Lecture 15
Urea – Part 2

The urea production processes are continued below:

Ammonia stripping process

NH3 and CO2 are converted to urea via ammonium carbamate at a pressure of 150bar and a temperature of 180°C. A molar ratio of 3.5 is used in the reactor giving a CO2 conversion of 65%. The reactor effluent enters the stripper where a large part of the unconverted carbamate is decomposed by the stripping action of the excess NH3. Residual carbamate and CO2 are recovered downstream of the stripper in two successive stages operating at 17 and 3.5bar respectively. NH3 and CO2 vapours from the stripper top are mixed with the recovered carbamate solution from the High Pressure (HP)/Low Pressure (LP) sections, condensed in the HP carbamate condenser and fed to the reactor. The heat of condensation is used to produce LP steam. The urea solution leaving the LP decomposition stage is concentrated in the evaporation section to a urea melt.
Figure 2 – Block Diagram of a Total Recycle NH3 Stripping Urea Process
Advanced cost & energy saving (ACES) process

In this process the synthesis section operates at 175bar with an NH3/CO2 molar ratio of 4 and a temperature of 185 to 190°C. The reactor effluent is stripped at essentially reactor pressure using CO2 as the stripping agent. The overhead gas mixture from the stripper is fed to two carbamate condensers in parallel where the gases are condensed and recycled under gravity to the reactor along with absorbent solutions from the HP scrubber and absorber. The heat generated in the first carbamate condenser is used to generate 5bar steam and the heat formed in the second condenser is used to heat the solution leaving the stripper bottom after pressure reduction. The inerts in the synthesis section are purged to the scrubber from the reactor top for recovery and recycle of NH3 and CO2. The urea solution leaving the bottom of the stripper is further purified in HP and LP decomposer operating at approx. 17.5bar and 2.5bar respectively. The separated NH3 and CO2 are recovered to the synthesis via HP and LP absorbers. The aqueous urea solution is first concentrated to 88.7%wt in a vacuum concentrator and then to the required concentration for prilling or granulating.

Isobaric double recycle (IDR) process

In this process the urea synthesis takes place at 180-200bar and 185-190°C. The NH3/CO2 ratio is approximately 3.5-4, giving about 70% CO2 conversion per pass. Most of the unconverted material in the urea solution leaving the reactor is separated by heating and stripping at synthesis pressure using two strippers, heated by 25bar steam, arranged in series. In the first stripper, carbamate is decomposed/stripped by ammonia and the remaining ammonia is removed in the second stripper using carbon dioxide as stripping agent. Whereas all the carbon dioxide is fed to the plant through the second stripper, only 40% of the ammonia is fed to the first stripper. The remainder goes directly to the reactor for temperature control. The ammonia-rich vapours from the first stripper are fed directly to the urea reactor. The carbon dioxide-rich vapours from the second stripper are recycled to the reactor via the carbamate condenser, irrigated with carbamate solution recycled from the lower-pressure section of the plant.
The heat of condensation is recovered as 7bar steam which is used down-stream in the process. Urea solution leaving the IDR loop contains unconverted ammonia, carbon dioxide and carbamate. These residuals are decomposed and vaporised in two successive distillers, heated with low pressure recovered steam. After this, the vapours are condensed to carbamate solution and recycled to the synthesis loop. The urea solution leaving the LP decomposition for further concentration, is fed to two vacuum evaporators in series, producing the urea melt for prilling and granulation.

**Process Water Sources and Quantities**

A 1,000t.d-1 urea plant generates on average approximately 500m3.d-1 process water containing 6% NH3, 4% CO2 and 1.0% urea (by weight). The principal source of this water is the synthesis reaction where 0.3tonnes of water is formed per tonne of urea e.g.

\[ 2\text{NH}_3 + \text{CO}_2 \rightarrow \text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} \]

The other sources of water are ejector steam, flush and seal water and steam used in the waste water treatment plant.

