

**Study of Production of Ammonia from Natural Gas and Air**Aishwarya Nalawade¹, Pallavi Thorat², Shailendra Chaudekar³, V. D. Chitodkar⁴^{1,2,3,4} Department of Chemical Engineering, Bharati Vidyapeeth College of Engineering, Navi Mumbai

Abstract — Ammonia is an important nitrogenous material used as fertilizer. Most of ammonia is made synthetically. It is also obtained as by-product in some cases. Ammonia gas is used directly as fertilizer in heat treatment, paper pulping, nitric acid and nitrate manufacturing, nitric acid esters and nitro compound manufacture, explosive of various types and as a refrigerant. The most important field is of fertilizer. Importance of ammonia in this field is due to the fact that it is by far the simplest form of actual nitrogen which can be administrated and the most economical source of other nitrogen chemicals. Hence ammonia is the backbone of Nitrogen fertilizer processes. Its production is the first consideration in the initiation of a fertilizer industry. Great strides have been made in the last few years in the economy and efficiency of ammonia processes. The process available for its manufacture is Haber, Kellogg, Corl Bosch, Claude, Casale, and Fauser, Mont Cenis. The main raw material for the ammonia production is natural gas obtained from petroleum industry. The synthesis of ammonia from Nitrogen and hydrogen was first chemical reaction to be carried out under high pressure on commercial scale. This synthesis reaction has probably been studied more extensively and is better understood than any other high pressure reactions. This will be the subject of study in the project along with the designing of the project and analytical evaluation.

Keywords- Kellogg process, ammonia, nitrogen fixation, catalyst.

I. INTRODUCTION

Ammonia (NH₃), a colourless alkaline gas is lighter than air and possesses a unique, penetrating odour. The preparation of ammonium salts dates back to early Egyptians in the fourth century. Ammonia gas was first produced as a pure compound by priestly in 1774. The value of Nitrogen compounds as an ingredient of mineral fertilizers was recognized in 1840. Nitrogen is an essential element to plant growth and ammonia is the primary nitrogen source used in fertilizers. Until the early 1900s, the nitrogen source in farm soils was entirely derived from natural sources: from mineral resources such as Chilean nitrates, from manure and the putrefaction of vegetable waste; and from ammonium sulphates from coal coking, seed meals, sewage sludge and food processing by products.

The synthesis of ammonia directly from hydrogen and nitrogen on a commercial scale was pioneered by Haber and Bosch in 1913, for which they were awarded Nobel prizes. Before start of the world war I, most ammonia was obtained by the dry distillation of nitrogenous vegetables and animal products by the reduction of nitrous acid and nitrites with hydrogen and also by the decomposition of ammonium salts by alkaline hydroxides or by quicklime, the salt most generated used being the chloride (ammonium chloride). The Romans gave the name Sal Ammoniacus [salt of Ammonia] or [salt of Amun] to the ammonium chloride deposits that they collected near the Temple of Amun in ancient Libia. In the form of Sal ammoniac ammonia was important to the Muslim chemists as early as 8th century, first mentioned by the Persian chemist Jabiribn Hayyan and to the European chemist since the 13th century being mentioned by Albertus Magnus. It was also used by dyers in the Middle Ages in the form of Fermented urine to alter the colour of vegetable dyes. In the 15th century, Basilius Valentinus showed that ammonia could be obtained by the action of alkalis on Sal ammoniac. At a later period, when Sal ammoniac was obtained by distilling the hooves and horns of oxen and neutralizing the resulting carbonate with hydrochloric acid, the name, "spirit of hartsh horn" was applied to ammonia. Gaseous ammonia was first isolated by Joseph Priestley in 1774 and was termed by him "alkaline air". Eleven years after, in 1785, Claude Louis Berthollet ascertained its composition.

The Haber-Bosch process to produce ammonia from the nitrogen in the air was developed by Fritz Haber and Carl Bosch in 1909 and patented in 1910. It was first used on an industrial scale in Germany during world war I following the allied blockade that cut off the supply of nitrates from Chile. The ammonia was used to produce explosives to sustain war efforts. Prior to the availability of Natural gas, hydrogen as a precursor to ammonia production was produced via the electrolysis of water or using the chloroalkali process. With the advent of the steel industry in the 20th century ammonia becomes a by-product of the production of coking coal. Today, most ammonia is produced on a large scale by the Haber process with capacities of up to 3300MTPD. In the process, N₂ and H₂ gases are allowed to react pressure of 200 bars.

II. MATERIALS AND METHODS

Materials used:-

Physical and Chemical Properties of Natural Gas:-

- It is a fossil fuel formed from plant and animal remains millions of years ago.
- It is hydrocarbon component with methane as a major component.
- It is colourless and odourless. For security during transportation or processing, a commercial odorant is added to allow users to detect the gas for safety.
- It is lighter than air with a specific gravity of about 0.6-0.8. If leaks, it disperses upward and dissipates into the air quickly.
- It is inflamed during a range of 5-15% by volume of gas in air. The self-ignition temperature of natural gas is 537-540 Celsius degrees.
- As it is a clean fuel with cleaner burning nature, natural gas has lower environmental impact when compared with other types of fuel.

