FERTILIZERS TECHNOLOGY

CHEM 0905554

Second Semester 22/23

CHAPTER 8

UREA PRODUCTION


O
C
H2N
NH2

USES

- Urea is used as a fertilizer because of its high nitrogen content and its ability to readily convert to ammonia in the soil.
- It is incorporated into many mixed fertilizers. It can be applied alone to soil or sprayed onto foliage.
- Methylene-Urea fertilizers are created when urea is treated with formaldehyde. This process allows the nitrogen to release slowly, continuously and uniformly.
- Urea is used as a significant part of livestock food to meet protein requirements.

USES

- Urea-formaldehyde resin is created when the two (2) components are heated in the presence of mild alkalis. They undergo a condensation reaction that combines them and forms a water-soluble polymer. This polymer is used to formulate adhesives and coating agents or when mixed with other substances to produce powders that can be molded into solid objects.
- Urea is also used in the Power Industry as a reducing agent. When it is appropriately mixed with combustion air, it reduces NOx emissions.

PHYSICAL DATA

- Odorless or slight ammonia odor
- pH: 7.2 (10 % water solution)
- Decomposes at 270.8°F (132.7°C); decomposes into ammonia and carbon dioxide.
- If burned, emits small amounts of nitrogen oxides.
- Solubility in water is 119g per 100g water at 77°F (25°C)
- Specific gravity: 1.34 at 68°F (20°C); heavier than water
- Molecular weight: [$CO(NH_2)_2$] 60.06

STORAGE AND HANDLING

- Urea is not listed as a Hazardous Material by the Department Of Transportation (DOT), Transport Canada (TC), International Maritime Organization (IMO) and the United Nations (UN).
- Urea is most commonly stored in silos or warehouses.
- A hopper or pneumatic truck is used in the transport and delivery of urea.

UREA PELLETS (SOLID)

- Urea is approximately up to 56% in terms of nitrogen content.

ADVANTAGES:

- Eliminates requirement for large storage systems and requires less handling for delivery and storage.

DISADVANTAGES:

- Adds to system complexity because of the need for de-mineralized water and these systems typically have higher operating and maintenance costs.

UREA LIQUID

- Urea liquid is similar to Aqua Ammonia as it can be directly injected into system processes.

ADVANTAGES:

- It eliminates system complexity because there is no need to convert the urea to ammonia.

DISADVANTAGES:

- It increases product cost due to the dilution factor and requires containment areas in the event of liquid releases.

UREA ($CO(NH_2)_2$) PRODUCTION

- The commercial synthesis of urea involves the combination of ammonia and carbon dioxide at high pressure to form Ammonium Carbamate.
- This is a fast, exothermic reaction that goes to completion.
- The Ammonium Carbamate goes through dehydration by the application of heat to form urea and water.
- This is a slow, endothermic reaction that does not go to completion.

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PROCESS OPERATING VARIABLES

TEMPERATURE

- Conversion of ammonium carbamate to urea in the absence of excess ammonia increases with temperature to a maximum of about 50% at 170 - 190 ºC when the pressure is sufficiently high to keep the reactants in the liquid state.
- The rate of reaction increases with temperature: it is slow at 150 ºC and below and quite rapid at 210 ºC.
- A satisfactory approach to equilibrium can be obtained in the temperature range of 180 - 200 ºC.
- Corrosion difficulties increase with temperature, and a range of 180 - 210ºC is generally accepted as optimum for most processes

PRESSURE

- At constant temperature, conversion increases with pressure up to the critical point which is the point at which the vapor phase is substantially eliminated, and the reactants are in the liquid state.
- A further increase in pressure is not beneficial.
- The critical temperature is a complex function of the temperature and composition of the reactor’s content.
- For example, at 150^{o}C a pressure of about 100 atm might be near optimum for a stoichiometric NH_3:CO_2 ratio, but at this temperature the rate of reaction is unacceptably slow.
- At the preferred temperature of 180 - 210^{o}C, pressures of 140 - 250 atm are commonly used.

MOLE RATIO OF NH_3:CO_2

- Excess NH_3 above the stoichiometric mole ratio of 2 favors the rate of the reaction.
- The percentage of CO_2 converted to urea is increased but the percentage of HN_3 converted to urea is decreased.
- Because recycling of excess NH_3 is relatively simple, most processes use 50% or more excess ammonia.
- Today all processes account for a balance of both CO_2 and NH_3 conversion to reduce total recycling to a minimum plantwide.

