

Study on the Production of Urea by Snam Ammonia Stripping Process and Stami Carbon Dioxide Stripping Process

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Abstract— Urea is the most convenient form for fixed nitrogen. Urea has the highest nitrogen content available in a solid fertilizer (46 %) [NFL-Guna (M.P),Plant data]. It is easy to produce as prills or granules and easily transported in bulk or bags with no explosive hazard. It leaves no salt residue after use on crops. Its specific gravity is 1.335[Dryden's Outlines of chemical technology, 3rd-edition.New Delhi:Affiliated East west press private Limited,2004], decomposes on boiling point and is fairly soluble in water. The principal raw materials required for this purpose are NH₃ & CO₂.Two reactions are involved in the formation of urea. In first step carbon dioxide and ammonia is reacted at high pressure to form ammonia carbamate. This reaction is highly exothermic [Pozin M E. Fertilizer Manufacture. Moscow: Khimia, 1974].



In the second step decomposition of ammonia carbamate has been taken place and this reaction is endothermic in nature.



Keywords: Urea, Snam Ammonia Stripping Process and Stami Carbon Dioxide Stripping Process, Biuret

I. INTRODUCTION

Fertilizer is generally defined as any organic or inorganic, natural or synthetic material, which supplies one or more of the chemical elements required for the plant growth". The aim of the fertilizer industry is to provide the primary and secondary nutrients for plant growth. Primary nutrients are normally supplied through chemical fertilizers. They are chemical compounds containing one or more of the primary nutrients and are generally produced by chemical reactions. The primary nutrients are Nitrogen, Phosphorus and Potassium. However, their concentration in a chemical fertilizer is expressed as a percentage of total nitrogen (N), available phosphate (P₂O₅) and soluble K₂O. If a nutrient is missing in a fertilizer, it is represented by a zero. For Ex. ammonium sulphate is represented by 20.6-0-0.

Urea is an important nitrogenous fertilizer. Its utilization is increasing steadily, it being the preferred nitrogen fertilizer worldwide. It is used in solid fertilizer, liquid fertilizer, formaldehyde resins and adhesives. Rouelle first discovered urea in urine in 1773. His discovery was followed by the synthesis of urea from ammonia and cyanic acid by Woehler in 1828. This is considered to be the first synthesis of an organic compound from an inorganic compound. In 1870, Bassarow produced urea by heating ammonium carbamate in a sealed tube that is dehydration. The chemical formula of, NH₂CONH₂, indicates that urea can be considered to be the amide of carbonic acid NH₂COOH, or the diamide of carbonic acid CO(OH)₂.

II. PROCESS

Ammonia & CO₂ are compressed separately and fed to the high pressure (180 atms) autoclave. The autoclave must be water cooled due to the highly exothermic nature of the reaction. A mixture of urea, ammonium carbamate, H₂O and unreacted (NH₃+CO₂) is produced. After reaction liquid effluent is let down to 27 atms and fed to a special flash-evaporator containing a gas-liquid separator and condenser. Unreacted NH₃, CO₂ & H₂O are thus removed & recycled. An aqueous solution of carbamate-urea is passed to the atmospheric flash drum where further decomposition of carbamate takes place. The off gases from this step can either be recycled or sent to NH₃ processes for making chemical fertilizer. The 80 % aqueous urea solution can be used as it is, or sent to a vacuum evaporator to obtain molten urea containing less than 1 % water. The molten mass is then sprayed into a prilling tower. To avoid formation of biuret and keep it less than 1 % and the temperature must be kept just above the melting point of urea for processing times of 1-2 seconds. Here we discussed two processes for the manufacture of urea are[Shreeve R N. Chemical process industries,3rd edition. New York : McGraw Hill book company,1967) :

