pressure Swing Adsorption
PEM	Proton Exchange Membrane
ASU	Air Separation Unit
FBM	The Bare Module cost Factor
CBM	which includes bot direct and indirect costs for the equipment
$F_{p.vessel}$	used to determine the costs of ammonia synthesis reactor and the flash drum
FM	Also used to cost equipment
COM	The Cost of Manufacturing
DMC	The Sum of The Direct Costs
FMC	The Fixed Costs
GE	The General Expensive
N_{OL}	Number of Operation per Shift
P	The Number of Processing Steps that Include Solids Handling
N_{np}	The number of nonparticulate processing steps, including compressors, towers, heat exchangers, reactors and heaters
Y	The operating labor in units of hours/ton per processing step
X	The plant capacity per day
B	A constant related to the process type

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