1. BRIEF HISTORY OF AMMONIA [1]

Nitrogen is an essential element for life on Earth and a crucial nutrient to sustain plant life; it is present in the atmosphere in the form of the diatomic molecule N\textsubscript{2} (N≡N). The triple bond is remarkably strong and its dissociation requires a large amount of energy (945 kcal/mol). Thus, even though it is abundantly available in the air at about 78% by volume, it is hard to use. Humans learned how to convert nitrogen into ammonia synthetically over 100 years ago in a process discovered by Fritz Haber. The technology was purchased by BASF and the German chemist Carl Bosch scaled it up to industrial level. Both scientists were awarded the Nobel Prize for their critical research and the synthesis of ammonia is now known as the Haber-Bosch process, which takes place from the reaction between nitrogen and hydrogen:

\[ \text{N}_2 (g) + 3\text{H}_2 (g) \leftrightarrow 2\text{NH}_3 (g) \]  

(1)

The conversion typically occurs at temperatures between 300-550 °C, and under extremely high pressure between 150-300 bar. Thermodynamically, the formation of ammonia is favored at low temperatures and high pressure. However, because the reaction rate is very low, both high temperature and pressure are used in the presence of an iron-based catalyst to lower the activation energy of the reaction, which is, in the case of ammonia, the energy required to dissociate molecular nitrogen. Above 750 bar, the conversion to ammonia can reach 100%. However, the amount of energy required to maintain this exceedingly high pressure is not practical and presents unreasonable safety concerns. Because of this, 150-300 bar is typically used. For example, at a temperature of 475 °C and 200 bar, the yield of ammonia generally ranges from 10-20%, which is low, but the costs of running the plants are also contained.

2. GLOBAL AMMONIA MARKET [1]

On a global scale, approximately 82% of ammonia is used for the production of fertilizers and nearly half of this is used for the synthesis of Urea (Figure 1). Ammonium nitrate, di-ammonium phosphate (DAP) and mono-ammonium phosphate (MAP) are other common fertilizers that are manufactured from ammonia. Only 18% of ammonia is employed for uses other than agriculture. This fraction is used as the precursor for the synthesis of important nitrogen-containing compounds like acrylonitrile, amino acids, hydrogen cyanide, hydrazine, hydroxylamine and many more. In the United States, because agriculture practices are highly developed, over 40% of ammonia is used directly for agricultural applications.
Figure 1: Ammonia is predominantly used for fertilizer production (82% in 2013).

The global market of ammonia is highly fragmented (Figure 2). In 2013, China was the world’s largest producer of ammonia with a market share of more than 30%, producing nearly 70 million metric tons per year. India followed with 7.1% market share, Russia with 6.1% and the United States with 6.0%. The I.R. Iran with seven active plants, produced about 3.0 million metric tons per year of ammonia with a market share of more than 1.5%\textsuperscript{1}.

Figure 2: Ammonia production capacity by region- 2013 market share.

\textsuperscript{1}Iran’s Petrochemical Industry Report, 2014
Historically, the production of ammonia has steadily increased over the past 100 years at a 2% growth rate. However, due to a strong increase in fertilizer demand, the ammonia market is expected to grow at an unprecedented 3.1% compound annual growth rate (CAGR) in the next five years and reach global revenues of over $100 billion in 2019.

3. AMMONIA PRODUCTION PROCESSES [2]

The typical size of a large single-train ammonia plant is 1,000-1,500 ton/day, although capacities of 1,800 ton/day and above are not uncommon for new plants.

Natural gas is the typical feedstock used for ammonia production in all countries, except for India and China. Steam reforming of natural gas is the most efficient route, with about 77% of world ammonia capacity being based on steam reforming of natural gas.

The ammonia synthesis process is principally independent of the type of synthesis gas production process, but synthesis gas quality influences the loop design and operating conditions. A block diagram of the conventional ammonia plant based on steam reforming process is shown in Figure 3.