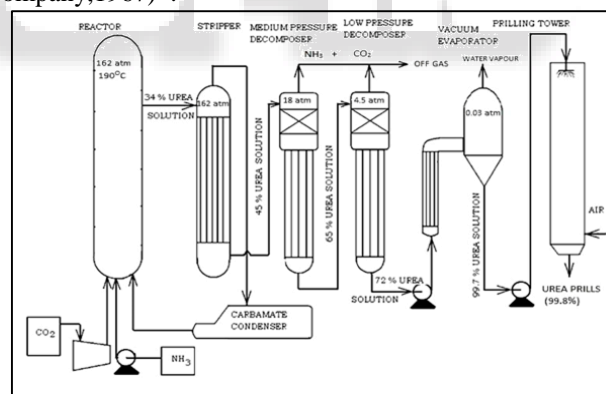


Fig. 1: Snamprogetti process for manufacture of urea

A. Snam Progetti (Italy):

This process is based on the principle of the internal carbamate recycle technique and is commonly called the Snam ammonia stripping process. The basic difference between the Snam process & the conventional carbamate solution recycle urea processes is that in this case the unconverted carbamate is stripped and recovered from the urea synthesis reactor effluent solution at reactor pressure, condensed to an aqueous solution in a steam producing high pressure condenser, & recycle back to the reactor by gravity. A part of the liquid NH₃ reactor feed, vaporized in a steam heated exchanger, which is used as inert gas to decompose & strip ammonium carbamate in the steam heated high pressure stripper. The reactor operates at about 130 atm & 180-190 °C.

The stripper operates at about 130 atm & 190°C. The stripper off-gas is condensed in a vertical shell & tube condenser, operating at about 130 atm & 148-160°C. Low pressure steam is produced in the high pressure carbamate condenser. The product urea solution, which is leaving from the stripper & still containing 2-3 % of residual unreacted carbamate, is further degassed in a low pressure decomposition-absorption system. The recovered ammonical solution of ammonium carbamate is pumped back to the reactor [Brownell L E & young E H. Process Equipment Design. New York: John Wiley & Sons, 1968].

1) Reactions

As the formation of urea from ammonia & carbon dioxide takes place through reversible reactions with formation of ammonium carbamate as intermediate product. So, economy of any urea manufacturing process depends on how we recycle carbamate to the reactor. In Snamprogetti process of urea manufacturing accomplishes the recycle of carbamate by stripping process.

Recycle of carbamate



As the reaction is reversible, the decomposition of ammonium carbamate involves increase in volume & absorption of heat. Thus this reaction will be favored by decrease in pressure & increase in temperature. Moreover, decreasing the partial pressure of either of the products will also favor the forward reaction. The process based on first principle of decrease in pressure & decrease in temp is called conventional process, whereas the process based on increase/decrease of partial pressures of NH₃ or CO₂ is called stripping process. The equilibrium rate constant can be correlated by partial pressure of ammonia and carbon dioxide by the following reaction [Joshi M V. Process Equipment Design, 3rd edition. New delhi: Mcmillan India Limited, 2001].

$$K = (p_{\text{NH}_3})^2 \cdot (p_{\text{CO}_2}),$$

where K is equilibrium constant

The stripping process depends on stripping agent CO₂ or NH₃ as stripping agent. If CO₂ is selected, it is to be supplied to the decomposers/stripper as in Stamicarbon CO₂ stripping process. While if NH₃ is selected, it is to be obtained from the system itself because excess NH₃ is present in the reactor as in Snam's process. CO₂ stripping is advantageous because introducing CO₂ increase in partial pressure of carbon dioxide (p_{CO₂}). So partial pressure of ammonia p_{NH₃} will be reduced to maintain total pressure constant as P = p_{CO₂} + p_{NH₃}.

At a particular temp. equilibrium constant (K) is constant. So when partial pressure of ammonia p_{NH₃} is reduced to keep K constant, carbamate will be reduced much faster by decomposition as p_{NH₃} appears in the equilibrium equation with a power of two. Selection of 1st stage decomposition should be being such a way that minimum water evaporates because the recovered gases go along with the carbamate to reactor again & if water enters reactor, production will be affected adversely due to hydrolysis of urea. So, stage wise decomposition of carbamate is done. Second consideration in favor of isobaric stripping is that higher carbamate recycle pressure results in condensation at higher temp & that recovery in the form of low pressure steam.