OTHER FACTORS

- The presence of water decreases conversion; therefore, most processes are designed to minimize the amount of water recycled to the reactor.
- The presence of small amounts of oxygen decreases corrosion; all processes use this method minimizing corrosion.

AVAILABLE PROCESSES

1. Advanced cost and energy saving process (ACES)
2. Carbon dioxide stripping process
3. Ammonia stripping process
4. Isobaric double recycle (IDR) process

AVAILABLE PROCESSES

- Urea is produced from ammonia and carbon dioxide in two equilibrium reactions:

$$2NH_3 + CO_2 \longleftrightarrow NH_2COONH_4\ (ammonium\ carbamate)$$

$$NH_2COONH_4 \longleftrightarrow NH_2CONH_2 (urea) + H_2O$$

- The urea manufacturing process, shown schematically in the next slide is designed to maximize these reactions while inhibiting biuret formation:

$$2NH_2CONH_2 \longleftrightarrow NH_2CONHCONH_2 (biuret) + NH_3$$

- This reaction is undesirable, not only because it lowers the yield of urea, but because biuret burns the leaves of plants.
- This means that urea which contains high levels of biuret is unsuitable for use as a fertilizer.

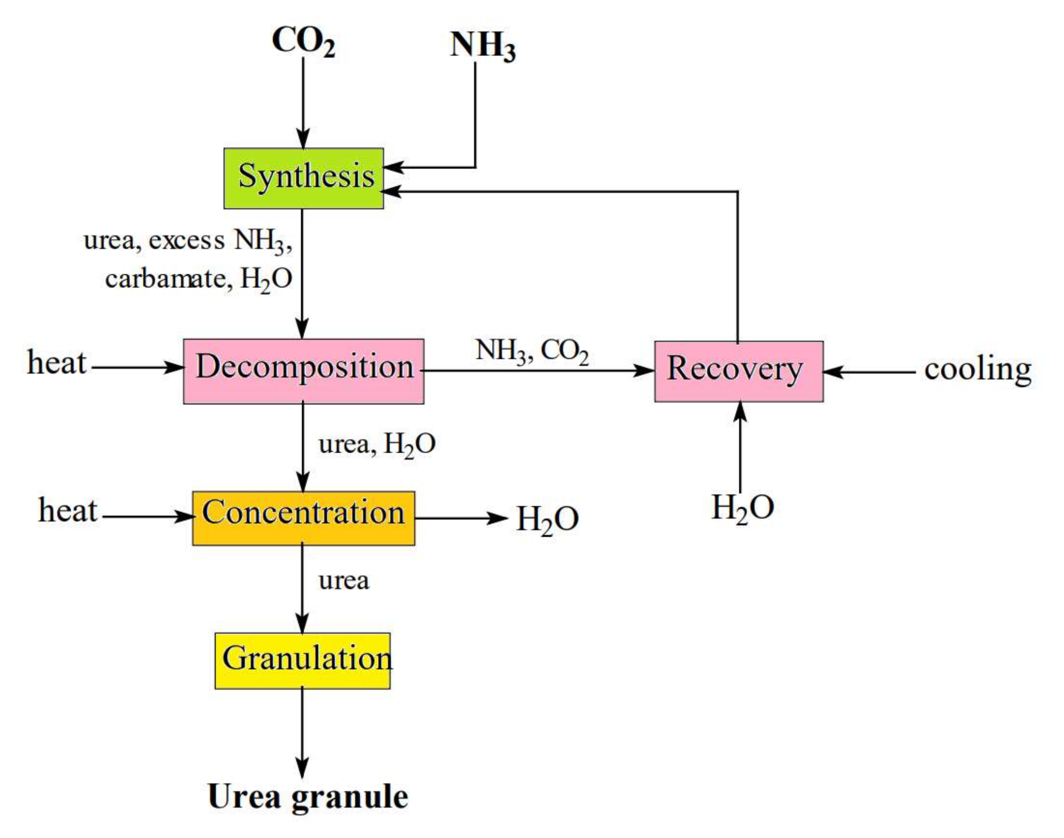
1- ADVANCED COST AND ENERGY SAVING (ACES) PROCESS

- In this process the synthesis section operates at 175 bar with an NH_3/CO_2 molar ratio of 4 and a temperature of 185 to 190 ^oC.
- The reactor effluent is stripped at essentially reactor pressure using CO_2 as 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 5 bar steam and the heat formed in the second condenser is used to heat the solution leaving the stripper bottom after pressure reduction.

