Fertilizers Industry

Chemical fertilizers are a class of substances which are added to the soil to make up and to provide the elements necessary for the growth of plants. These may include naturally occurring inorganic or organic substances or such substances prepared synthetically. These are in a way considered superior to the natural manures like decayed animal wastes and leaf and plant manures which cannot supply the various elements in correct and suitably adjusted proportions according to the needs of the plants.

Besides carbon, hydrogen and oxygen which the plants take from air and water, the other major requirements of growing plants are *nitrogen, phosphorus* and *potassium.*

These elements are required by the plants for their normal growth, proper maintenance and high yield of produce, in bulk because they are not only the constituents of plants enzymes, co-enzymes, hormones or activators but also make the very plant roots, stem, leaves, fruits, vegetables, grains, seeds etc. In addition to N, P and K, plants need a number of elements for their proper growth and maintenance. in very small quantities which act as activators for enzymes, e.g., Mn, Mg, Co, Zn, Cu, Fe etc. These are called *trace elements.* Their deficiency in the soil normally does not take place and are, therefore, not required to be regularly added to the soil except certain areas or region which may be deficient in one or more of these elements.

Besides the above mentioned elements, there are some elements and compounds such as gypsum which make the availability of fertilizers to the plants easier. These substances are known as *stimulants.*

Role of Fertilizers in Agriculture

Plants need the various 'substances such as water, nitrogen compound phosphorus compounds, potassium compounds etc., all in fair quantities, for their proper growth and maintenance. Iron, lime, magnesium and sulphur compounds are also required in small quantities. These substances stimulate the processes of metabolism in the plant cells, growth of plants and specially its fruits, increase the content of valuable materials (e.g. starch, proteins etc.) and increase resistance to frost, draught and various diseases. By consuming these elements, the soil becomes exhausted. Each year fertilizers (or manures), which are chemical substances serving as food materials to the soil, are added to the soil to replenish the loss suffered by it oil account of growth of plants. The plants, so essential to our life, require food for nourishment. All these plant foods are supplied by nature. Plants draw their requirement from the soil by means of their roots.

Application of fertilizers to the soils increases the fertility of the soils – hence plants products have to be sustained on normal land by replenishing and can be increased above normal level by applying larger amounts of fertilizers. Fertilizers also help to maintain the pH of the soil near 7 to 8 which is optimal for plant health and growth.

Today the increase of food production has become essential on account of the enormous growth of population. This is a problem of every country and the challenge of increased production is being met by larger and larger production of fertilizers.

Classification of Fertilizers

Fertilizers are classified according to the nature of the elements like P and K, they provide to the soil. This classification gives the following types of fertilizers;

(1) **Nitrogen Fertilizers.** These fertilizers mainly supply nitrogen to the plants of soil. Ammonium sulphate, calcium ammonium nitrate, urea etc. are the example of nitrogenous fertilizers.

(2) **Phosphate Fertilizers.** These fertilizers provide phosphorus to the soil Superphosphate of lime, triple superphosphate and phosphate slag are the examples of phosphate fertilizers.

(3) **Potash Fertilizers.** These fertilizers supply potassium to the plants. KCl, KNO_3), K_2SO_4 etc. are the important examples.

(4) **NP Fertilizers.** These fertilizers contain two elements namely nitrogen and phosphorus. These are obtained by mixing together nitrogenous and phosphate fertilizers in suitable proportions. Examples of NP fertilizers are: dihydrogen ammoniated phosphate, $NH_4H_2PO_4$, calcium superphosphate nitrate, $Ca(H_2PO_4)_2.2Ca(NO_3)_2$

(5) **Complete Fertilizers.** These fertilizers supply all the three essential elements namely nitrogen, phosphorus and potassium to the soil and are produced by mixing nitrogenous, phosphate and potash fertilizers in suitable proportions. It is observed that these fertilizers produce much better results. These are also known as mixed fertilizers or NPK fertilizers.

Here we shall discuss only nitrogenous and phosphate fertilizers.

Nitrogenous Fertilizers

These fertilizers mainly supply nitrogen to the plants or soils. Most of them are synthetic products and nitrogen is present in the fertilizers either as NO_3^- ion or amide or NH_4^+ ion. All the nitrogenous fertilizers are soluble in water and are readily available to plants.

