



Nitrogen Industry

Chemical Process technology

CHE F419

2/17/2016

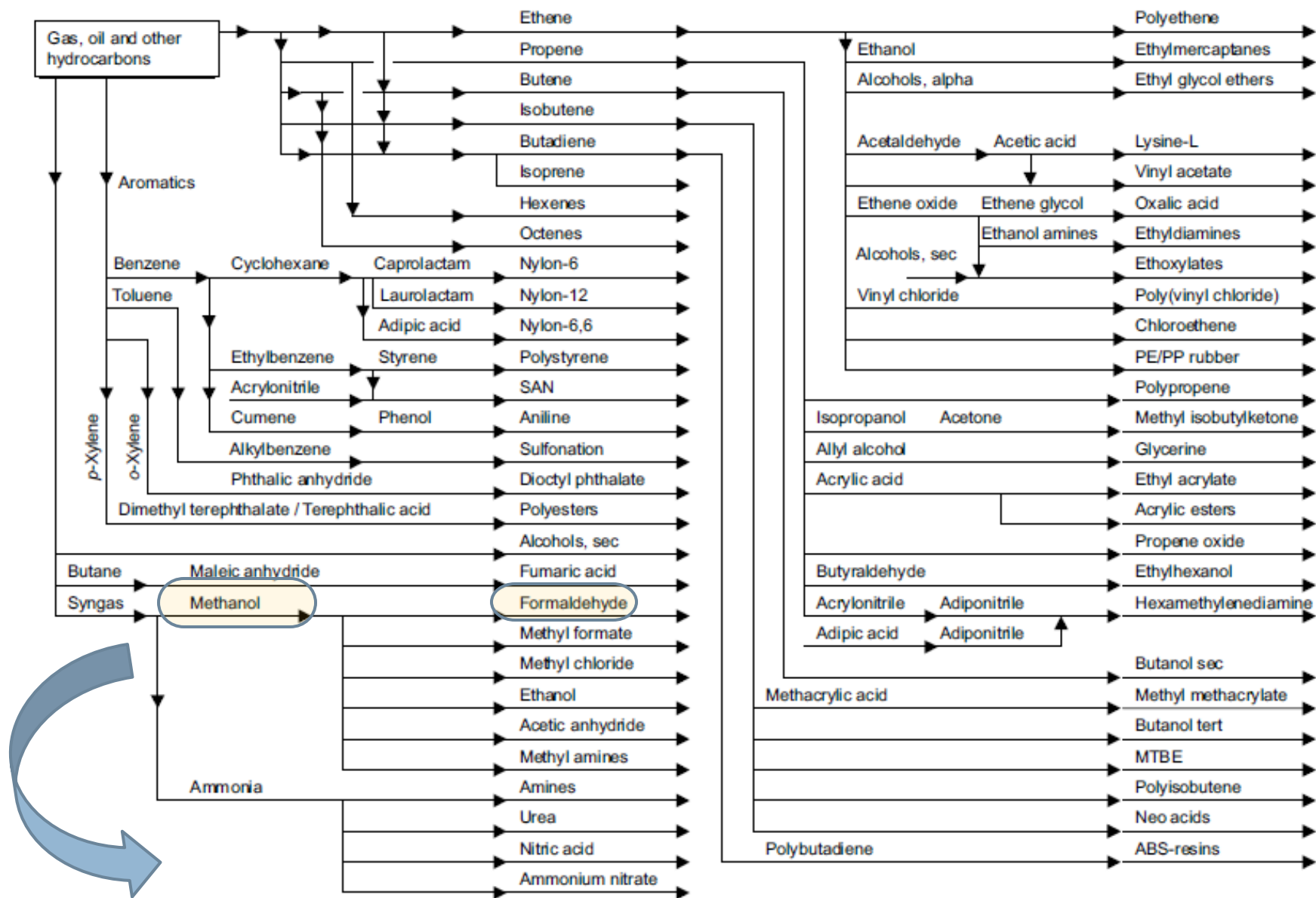


Figure 2.2 Survey of the petrochemical industry.

Nitrogen Industry

- The production of nitrogen is a major branch of the fertilizer industry and it opens up a most important segment of the chemical industry.
 - ▣ Pure nitrogen may be obtained by separation from air by liquid air distillation.
 - ▣ By consumption of the oxygen of air by burning of fuel, which leaves nitrogen residue.
- Nitrogen, however, is a rather inert element; it is difficult to get it to combine with any other element.
- Haber succeeded in getting nitrogen to combine with hydrogen by the use of high pressure, moderately high temperatures, and a catalyst.
- Ammonia; Nitric acid, Ammonium nitrate/chloride, Urea

Ammonia

- **Ammonia or azane** is a compound of nitrogen and hydrogen with the formula NH_3 .
- Colorless gas with a **characteristic pungent smell**
- **Soluble in water** (aq. Solution : weak acid)
- Ammonia contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to food and fertilizers.
- **End uses**
 - ▣ Direct application as fertilizer
 - ▣ Urea, Ammonium phosphates, nitrate, sulfate
 - ▣ Production of nitric acid, amines, nitriles.
 - ▣ Environmental application: removal of NO_x from flue gases of power plants.
- Nitrogen consumption in fertilizer (80% of NH_3 production)
 - Mixed fertilizers (NPK)
 - Chemical nitrogen fertilizer

Applications of Ammonia

- Refrigeration
- HNO_3 (ostwald)
- Ammonium sulphate
- Ammonium nitrate
- Silk manufacturing
- Cleansing agent for remaining grease in dry cleaning
- Solvay process
- Fertilizers
- Explosives (TNT etc)