Density – 12.246 kg/m³

Boiling point - -158oC/115°K

Calorific value – 49311.2 kJ/kg

Specific volume – 0.00231m³/kg

Critical temperature – 190.7°K

Critical pressure – 7.500 Kpa

Ignition point – 593

Flammability limits – 4-16 % (volume% in air)

Maximum flame velocity – 0.3m/s

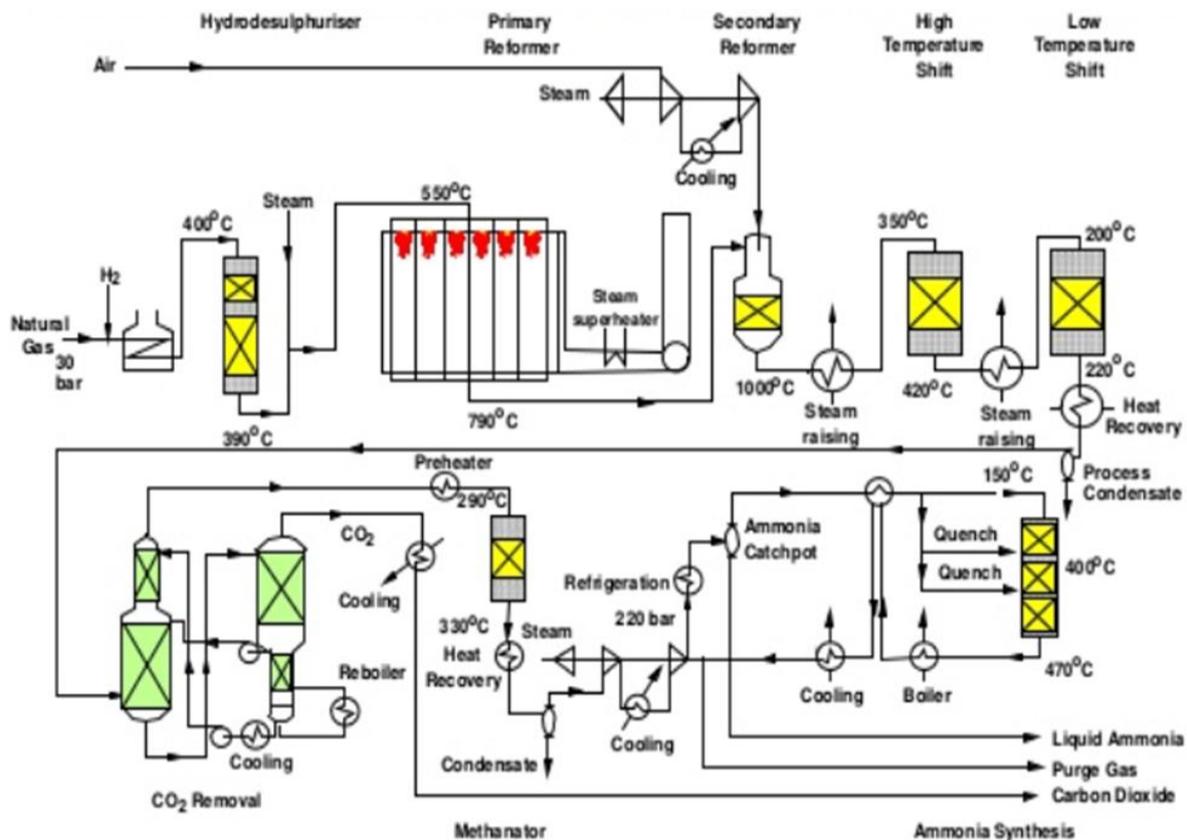


Fig 1: Process diagram

In the process natural gas is used for production of nitrogen and hydrogen. The purified nitrogen and hydrogen is thus reacted to give ammonia gas. In commercial production sulphur free natural gas is mixed with steam in the volume based ratio of 3.7:1 and compressed to 40atm. The mixture is preheated with the recycled flue or effluent gases and fed into the furnace. At 800-850°C in the presence of iron catalyst promoted with other metal oxides conversion of methane takes place with the formation of CO. The residual gas is mixed with air and fed into shaft converter to get complete conversion. The waste heat is utilized for the steam generation and ethanolamine which are used in CO₂ and H₂S removal. The exit gas containing poison was regenerated in the methanator at 280-350°C which ultimately used for

heating the feed water. Purified N_2 and H_2 mixture was compressed to 300atm at 320 to 380°C in the presence of catalyst converted to NH_3 . 14-20% conversion per pass was achieved.

NH_3 condensed and separated from exit gas, whereas unconverted N_2 and H_2 gases were recycled along with the fresh gases. Ammonia synthesis is being exothermic the process requires an effective temperature control system at every stage of reaction.

Desulphurization

The Sulphur compounds in the process gas are converted into hydrogen sulphide using hydrogen and a catalyst made up of cobalt & molybdenum oxides. There are 10te of catalyst in the vessel. A hydrogen rich gas stream from the synthesis loop supplies the hydrogen. This is taken from the re-cycle stage of the Synthesis gas compressor. The hydrogen sulphide formed is removed by absorption onto zinc oxide forming zinc sulphide and is retained in these two vessels. There are Zinc Oxide in the two vessels.

Primary Reformer

In the primary reformer steam and natural gas are added in a steam to gas ratio of 3:1. So 100te steam and 33te of natural gas per hour are added to the primary reformer at a pressure of 32bar. Before entering the catalyst filled tubes the mixture is pre-heated to 500°C by the combustion gases leaving the reformer furnace. The reforming takes place in 520 tubes filled with promoted nickel oxide catalyst (22te) and the temperature of reaction is 820°C. This reaction is takes in heat. Heat is supplied by burning natural gas in 198 burners in the roof of the furnace. There are also 11 burners surrounded by firebricks on the floor of the furnace at the outlet end of the reformer tubes. The process gases and steam flows downward in the catalyst filled tubes. The tubes are divided into ten rows of 52 tubes. 51 of these in each row of tubes are filled with catalyst but one tube in the middle of each row is a riser and does not contain catalyst. This tube has no restriction and is capable of transporting the total flow from the other 51 catalyst filled tubes upwards. The tubes are welded into a common header along the bottom to allow the gases leaving the catalyst filled tubes to run to the empty tube which carries the gases in the opposite direction up to another header meeting the other outlets of other rows. So there are 10 risers taking reformed gases to a common header going on to feed the secondary reformer

Secondary Reformer

The next step is the addition of air and steam. This is pre-heated by waste heat from the combustion gases to 455°C. The air is the source of nitrogen for the ammonia synthesis. The volume of air is designed to give a Hydrogen to Nitrogen ratio of 3:1 ($H_2:N_2$) in the gas stream following the removal of carbon oxides, steam and methanol. This air and steam at 455°C meets the mixture of steam and gas from the primary reformer at 825°C at an inverted burner at the top of the secondary reformer (40te NiO catalyst). The remaining methane is reformed and the temperature increases to 920°C at the exit. This vessel is surrounded by water jackets to keep the metal surface cool. Approx. composition: 57% H_2 , 22% N_2 , 13% CO, 7% CO_2 , 0.3% CH_4 . The gases exit the secondary reformer through two waste heat boilers 101C A&B each producing 100 te steam per hour. The boilers are high heat flux Bayonet/scabbard type boilers. They are followed by a shell and tube boiler 102C 50te/hr capacity. These exchangers utilize the excess heat in the process stream.