![Block diagram of ammonia production based on the steam reforming process.](image)
The primary and secondary reformers in ammonia plants are almost the same as methanol plants. The main difference is that, the air is used instead of oxygen in the secondary reformer (ATR). In addition no CO$_2$ sources is used as reformer feed, because the objective of reformer units is to maximize the H$_2$ and minimize the CO and CO$_2$ production.

Water, carbon monoxide and carbon dioxide, all of which poison the iron catalyst used in the ammonia synthesis, must be removed from the synthesis gas.

**Carbon monoxide removal (water-shift conversion)**

The process gas from the secondary reformer contains 12-15% CO (dry gas base) and most of the CO is converted in the shift section according to the reaction:

$$\text{CO + H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H_R = -41 \text{ kJ/mol} \quad (2)$$

In the High Temperature Shift (HTS) conversion, the gas is passed through a bed of iron oxide/chromium oxide catalyst at around 400°C, where the CO content is reduced to about 3% (dry gas base), limited by the shift equilibrium at the actual operating temperature. There is a tendency to use copper containing catalyst for increased conversion.

The gas from the HTS is cooled and passed through the Low Temperature Shift (LTS) converter. This LTS converter is filled with a copper oxide/zinc oxide-based catalyst and operates at about 200-220°C. The residual CO content in the converted gas is about 0.2-0.4% (dry gas base). A low residual CO content is important for the efficiency of the process.

**Water removal**

The gas mixture is further cooled to about 40°C, at which temperature the water condenses and is removed.

**Carbon dioxide removal**

The CO$_2$ is removed in a chemical or a physical absorption process. The solvents used in chemical absorption processes are mainly aqueous amine solutions; Mono Ethanolamine (MEA), Activated Methyl Di-Ethanolamine (aMDEA) or hot potassium carbonate solutions. Physical solvents are glycol di-methylethers (Selexol), propylene carbonate and others. The MEA process has a high regeneration energy consumption and is not regarded as a good process.

For new ammonia plants the following CO$_2$ removal processes are currently recommended:

- aMDEA 2-stage process, or similar
- Benfield process (HiPure, LoHeat), or similar
- Selexol or similar physical absorption processes

Residual CO$_2$ contents are usually in the range of 100-1,000 ppmv, dependent on the type and design of the removal unit. Contents down to about 50 ppmv are achievable.
Methanation

The small amounts of CO and CO\(_2\), remaining in the synthesis gas, are poisonous for the ammonia synthesis catalyst and must be removed by conversion to CH\(_4\) in the methanator:

\[
\begin{align*}
\text{CO} + 3\text{H}_2 & \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (3) \\
\text{CO}_2 + 4\text{H}_2 & \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad (4)
\end{align*}
\]

The reactions take place at around 300°C in a reactor filled with a nickel containing catalyst. Methane is an inert gas in the synthesis reaction of ammonia.

Synthesis gas compression and ammonia synthesis

Modern ammonia plants use centrifugal compressors for synthesis gas compression, usually driven by steam turbines, with the steam being produced in the ammonia plant. The refrigeration compressor, needed for condensation of product ammonia, is also usually driven by a steam turbine.

The synthesis of ammonia takes place on an iron catalyst at pressures usually in the range of 100-250 bar and temperatures in the range of 350-550°C:

\[
\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3 \quad \Delta H_R = -46 \text{ kJ/mol} \quad (5)
\]

Only 20-30% is reacted per pass in the converter due to the unfavorable equilibrium conditions.

The ammonia that is formed is separated from the recycle gas by cooling/condensation, and the reacted gas is substituted by the fresh make-up synthesis gas, thus maintaining the loop pressure. In addition, extensive heat exchange is required due to the exothermic reaction and the large temperature range in the loop. A newly developed ammonia synthesis catalyst containing ruthenium on a graphite support has a much higher activity per unit of volume and has the potential to increase conversion and lower operating pressures.