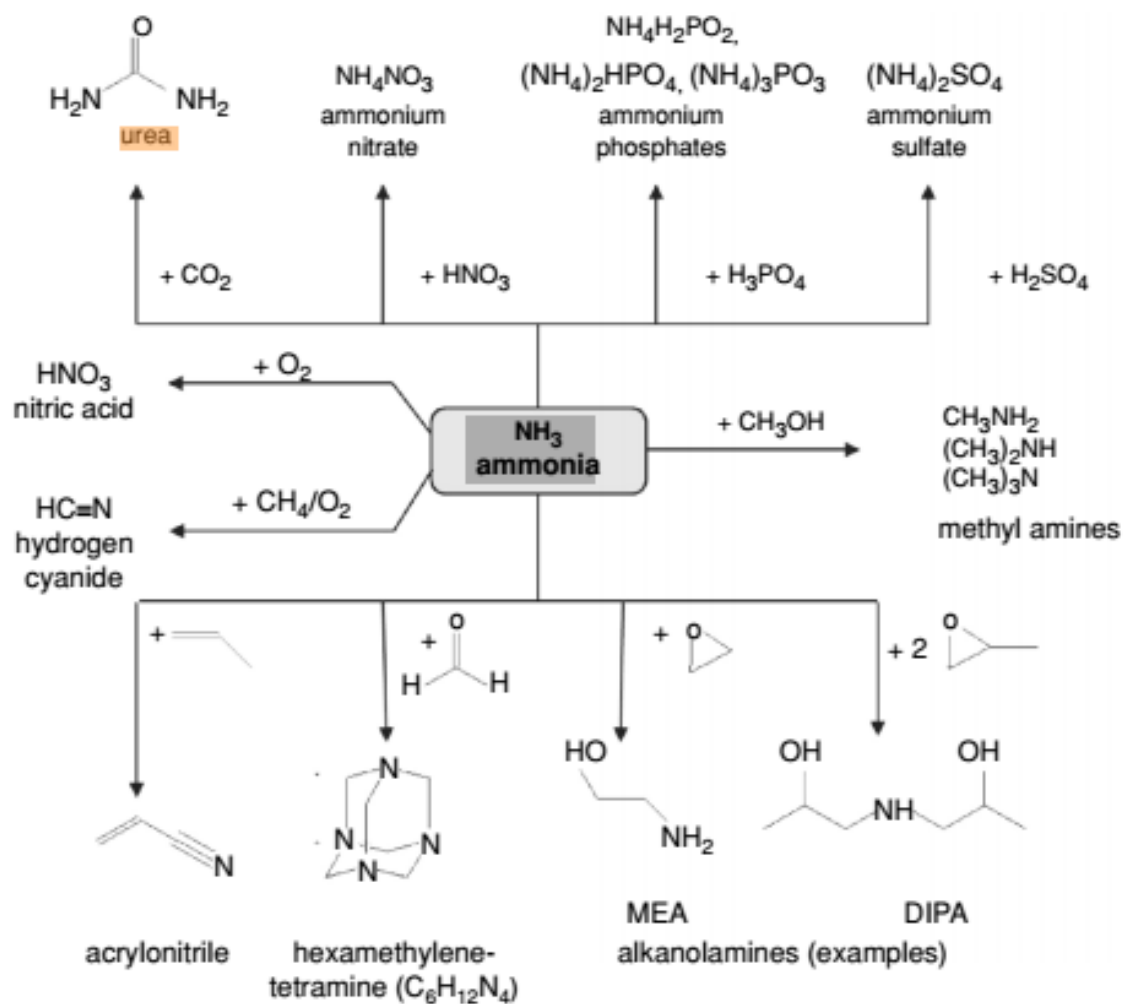


Figure 6.2 Fertilizers and chemicals from ammonia.



Photograph Copyright by Deb McClintock

Upper Left: *Pseudevernia intensa*;

Lower Left: *Xanthoparmelia chlorochroa*;

Lower Right: *Usnea(?) cavernosa*;

Upper Right: *Teloschistes exilis*.

A: ammonia solution. B: simmering water.

C: lichen B re-extracted in ammonia. D: alcohol.

Principle of Ammonia Synthesis

The Haber or Haber-Bosch Process

- The ammonia synthesis reaction is represented by

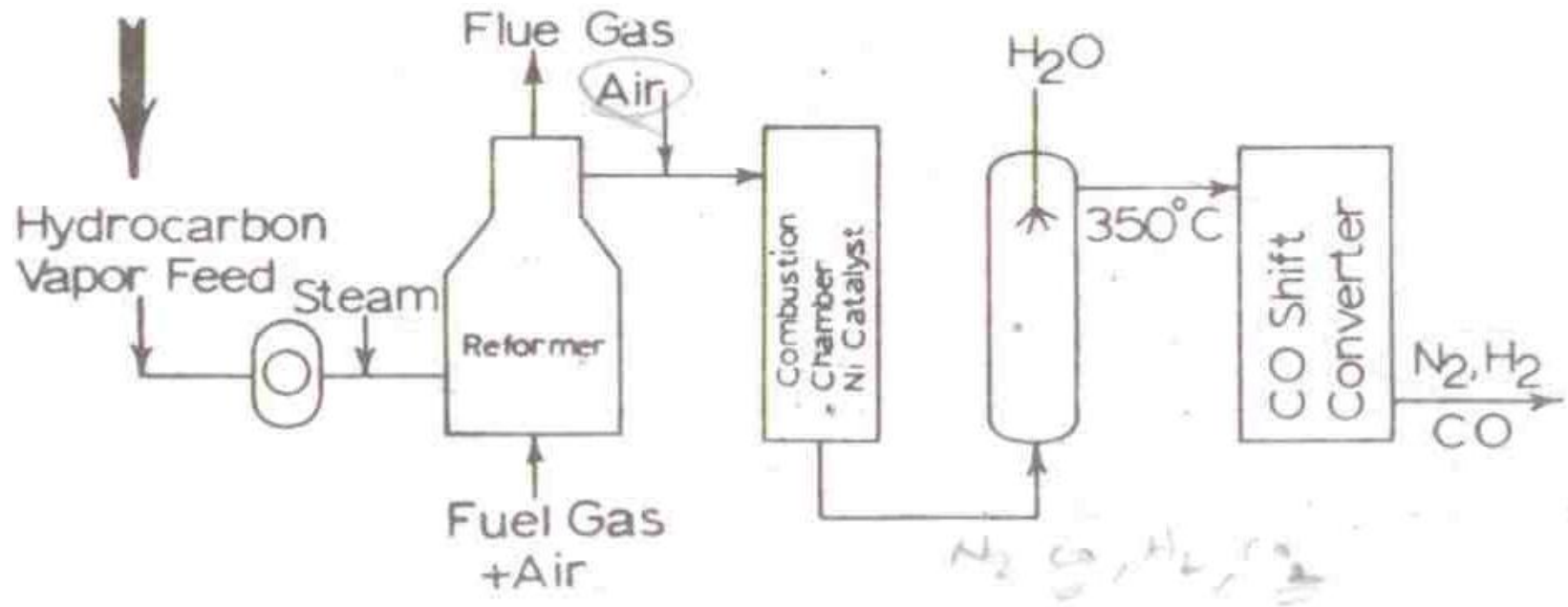


- Increase in the pressure on this system increases the equilibrium ammonia concentration.
- While raising the synthesis temperature gives a faster rate, it also displaces the equilibrium to the left, giving smaller potential conversion.
- Condition used for most synthesis ammonia process
 - ▣ $P = 100\text{-}300 \text{ atm}$
 - ▣ $T = 400\text{-}500 \text{ }^\circ\text{C}$
- Catalyst : Promoted iron oxide catalyst – Update Ruthenium on Carbon

Process Selection

- Feedstocks for Ammonia synthesis by air distillation
 - ▣ Cryogenic low temperature technology
 - ▣ Feasible only for small ammonia plant (100 tonne/day) or where abundant hydrogen is available.
- Ammonia feedstocks by reforming and secondary reforming (from coal, petroleum and natural gas)
 - ▣ Coal as a source via water gas ($\text{CO} + \text{H}_2$) reaction : higher capital investment, environmental problem
 - ▣ Natural gas reforming: can use any kind of petroleum feed stock, easier to clean prior to use, less emission

Process flow sheet (Text book)



STEAM REFORMING

In steam reforming, hydrogen is produced by reforming the hydrocarbon feedstock, producing synthesis gas containing a mixture of carbon monoxide and hydrogen. The carbon monoxide is then reacted with steam in the water-gas-shift reaction to produce carbon dioxide and hydrogen. The carbon dioxide is recovered for urea production, exported as co-product, or vented to the atmosphere. In the final synthesis loop, the hydrogen reacts with nitrogen to form ammonia.

