Fertilizer

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Being an agricultural nation, production of fertilizer is given the highest national priority only after Defence and population control.

PLANT NUTRIENTS

Plants require following nutrient elements for their growth

a) **Natural nutrients**

Carbon, hydrogen and oxygen are derived from air and water and so these are called natural nutrients.

b) **Primary nutrients**

Nitrogen, phosphorus and potassium are consumed in large amounts by the plants for their growth and so these are called primary nutrients.

c) **Secondary nutrient**

Calcium, magnesium and sulfur which occur to a limited extent in all soils, are called secondary nutrients.

d) **Micronutrients**

Zinc, boron, copper, manganese, chlorine, iron and molybdenum are required in little amount by the plants and so these are called micro nutrients.

Nitrogen, potassium and phosphorus containing minerals are principally important for normal plant life. These elements stimulate processes of metabolism in the plant cells, growth of the plant and especially its fruits, increase the content of valuable plant components such as starch of potatoes, sugars of beets, fruits and berries, proteins of grains and increase resistance to frost, drought and diseases.

Magnesium

Magnesium carried out the phosphates which are important for the formation of phospholipids and in the synthesis of nucleoproteins. Magnesium is also a mineral constituent of chlorophyll and makes up 2.7% of the weight of chlorophyll.

Deficiency of magnesium is removed by the naturally occurring magnesium salt present in soil. Dolomitic limestone is used to supplement the natural supply.

Calcium

Calcium acts as a plant nutrient and soil amendment to correct soil acidity. It is found as plant constituent in the cell walls of leaves in the form of calcium pectate. Calcium is closely associated with the growth of the flowers. The deficiency of calcium also prevents normal development of buds and tips. Calcium is also found in cell sap either in the ionic form or as salts of organic acids. Application of calcium to the soils corrects the soil's acidity rather than supplying a nutrient.

Sulfur

It is present in many proteins in the form of methionine and cystine which contain 21.5 and 26.7% sulfur respectively. A deficiency of sulfur decreases the plant growth accompanied by extensive yellowing of green parts. The sulfur needs of the plants are small and supplied by soil compounds, from industrial gases that distribute sulfur compounds, or from sulfates supplied in fertilizers.

Iron

Iron is used in certain respiratory enzyme systems by plants, mainly, catalyse, cytochrome and peroxidase. A deficiency of iron causes leaves to turn white and growth to cease. Iron deficiency is noted in the growth of citrus and in crops such as soyabeans and peanuts.

Boron

It is required in extremely small amounts by plants. Its function is obscure, but accumulation of carbohydrates and water soluble amino compounds in plants efficient in boron suggests that boron is of some importance in protein synthesis.

Zinc

It is involved in enzyme systems in the plant, particularly carbonic anhydrase and carboxylase

Manganese

It is found in active regions of the plant and acts as an oxidising agent for iron. Deficiencies of manganese usually occur in organic soils and in alkaline or highly acidic soils.

Copper

Copper is associated with some of the plant enzyme systems, such as polyphenol oxidase and ascorbic acid oxidase. Deficiencies are generally associated with organic soils

Chlorine

It is the most recent addition to the essential nutrient list. It has been observed that the deficiency of chlorine can cause wilt chlorosis (yellowing of green plants) and necrosis. Chlorine in small amounts also stimulates growth of crops like barley, alfalfa and tobacco.

Molybdenum

It is associated with the functioning of one or more of the plant enzyme systems, especially nitrate reducing enzymes

NEED FOR FERTILIZER ?

CLASSIFICATION

Based on their chemical composition

- **Organic products:** Produced out of wastes of animal husbandry (stable manure, slurry manure, etc.), plant decomposition products (compost, peat, etc.), or products from waste treatment (composted garbage, sewage sludge, etc.).
- **Mineral fertilizers:** Contains inorganic or synthetically produced organic compounds.
- **Synthetic soil conditioners:** It's main function is to improve the physical properties of the soil.