ADVANCED COST AND ENERGY SAVING (ACES) PROCESS

- The inerts in the synthesis section are purged to the scrubber from the reactor top for recovery and recycle of NH_3 and CO_2.
- The urea solution leaving the bottom of the stripper is further purified in HP and LP decomposers operating at approx. 17.5 bar and 2.5 bar respectively.
- The separated NH_3 and CO_2 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.

SCHEMATIC REPRESENTATION OF UREA SYNTHESIS


CO_2

NH_3

Synthesis

urea, excess NH_3, carbamate, H_2O

heat

Decomposition

NH_3, CO_2

Recovery

cooling

urea, H_2O

heat

Concentration

H_2O

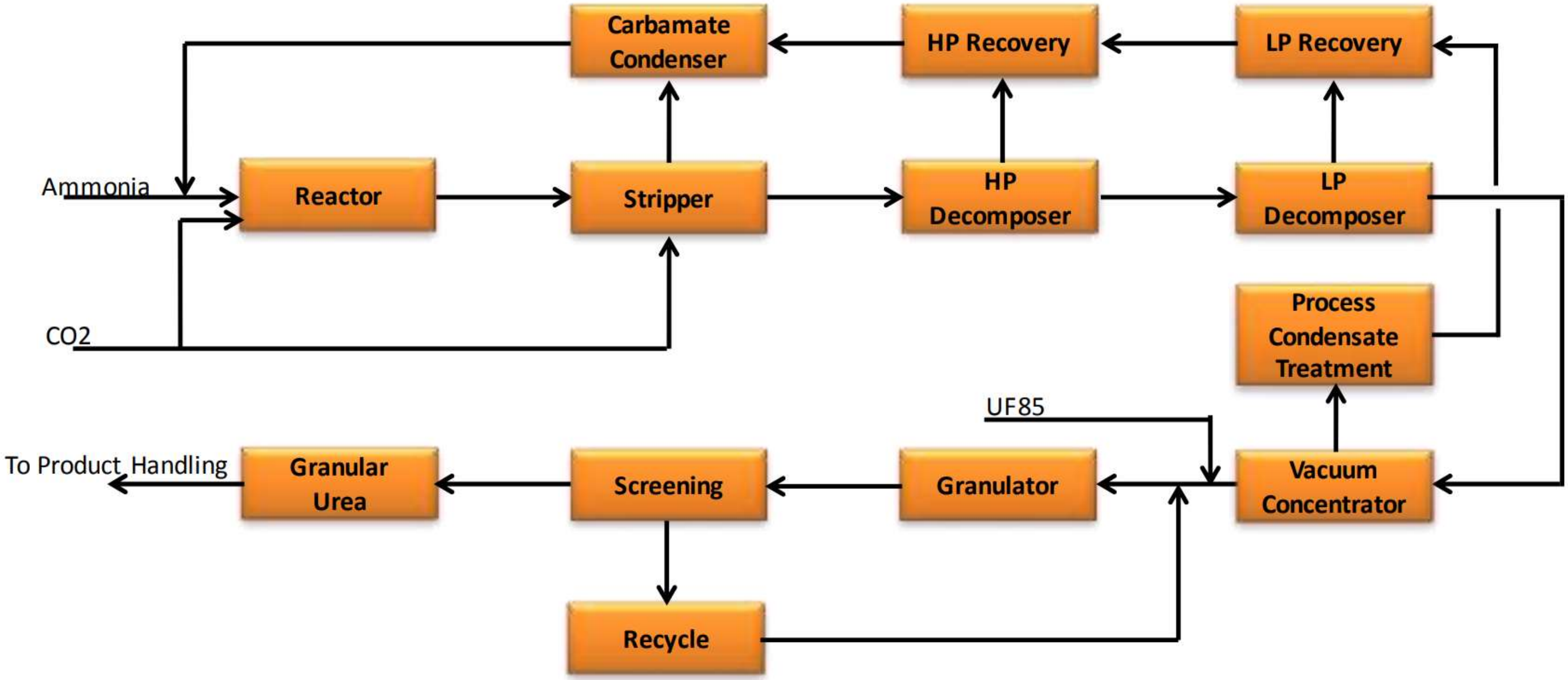
H_2O

urea

Granulation

Urea granule

SCHEMATIC REPRESENTATION OF UREA SYNTHESIS



UREA PROCESS FLOW

Urea process is characterized by the following main process steps:

A. Urea synthesis, NH_3 & CO_2 recovery section at higher pressure

B. Urea purification along with NH_3, CO_2 recovery at two lower pressures

C. Urea concentration

D. Process condensate treatment

E. Granulation.

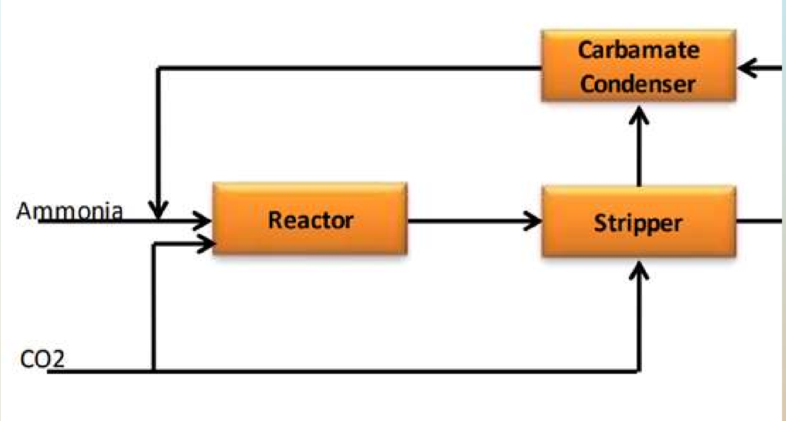
UREA PRODUCTION PROCESS

A. UREA SYNTHESIS , NH_3, CO_2 RECOVERY AT HIGH PRESSURE

- Urea is produced through the reaction of ammonia and carbon dioxide.
- The ammonia and carbon dioxide react to form ammonium carbamate, a portion of which dehydrates to urea and water.
- The fraction of ammonium carbamate that dehydrates is determined by the ratios of various reagents, the operating temperature, pressure and the residence time in the reactor.
- The reaction products leaving the reactor flow to a stripper, a vertical tube falling film decomposer in which the liquid, distributed on the heating surface as a film, flows by gravity to the bottom.

UREA PRODUCTION PROCESS

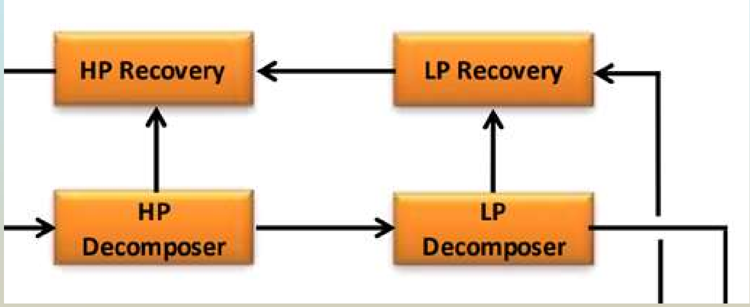
- As the liquid film flows, it gets heated and decomposition of carbamate through surface evaporation takes place.
- Generated vapors (essentially ammonia and carbon dioxide) are removed by flowing to the top of the stripper.
- This gaseous stream with the recovered solution from the downstream sections is condensed and recycled to the urea reactor by means of carbamate ejector.



UREA PRODUCTION PROCESS

B. UREA PURIFICATION AND NH_3, CO_2 RECOVERY AT TWO LOWER PRESSURES

- Urea purification and overhead vapors recovery take place in two stages at decreasing pressures.
- The exchangers where urea purification occurs are called decomposers.
- In these equipment, the residual carbamate decomposition takes place.



UREA PRODUCTION PROCESS

B. UREA PURIFICATION AND NH_3, CO_2 RECOVERY AT TWO LOWER PRESSURES

- The decomposed carbamate vapors are condensed and recycled back to the synthesis loop while the inerts are washed in the washing column before being sent to the flare stack.
- The urea solution exiting this section is purified to generate Urea solution of 69-71 wt %.