In steam reforming ammonia plants there is a surplus of high-level heat that is produced in primary reforming, secondary reforming, shift conversion and ammonia synthesis. Most of the waste heat is recovered for producing high pressure steam that is used in turbines for driving compressors, pumps and fans. In general, all the high pressure steam will be used in steam turbines for driving the synthesis gas compressor. Modern steam reforming ammonia plants do not import energy for driving the mechanical equipment. Energy is in many cases exported in the form of steam or electricity to other consumers (IPTS/EC, 2007).

The natural gas use in a an ammonia plant using the steam reforming process ranges between 28 and 35.5 GJ/tonne, of which about 20-22 GJ/tonne of ammonia is used as feedstock, 7.2-9.0 GJ/tonne is fuel consumed in the primary reformer, and the remaining 0.5-4.2 GJ/tonne is used in auxiliary boilers and others.

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Conventional steam reforming of natural gas includes desulphurization, primary reforming and secondary reforming processes.

Desulphurization:

The feedstock used for the production of ammonia may contain sulphur and sulphur compounds which are harmful for the catalyst used in subsequent process steps and therefore need to be removed. Typically, feedstocks may contain up to 5 mg S/Nm³ of sulphur compounds. In desulphurization, the pre-heated (350-400°C) and untreated feed-gas enters a vessel that usually contains a cobalt molybdenum catalyst where the sulphur compounds are hydrogenated to H₂S. The hydrogen needed for the reaction is usually recycled from the synthesis section. The hydrogenated sulphur compounds are then adsorbed on pelletized zinc oxide. After desulphurization, the feed-gas sulphur concentration drops to less than 0.1 ppm.

Primary Reforming:

The feed-gas, after being treated in a desulphurization vessel, is mixed with process steam. The preheated mixture enters the primary reformer at a temperature of 400-600°C. In certain new and revamped ammonia plants the preheated steam/gas mixture is passed through an adiabatic pre-reformer before entering the primary reformer, where it is then reheated in the convection section (EFMA, 2000).

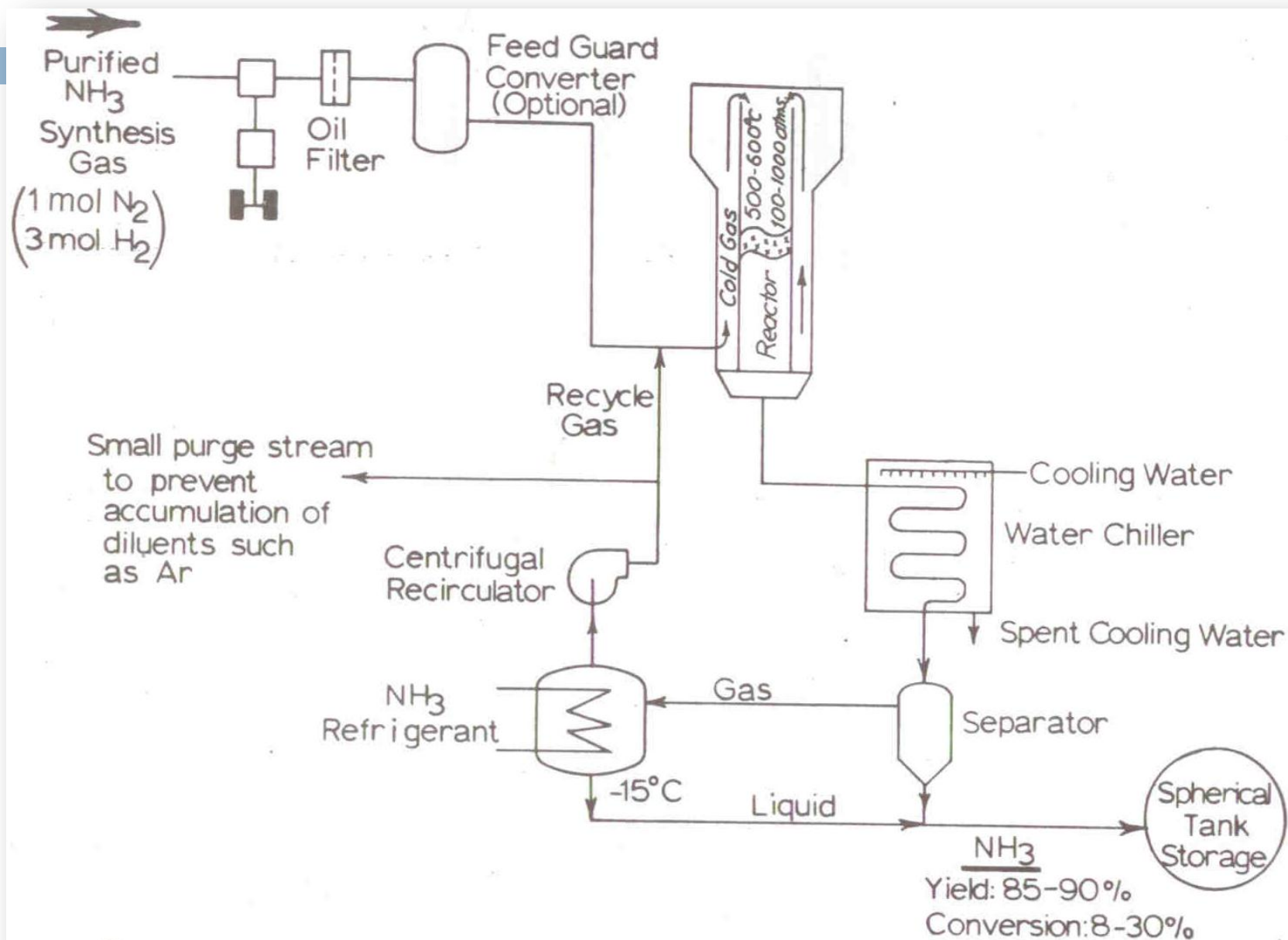
Primary reformers consist of a large number of high-nickel chromium alloy tubes which are filled with a nickel-containing reforming catalyst (see Figure 3). In conventional steam reforming, the hydrocarbon conversion rate in the primary reformer is about 60%.

The reaction is highly endothermic:

Natural gas or other types of burners provide heat to the process. About half of the heat supplied to the primary reformer is consumed in the reaction. The remaining half is contained in the flue gases and used in the convection section of the reformers for the preheating of process streams. The flue gases leaving the primary reformer convection section compose the most significant source of the plant's emissions. These emissions mainly consist of CO₂, NO_x, and small amounts of SO₂ and CO (EFMA, 2000). The typical fuel use in the primary reformer (including steam generation) ranges between 7.2 and 9.0 GJ/tonne of ammonia (IPTS/EC, 2007). Natural gas consumption in energy efficient ammonia plants is about 6.8 GJ/tonne of ammonia (Ullmann's, 2011).