Synthesis loop arrangements differ with respect to the points in the loop at which the make-up gas is delivered and the ammonia and purge gas are taken out. The best arrangement is to add the make-up gas after ammonia condensation and ahead of the converter. The loop purge should be taken out after ammonia separation and before make-up gas addition. This configuration is dependent on the make-up gas being treated in a drying step before entering the loop. A make-up gas containing traces of water or carbon dioxide must be added before ammonia condensation, with negative effects both to ammonia condensation and energy.

Conventional reforming with methanation as the final purification step, produces a synthesis gas containing inerts (methane and argon) in quantities that do not dissolve in the condensed ammonia. The major part of these inerts is removed by taking out a purge stream from the loop. The size of this purge stream controls the level of inerts in the loop to about 10-15%. The purge gas is scrubbed with water to remove ammonia before being used as fuel or before being sent for hydrogen recovery.
Ammonia condensation is far from complete if cooling is with water or air and is usually not satisfactory (dependent on loop pressure and cooling medium temperature). Vaporizing ammonia is used as a refrigerant in most ammonia plants, to achieve sufficiently low ammonia concentrations in the gas recycled to the converter. The ammonia vapors are liquefied after recompression in the refrigeration compressor.

**Steam and power system**

Steam reforming ammonia plants have high-level surplus heat available for steam production in the reforming, shift conversion, and synthesis sections, and in the convection section of the primary reformer. Most of this waste heat is used for high pressure steam production for use in turbines for driving the main compressors and pumps and as process steam extracted from the turbine system.

A modern steam reforming ammonia plant can be made energetically self-sufficient if necessary, but usually a small steam export and electricity import are preferred.

4. **UREA PRODUCTION PROCESSES [3]**

The commercial synthesis of urea (CON₂H₄) involves the combination of ammonia and carbon dioxide at high pressure to form ammonium carbamate (CO₂N₂H₆) which is subsequently dehydrated by the application of heat to form urea and water.

\[
2\text{NH}_3 + \text{CO}_2 \leftrightarrow \text{NH}_2\text{COONH}_4 \quad (6)
\]

\[
\text{NH}_2\text{COONH}_4 \leftrightarrow \text{CO(NH}_2)_2 + \text{H}_2\text{O} \quad (7)
\]

Reaction (6) is fast and exothermic and essentially goes to completion under the reaction conditions used industrially. Reaction (7) is slower and endothermic and does not go to completion. The conversion (on a CO₂ basis) is usually in the order of 50-80%. The conversion increases with increasing temperature and NH₃/CO₂ ratio and decreases with increasing H₂O/CO₂ ratio.

The design of commercial processes has involved the consideration of how to separate the urea from the other constituents, how to recover excess NH₃ and decompose the carbamate for recycle. Attention was also devoted to developing materials to withstand the corrosive carbamate solution and to optimize the heat and energy balances.

The simplest way to decompose the carbamate to CO₂ and NH₃ requires the reactor effluent to be depressurized and heated. The earliest urea plants operated on a “Once Through” principle where the off-gases were used as feedstocks for other products. Subsequently “Partial Recycle” techniques were developed to recover and recycle some of the NH₃ and CO₂ to the process. It was essential to recover all of the gases for recycle to the synthesis to optimize raw material utilization and since recompression was too expensive an alternative method was developed. This involved cooling the gases and re-combining them to form carbamate liquor which was pumped back to the synthesis. A series of loops involving carbamate decomposers at progressively lower pressures and carbamate condensers were used. This was known as the “Total Recycle Process”. A basic consequence of recycling the
gases was that the NH$_3$/CO$_2$ molar ratio in the reactor increased thereby increasing the urea yield.

Significant improvements were subsequently achieved by decomposing the carbamate in the reactor effluent without reducing the system pressure. This “Stripping Process” dominated synthesis technology and provided capital/energy savings. Two commercial stripping systems were developed, one using CO$_2$ and the other using NH$_3$ as the stripping gases.

Since the base patents on stripping technology have expired, other processes have emerged which combine the best features of Total Recycle and Stripping Technologies. For convenience total recycle processes were identified as either “conventional” or “stripping” processes. Block flow diagram for CO$_2$ stripping total recycle processes is shown in Figure 4.