Composition of Nitrogenous Fertilizers;

Typical nitrogenous fertilizers are:

1. Ammonia	82% N
2. Urea	46% N
3. Ammonium nitrate	33% N
4. Ammonium sulphate	21 % N
5. Ammonium chloride	26% N
6. Ammonium sulphur nitrate	26% N
7. Calcium ammonium nitrate	26% N
8. Mono-ammonium phosphate	11 % N
9. Diammonium phosphate	16% N
10.Nitrophosphate	20% N

Ammonia

Ammonia usually exists as a colourless gas but may be preserved as a colourless liquid or ice like solid. It can be obtained by either of the following methods,

(i) **From ammonium salts.** Ammonia is prepared in the laboratory by heating an ammonium salt with a base. .

$$2NH_4^+ + OH \longrightarrow 2NH_3 + H_2O$$

$$2NH_4^+ + CaO \longrightarrow Ca^{2+} + 2NH_3 + H_2O$$

(ii) **From ammonical liquor.** Coal contains about 1.5 percent of decayed nitrogen of ancient vegetables and when coal is carbonized, ammonia passes along with the coal gas in form of its compounds with H_2S, HCN, HCl, H_2S0_4 etc. and comes in the ammonical liquor. When this liquor is heated with lime in a current of steam, some of the ammonium salts are decomposed by the action -of heat alone and the rest under the influence of lime to give out ammonia gas.

$$NH_4HS \rightleftharpoons NH_3 + H_2S$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$$

(jii) From air. The nitrogen obtained from air is converted to ammonia by the Haber's process or the Cyanamide process.

(a) Haber's Process (Cyanamide Process)

Most of the commercial ammonia is now prepared 'by fixing atmospheric nitrogen. When nitrogen and hydrogen are passed over an iron catalyst at 500°C under a pressure of about 200 atm; ammonia is formed.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \triangle H = 46\ kcal/mole^{-1}$$

In the actual process the required hydrogen is obtained from water gas and nitrogen from the fractional distillation of liquid air. The mixture of nitrogen and hydrogen (1:3 by volume) is also obtained from an appropriate mixture of water gas and producer gas by blowing steam and air over hot coke alternately. Steam is added to this mixture and the whole is passed over heated iron, oxide at 500°C and 20-30 atmospheric pressure, carbon monoxide being converted to carbon dioxide.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

CO_2 is removed by water under pressure and residual CO by ammonical sodium formate (at 250 atm) or by ammonical cuprous chloride. By suitable adjustment of the process, a mixture of nitrogen and hydrogen in the required proportion' of 1:3 is obtained.