Secondary Reforming:

In secondary reforming the nitrogen needed for the production of ammonia is added and the reforming of the hydrocarbon feed is completed (only about 60% of the feed-gas was reformed in the primary reformer). In order to increase the conversion rate, high temperatures are required. This is achieved with the internal combustion of part of the reaction gas and the process air, which is also the source of nitrogen, before it passes over to the nickel containing catalysts. The supplied air is compressed and heated at the convection section of the primary reformer at a temperature of 500-600°C. The gas outlet temperature is about 1000°C and about 99% of the primary reformer hydrocarbon feed is converted. The residual methane content is about 0.2-0.3% (dry gas base). Heat is removed with the use of a waste heat boiler and the gas is cooled down to approximately 330-380°C (IPTS/EC, 2007).



Carbon Capture and Storage


5.3.8 Carbon Capture and Storage (CCS)

Significant research, development, and demonstration efforts are ongoing with respect to CCS as a greenhouse gas mitigation option. The idea is to capture large-scale carbon dioxide emissions and store the gas underground so that it is not released into the atmosphere. Instead of carbon dioxide storage, some of the captured carbon dioxide could be used as a chemical feedstock, for example in the production of methanol or urea.

In coal-based technologies, there are basically three routes to carbon capture:

- post-combustion (recovering CO₂ from flue gases);
- oxy-fuel combustion (combustion in oxygen instead of air); and
- pre-combustion (extracting CO₂ before the fuel is burned).

Post-combustion is the route that would be applied to conventional pulverized-coal combustion power plants. Carbon dioxide is captured from the flue gases that mostly consist of nitrogen and water vapor, with only 15% or less being carbon dioxide. Carbon dioxide capture can be done by absorption in methanol or in amine-based solutions (Section 5.4). In principle, post-combustion capture is applicable to all types of power plants. However, the low pressure, large volume, and low concentration of carbon dioxide lead to huge capture systems with large energy consumption.



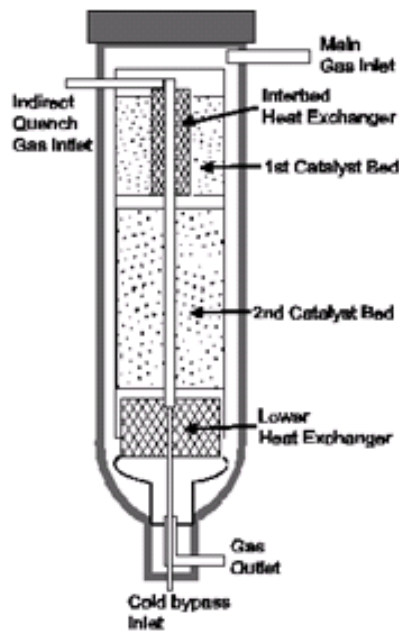
In oxy-fuel combustion, the fuel, in this case coal, is burned in (nearly) pure oxygen instead of air, eliminating the large amount of nitrogen from the flue gas, which mostly consists of carbon dioxide and water vapor. The latter is condensed through cooling, resulting in an almost pure stream of carbon dioxide. The main problems with this technology are the high investment costs and the large energy consumption in the production of oxygen.

Pre-combustion carbon capture has been integrated with gasification for several years, but more as a hydrogen purification step in the production of syngas for the manufacture of chemicals and synfuels than as a carbon capture step. The most common method is converting (part of the) carbon monoxide in the syngas into carbon dioxide and hydrogen via the water–gas shift reaction, followed by absorption of carbon dioxide in methanol or amine-based solutions (Section 5.4). Possible alternatives are the use of membrane technology or pressure swing adsorption (Section 6.1.6). The resulting carbon dioxide emissions can be pulled off in a relatively pure stream, while the formed hydrogen can be combusted or used in the production of chemicals.

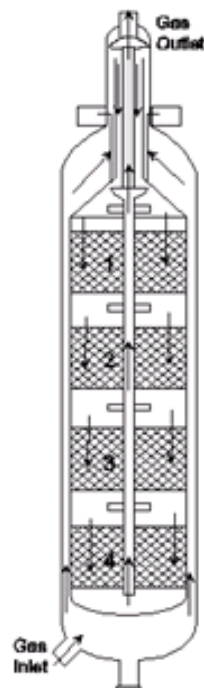
□ Ammonia Synthesis

- Nitrogen and hydrogen (obtain from any route) are required in mole ratio 1:3, raised to very high pressure 100-900 atm range (centrifugal compressor).
 - Material of construction: Steel (hydrogen embrittlement)
- Commercial Synthesis Reactor
 - Pressure vessel with sections for catalyst beds and heat exchangers
 - Cold feed gas is added in quench reactor
 - The heat produced is removed between the catalyst beds by heat exchanger
- Product recovery (Condensation)
 - Ammonia is condensed from this gas mixture by cooling the gases
 - At high pressure (converter exit pressure) ammonia condenses easily
 - It can be absorbed in water if solution to be marketed.