The principal sources of urea, NH3 and CO2 in the process water are:

- Evaporator condensate

The NH3 and urea in the evaporator condensate are attributable to:

- The presence of NH3 in the urea solution feed to the evaporator
- The formation of biuret and the hydrolysis of urea in the evaporators, both reactions liberating NH3

\[ 2\text{CO(NH}_2\text{)}_2 \rightarrow \text{H}_2\text{NCONHCONH}_2 + \text{NH}_3 \]

\[ \text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2 \]

- Direct carry over of urea from the evaporator separators to the condensers (physical entrainment)
- The formation of NH3 from the decomposition of urea to isocyanic acid

\[ \text{CO(NH}_2\text{)}_2 \rightarrow \text{HNCO} + \text{NH}_3 \]

The reverse reaction occurs on cooling the products in the condensers

- Off-gases from the recovery/recirculation stage absorbed in the process water
– Off-gases from the synthesis section absorbed in the process water
– Flush and purge water from pumps
– Liquid drains from the recovery section

The purpose of the water treatment is to remove NH3, CO2 and urea from the process water and recycle the gases to the synthesis. This ensures raw material utilisation is optimised and effluent is minimised.

2.4 Prilling and Granulation

In urea fertilizer production operations, the final product is in either prilled or granular form. Production of either form from urea melt requires the use of a large volume of cooling air which is subsequently discharged to the atmosphere.

2.4.1 Prilling

The concentrated (99.7%) urea melt is fed to the prilling device (e.g. rotating bucket/shower type spray head) located at the top of the prilling tower. Liquid droplets are formed which solidify and cool on free fall through the tower against a forced or natural updraft of ambient air. The product is removed from the tower base to a conveyor belt using a rotating rake, a fluidised bed or a conical hopper. Cooling to ambient temperature and screening may be used before the product is finally transferred to storage.

The design/operation of the prilling device exerts a major influence on product size. Collision of the molten droplets with the tower wall as well as inter-droplet contact causing agglomeration must be prevented. Normally mean prill diameters range from 1.6-2.0mm for prilling operations. Conditioning of the urea melt and “crystal seeding” of the melt, may be used to enhance the anti-caking and mechanical properties of the prilled product during storage/ handling.
2.4.2 Granulation

Depending on the process a 95-99.7% urea feedstock is used. The lower feedstock concentration allows the second step of the evaporation process to be omitted and also simplifies the process condensate treatment step. The basic principle of the process involves the spraying of the melt onto recycled seed particles or prills circulating in the granulator. A slow increase in granule size and drying of the product takes place simultaneously. Air passing through the granulator solidifies the melt deposited on the seed material. Processes using low concentration feedstock require less cooling air since the evaporation of the additional water dissipates part of the heat which is released when the urea crystallizes from liquid to solid.

All the commercial processes available are characterised by product recycle, and the ratio of recycled to final product varies between 0.5 and 2.5. Prill granulation or fattening systems have a very small recycle, typically 2 to 4%. Usually the product leaving the granulator is cooled and screened prior to transfer to storage. Conditioning of the urea melt prior to spraying may also be used to enhance the storage/handling characteristics of the granular product.

Urea: Safety

Urea can be irritating to skin, eyes, and the respiratory tract. Repeated or prolonged contact with urea in fertilizer form on the skin may cause dermatitis.

High concentrations in the blood can be damaging. Ingestion of low concentrations of urea, such as are found in typical human urine, are not dangerous with additional water ingestion within a reasonable time-frame. Many animals (e.g., dogs) have a much more concentrated urine and it contains a higher urea amount than normal human urine; this can prove dangerous as a source of liquids for consumption in a life-threatening situation (such as in a desert).
Urea can cause algal blooms to produce toxins, and its presence in the runoff from fertilized land may play a role in the increase of toxic blooms.\textsuperscript{[20]}

The substance decomposes on heating above melting point, producing toxic gases, and reacts violently with strong oxidants, nitrites, inorganic chlorides, chlorites and perchlorates, causing fire and explosion.