Methanation

Ammonia Plant Methanation The gases leaving the Benfield go through knock out pots to remove water before going on to the methanator where the small traces of carbon oxides are converted to methane (Carbon oxides and water are poisons to the iron catalyst in the synthesis converter and must be removed). The catalyst in the methanator is the same material, promoted nickel oxide, as that in the reformer tubes. However, the reaction is the reverse of that in the primary reformer and this is possible because there is no water present in the process stream going through the methanator. The reaction here generates heat when carbon oxides and hydrogen recombine to form methane (Methane is not a poison to the synthesis catalyst). The gases are then cooled by boiler feed water before going on to the first compression stage of the 103J compressor. Methane is introduced from the air through the secondary reformer. They are removed through a Hydrogen Recovery unit where the ammonia is scrubbed with water and sent to the urea plant for reuse. The hydrogen is separated in a set of prisms by diffusion and recycled to make more ammonia. The methane is burned with the fuel gas.

Ammonia Synthesis

The 103J compressor has three compression stages, stage 1, stage 2 and recycle. The process gases in the synthesis loop recirculate in the ammonia rich loop, between the synthesis converter and the 106F (ammonia, knock out vessel). The gasses leaving the 106F now low in ammonia and containing make up gas from the second stage of the 103J return to the synthesis converter via the recycle stage of the 103J. Ammonia is made up of 3 molecules of hydrogen and 1 molecule of

Nitrogen. Heat is generated by this reaction so low temperature would favour the reaction, however the temperature is maintained high to get a faster generation of a smaller percentage of ammonia followed by rapid removal of over 90% of the ammonia after it is formed. Once the synthesis reaction is established and the catalyst is fully reduced the gases entering the synthesis converter catalyst contain 1.5% ammonia the process stream leaving the synthesis converter contains 17% ammonia. Because the reaction gives out heat and temperatures above 550°C will damage the catalyst the temperature is controlled between 350°C and 500°C by gas flow through the catalyst bed in the synthesis converter. The synthesis converter was one of the most significant modifications that improved the efficiency of the plant. The original converter was configured to have a gas flow axially through the vessel. This was modified to give radial flow through the catalyst, which gave a shorter path with lower pressure differential. A smaller particle size catalyst could also be used. This modification increased the ammonia concentration at the outlet of the converter from 14% to 17%.

Storage

Ammonia Plant Storage The ammonia is sent for storage in two refrigerated tanks each with a capacity of 15,000T. The tanks have a separate refrigeration plant to maintain the temperature at -33°C. The tanks are mild steel and are enclosed in a concrete capsule with a 1 meter gap between the concrete and the tank. There is a pumping system for loading trains and sea going tankers. It is also possible to import ammonia by ship if required.

Mass Balance:-

$$\text{Ammonia Production} = 2000 \text{ MTPD} = 4901.96 \text{ kmol/hr}$$

$$\text{N}_2 + 3\text{H}_2 \qquad \qquad \qquad 2 \text{NH}_3$$

Let % conversion = 20%

Which means, 1 kmol N₂ forms 2x0.2 = 0.4 kmol NH₃

Assuming losses = 8%

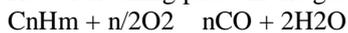
$$\text{Ammonia production} = 4901.96 / 0.92 = 5328.22 \text{ kmol/hr}$$

$$\text{Hence, N}_2 \text{ required} = 5328.22 / 0.4 = 13320.55 \text{ kmol/hr}$$

$$\text{Air required} = 13320.55 \times 100 / 79 = 16861.45 \text{ kmol/hr}$$

$$\text{Similarly, H}_2 \text{ required} = 3 \times 13320.55 = 39961.65 \text{ kmol/hr}$$

Reaction taking place in the gasifier is



At high temperature



Composition is given in weight percent.

$$\text{C} = 84.98\%$$

$$\text{H} = 12.07\%$$

$$\text{S} = 1\%$$

$$\text{N} = 0.4\%$$

$$\text{O} = 1.5\%$$

Composition of gases coming out of the gasifier is given as-

$$\text{CO} = 42\%$$

$$\text{H}_2 = 51.23\%$$

$$\text{H}_2\text{S} = 0.23\%$$

$$\text{CO}_2 = 5.7\%$$

$$\text{N}_2 = 0.18\%$$

$$\text{Ar} = 0.02\%$$

$$\text{CH}_4 = 0.5\%$$

Material balance across H₂S absorber

Basis: 100 kmole of Raw gas

$$\text{CO} = 42 \text{ kmole}$$

$$\text{H}_2 = 51.23 \text{ kmole}$$

$$\text{H}_2\text{S} = 0.23 \text{ kmole}$$

$$\text{CO}_2 = 5.7 \text{ kmole}$$

$$\text{N}_2 = 0.18 \text{ kmole}$$

$$\text{Ar} = 0.09 \text{ kmole}$$

Now, maximum concentrations of H₂S in H₂S free raw gas is limited to 0.3 ppm.

