Study of Production of Ammonia from Natural Gas

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Abstract— Ammonia is a compound of nitrogen and hydrogen with the formula NH3. 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 the 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's, Carl Bosch, Claude and Mont Cenis. This will be the subject of study in the project along with the designing of the project and analytical evaluation.
Key words: Ammonia, Nitrogen Fixation, Catalyst

I. INTRODUCTION

Ammonia is a compound of nitrogen and hydrogen with the formula NH_3. Ammonia is a colourless gas with a characteristic pungent smell. It contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to food and fertilizers. Ammonia, either directly or indirectly, is also a building block for the synthesis of many pharmaceutical products or is used in many commercial cleaning products. Fixed nitrogen from the air is the major ingredient of fertilizers which makes intensive food production possible. During the development of inexpensive nitrogen fixation processes, many principles of chemical and high-pressure processes were clarified and the field of chemical engineering emerged. Before synthetic nitrogen fixation, wastes and manures of various types or their decomposition products, and ammonium sulphate, which is a by-product from the coking of coal, were the primary sources of agricultural nitrogen. Chilean saltpetre, saltpetre from human and animal urine, and later ammonia recovered from coke manufacture were some of the important sources of fixed nitrogen. During the first decade of the twentieth century, the worldwide demand for nitrogen-based fertilizers far exceeded the existent supply. The largest source of the chemicals necessary for fertilizer production was found in a huge guano deposit (essentially sea bird droppings) that was 220 miles in length and five feet thick, located along the coast of Chile. Scientists had long desired to solve the problem of the world's dependence on this fast disappearing natural source of ammonia and nitrogenous compounds.

II. MATERIALS & METHODS

A. Materials Used

1) Physical and Chemical Properties of Natural Gas:-

- It's a fossil fuel formed from plant and animal remains millions of years ago.
- It is a 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 537-540ºC.
- As it is a clean fuel with cleaner burning nature, natural gas has lower environmental impact when compared with other types of fuel.
  - Density – 12.251 kg/m^3
  - Boiling point - 158.24ºC/115ºK
  - Calorific value – 49311.2 kJ/kg
  - Specific volume – 0.00231m^3/kg
  - Critical temperature – 190.7ºK
  - Critical pressure – 7.500 KPA
  - Ignition point – 580
  - Flammability limits – 4-16 % (volume% in air)
  - Maximum flame velocity – 0.3m/s

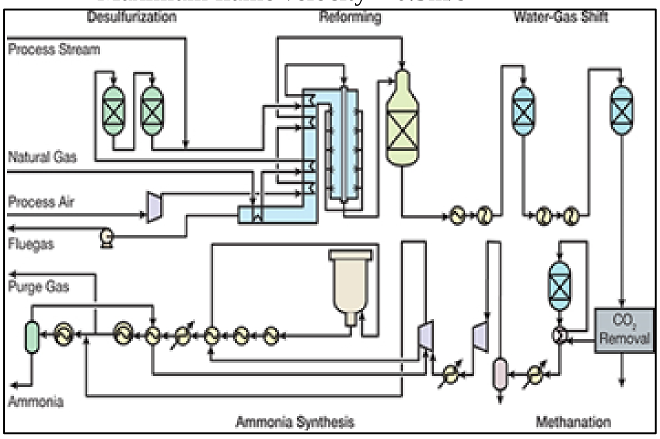

Fig. 1: Process diagram

In this 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 40 ATM.

The mixture is preheated with the recycled flue or effluent gases and fed into the furnace. At 800-850ºC in the presence of an iron catalyst promoted with other metal oxide conversion of methane takes place with the formation of CO. The residual gas is mixed with air and fed into shift converter to get complete conversion. The waste heat is utilized for the steam generation and ethanolamine which are used in CO_2 and H_2S removal. The exit gas containing poison was regenerated in the methanator at 280-350ºC which ultimately used for heating the feed water. Purified N_2 and H_2 mixture was compressed to 300atm at 320 to 380ºC 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 the reaction.

B. Desulphurization

The Primary Reforming catalyst is poisoned by sulphur and for this reason all sulphur compounds need to be removed from the incoming natural gas. Natural gas may contain 10 PPM of sulphur and may contain such “reactive” sulphur compounds as hydrogensulphide (H_2S), Mercaptan (RSH), Disulphides (R_2S_2) and cyclic sulphides etc. The converter reduces the sulphur content to < 0.05 PPM.