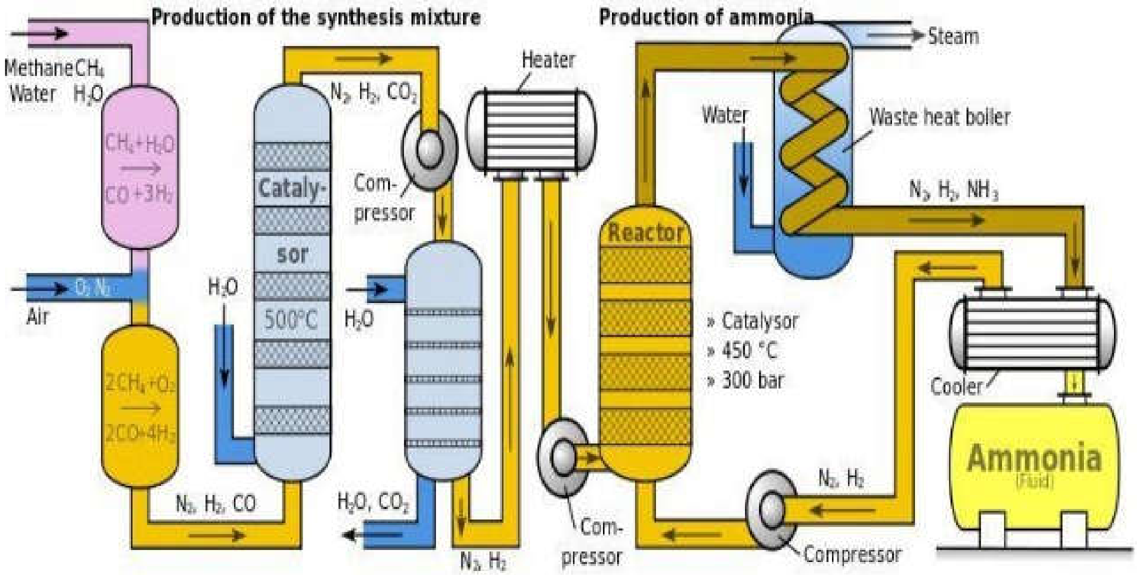

Fig 1. Haber's process for the synthesis of ammonia

The gas mixture is compressed and then passed into the catalytic chamber which consists of a steel tower containing thin walled steel tubes packed with the catalyst (Fig. 1). The incoming gases pass up in between these tubes so as to get heated and then enter down through them. The temperature of the catalytic tubes is maintained at 500°C by' heating-them electrically. The issuing gas containing about 10 per cent ammonia is cooled and liquid ammonia condenses. The unconverted nitrogen and hydrogen are returned to the inlet and passed again over the catalyst. According to *Le-Chatelier's principle*, the most favorable conditions for the synthesis of ammonia are:

- High pressure due to decrease in volume (200 atm).
- Low temperature due to exothermic nature of the reaction. (500-600ºC in the presence of suitable catalyst).

(b) Cyanamide Process

In this process the air is passed or calcium carbide heated to about 800°C when nitrogen combines to form calcium cyanamide;

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

Properties and Uses

Ammonia is a colourless gas with characteristic smell. It can be liquefied in a bath maintained at -40°C). The liquid boils at -33.2°C. Liquid ammonia resembles water in its physical behavior, being highly associated because of the polar nature and strong H-bonding. Ammonia is utilized for;

(i) manufacture of urea
(ii) manufacture of ammonium sulphate
(iii) manufacture of ammonium nitrate, and
(iv) oxidation to nitric acid

2. Urea

Urea (carbamide) is a high quality nitrogenous fertilizer with 46.6% nitrogen contents. It is also used as a nitrogen containing admixture to animal feed. It is synthesized from ammonia (NH_3) and carbon dioxide (CO_2). The manufacturing process consists of the following steps:

(i) Production of NH_3
(ii) Production of CO_2
(iii) Chemical reaction between NH_3 and CO_2
(iv) Distillation and processing to end product.

(i) Production of NH_3

(a) Haber's Process.

N_2 is obtained from air by burning any combustible material which utilizes O_2 leaving N_2 or by liquefaction of air. H_2 gas is obtained by cracking of natural gas or by heating the natural gas with steam in the presence of Ni as catalyst.

$$(N_2 + O_2) \text{ air} + C \longrightarrow CO_2 + N_2$$

$$CH_4 \longrightarrow C + 2H_2$$

$$CH_4 + 2H_2O \xrightarrow{Ni} CO_2 + 4H_2$$

CO_2 is obtained as a bye product which is used in the manufacture of urea. N_2 and H_2 gases obtained from above methods are mixed in the ratio 1:3 heated to optimal temperature 450-500°C and pressure 200 atm. in the presence of $Fe_2 0_3$ – Al_2O_3 as catalyst.

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

(b) From Coal

When coal is heated in closed retorts to red heat (1000°C) in the absence of air or O_2, it produces coal gas, coal tar and coke as major fractions. Ammonium salts such as $(NH_4)_2CO_3$, $(NH_4)_2S$, $(NH_4)HS$, NH_4CN, $(NH_4)_2SO_4$ and NH_4Cl present in ammonical liquor, are obtained as byproducts, which on heating or treatment with lime produce NH_3 gas.

$$NH_4HS \xrightarrow{\triangle} NH_3 + H_2S$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O$$

(c) Production of CO_2

Carbon dioxide is obtained by igniting C obtained from natural gas.

$$C + O_2 \longrightarrow CO_2$$

(d) Reaction between NH_3 and CO_2

NH_3 and CO_2 obtained are reacted with each other in reaction tower as under;

$$CO_2 + 2NH_3 \rightleftharpoons NH_2COONH_4$$

Ammonium carbamate

On dehydration, ammonium carbamate produces liquid urea.

$$NH_2COONH_4 \xrightarrow{\triangle} NH_2COONH_2 + H_2O$$

Urea

The conversion ratio increases with temperature.