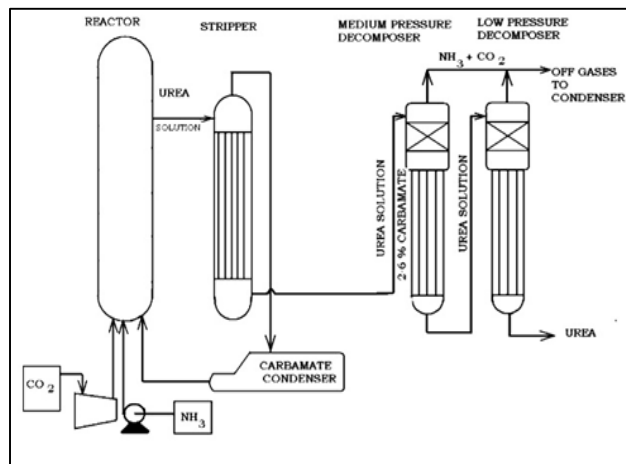


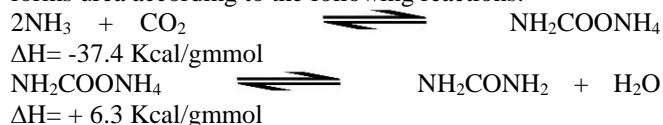
Fig. 2: Stamicarbon process

B. Stamicarbon (Holland):

The novelty of the CO₂ stripping process consists of the fact that the reactor effluent is not let down to a lower pressure as in the conventional liquid recycle urea process, but is stripped at synthesis pressure by the gaseous CO₂ reactor feed stream in a steam heated vertical heat exchanger. The high pressure stripper operates at about 140 atm & 190°C. The stripped urea solution still contains about 15 % of the unconverted carbamate, & it is let down to about 3 atm for further degassing in the steam heated low pressure decomposer at about 120°C. The off gas recovered is condensed with cooling water in the low pressure condenser, operating at about 65°C & 3 atm. The solution thus obtained is pumped to the high pressure condenser by means of high pressure carbamate pump. The off gas recovered from the high pressure stripper is condensed in the high pressure condenser, which operates at about 170°C & 140 atm. The heat of condensation is removed on the shell side of the condenser by vaporizing the equivalent amount of condensate. The 3.4 atm steam thus produced can be reused in another section of the plant. The mixture of gas & liquid generated from the high pressure condenser is fed to the reactor for total CO₂ condensation to carbamate & subsequent conversion to urea. The inerts are vented from the reactor through a water cooled vent condenser. The reactor effluent, at about 185°C & 140 atm, is fed to the high pressure stripper as described above.

1) Reactions

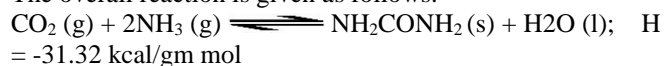
In the reactor, when liquid ammonia reacts with compressed Carbon dioxide (at 162 atm) at high temperature & pressure forms urea according to the following reactions:



The reactions are reversible in nature only partial conversion occurs in the reactor. Urea solution consisting of Urea, Carbamate, Water & unconverted CO₂ & NH₃ are fed into the stripper where stripping action of NH₃ favors decomposition of carbamate, and hence 80% of carbamate is decomposed here. Pressure in the stripper is same as that of the reactor. Urea solution from the stripper is sent to Medium pressure decomposer where Urea purification takes place by the dehydration of the Carbamate. Urea solution is further purified in Low pressure decomposer. Off gases from the

Medium Pressure decomposer & Low Pressure decomposer are sent to the Medium pressure condenser & Medium pressure absorber for the recovery of unconverted Ammonia. In this way 71.12% of Urea solution resulting from Low Pressure decomposer is sent to Vacuum concentrators operating in two stages i.e. 1st Vacuum evaporator and 2nd Vacuum evaporator. Finally, 98 % molten urea is sent to the Prilling Towers where Urea prills are formed by passing a current of cold air from the bottom in the tower. Proper size Urea prills are sent to bagging section through belt conveyors. In bagging section, coating of Urea prills may be done. Oversized Urea prills or lumps are sent to lump dissolving tank.