Based on their nutrient content

- **Micronutrient fertilizers:** Containing nutrients required in small quantities by plants.
- **Straight fertilizers:** Containing one primary nutrient, and
- **Compound fertilizer:** Also known as complex or multi-nutrient fertilizers. It contains several primary nutrients and sometimes micronutrients.

Based on the source

Fertilizers can be obtained from natural and artificial sources

a) Natural organic fertilizers

- **Animal matter:** Powdered dry fish and red dry blood from the slaughter house are important nitrogenous fertilizers.
- **Farm yard manures:** Typical farmyard manure consists of cow dung, sheep dung and human excretions.
- **Guano:** Guano is a classic example of complete fertilizer and it is a mixture of bird 's excrement, fish refuge and fish hones.
- **Plant matter:** Oil cakes from cotton seed meal; linseed meal and caster cake belong to this class and contain 7%, 5.5% and 6% of nitrogen respectively.

b) Natural inorganic fertilizers

- **Rock Phosphates:** Finely divided rock phosphate, although insoluble in water, weathers rapidly and may be used directly. Bone metal is another source which supplies phosphorus but phosphorus is exclusively supplied by the artificial sources.
- **Chile Saltpetre:** Chilean deposits would not last for more than 250 years, even at present about 83% of the world's requirements of $NaNO_3$ come from artificial sources.
- **Potassium Salts:** Natural potassium sources are wood ash (containing 5-6% potash) and waste materials of sugar beet crops.

c) Artificial fertilizers

- Phosphorus fertilizer
- Nitrogenous fertilizer
- Potassium fertilizer

Three major components in chemical fertilizer

N – Nitrogen
(facilitates early stages of growth / development of stems & leaves)

P – Phosphorous
(stimulate early growth, accelerates seeding / fruit formation, plays important role in the ADP-ATP cycle)

K – Potassium
(development of starches of underground vegetables / grains, sugar components & fibrous materials in the plant, provides immunity towards diseases.

Requisite as fertilizer

The chief requisites of a fertilizer are

- Must be soluble in water
- The element present in the compound must be easily available to the plant
- Should be cheap
- Should not be toxic to plant
- Should be stable for long time
- Should maintain the pH of the soil in the vicinity of 7 to 8.

The most important factor of fertilizers is the movement of water in the soil. Application of lime opens the pores of the soil and enables a free circulation of water.

Fertilizer ratio

Commercial fertilizer has specific ratio of nutrients. It is defined as the relative proportion of primary nutrients in a fertilizer grade divided by the highest common denominator for the grade, expressed in the order N, P and K. For instance, a fertilizer with 5-10-15 grade has 1-2-3 ratio, whereas a fertilizer with 10-20-20 grade has 1-2-2 ratio. The grade 16-12-20 has a ratio of 4-3-5 of N, P and K, respectively.

Source of Nitrogen :

Ammonia, Ammonium salts, Urea, Nitrates

Source of Phosphorous :

phosphate salts : Calcium phosphate
Ammonium phosphate

Source of Potassium :

Potash (Potassium chloride)

[Natural sources of these components ?]

AMMONIA production

Chemical reaction : $N_2 + 3H_2 \overset{Fe}{\rightleftharpoons} 2NH_3$

$(\Delta H = -91.41 \text{ kcal})$

Source of raw materials:

H_2 from water gas / steam reforming of methane

N_2 from air-liquefaction process

Le-Chatelier's principle !