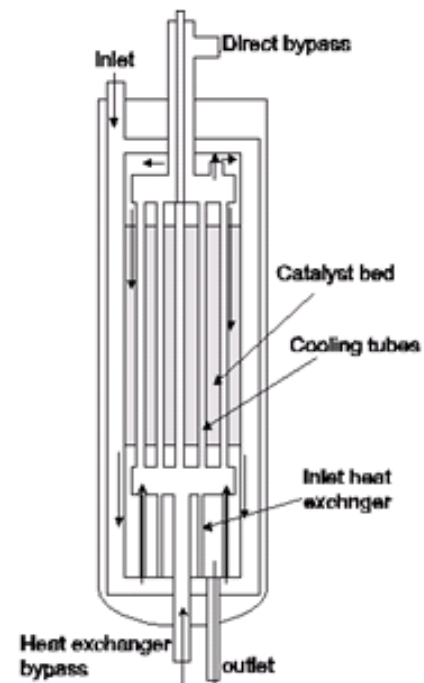
Ammonia synthesis reactor design



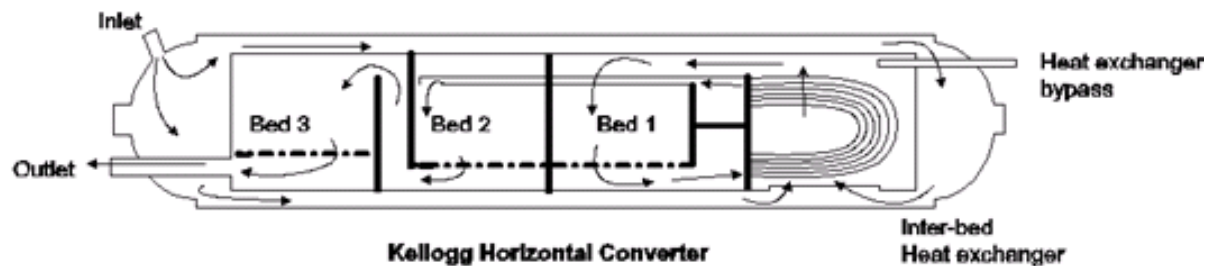
Topsoe S 200 Radial Converter



Kellogg Quench Converter



Tube Cooled Converter



Kellogg Horizontal Converter

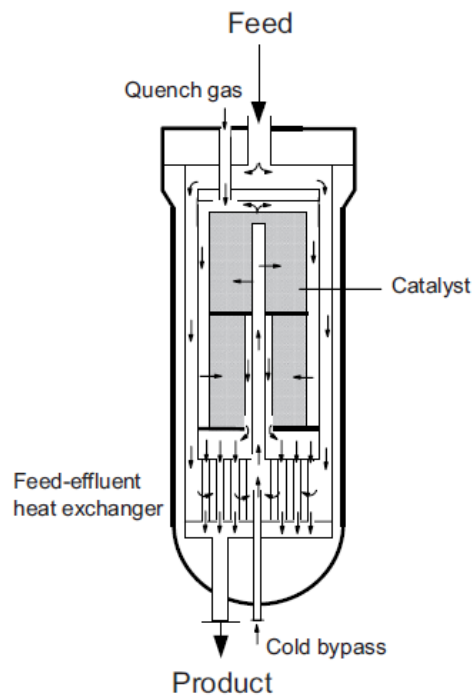


Figure 6.6 Haldor Topsøe radial flow reactor.

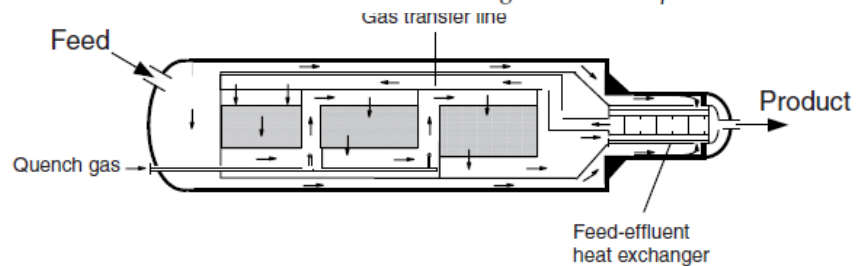
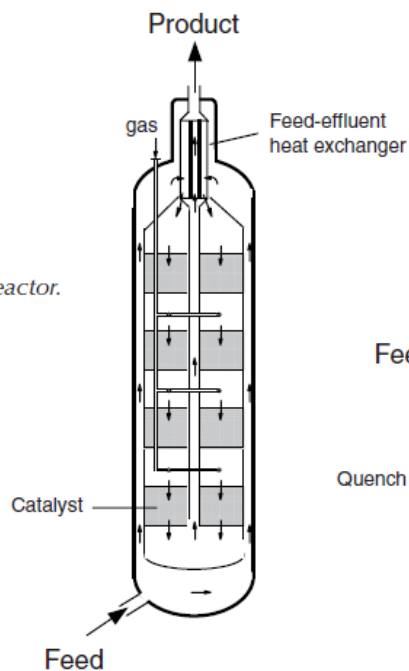


Figure 6.5 Kellogg quench reactors; vertical (left) and horizontal (right).

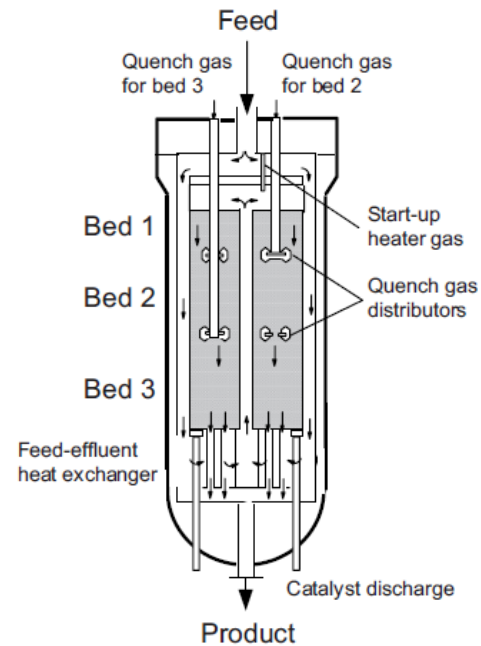


Figure 6.4 ICI quench reactor

□ Catalyst development

▣ To date catalysts are based on Iron oxide

- promoted by alkali K_2O (1-2%) and metal oxide (Al_2O_3)
- Al_2O_3 support to prevent sintering
- Potassium reduces the activation energy of dissociation

▣ Kellogg : Commercialized the Kellogg advanced Ammonia process using ruthenium on a graphite support

□ Process design modifications

- ▣ Modern trend toward: lower pressure & increased flow rates
- ▣ Large single-train plant

Fertilisers :

Nitrogen

- Ammonia
- Urea
- Ammonium Nitrate
- Calcium Cyanamide
- Ammonium Sulphate
- Calcium Nitrate
- Calcium Ammonium Nitrate
- Potassium Nitrate
- Ammonium Chloride

Phosphatic

- Calcium phosphate
- Single Superphosphate (SSP)
- Triple Superphosphate (TSP)
- Ammonium phosphate
- Monoammonium phosphate (MAP)
- Diammonium phosphate (DAP)
- Nitrophosphate

Potash

- Potassium chloride
- Potassium carbonate
- Sylvinite (mixture of KCl and NaCl)
- Carnallite
- Kainite
- Langbeinite
- Nitre or Indian Saltpetre
- Source of Potash – bitterus left over salt discovery and molasses/distillery slop.

UREA (NH_2CONH_2)

Organic compound

Also known as Carbamide

PROPERTIES:

Mol. Wt : 60.05

M.P : 132.7 °C

B.P : Decomposes

Fairly soluble in water

Colorless

Odorless

47% nitrogen

USES:

- solid as well as liquid nitrogen fertilizers.
- Plastics in combination with formaldehyde and furfural.
- adhesives.
- coatings, textile anti shrink compounds, ion-exchange resins.
- as an intermediate for ammonium sulfamate, sulfamic acid, and the phthalocyanine pigments

Process routes & Reactions

Method of production :

Ammonium cyanate heating: $\text{NH}_4\text{OCN} \rightarrow \text{NH}_2\text{CONH}_2$

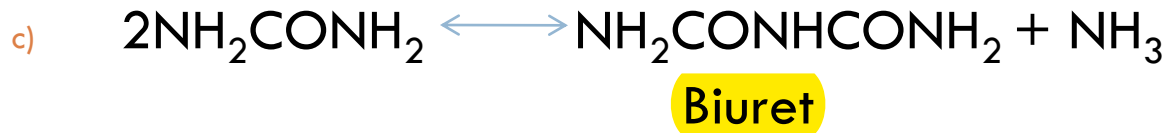
Ammonium carbamate decomposition process.

