AMMONIA

Ammonia finds a very important place in the manufacturing of many materials. It has many applications such as direct use as fertilizer, in the manufacturing of fertilizers like urea, ammonium sulfate, di-ammonium phosphate, sodium nitrate, ammonium nitrate etc., and in the manufacturing of nitric acid and chemical compounds like acrylonitrile, caprolactum, nylon 6 and nylon 6/6. It is also used as refrigerant for refrigeration systems and large scale air-conditioning systems.

Ammonia, a colourless gas at atmospheric conditions is a toxic and explosive. In liquid form, it’s boiling and freezing points are respectively -33 °C and -77 °C at atmospheric pressure.

The different raw materials used for production of ammonia are Natural Gas, Naphtha, Fuel Oil, and byproducts from chemical plants like Cock Oven Gas, Refinery Gas etc. The quantity and place of byproducts like Coke Oven Gas, Refinery Gas etc. mainly depends on the production in the chemical plants. So, they are not effective to use for continuous production of ammonia. The fuel oil is heavier than natural gas and naphtha. As the molecular weight of the raw material increases, the difficulty and cost of processing in ammonia production increase. So, at present the application of fuel oil as raw material in ammonia production is negligible. The natural gas, naphtha and fuel oil are compared based on the percentages of carbon, hydrogen and sulfur present in them Table I.1.
Table 1.1 Constituent Elements of Raw Materials Available for Production of Ammonia

<table>
<thead>
<tr>
<th>Elements present in Raw Material</th>
<th>Natural Gas</th>
<th>Naphtha</th>
<th>Fuel Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>73.4 %</td>
<td>83.8 %</td>
<td>87.2 %</td>
</tr>
<tr>
<td>Hydrogen (required for Ammonia Production)</td>
<td>22.76 %</td>
<td>16.2 %</td>
<td>9.9 %</td>
</tr>
<tr>
<td>Sulfur (Impurity, To be removed)</td>
<td>3.25 %</td>
<td>5.1 %</td>
<td>8.8 %</td>
</tr>
<tr>
<td>Hydrogen to Carbon Ratio</td>
<td>0.31</td>
<td>0.19</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Generally, it is stated that the most effective and economical raw material for production of ammonia is the one with highest Hydrogen to Carbon ratio. Thus, natural gas is the most effective and economical raw material for the production of ammonia. In places where natural gas is not available, naphtha is the next best alternative for production of ammonia. Ammonia is one of the important raw materials to manufacture Urea. Most commonly the urea manufacturing plant consists of a sub chemical unit to manufacture ammonia. Ammonia production is a highly energy consuming process requiring from 35 to 50 GJ of energy per ton of ammonia production depending on the raw material used and process involved.

1.1 Manufacture of Ammonia

There are four basic processes to manufacture ammonia. They are Herber-Bosch process, coal based partial oxidation process, heavy hydrocarbon based partial oxidation process and steam reforming process.

1.1.1 Heber-Bosch process

In the original Heber-Bosch process, the hydrogen source was coke derived from coal. In this process, coke is first blasted with air and the heat liberated by the formation of carbon dioxide raises the coke to incandescence. The products combustion leaves the system by going to the atmosphere. Steam is added next to
produce water gas containing carbon dioxide, carbon monoxide, and hydrogen. The nitrogen is usually furnished by adding a sufficient quantity of the combustion products from the blasting step to the gas is converted to hydrogen and carbon dioxide by reaction with steam over a catalyst and the converted gas is stored in another gas holder, compressed and scrubbed using an ammoniac cuprous solution to remove unconverted carbon monoxide. The resultant, relatively pure gas, consisting of three parts hydrogen to one part nitrogen, is then fed as makeup gas to the synthesis loop.

I.1.2 Coal-based partial oxidation processes

Two commercially established processes utilizing coal feeds are the Lurgi process and the Koppers-Totzek process.

In the Lurgi process, coal is gasified in a fixed bed reactor using oxygen and steam at about 2000-3000 kN/m² pressure. The steam and oxygen enter the gasifier through slots in a rotary grate while the coal is charged through specially designed lock hoppers and distributed evenly over the cross section of the gasifier. Ash is removed in a non-slugging operation by the rotary grates. Gasification temperatures range from about 560 °C to 620 °C depending on the feed characteristics. Because the gasification temperature is in the intermediate range and the operating pressure is relatively high, the methane and carbon dioxide content from a typical Lurgi gasifier are 10-11% and about 28% respectively. The crude gas from the Lurgi gasifier is treated in several processing steps including waste heat recovery, shift conversion, removal of tars phenols, and other by products, Retinol treatment for carbon dioxide and sulfur removal, liquid nitrogen scrubbing to produce highly purified synthesis gases.
The Koppers-Totzek dilute phase gasification takes place at low pressure and much higher temperature essentially ensuring complete hydrocarbon conversion. A homogeneous mixture of pulverized coal, oxygen and steam reacts producing a flame zone temperature of about 1925 °C. Subsequent steam and carbon endothermic reactions reduce the temperature to around 1480 °C. Residual methane levels of 0.1% and less are realized. Depending on the reactivity of the coal, up to 99% of the carbon is gasified; the bulk of the resultant gases consist of hydrogen and carbon monoxide. The crude washing, compression, sulfur removal, shift conversion, carbon dioxide removal, nitrogen scrubbing, compression and synthesis.

I.1.3 Heavy Hydrocarbon-based Partial Oxidation processes

Two major partial oxidation processes are commercially available, the Shell process and the Texaco process. Operating conditions in the gas generator vary from 1200 °C to 1370 °C and from 3100 kN/m² to 8270 kN/m².

Preheated hydrogen feed and oxygen are mixed with steam and fed to the combustion chamber of the reactor. A non-catalytic flame reaction produces the raw synthesis gas. The hot reactor effluent is cooled by generating high pressure steam is specially designed waste heat boilers. In spite of the presence of free carbon in the gas, the design ensures that heat transfer surfaces remain clean even after prolonged operation. The raw synthesis gas is then routed to the carbon removal system, consisting of a carbon catcher and gas cooler scrubber, where the carbon produced in the reactor is removed as water slurry. The carbon is transferred to the oil from carbon oil pellets in a device called a palletizer. The resultant pellets are re-slurred with oil feed in a homogenizer and recycled as dilute slurry to the reactor.
Preheated hydrogen feed along with oxygen and steam are fed to the reactor using a hot water steam from the scrubber. The water quenches cools the resultant mix tire is regenerated in the naphtha stripper. From the stripper overheads, naphtha stripper containing carbon is recycled to the reactor. The water from naphtha separator, after degassing, is routed back to the scrubber and the clean raw synthesis gas is available for further processing.

1.1.4 Steam Reforming Process

At present 75-80 % of ammonia produced in the world is produced from steam reforming operations and approximately 65-70 % of these use natural gas as feed. The feedstock, ranging from natural gas to naphtha, is first de-sulfurized, mixed with steam and reformed in the primary reformer. The remaining carbon dioxide and carbon monoxide are removed by reaction of hydrogen to produce methane and water in a methanation step. The synthesis gas is then compressed and ammonia is produced.

Advantages:

Ammonia production using steam reforming process has the following advantages:

(i) The steam reforming process generates more hydrogen than partial oxidation process.

(ii) Steam reforming process requires less feed than partial oxidation process.

(iii) Production of ammonia from coal plants is more costly than conventional gas based processes, because of the extensive solid handling and effluent treatment facilities required and

(iv) Steam reforming process generates less pollution than other processes.