Major engineering challenges

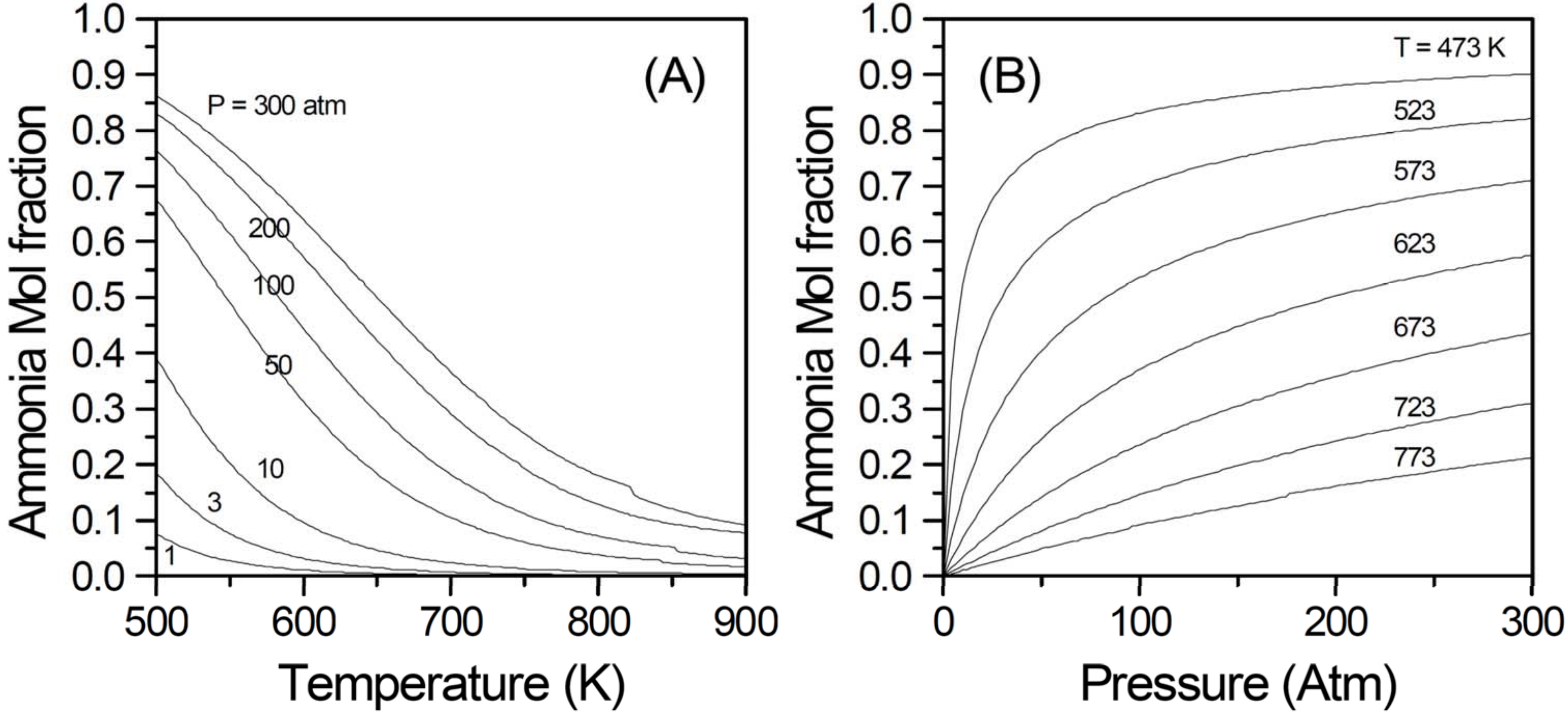
High equilibrium yield can be obtained for <u>high pressure</u> & <u>low temp.</u>

$$[NH_3]^2 = k_p\,[N_2][H_2]^3$$

where k_p is the rxn equil. constant.