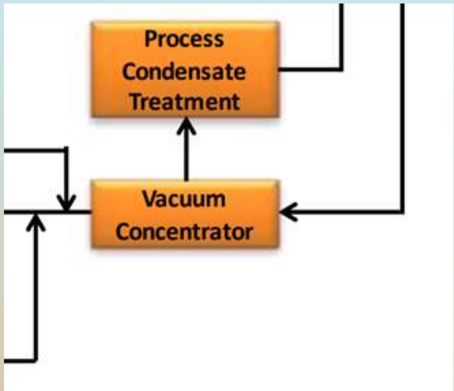
UREA PRODUCTION PROCESS

C. UREA CONCENTRATION SECTION

- In order to granulate Urea, concentrated Urea solution of 97 wt% is necessary.
- This is achieved in vacuum concentration stage.
- The Urea solution leaving the purification sections having about 70% wt Urea, along with the Urea solution recycle coming from granulation unit, is sent to the Urea concentration section.
- The concentration happens in vacuum conditions employing vacuum generation system.
- The concentrated Urea solution (~97 % by wt.), is sent to granulation unit, after mixing with UF85 additive (Urea Formaldehyde Concentrate) as anti-caking agent.

UREA PRODUCTION PROCESS

D. PROCESS CONDENSATE TREATMENT

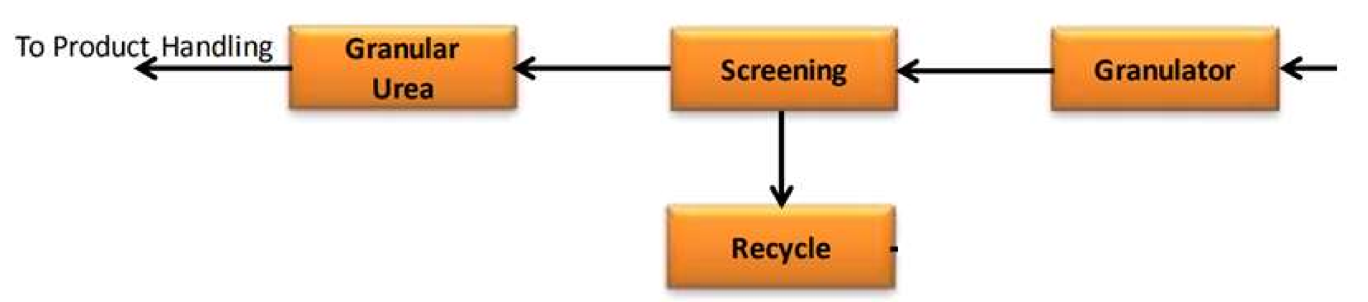


- The process condensates containing NH_3, CO_2 and Urea coming out from vacuum system is treated in this section to ensure that the condensate is almost free-of contaminants.
- The treated process condensate is further sent to the Polishing unit.
- The NH_3 & CO_2 separated from the process condensate stripper are mixed with the Low Pressure Decomposer overhead vapors, condensed and further recycled back to the synthesis loop.

UREA PRODUCTION PROCESS

E. GRANULATION

- The Urea solution is fed on the Urea seeds in the granulator bed through the multi spray nozzles to enlarge the recycle particles (seeds) through agglomeration of the solution to seeds.
- The water in the feed Urea solution is evaporated in the granulator.
- The enlarged granules are cooled to a suitable temperature by fluidizing air on the internal fluidized beds in the granulator.



UREA PRODUCTION PROCESS

- Urea granules produced in the granulator are screened to separate the product size granules from over and under size granules through the double deck screen.
- Small sized granules are recycled back to the granulator as the seed and oversized granules are crushed through the double roller type crusher and recycled back to the granulator together with the under sized granules as the seeds.
- Exhaust air from the granulator and cooler is scrubbed in the wet type dust scrubber to recover the Urea dusts in the exhaust air.
- The water used in the dust scrubber to dissolve the urea dust is recycled back to the Urea plant to recover the Urea by evaporating the water.

UREA GRANULE SPECIFICATIONS

Component	Concentration
Nitrogen	46 % minimum by weight
Biuret	1.0 % minimum by weight
Moisture content	0.3 % minimum by weight
Sizing	90 % 2 – 4 mm by weight

2- CARBON DIOXIDE STRIPPING PROCESS

- In all CO_2 stripping processes, ammonia and carbon dioxide are fed directly to the synthesis section.
- Optimum process conditions of approx. 140 bar and 180 °C are maintained.
- Carbon dioxide, to which a small quantity of air is added to prevent corrosion, is compressed to synthesis pressure in a multistage compressor, while the ammonia pressure is raised by a high-pressure pump.
- Hydrogen is removed from the fresh carbon dioxide feed stream in the H_2 removal reactor located between the compression stages.