Amount of H₂S to be removed = 0.23 kmole

In H₂S free gas

$$\text{H}_2 = 51.23 \text{ kmole} \quad \% \text{ of H}_2 = 51.23 / 99.77 \times 100 = 51.34$$

$$\text{CO} = 42 \text{ kmole} \quad \% \text{ of CO} = 42 / 99.77 \times 100 = 42.09$$

$$\text{H}_2\text{S} = 0.3 \text{ ppm \% of H}_2\text{S} = 0.3 \text{ ppm}$$

$$\text{CO}_2 = 5.77 \text{ kmole \% of CO}_2 = 5.77/99.77 \times 100 = 5.78$$

$$\text{CH}_4 = 0.5 \text{ kmole \% of CH}_4 = 0.5/99.77 \times 100 = 0.501$$

$$\text{N}_2 = 0.18 \text{ kmole \% of N}_2 = 0.18/99.77 \times 100 = 0.18$$

$$\text{Ar} = 0.09 \text{ kmole \% of Ar} = 0.09/99.77 \times 100 = 0.09$$

$$\text{Total no. of moles} = 51.23 + 42.09 + 5.77 + 0.5 + 0.18 + 0.09 = 99.77 \text{ kmole}$$

Material balance across CO shift converter

Basis: 100 kmol of H₂S free gases

Now since 97% of CO is converted in converter

$$\begin{aligned} \text{Therefore kmoles of CO}_2 \text{ in product} &= 5.78 + 42.09 \times 0.97 \\ &= 5.78 + 40.8 = 46.6 \text{ kmoles} \end{aligned}$$

$$\text{similarly, kmoles of H}_2 \text{ in the Product} = 51.34 + 40.8 = 92.14$$

$$\text{K mole of CO} = 42.09 - 40.4 = 1.26$$

$$\text{K mole of H}_2\text{S} = 0.3 \text{ ppm}$$

$$\text{K mole of CH}_4 = 0.501 \text{ kmole}$$

$$\text{K mole of Ar} = 0.09 \text{ kmole}$$

$$\text{K mole of N}_2 = 0.18 \text{ kmole}$$

$$\begin{aligned} \text{Total no of moles in the product stream} &= (46.4 + 92.14 + 1.26 + 0.501 + 0.09 + 0.18) \\ &= 140.77 \text{ kmole} \end{aligned}$$

$$\text{H}_2 \text{ in the product} = 92.14/140.77 \times 100 = 65.45\%$$

$$\text{CO}_2 \text{ in the product} = 46.6/140.77 \times 100 = 33.1\%$$

$$\text{H}_2\text{S} = 0.3 \text{ ppm}$$

$$\text{CH}_4 = 0.501/140.77 \times 100 = 0.36\%$$

$$\text{Ar} = 0.09/140.77 \times 100 = 0.063\%$$

$$\text{N}_2 = 0.18/140.77 \times 100 = 0.13\%$$

Material balance across CO₂ Absorber

Basis 100 mole of converted gas

Taking efficiency of the absorber to be 92%

$$\begin{aligned} \text{CO}_2 \text{ to be removed} &= 0.92 \times 33.1 \\ &= 30.45 \text{ kmole} \end{aligned}$$

$$\text{CO}_2 \text{ in the product stream} = 2.65 \text{ kmole}$$

$$\begin{aligned} \text{Total number of moles in the product stream} \\ &= (2.65 + 65.45 + 0.89 + 0.13 + 0.06 + 0.36) = 69.54 \text{ kmole} \end{aligned}$$

$$\text{CO}_2 = 2.65/69.54 \times 100 = 3.8$$

$$\text{H}_2 = 65.45/69.45 \times 100 = 94.2$$

$$\text{CO} = 0.89/69.45 \times 100 = 1.3$$

$$\text{CH}_4 = 0.36/69.45 \times 100 = 0.518$$

$$\text{N}_2 = 0.13/69.45 \times 100 = 0.19$$

$$\text{Ar} = 0.064/69.45 \times 100 = 0.09$$

$$\text{H}_2\text{S} = 0.3 \text{ ppm}$$

Material balance across Adsorber

The main function of absorber is to adsorb H₂S, CO & CO₂. They are reduced to an amount which is negligible.

$$\text{Moles remained} = 100 - 3.8 - 1.3 = 94.9 \text{ kmole}$$

% of gas after adsorption

$$\text{H}_2 = 94.2/95 \times 100 = 99\%$$

$$\text{CH}_4 = 0.54$$

$$\text{Ar} = 0.095$$

$$\text{N}_2 = 0.19/95 = 0.2$$

N₂ is added in such a way that

H₂: N₂ becomes 3 : 1

Suppose x mole of N₂ is added

$$99 = (0.18 + x) \times 3$$

$$x = 32.80$$

$$\text{Total no of moles} = 99 + 32.80 + 0.54 + 0.095 = 132.43 \text{ kmole}$$

$$\text{\% of N}_2 \text{ in the product} = 32.80/132.43 \times 100 = 24.76 \%$$

$$\text{\% of H}_2 \text{ in the product} = 99/132.43 \times 100 = 74.76\%$$

$$\text{\% of Ar} = 0.072\%$$

$$\text{\% of CH}_4 = 0.54/132.43 \times 100 = 0.4\%$$

Material balance across NH₃ Separator

Now in NH₃ Separator 3 streams are there out of which 2 are going out and one is making in the stream that moves in F13 & stream that gives main product is F14 & F 15.

F16 is recycle stream moving to compressor.