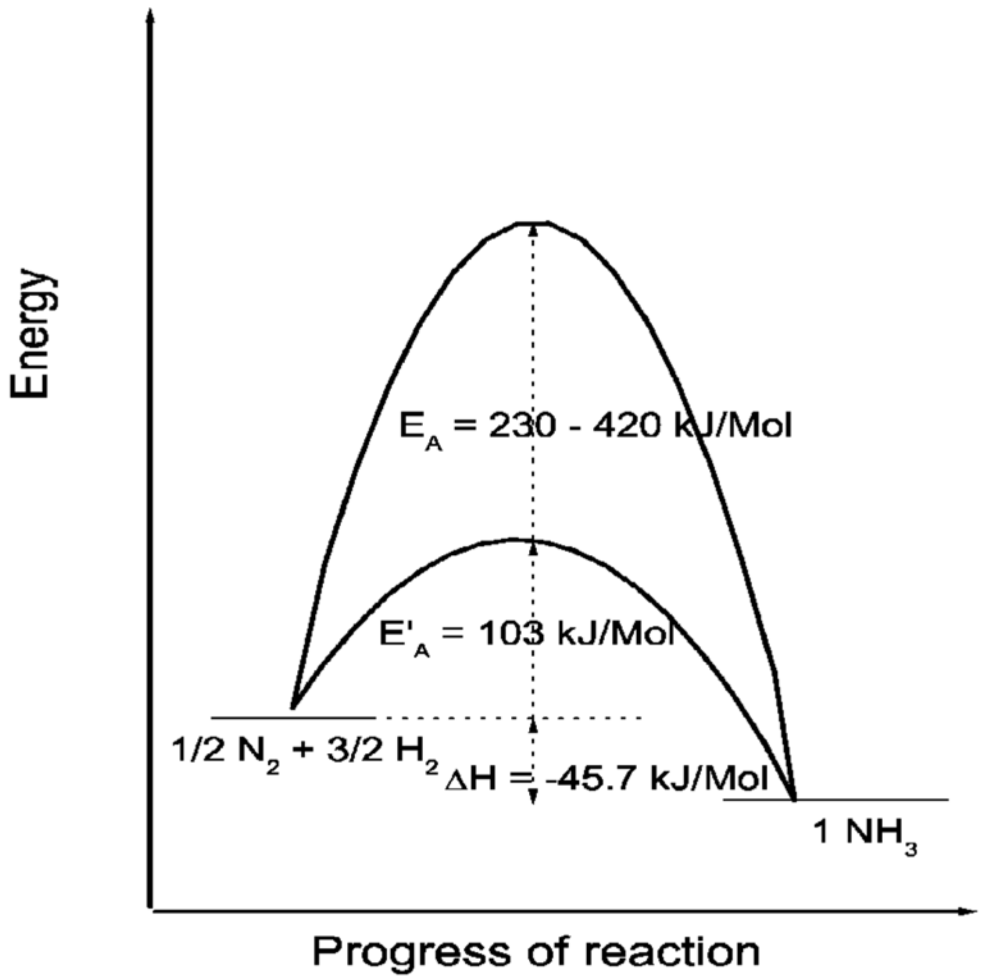
In terms of yield/mole fraction: $Y_{NH_3} = P_T\left[k_p Y_{N_2} Y_{H_2}^3\right]^{1/2}$

$$RT \ln k_p = a_0 + a_1 T - a_2 T^2 + a_3 T^3 - bT \ln T$$



1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Ammonia Mol fraction
(A)
P = 300 atm
200
100
50
10
3
1
500
600
700
800
900
Temperature (K)
(B)
T = 473 K
523
573
623
673
723
773
0
100
200
300
Pressure (Atm)

But rxn equilibrium is not the whole story !



Operating temp. is generally 500-550°C for Haber-Bosch process.

A significant amount of energy is required for the activation energy / kinetics

Process optimization is thus reduced to maximisization of the space velocity (V) instead of the product yield.

$$x \propto \frac{1}{V^n}$$

fraction of NH_3 in the product gases

< 1 correct temp.

> 1 ~~too~~ low temp. because of high velocity gas cooling.

$$Y = V \cdot x \approx V^{(1-n)}$$

amt. of ammonia obtained per unit vol. of catalyst per unit time.