**Figure 4: Block diagram of a Total Recycle CO2 Stripping Urea Process.**
The urea solution arising from the synthesis/recycle stages of the process is subsequently concentrated to a urea melt for conversion to a solid prilled or granular product.

Improvements in process technology have concentrated on reducing production costs and minimizing the environmental impact. These included boosting CO$_2$ conversion efficiency, increasing heat recovery, reducing utilities consumption and recovering residual NH$_3$ and urea from plant effluents. Simultaneously the size limitation of prills and concern about the prill tower off-gas effluent were responsible for increased interest in melt granulation processes. Some or all of these improvements have been used in updating existing plants and some plants have added computerized systems for process control. New urea installations vary in size from 800 to 2,000 mtd and typically would be 1,500 mtd units.

**Carbon dioxide stripping process**

NH$_3$ and CO$_2$ are converted to urea via ammonium carbamate at a pressure of approximately 140 bar and a temperature of 180-185°C. The molar NH$_3$/CO$_2$ ratio applied in the reactor is 2.95. This results in a CO$_2$ conversion of about 60% and an NH$_3$ conversion of 41%. The reactor effluent, containing unconverted NH$_3$ and CO$_2$ is subjected to a stripping operation at essentially reactor pressure, using CO$_2$ as stripping agent. The stripped-off NH$_3$ and CO$_2$ are then partially condensed and recycled to the reactor. The heat evolving from this condensation is used to produce 4.5 bar steam some of which can be used for heating purposes in the downstream sections of the plant. Surplus 4.5 bar steam is sent to the turbine of the CO$_2$ compressor.

The NH$_3$ and CO$_2$ in the stripper effluent are vaporized in a 4 bar decomposition stage and subsequently condensed to form a carbamate solution, which is recycled to the 140 bar synthesis section. Further concentration of the urea solution leaving the 4 bar decomposition stage takes place in the evaporation section, where a 99.7% urea melt is produced.

**Prilling and Granulation**

In urea fertilizer production operations, the final product is in either prilled or granular form. Production of either form from urea melt requires the use of a large volume of cooling air which is subsequently discharged to the atmosphere. A block diagram of the prilling and granulation processes is shown in Figure 5.
Figure 5: Block Diagram for Urea Granulation and Prilling Processes.

**Prilling**

The concentrated (99.7%) urea melt is fed to the prilling device (e.g. rotating bucket/shower type spray head) located at the top of the prilling tower. Liquid droplets are formed which solidify and cool on free fall through the tower against a forced or natural up-draft of ambient air. The product is removed from the tower base to a conveyor belt using a rotating rake, a fluidized bed or a conical hopper. Cooling to ambient temperature and screening may be used before the product is finally transferred to storage.

The design/operation of the prilling device exerts a major influence on product size. Collision of the molten droplets with the tower wall as well as inter-droplet contact causing agglomeration must be prevented. Normally mean prill diameters range from 1.6-2.0 mm for prilling operations.

**Granulation**

Depending on the process a 95-99.7% urea feedstock is used. The lower feedstock concentration allows the second step of the evaporation process to be omitted and also simplifies the process condensate treatment step. The basic principle of the process involves the spraying of the melt onto recycled seed particles or prills circulating in the granulator. A slow increase in granule size and drying of the product takes place simultaneously. Air passing through the granulator solidifies the melt deposited on the seed material. Processes using low concentration feedstock require less cooling air since the evaporation of the
additional water dissipates part of the heat which is released when the urea crystallizes from liquid to solid.

All the commercial processes available are characterized by product recycle, and the ratio of recycled to final product varies between 0.5 and 2.5. Prill granulation or fattening systems have a very small recycle, typically 2 to 4%. Usually the product leaving the granulator is cooled and screened prior to transfer to storage. Conditioning of the urea melt prior to spraying may also be used to enhance the storage/handling characteristics of the granular product.

References

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3- European Fertilizer Manufactures’ Association, Booklet No. 5: Production of urea and urea ammonium nitrate, 2000.