C. Primary Reformer

Primary Reformer contains tubes and burners with rectangular structure. It contains 4 rows having 33 tubes in each total is 132. It also contains 5 rows of 9 burners in each rows total is 45 burners between the reforming tubes harps. There are 18 Side burners and 27 center burners . Primary reformer is used to convert hydrocarbons into a mixture of CO_2, CO, H_2, N_2 & inert. The desulphurized natural gas is reacted with steam over reforming catalyst to give a gas containing hydrogen, carbon monoxide, carbon dioxide and methane. Here in plant top fired reformer is used for synthesis gas and steam formation. The desulphurized natural gas is reacted with steam over the reforming catalyst to produced a gas containing H_2, CO, CO_2, and CH_4. Here natural gas containing 98.64% of methane and at outlet 12.44% of methane at 750 degree C. Usually this carbon is removed by prolonged heating of catalyst with a mixture of Steam and air at about 750 degree C.

D. Secondary Reformer

The gas outlying the primary reformer enters the secondary reformer where the conversion of methane is continued in auto-thermal condition. The air is compressed in a motor driven centrifugal air compressor and discharge at 32.5kg/cm^2g& 180 degree C. The temperature of process air is raised in NG/PA heater. Process air is fed to secondary reformer at a pressure of 31.5kg/cm2 and temperature of 485 degree C. The heated mixture then flows through a single bed nickel oxide catalyst, the methane reacting with the excess steam with to produce further H_2, CO, CO_2.

E. Methanation

Methanation is the process in which the residual CO & CO_2 slipped from LT shift converter and CO_2 Absorber respectively are converted into METHANE. CO & CO_2 oxide Ammonia synthesis catalyst deactivate thus the gases are known as poison to referred catalyst. Methanation reaction is highly exothermic reaction. The gas from CO_2 removal section is fed to ammonia synthesis loop i.e. Decarbonated gas must have the value of CO & CO_2 less than 5 PPM. Methanation is required to bring down the tolerable level of CO & CO_2 less than 5 PPM to avoid ammonia synthesis catalyst poisoning.

F. Ammonia Synthesis

By the turn of the 19th century, complete understanding and application of the law of mass action kinetics and chemical equilibria enabled chemists to investigate the synthesis of ammonia more systematically. From the equilibrium data measured it was obvious that, at normal pressure, the reaction temperature should be kept well below 300°C in order to obtain even a small percentage of ammonia. For this temperature range, however, no catalyst was available. By increasing the pressure to 75 bar the equilibrium conditions improved, but even at this pressure, and an operating temperature of about 600°C, most known catalysts at that time led to a very low ammonia concentration. It was Haber who finally over-came his colleagues’ excessive pre-occupation with unfavourable equilibrium concentrations. Firstly, he recognized that much higher pressures had to be employed and he constructed a small laboratory apparatus for the continuous production of ammonia. Secondly, and perhaps more importantly, he developed the concept of a recycle process. The amount of ammonia formed in a single gas pass is much too small to be of interest for the economic production of ammonia. Haber, therefore, recycled his gas over the catalyst after separating the ammonia formed by condensation. The gas lost by conversion was compensated with a fresh gas input and the mixture was recycled under pressure. Synthesis gas ammonia production requires a high purity mixture of three volumes or moles of hydrogen to one volume mole of nitrogen. Hydrogen for the synthesis gas is produced by catalytically reforming natural gas with steam at high temperature. Nitrogen is supplied by injecting air at elevated temperature; the oxygen content is completely consumed by oxidising a part of the combustible in the gas stream.

G. 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 1meter 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.

H. Industrial importance and uses

1) Fertilizers: - Liquid fertilizer consists of ammonia, ammonium nitrate, urea, and aqua ammonia, also used to produce the ammonium and nitrate salts.
2) 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.
3) Petroleum industry:- Utilizes ammonia in neutralizing the acid constituents of crude oil and for the protection of the equipment from corrosion.

4) Mining industry: - Uses ammonia for the extraction of metals such as copper, nickel and molybdenum from their ores.
5) Pulp and paper industry: - Uses ammonia for pulping wood and as casein dispersant in the coating of the paper.

I. 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 1 atm conditions.
    2) Presence of chlorine higher than ammonia causes chlorine to react with ammonia and form a violently explosive compound.

J. Safety in ammonia plants

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

III. Conclusion

Ammonia is one among the largest volume inorganic chemicals in the chemical process industries and used mainly for production of fertilizers using steam reforming of natural gas. Large release of ammonia due to accidents and vessel failures etc. has decreased considerably in the last three decades. problems and failures do occurs frequently in the ammonia plant even after following the inherently safer design philosophy and risk assessment. Major areas of concerns/failures are reforming and synthesis loop causing fires and shutdowns. 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.

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