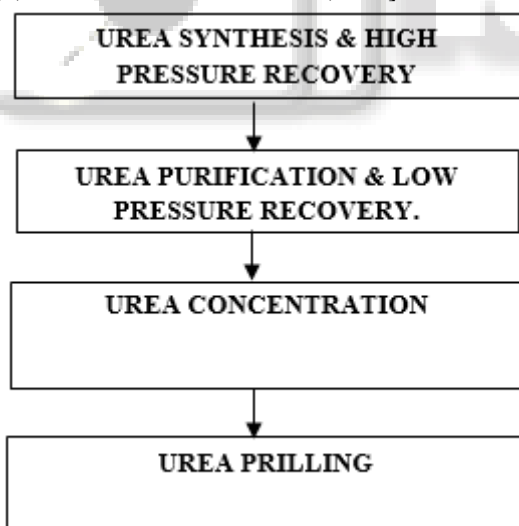
The overall reaction is given as follows: -



As the reactions shows the releasing heat of 31.32 kcal/gm mol at standard conditions of 1 atm pressure & 25°C which means the reaction is exothermic. But in actual situation in plant heat available in a urea synthesis reaction will be only 5.74 kcal/gm mol as a lot of the heat lost in evaporation of liquid NH₃, evaporation of water & melting of urea and some energy is also consumed in feeding CO₂ & NH₃ at high temperature & pressure, in recycling of carbamate, in vacuum concentration of urea, for operating different pumps & compressors etc. which altogether makes the urea production energy consuming.

III. DISCUSSION

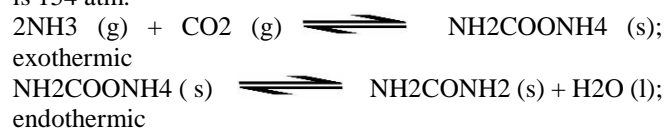
The urea production process takes place through the following steps [Bhattacharyya B C. Chemical Equipment Design, 1st edition. New Delhi: CBS, 2003] :



A. Urea Synthesis & High Pressure Recovery

Urea is synthesized from liquid ammonia & gaseous carbon-di-oxide. The carbon dioxide drawn from battery limits at about 1.6 atm pressure & about 40°C temp is compressed in a centrifugal compressor up to 162 atm. A small quantity of air is added to the CO₂ compressor suction in order to passivate the stainless steel surfaces. Thus protecting them from corrosion due both to the reagent & the reaction product. The liquid ammonia coming directly from battery limits is collected in the ammonia receiver tank from where it is drawn

to & compressed at about 23 atm pressure by means of centrifugal pump. Part of this ammonia is sent to medium pressure absorber & remaining part enters the high pressure synthesis loop. The NH₃ of this synthesis loop is compressed to a pressure of about 240 ata. Before entering the reactor, it is used as a riving fluid in the carbamate ejector, where the carbamate coming from carbamate separator is compressed up to synthesis pressure. The liquid mixture of ammonia & carbamate enters the reactor where it reacts with compressed CO₂. In the reactor the NH₃ & gaseous CO₂ react to form ammonium Carbamate, a portion of which dehydrates to form urea & water. The fraction of carbamate that dehydrates is determined by the ratios of various reactants, operating temp, the residence time in the reactor & reaction pressure. The mole ratio of NH₃ / CO₂ is around 2:1, the mole ratio of water to CO₂ is around 0.67: 1, temperature is 190°C and pressure is 154 atm.



The 1st reaction occurs rapidly & is completed. The 2nd reaction occurs slowly & determines the reactor volume. Urea reactor is a plug flow type with 10 no's of sieve trays to avoid back mixing & to avoid escape of gaseous CO₂ which must react in the lower part of the reactor. Stage wise decomposition is carried out to reduce water carry over to the reactor which could adversely affect conversion.