Suppose the moles of F 13 stream are as follows

$$N_2 = a$$

$$H_2 = 3a$$

$$NH_3 = b$$

$$Ar = c$$

$$CH_4 = d$$

Now solubility of H₂, N₂, Ar, NH₄ in liquid NH₃ is given as

Solubility of H₂ = 0.0998 cm³ of H₂ at NTP/gm of liq NH₃

Solubility of N₂ = 0.1195 cm³ of N₂ at NTP/gm of liq NH₃

Solubility of Ar = 0.154 cm³ of Ar at NTP/gm of liq NH₃

Solubility of CH₄ = 0.304 cm³ of CH₄ at NTP/gm of liq NH₃

For F 14 stream

$$H_2 = 0.0998/22414 \times 17 \times 3a \times 22 \times 298/273$$

$$= 5.45 \times 10^{-3}a$$

$$N_2 = 0.1195/22414 \times 17 \times a \times 22 \times 298/273$$

$$= 2.18 \times 10^{-3}a$$

$$Ar = 0.154/22414 \times 17 \times c \times 22 \times 298/273$$

$$= 2.8 \times 10^{-3}c$$

$$CH_4 = 0.304/22414 \times 17 \times d \times 22 \times 298/273$$

$$= 5.54 \times 10^{-3}d$$

Now we want 2000 MTPD production

Therefore NH₃ production in F 14

$$= 2000 \times 1000/(17 \times 24)$$

$$= 4901.96 \text{ kmole/hr}$$

Now for F15 stream

Equilibrium of NH₃ in gas phase with liq. NH₃ in separator = 5.9%

Assuming that total inert conc. In stream from the separator = 5%

$$H_2 + N_2 = 100 - 5.9 - 5 = 89.1\%$$

$$H_2 = \frac{3}{4} \times 89.1 = 66.83\%$$

$$N_2 = \frac{1}{4} \times 89.1 = 22.28\%$$

$$NH_3 = 5.9\%$$

$$Ar + CH_4 = 5\%$$

Since CH₄ is 2.5 times the Ar.

$$Ar = 1.43\%$$

$$CH_4 = 3.57\%$$

Now applying material balance on NH₃ separator

$$F_{13} = F_{14} + F_{15}$$

$$H_2 \text{ balance : } 3a = 0.6683 F_{15} + 5.45 \times 10^{-3}a \quad (1)$$

$$N_2 \text{ balance : } a = 0.2228 F_{15} + 2.18 \times 10^{-3}a \quad (2)$$

$$NH_3 \text{ balance : } b = 2450.98 + 0.059 F_{15} \quad (3)$$

$$CH_4 \text{ balance : } d = 5.54 \times 10^{-3}d + 0.0357 F_{15} \quad (4)$$

$$Ar \text{ balance : } c = 2.8 \times 10^{-3}c + 0.0143 F_{15} \quad (5)$$

From (5)

$$0.9945d = 0.0357 F_{15} \quad (6)$$

$$d = 0.0359 F_{15}$$

From eqn. (1)

$$2.99478 a = 0.6683 F_{15} \quad a = 0.223 \times F_{15} \quad (7)$$

From eqn. (4)

$$0.9972 c = 0.0143 F_{15}$$

$$c = 0.01434 F_{15} \quad (8)$$

Now total moles in product stream F14

$$= 4901.96 + (2.18 + 5.45) \times 10^{-3} \times 0.223 \times F_{15} + 2.8 \times 10^{-3} \times 0.0143 F_{15} + 5.54 \times 10^{-3} \times 0.0359 F_{15}$$

$$= 4901.96 + 1.9404 \times 10^{-3} F_{15}$$

$$\eta \text{ of } NH_3 \text{ separator} = 98.5\%$$

Therefore

$$4901.96 = 0.985$$

$$4901.96 + 1.9404 \times 10^{-3} F_{15}$$

$$4901.96 = 2414.22 + 1.9113 \times 10^{-3} F_{15}$$

$$F_{15} = \frac{2487.74}{0.0019113} \text{ kmol/hr}$$

From (7)

$$a = 5133.7 \text{ kmol/hr}$$

From (8)

$$c = 330.12 \text{ kmol/hr}$$

From (6)

$$d = 826.45 \text{ kmol/hr}$$

& from (3)