Raw materials used: CO_2 and NH_3

Chemical reactions:



Undesired side reaction



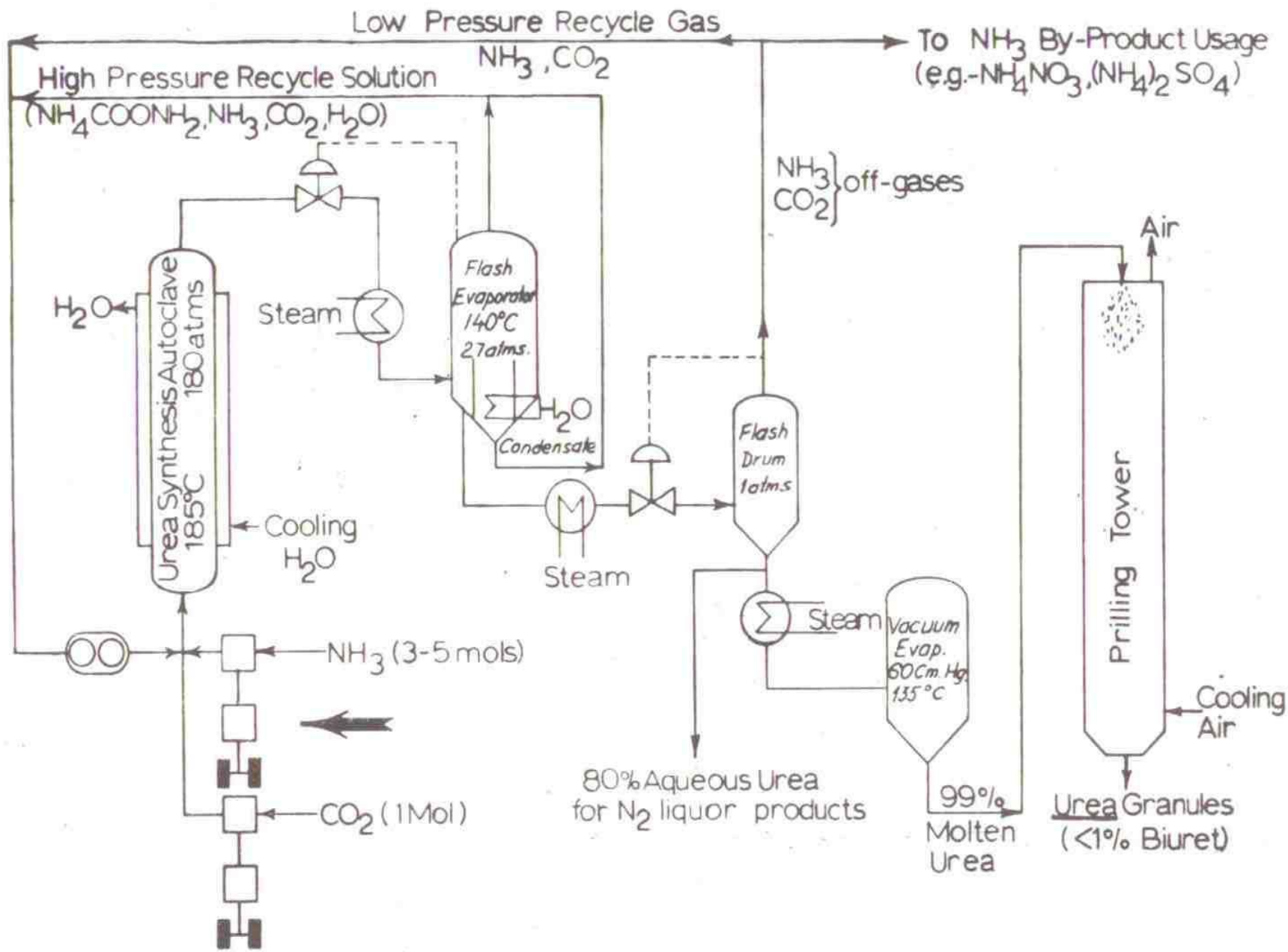
□ Process Steps:

▣ Solution synthesis

- Ammonia and carbon dioxide are reacted to form ammonium carbamate. Typical operating conditions include temperatures from 180 to 200°C, pressures from 140 to 250 atmospheres $\text{NH}_3:\text{CO}_2$ molar ratios from 3:1 to 4:1.
- The carbamate is then dehydrated to yield 70 to 80 percent aqueous urea solution.

▣ Solid Formation: (Prilling / Granulation)

- **Prilling:** It is a process by which solid particles are produced from molten urea. Molten urea is sprayed from the top of a prill tower. As the droplets fall through a countercurrent air flow, they cool and solidify into nearly spherical particles.
- **Granulation:** Granular urea is generally stronger than prilled urea, both in crushing strength and abrasion resistance. In drum granulation, solids are built up in layers on seed granules placed in a rotating drum granulator/cooler approximately 4.3 meter in diameter.
- **Clay Coating:** Used to reduce product caking and urea dust formation