CARBON DIOXIDE STRIPPING PROCESS

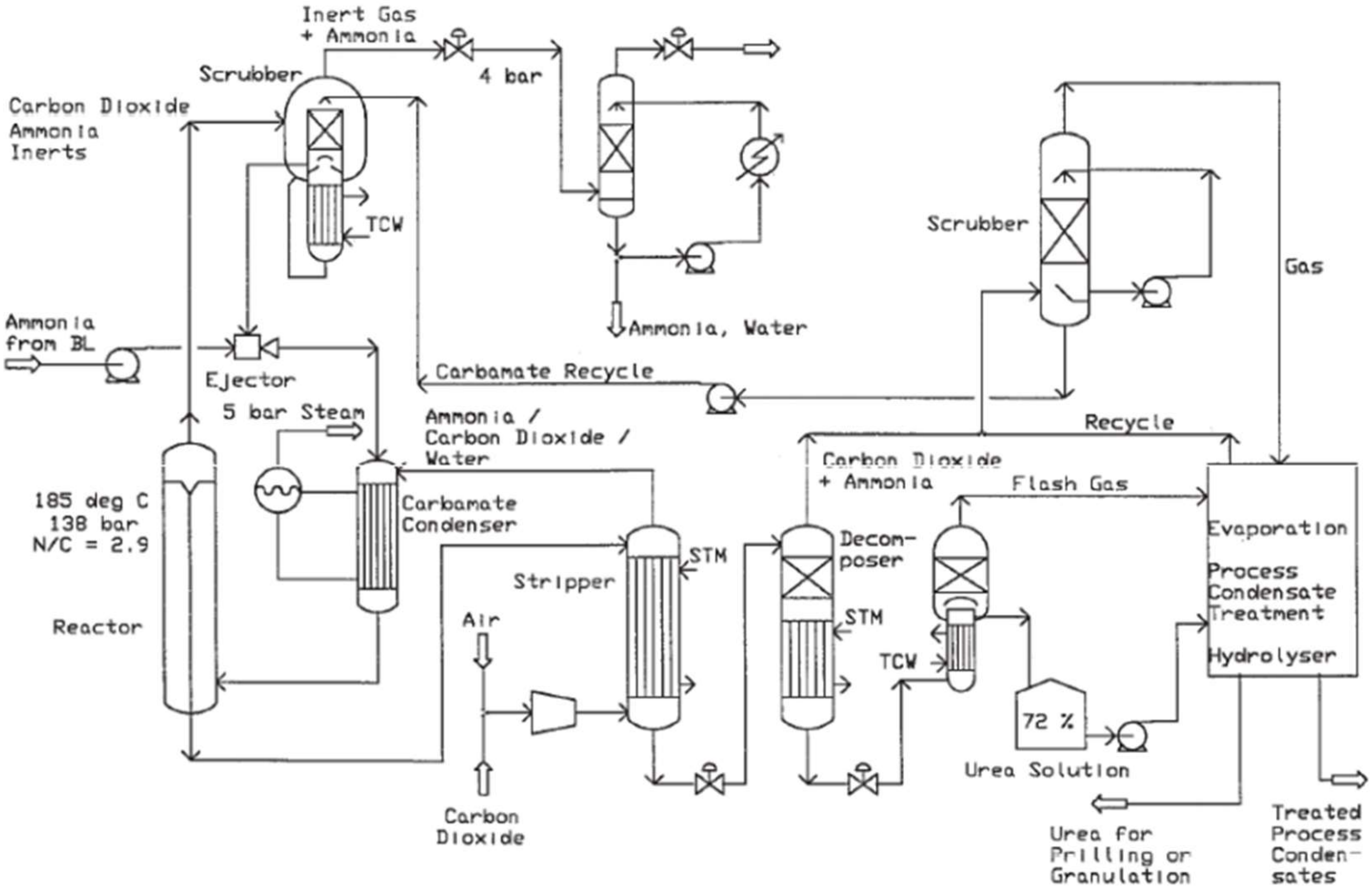
- The exothermic condensation to ammonia carbamate as well as the endothermic dehydration of the carbamate to urea and water takes place in the synthesis section.
- The reaction described results in a chemical equilibrium; part of the ammonia and carbon dioxide is not converted to urea and water.
- For this reason, the reaction mixture is subjected to a stripping process, using carbon dioxide to strip off the unreacted ammonia.
- This design feature is highly effective because of its low energy requirement and retention of unconverted reactants in the synthesis section.