$$b = 4299.24 \text{ kmol/hr}$$

Now for F-13 stream

$$H_2 = 3 \times 5133.7 = 15401.1 \text{ kmol/hr}$$

$$N_2 = 5133.7 \text{ kmol/hr}$$

$$NH_3 = 4299.24 \text{ kmol/hr}$$

$$Ar = 330.12 \text{ kmol/hr}$$

$$CH_4 = 826.45 \text{ kmol/hr}$$

$$\text{Total no of moles} = 25990.61 \text{ kmol/hr}$$

$$H = \frac{15401.1}{25990.61} = 59.26\%$$

$$N_2 = 19.75\%$$

$$NH_3 = 16.52\%$$

$$Ar = 1.28\%$$

$$CH_4 = 3.18\%$$

For F14 stream

$$NH_3 = 4901.96 \text{ kmol/hr}$$

$$H_2 = 5.45 \times 10^{-3} a$$

$$= 5.45 \times 10^{-3} \times 5133.7 = 27.98 \text{ kmol/hr}$$

$$N_2 = 2.18 \times 10^{-3} x$$

$$a = 2.18 \times 10^{-3} \times 5133.7$$

$$= 11.19 \text{ kmol/hr}$$

$$CH_4 = 5.54 \times 10^{-3} x d$$

$$= 5.54 \times 10^{-3} \times 826.45$$

$$= 4.58 \text{ kmol/hr}$$

$$Ar = 2.8 \times 10^{-3} c$$

$$= 2.8 \times 10^{-3} \times 330.12$$

$$= 0.924 \text{ kmol/hr}$$

$$\text{Total no of moles in product} = 2985.67 \text{ kmol/hr}$$

$$NH_3 = \frac{4901.96}{4946.634} \times 100 = 99.09\%$$

$$H_2 = \frac{27.98}{4946.634} \times 100 = 0.56\%$$

$$N_2 = \frac{11.19}{4946.634} \times 100 = 0.22\%$$

$$CH_4 = \frac{4.58}{4946.634} \times 100 = 0.092\%$$

$$Ar = \frac{0.924}{4946.634} \times 100 = 0.018\%$$

Material balance across NH₃ converter

Suppose in F12 stream

$$N_2 = x \text{ kmole}$$

$$H_2 = y \text{ kmole}$$

$$NH_3 = z \text{ kmole}$$

Assuming 20% conversion

For N₂ balance

$$X [1 - 0.2] = 5133.7$$

$$X = N_2 = 6417.125 \text{ kmol/hr}$$

$$H_2 = 3 \times 6417.125 = 19251.4 \text{ kmol/hr}$$

$$NH_3 \text{ formed} = 2 \times 0.2 \times 6417.125$$

$$= 2566.85 \text{ kmol/hr}$$

$$\begin{aligned} \text{NH}_3 \text{ in F12} &= 4299.24 - 2144.48 \\ &= 1732.4 \text{ kmol/hr} \\ \text{CH}_4 \text{ in F12} &= 826.45 \text{ kmol/hr} \\ \text{Ar in F12} &= 330.12 \text{ kmol/hr} \\ \text{Total no of moles in F12} &= 28557.5 \text{ kmol/hr} \\ \text{N}_2 &= \frac{6417.125 \times 1000}{28557.5} = 22.47\% \\ \text{H}_2 &= \frac{19251.4 \times 1000}{28557.5} = 67.42\% \\ \text{NH}_3 &= \frac{1732.4 \times 1000}{28557.5} = 6.04\% \\ \text{CH}_4 &= \frac{826.45 \times 1000}{28557.5} = 2.89\% \\ \text{Ar} &= \frac{330.12 \times 1000}{28577.5} = 1.17\% \end{aligned}$$

Applying material balance across compressor

$$F11 + F16 = F12$$

$$F11 + F16 = 28557.5$$

Applying H₂ balance

$$0.7476 F11 + 0.6683 F16 = 0.6742 \times 28557.5$$

$$0.7476 [28557.5 - F16] + 0.6683 F16 = 0.6742 \times 28557.5$$

$$\text{Therefore } F16 = 26432.79 \text{ kmol/hr}$$

$$\text{Recycle} = 26432.79 \text{ kmol/hr}$$

$$F11 = 28557.5 - 26432.79$$

$$= 2124.79 \text{ kmol/hr}$$

Suppose the kmole of feed gases coming from absorber is A

$$A \times 0.99 = 2124.71 \times 0.7476$$

$$A = 1588.43 \text{ kmol/hr}$$

$$\text{Amt of N}_2 \text{ Added} = 2124.71 \times 0.2476$$

$$= 526.1 \text{ kmol/hr}$$

Across the absorber applying overall material balance.

H balance,

$$F10 \times 0.942 \text{ kmol/hr}$$

$$F10 = 1422.8025 \text{ kmol/hr}$$

Applying material balance across CO₂ removal $F8 \times 0.6545 = F10 \times 0.942$

$$F8 = \frac{1422.8025 \times 0.942}{0.6545} = 2047.79 \text{ kmol/hr}$$

$$0.6545$$

Applying material balance across shift converter

$$F7 \times 0.534 = 2286.17 \times 0.6545$$

$$F7 = 2914.49 \text{ kmol/hr}$$

Applying material balance across H₂S removal

$$F5 \times 0.5123 = 2914.49 \times 0.5134$$

$$F5 = 2920.75 \text{ kmol/hr}$$

$$\text{H}_2\text{S removed} = 2920.75 \times 0.0023 - 2914.49 \times 0.3 \times 10^{-4}$$

$$= 6.63 \text{ kmol/hr}$$

For H₂S gas

$$W = 0.094, \quad TC = 373. \text{ K} \quad PC = 89.63 \text{ bar}$$

$$P = 49 \text{ bar} \quad T = -220C = 2510K$$

$$Tr = \frac{257}{373.5} = 0.67$$

$$Pr = \frac{49}{39.63} = 0.55$$

$$B0 = 0.083 - \frac{0.422}{(0.67)^{1.6}} = -0.59$$

$$mk \text{ kg/m}^2 B = 0.139 - \frac{0.172}{(0.67)^{4.2}} = -0.78$$

$$Z = 1 - \frac{0.59 \times 0.55}{0.67} = 0.52$$

$$PV = Z n RT$$

$$49 \times V = 0.082 \times 0.55 \times 251 \times 5.94$$

$$V = 1.297 \text{ m}^3$$

Solubility of H₂S in Methanol

$$= \frac{60 \text{ m}^3 \text{ of H}_2\text{S}}{\text{m}^3 \text{ of methanol}} \text{ at } -220\text{C} \text{ \& } 49 \text{ atm}$$

Weight of methanol required

$$= \frac{1.534}{60} = 2.56 \times 10^{-2} \times 1215$$

$$= 31.1 \text{ kg}$$

$$\text{kmol of methanol required} = \frac{31.1}{32} = 0.97 \text{ kmol/hr}$$

3% by weight of carbon is converted into coke, therefore only 97% of carbon is present in raw gas.

$$\text{Coke formed} = 20556.22 \times 0.8489 \times 0.03$$

$$= 523.5 \text{ kmol/hr}$$

Applying mass balance across carbon recovery unit;\

$$F_3^* = F_5^* - \text{mass of coke formed}$$

(* denotes mass per unit time)

$$F_3^* = 2920.75 \times 14.6 - 523.5 \times 12 = 36361 \text{ kg/hr}$$

Applying mass balance across gasifier

$$F_1^* = F_3^* - F_2^* = 36361 - 462.42 \times 32 = 21564 \text{ kg/hr}$$

Hence, Fuel Oil requirement = 21,564 kg/hr

COST ESTIMATION

Cost estimation is a specialized subject and profession in its own right. Chemical plants are built to make a profit. An estimate of the investment required and the cost of production needed before the profitability of project can be assessed.

Cost in plant can be classified as-

1. Fixed capital
2. Working capital

(1) Fixed capital:-

Fixed capital is the cost of the plant ready to start up. It includes

1. Design
2. Equipment and interaction
3. Piping instrumentation and control system
4. Building and structure
5. Auxiliary facilities such as utilities

(2) Working capital

Working capital is additional investment needed over and above fixed capital to start up the plant. It includes

1. Start up
2. Catalyst cost
3. Raw material
4. Finished product inventories

These costs are required to be corrected to the specific capacity and index price of the given year.