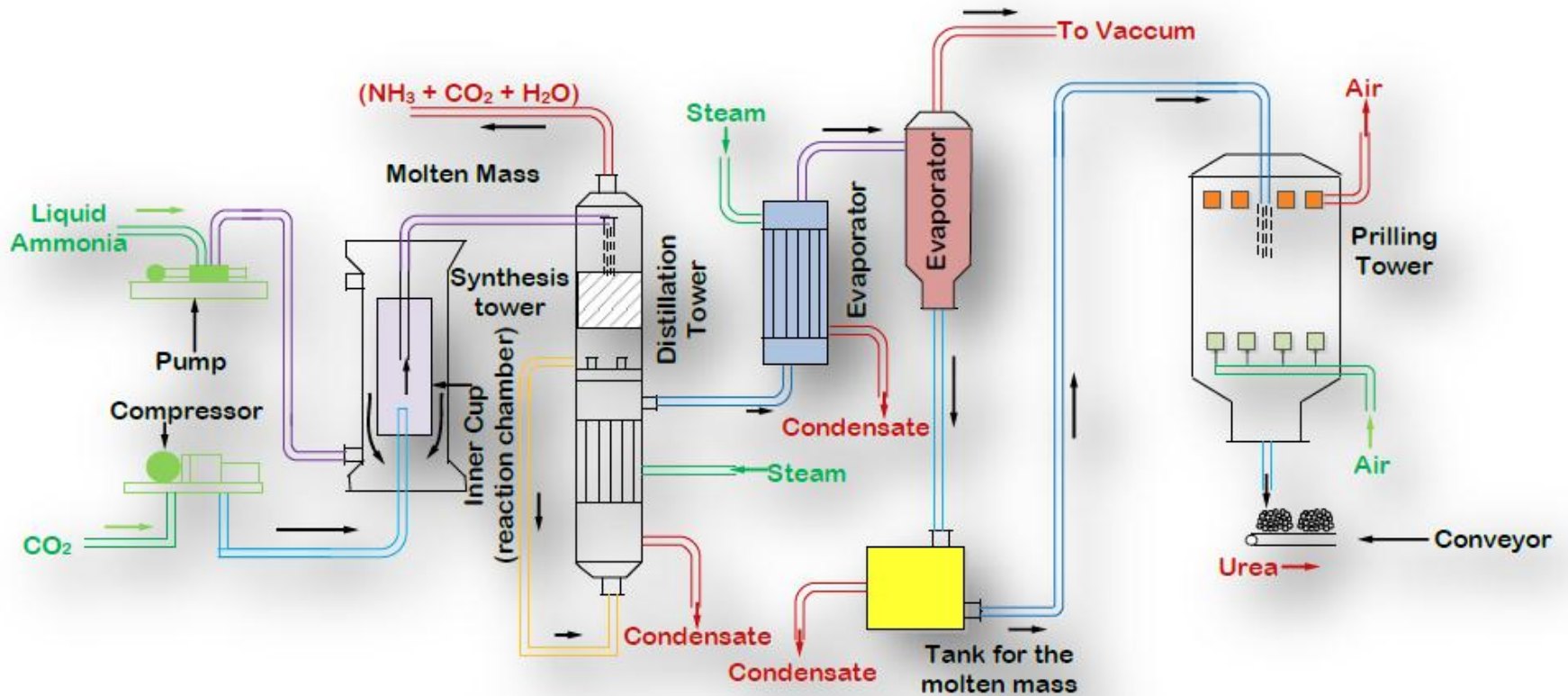


Figure: Manufacturing of Urea

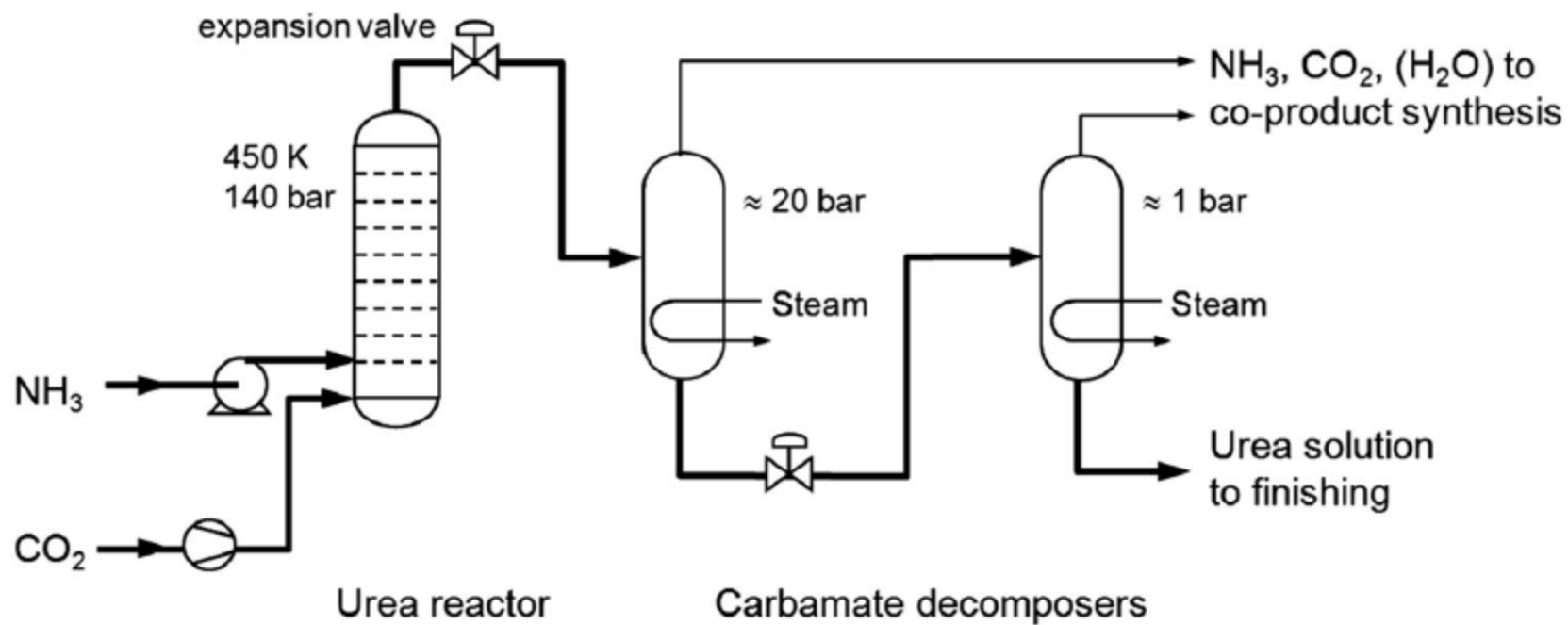
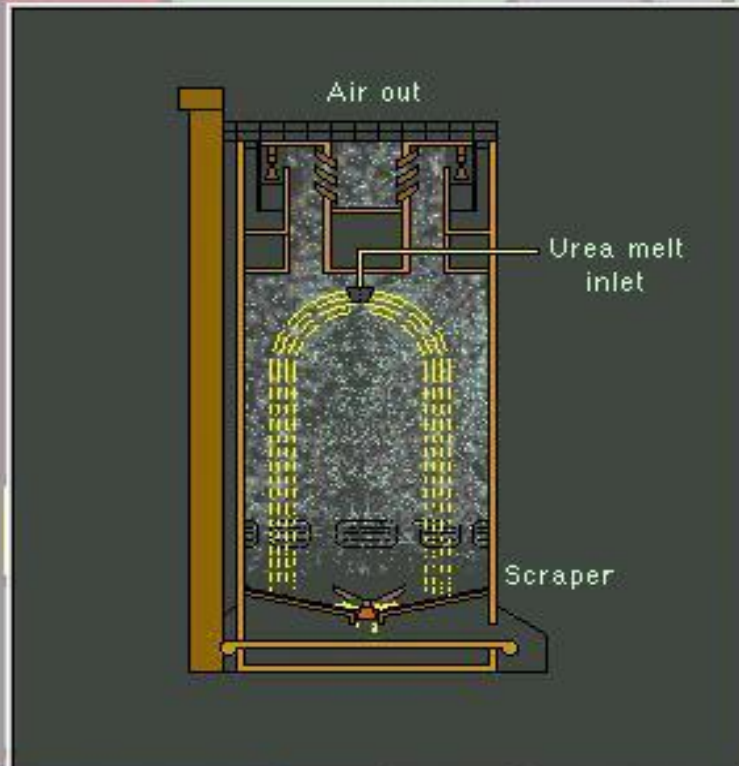
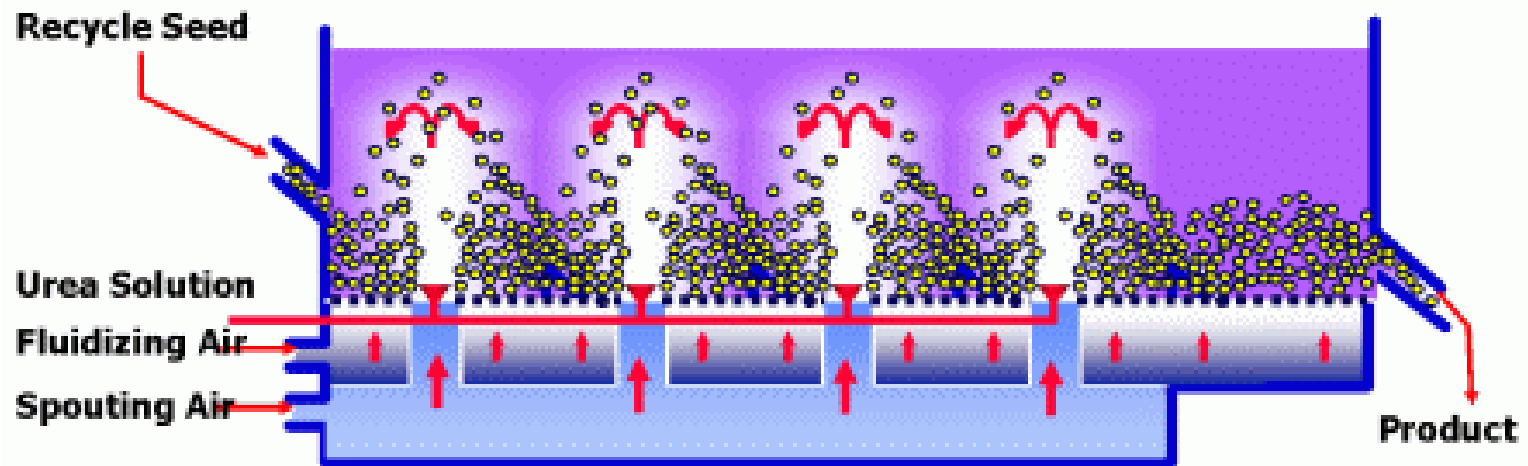