CARBON DIOXIDE STRIPPING PROCESS

- The stripper off gases are introduced into the high-pressure pool condenser together with the carbamate solution from the low- pressure scrubber and fresh ammonia.
- The heat released by the formation of carbamate in the high-pressure pool condenser is recovered to generate low- pressure steam.
- Subsequently, the mixture of gas and liquid flows into the urea reactor in which the main urea formation takes place.
- The liquid reaction mixture which leaves the reactor via an overflow is introduced into the stripper top.

CARBON DIOXIDE STRIPPING PROCESS

- The exhaust gases (inert gases, NH_3, CO_2 and H_2O), which are separated from the liquid at the reactor top, are scrubbed in the high- pressure scrubber with carbamate solution from the low-pressure recirculation section.
- Thus, most of the gases are recovered and returned to the pool condenser via the high-pressure ejector.
- The non-condensables withdrawn from the high-pressure scrubber are scrubbed in a low- pressure absorber, thereby minimizing ammonia emissions.


Inert Gas
+ Ammonia
4 bar
Scrubber
Carbon Dioxide
Ammonia
Inerts
TCW
Scrubber
Gas
Ammonia, Water
Ammonia
from BL
Ejector
5 bar Steam
Carbamate Recycle
Recycle
Ammonia /
Carbon Dioxide /
Water
Carbon Dioxide
+ Ammonia
Flash Gas
185 deg C
138 bar
N/C = 2.9
Carbamate
Condenser
Evaporation
Process
Condensate
Treatment
Hydrolyser
Decom-
poser
STM
Stripper
STM
Air
Reactor
TCW
72 %
Urea Solution
Carbon
Dioxide
Urea for
Prilling or
Granulation
Treated
Process
Conden-
sates

3- AMMONIA STRIPPING PROCESS

- NH_3 and CO_2 are converted to urea via ammonium carbamate at a pressure of 150 bar and a temperature of 180 ^{o}C.
- A molar ratio of 3.5 is used in the reactor giving a CO_2 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 NH_3.
- Residual carbamate and CO_2 are recovered downstream of the stripper in two successive stages operating at 17 and 3.5 bar respectively.

AMMONIA STRIPPING PROCESS

- NH_3 and CO_2 vapors 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.

4- ISOBARIC DOUBLE RECYCLE (IDR) PROCESS

- In this process reactor pressure is about 200 bar, the molar NH_3/CO_2 ratio is 4.5 and the reactor effluent temperature 185 to 190 ^oC.
- The conversion rates to urea in the reactor are 71% for CO_2 and 35% for NH_3 .
- Unconverted materials in the effluent from the reactor bottom are separated by heating and stripping in two consecutive decomposers operated at reactor pressure and heated by 25 bar steam.
- Carbamate is decomposed/stripped by NH_3 in the first stripper and the remaining NH_3 is evolved in the second stripper using CO_2 as stripping agent.

ISOBARIC DOUBLE RECYCLE (IDR) PROCESS

- The overheads from stripper 1 are fed directly to the reactor and the overheads from stripper 2 are recycled to the reactor via the carbamate condenser.
- Heat of condensation is recovered as 6 bar steam and used downstream in the process.
- Most of the CO_2 fed to the plant goes to the second stripper and the remainder goes directly to the reactor for fine temperature control when needed.
- About 40% of the NH_3 goes to the first stripper and the remainder to the upper and lower sections of the reactor in two streams.

ISOBARIC DOUBLE RECYCLE (IDR) PROCESS

- Unconverted carbamate, NH_3 and CO_2 leaving the stripper with the urea solution are recovered/vaporized in two successive distillers operating at 20 bar and 6 bar respectively.
- The vapors are condensed and recycled to the synthesis after condensation to carbamate solution
- The latent heat present in the 20-bar stage off gases is used as a heat source for the evaporation of water in the first stage evaporator.
- Further concentration of the urea solution leaving the LP decomposition stage is carried out in two vacuum evaporators in series, producing urea melt for prilling or granulating.