[10.1] Correction of index price

$$\text{Cost in yr. A} = \frac{\text{Cost in yr. B} \times \text{Cost index of yr. A}}{\text{Cost index of yr. B}}$$

Correction of capacity

$$C_2 = C_1 \left(\frac{S_2}{S_1} \right)^n$$

C₂ = Capital cost at capacity S₂

C₁ = Capital cost at capacity S₁

n = power factor

(From Peter Timmer Haus, page 186)

Ammonia plant capacity = 100,000 ton/yr.

Fixed capital investment = 24 x 10⁶\$ (Based on 1979) Power factor for ammonia = 0.55

Our plant capacity = 2000 MTPD

$$\text{Equation (2) } C_2 = C_1 \left(\frac{s_2}{s_1} \right)^n$$

Taking that our plant runs for 335 days /yr. deducting the time for normal shut down period

$$\text{Capacity} = 2000 \times 335 \text{ tons/yr.} = 670000 \text{ tons/yr.}$$

$$C_2 = 24 \times 10^6 \times \left(\frac{670000}{100000} \right)^{0.55}$$

$$= 3.841 \times 10^5 \$$$

Cost index = 2000
 From “chemical engineering” journal
 CI =585.9(based on 1979)

$$\text{Cost in yr. 2008} = \text{cost in yr. 1979} \times \frac{\text{C.I. 2016}}{\text{C.I.1979}}$$

Thus,
 Cost in yr. 2016 = $(3.841 \times 105) \times \frac{2000}{585.9}$
 = 1.31×106

From Peter Timer Haus –
 Working capital = 15% [fixed + working capital]

$$\text{W.C.} = \frac{\text{F.C.} \times 15}{85}$$

$$\text{W.C.} = 1.31 \times 15 \times \frac{106}{85}$$

$$= 1.388 \times 105$$

Therefore total capital investment
 = $1.31 \times 106 + 2.31 \times 105$
 = 1541000\$

Taking currency exchange rate as 1 \$ = 65 Rs
 Total capital investment
 = 1541000×65
 =Rs.100.016 crore

[A] DIRECT COST

Component	Given range	Assumed range	(%FCI)	Cost (Rs.crores)
Purchased equip.	15-40	25		116.25
Installation	06-14	09		41.85
Instrumentation	02-18	07		32.55
Piping	03-20	08		37.20
Electrical	02-10	05		23.25
building	03-18	05		23.25
Yarest	02-05	02		9.3
Service facilities	08-20	15		69.75
Land	01-02	01		4.6

Total direct cost = Rs. 358.05 crore

[B] INDIRECT COST

Engineer and supervision	04-25	10		46.5
Construction expenses	04-16	12		55.8
Contractor fee	02-06	02		9.3
Contingency	05-15	08		37.2

Total Indirect cost = Rs. 148.8 crore

COST OF REACTOR

$$\text{Volume of cylinder} = 3.14 \times 1 \times (\text{OD}^2 - \text{ID}^2) / 4$$

$$\text{OD} = 1.290\text{m}$$

$$\text{ID} = 1.212\text{m}$$

$$\text{Length, } l = 4.848\text{m}$$

Therefore,

$$\text{Vol of cyl. Material} = 0.743\text{m}^3$$

Density of Carbon Steel = 7820 kg/m³

Price of carbon steel = Rs 45/kg

Therefore, Cost of Reactor material = $0.743 \times 7820 \times 45 = 2.62$ lakh

CATALYST

Volume of catalyst = 18 m³

Price of catalyst = \$12/kg

Density of catalyst = 1200 kg/m³

Therefore, Cost of catalyst = $18 \times 1200 \times 12 \times 44 = 1.141$ Crores

Now, taking fabrication cost = 70% of total cost of equipment = $2.26 \times 0.7 / 0.3 = 5.273$ lakh

Hence, total cost of reactor (including catalyst) = $1.141 + 0.5273 + 0.262 = 1.22$ Crores

COST OF HEAT EXCHANGER

Volume of shell material = $3.14 \times \text{length} \times (\text{OD}^2 - \text{ID}^2) / 4$

OD = 1.115m

ID = 1.067m

Length = 16 ft = $16 \times 12 \times 0.0254$ m

Volume of shell material = 0.4012 m³

Volume of one tube = $3.14 \times \text{length} \times (\text{OD}^2 - \text{ID}^2) / 4$

OD = 0.0254m

ID = 0.0221m

Length = 16 ft

Volume of single tube = 6×10^{-4} m³

Total vol. of tubes = $6 \times 10^{-4} \times 730 = 0.4383$ m³

Density of material (carbon steel) = 7820 kg/m³

Cost of material = Rs 45/kg

Therefore, Cost of heat exchanger material = $(0.4012 + 0.4383) \times 7820 \times 45 = 2.954$ lakh

total cost of heat exchanger (including fabrication) = $2.954 \times 1 / 0.3 = 9.847$ lakh

INDUSTRIAL IMPORTANCE AND USES

AGRICULTURE INDUSTRIES: - Nearly 80% of all ammonia produced in the United States comes from agriculture industries. The chemical is a very valuable source of nitrogen which is necessary for the plant growth.

Although it can vary from plant to plant it is not uncommon to use up to 200lbs of ammonia per acre for each growing season. Common areas where ammonia is found in the agriculture business includes:-

- Fertilizers: - Liquid fertilizer consists of ammonia, ammonium nitrate, urea, and aqua ammonia, also used to produce the ammonium and nitrate salts.
- Livestock feeds: - Ammonia and urea are used as a source of protein to feed ruminating livestock animals such as cattle, sheep and goats.
- Crop protection: - Ammonia can also be used as a pre-harvest cotton defoliant, an antifungal agent on certain fruits and as a preservative for the storage of high-moisture corn.

METAL TREATING OPERATIONS: - Applications where protective atmospheres are required dissociated ammonia is used as nitriding, carbonitriding, bright annealing, furnace brazing, sintering, sodium hydride descaling, and atomic hydrogen welding.