Urea solution containing urea, carbamate, H₂O & unconverted CO₂ & NH₃ enters the high pressure stripper where the pressure is same as that of the reactor. The mixture is heated as it flows down the falling film exchangers. The CO₂ content of the solution is reduced by the stripping action of NH₃ as it boils out of the solution. The carbamate decomposition heat is supplied by 24 ata steam. The overhead gases from stripper and the recovered solution from the MP absorber, all flow to the high pressure carbamate condenser through mixer, where total mixture, except for a few inerts is condensed & recycled to the reactor by means of carbamate ejector. Condensing the gases at high temp & pressure permits the recovery of condensation heat in the production of steam at 4.5 ata in the high pressure carbamate condenser. From the top of the carbamate separator the incondensable gases come out consisting of inerts & a little quantity of NH₃ & CO₂ unreacted in the condenser. These are sent to the bottom of Medium Pressure decomposer.

B. Urea Purification & Low Pressure Recovery

Urea purification takes place in two stages at decreasing pressure as follows: 1st stage at 18 atm pressure, i.e, Medium Pressure decomposer 2nd stage at 4.5 atm pressure, i.e, Low Pressure decomposer Medium Pressure decomposer is falling film type. It is divided into 2 parts: Top separator, where the released flash gases, the solution enters the tube bundle & decomposition section where the residual carbamate is decomposed & required heat is supplied by means of 24atm steam condensate flowing out of the stripper. In decomposing section where the solution leaving the bottom of MP decomposer is expanded at 4.5 atm pressure & enters the Low Pressure decomposer. This is again divided in to two parts: top separator where the released flash gases are removed

before the solution enters the tube bundle. Decomposition section where the last residual carbamate is decomposed & the required heat is supplied by means of steam saturated at 4.5 atm.

C. Urea Concentration

After purification our objective is to reduce water content of urea to as low as 1 %. For the purpose a vacuum concentrator in two stages is provided. The solution leaving the Low Pressure decomposer bottom with about 72% urea is sent to the 1st vacuum concentrator operating at a pressure of 0.23 atm. The mixed phase coming out enters the gas liquid separator, wherefrom the vapors are extracted by the 1st vacuum system, while the solution enters the 2nd vacuum concentrator operating at a pressure of 0.03 atm. The two concentrators are fed by saturated steam at 4.5 atm. The mixed phase coming out enters the gas liquid separator, wherefrom the vapors are extracted by the 2nd vacuum system.

D. Urea Prilling

Molten urea leaving the 2nd vacuum separator is sent to the prilling bucket by centrifugal pump. The urea coming out of the bucket in the form of drops fall along the prilling tower & encounters a cold air flow which causes its solidification. The solid prills falling to the bottom of the prilling tower are sent through the screeners to retain lumps only, & then to belt conveyor which carries the product to the automatic weighing machine & to the urea storage sections. Urea lumps by the means of belt conveyor are recycled to the underground tank, where they are dissolved further.

IV. CONCLUSION

The Variables that effect the reactions are temperature, pressure, concentration, residence time and biuret formation.

A. Temperature

Process temperature is 185°C favors equilibrium yield at pressure of 180 atm. The conversion of ammonia to urea gradually increase as the temperature increase. However, after a particular temperature, depending pressure, the conversion suddenly drops with further increase in temperature. The pressure corresponding to this temperature (175-185 °C), is known as the decomposition pressure which is about 180 atm.

B. Pressure

The reaction is sufficiently slow at atmospheric pressure. However, it starts almost instantaneously at pressure of 100 atm. and temperature of 150°C. There is reduction in volume in the overall reaction and so high pressure favors the forward reaction. This pressure is selected according to the temperature to be maintained & NH₃: CO₂ ratio.

C. Concentration

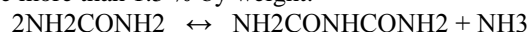
Higher the concentration of the reactants, higher will be the forward reaction according to the law of mass action. CO₂ being the limiting reagent higher NH₃: CO₂ ratio favors high conversion. Since, dehydration of carbamate results in urea production, so lesser H₂O: CO₂ ratio maintained for high conversion. Water intake to the reactor should be minimum.

D. Residence time

Since, urea reaction is slow and takes about 20 minutes' residence time to attain equilibrium, sufficient time is to be provided to get higher conversion.

E. Biuret formation

A problem faced during manufacture of urea is the formation of biuret. It is not a desirable substance because it adversely affects the growth of some plants. Its content in urea should not be more than 1.5 % by weight.



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