Figure 6.11 Once-through process for urea production.

Prilling Tower



- * To solidify urea melt to form urea prills
- * Urea droplets solidify due to counter current flow of cool air
- * Dedusting system at top of tower removes urea dust and NH_3 from air



Optimal Arrangement of Multi-stage Spouted Bed

- Round and Uniform Product
- High Drying Efficiency



MAJOR ENGINEERING PROBLEMS

1. Autoclave variable
 - ▣ Temperature, pressure, NH_3/CO_2 ratio
 - ▣ Heat dissipation in the autoclave : coils, wall cooling.
2. Carbamate decomposition and recycle
 - ▣ Low T, high P with short residence time
3. Production of granular urea
 - ▣ To avoid biuret formation: T, just above the melting point of urea with seconds residence time.
4. Corrosion
5. Process design modifications
 - ▣ Once through process
 - ▣ **Toyo Koatsu Process:** Combine ammonia and urea process. CO_2 is absorbed by mixture of hot carbamate and ammonia. The resulting mixture is passed to urea reactor.

AMMONIUM NITRATE

Properties:

Mol. wt- 80.05

M.P – 170°C

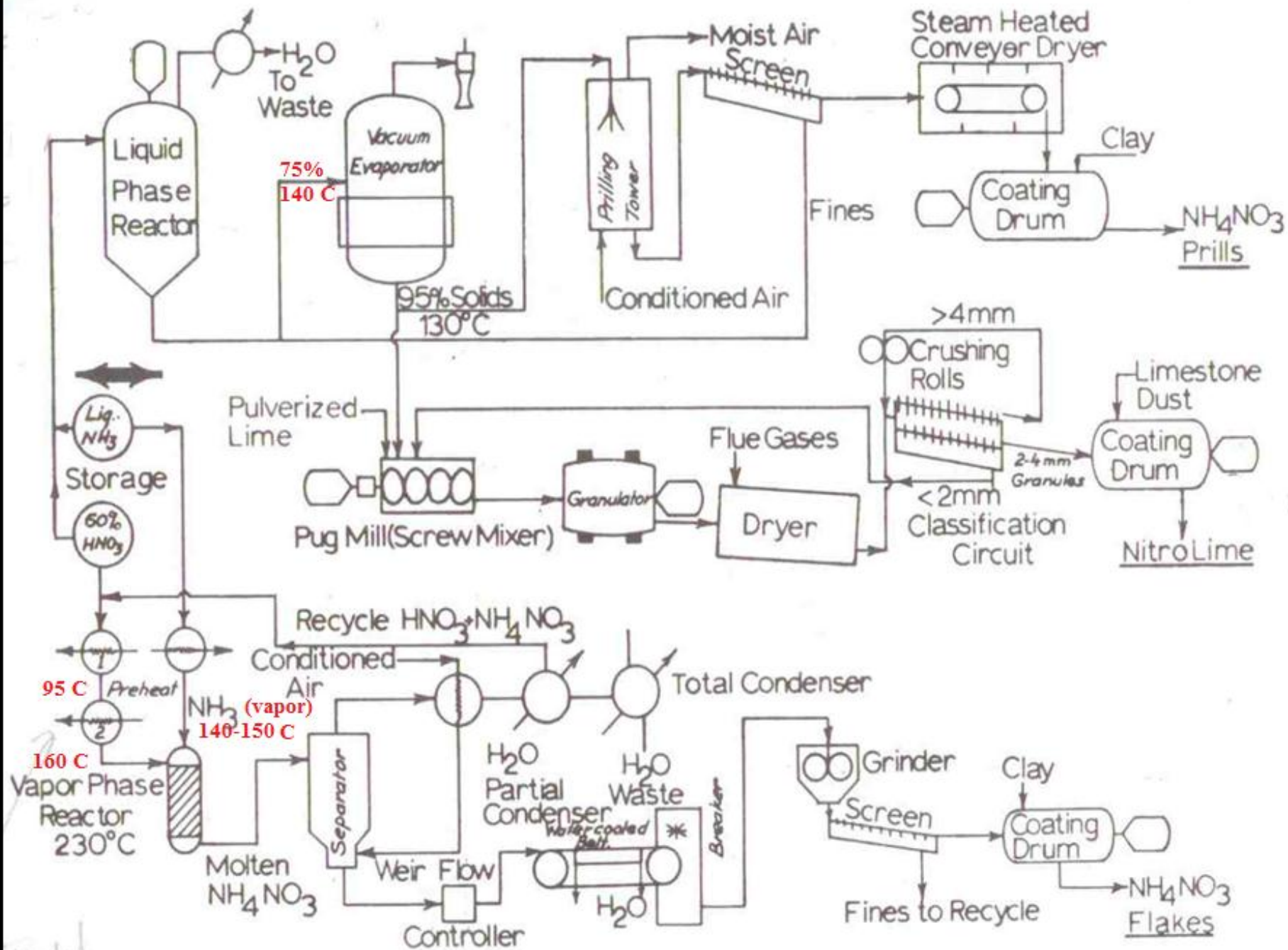
B.P – decomposes at 200 °C or higher

Uses:

In fertilizers, explosives, Nitrous oxide (as an aesthetic)

Production Process : Based on reaction of nitric acid and ammonia. Variation in methods are based on final solid form.

1. Prilling process
2. Crystallization process
3. Stengel process



Major engineering problem

1. Corrosion
2. Crystallization
3. Safety
 - ▣ Hot conc. Ammonium nitrate solution is explosively sensitized by traces of acid.
 - ▣ Care is taken to add sufficient ammonia to the wet melt to keep the pH above about 5.
4. Conditioned air requirement