PETROLEUM INDUSTRY: - Utilizes ammonia in neutralizing the acid constituents of crude oil and for the protection of the equipment from corrosion.

MINING INDUSTRY: - Uses ammonia for the extraction of metals such as copper, nickel and molybdenum from their ores.

STACK EMISSION CONTROL SYSTEMS: - Ammonia is used in stack emission control systems to neutralize sulphur-oxides from combustion of sulphur-containing fuels, as a method of NO_x control in both catalytic and non-catalytic applications and to enhance the efficiency of the electrostatic precipitators for particulate control.

PULP AND PAPER INDUSTRY: - Uses ammonia for pulping wood and as casein dispersant in the coating of the paper.

FOOD BEVERAGES, PETROLCHEMICAL AND COLD STORAGE INDUSTRIES: - Ammonia is a widely used refrigeration systems. It is also used as a source of nitrogen needed for the yeast and the micro-organisms.

RUBBER AND LEATHER INDUSTRY: - In rubber industry, the ammonia is used for the stabilization of natural and synthetic latex to prevent the premature coagulation. The leather industry uses the ammonia as a curing agent, as a slime and mold preventative in tanning liquors and as a protective agent for the leathers and furs in storage.

ELECTRONICS: - High purity ammonia is used for the electronic and for the semiconductor applications.

PHARMA AND BIOTECHNOLOGY: - Ammonia is used as a processing agent in the manufacturing of pharmaceuticals.

POWER AND ENERGY: - Purification of smoke gas in coal fired or oil fired power plants. With the presence of ammonia in a reactor the nitrogen oxides are converted into nitrogen and water while passing the reactor. In combination with chlorine, the ammonia is also used for the water purification.

HAZARDS OF AMMONIA

1. Toxic hazards: - In general ammonia gas under high concentration causes irritation to eyes.
2. Explosive Hazards: - Ammonia is explosive with air in the range of 16 to 25% by volume. Its auto ignition temperature is 651°C since such temperature are not encountered in practice; the chance of fire and explosive hazards due to ammonia is relatively remote. The presence of oil in mixture of ammonia with other combustible materials will increase the /fire hazard. The explosive range of ammonia is;
 1. Temperature and pressure higher than atm conditions.
 2. Presence of chlorine higher than ammonia causes chlorine to react with ammonia and form a violently explosive compound.

SAFETY IN AMMONIA PLANTS

- Wear ear plugs
- wear approved respirator & protective clothing
- Wear safety helmet, goggles, hand gloves, safety shoes.
- Keep away from heat, flames, spark & oxidizing material
- Keep area ventilated & report the leakage
- Keep people away from hazardous area.

III. CONCLUSION

Through extensive research and calculation, the processes were analysed and compared based on their associated costs, production value and environmental impact. The results produced throughout the project indicate that the process is less expensive and more environmentally responsible than current ammonia synthesis processes. The current process has an affiliated production cost of \$600 per ton of ammonia, resulting in a break-even point after approximately five years. However, is expected to reach a break-even point after less than two years of operation, with an affiliated production cost of \$232 of per ton. It has been predicted that, if this process were used to replace current processes for ammonia synthesis, the change could account for a 7% reduction in global greenhouse gas emissions. The results provide direction for research regarding the optimization of future ammonia and fertilizer production, indicated in the Recommended Future Research section of this chapter

REFERENCES

1. Fertilizers news – development in ammonia production technology – by D.Sen, Dec 24, 2011.
2. The fertilizer encyclopedia – by Sudha Gowariker, V.N.Krishnamurthy., 14 July, 2008, page no. 40.
3. History of industrial gases – by Ebbe Almquist 31 June, 2003.
4. Chemistry of petrochemical processes- 2nd edition, by Sami Mator and Zenis F. Hatch page no. 55-78.
5. Mc Graw – Hill series in chemical engineering, Sidney. D. Kirkpatrick, the chemical process industry , page no. 215-232.
6. Handbook on fertilizer technology by P. Sharma, page no. 28-75, Dec-2012.

7. GPCA fertilizer convection, steering the fertilizer industry through challenging times, 7th edition, 6 to 8th Sep., 2016, Dubai, UAE.
8. Indian Fertilizer Senario, Department of fertilizer Ministry of chemicals and fertiizers govt. of India, 2013- page no. 83.
9. Encyclopedia of chemical technology volume -2, by Wiley – Kirk – Othmer, page no. -638-691 (Ammonia).
10. Wikipedia ammonia production by T – Anthony, page no. 11.
11. Production of ammonia
12. [www.sbioinformatics.com/design-thesis ammonia](http://www.sbioinformatics.com/design-thesis-ammonia).
13. Dryden's outline of chemical technology 3rd edition, Gopal Rao, Marshil Sitting Prof. Haward University, Washington , page no. 01-08.
14. Erine, N.J, 2001. Africa in Perspective Natural gas offers, Nigeria Huge Potential Challenge oil and gas J (2 July), page no. 17
15. Perry, R.H., "Perry's Chemical Engineers Handbook", 6thEd., McGraw Hill Company, 1984.
16. McCabe Warren L., Smith Julian C., Harriot Peter, "UnitOperations of Chemical Engineering", 4th Ed., McGraw Hill,Inc., 1981.
17. Levenspiel Octave, "Chemical Reaction Engineering 2ndEd., Wiley Eastern Ltd., 1991.
18. Peters M.S., Timmerhaus K.D., "Plant Design andEconomics for Chemical Engineers", 4th Ed., McGraw Hill,1991.
19. Treybal R.E., "Mass Transfer Operations", 3rd Ed., McGrawHill Company, 1981.
20. Hesse, Herman C. and Rushton, J. Henry "ProcessEquipment Design" Affiliated East-West Press Pvt. Ltd.,New Delhi.
21. Richardson & coulson Vol 68. Operating Manual, "Ammonia Plant" of National Fertilizers ltd. Bathinda9. Elementary Principles of Chemical Processes by Felder