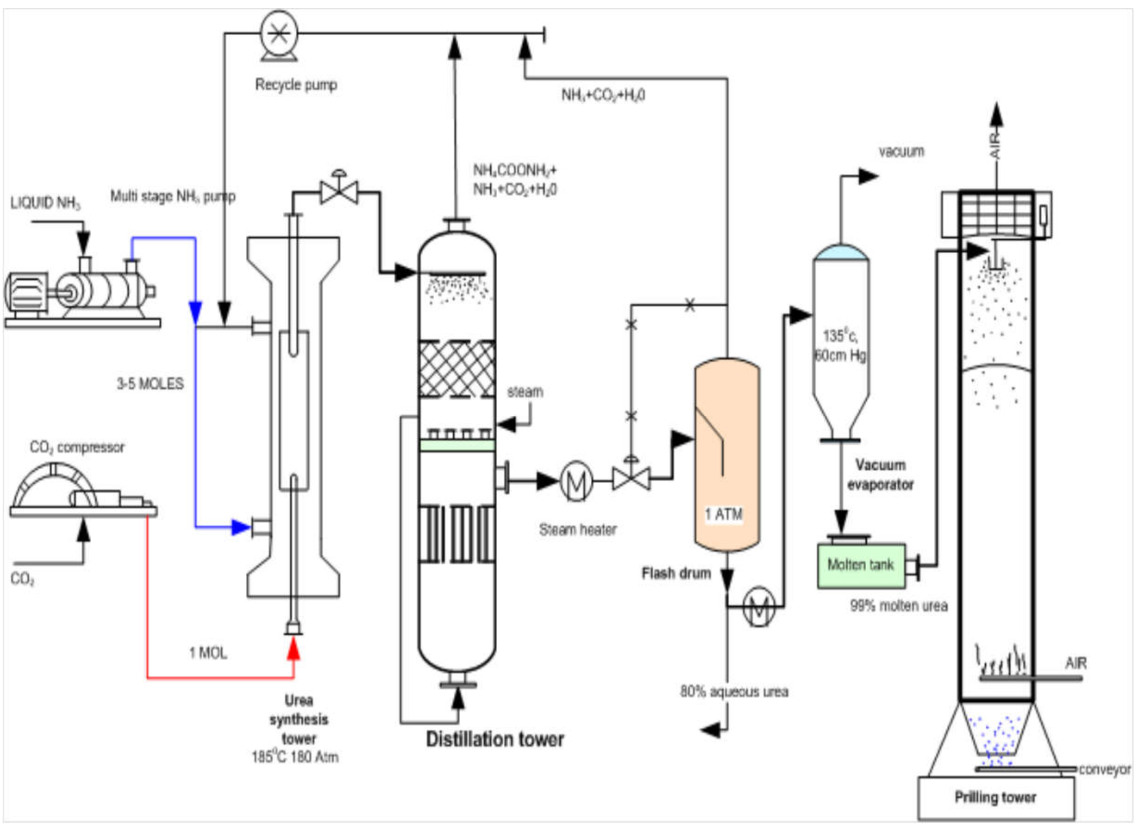

Fig 2. Flow sheet diagram for Urea manufacture

(iv) Processing to end product

According to Solvay process, 1 part compressed CO_2 is reacted with 2 parts liquid NH_3 at 180°C and 200 atm pressure. The reaction between

NH_3 and CO_2 results in a liquid mass known as ammonium carbamate. Dehydration of the carbamate takes place in tower made of alloy steel. This results in the formation of liquid urea. The conversion ratio increases with temperature. Since urea formed is in liquid state, hence high pressure is needed. The urea solution is concentrated in an evaporator and the urea is produced in the form of crystals or it is granulated in prilling tower, where concentrated solution is allowed to fall from the top of a high tower while a hot blast of air is blown in a counter current way. This evaporates excess water and urea. granules also called "prills" about 1116 to 118 inches in diameter fall at the bottom where they are packed.

Uses of Urea

Urea has the highest nitrogen content equal to 46.6%. This percentage of nitrogen is much higher than any other fertilizer. It does not change the pH of the soil and can be used to all types of soils and crops, since after its assimilation by plants through the interaction of nitrifying bacteria, it leaves behind only CO_2 in the soil.

$$NH_2COONH_2 + 3H_2O \longrightarrow CO_2 + 2NH_3$$

Ammonia is then converted to nitrates by oxidation.