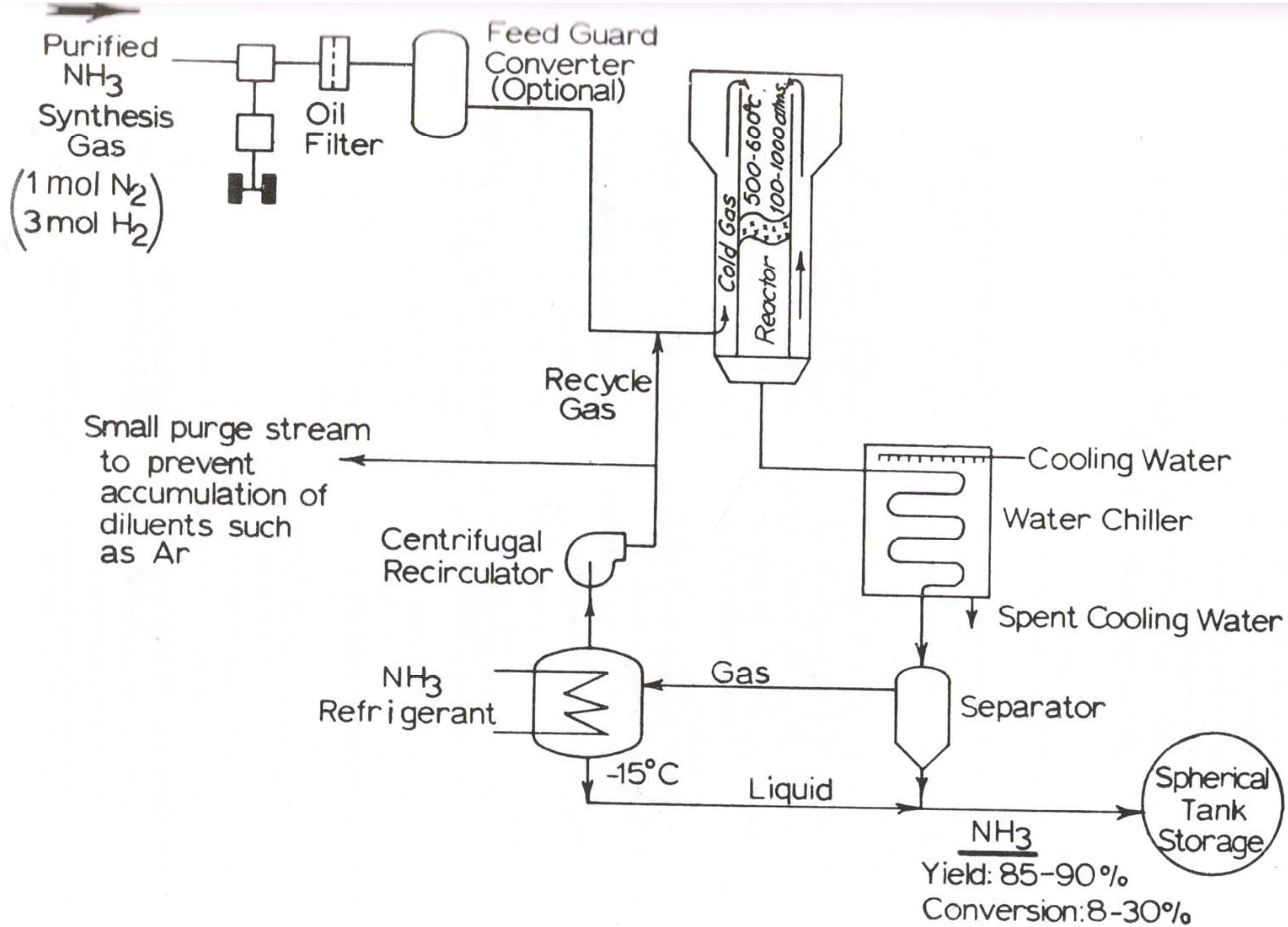
Catalyst

should allow improved yields @ low T & P

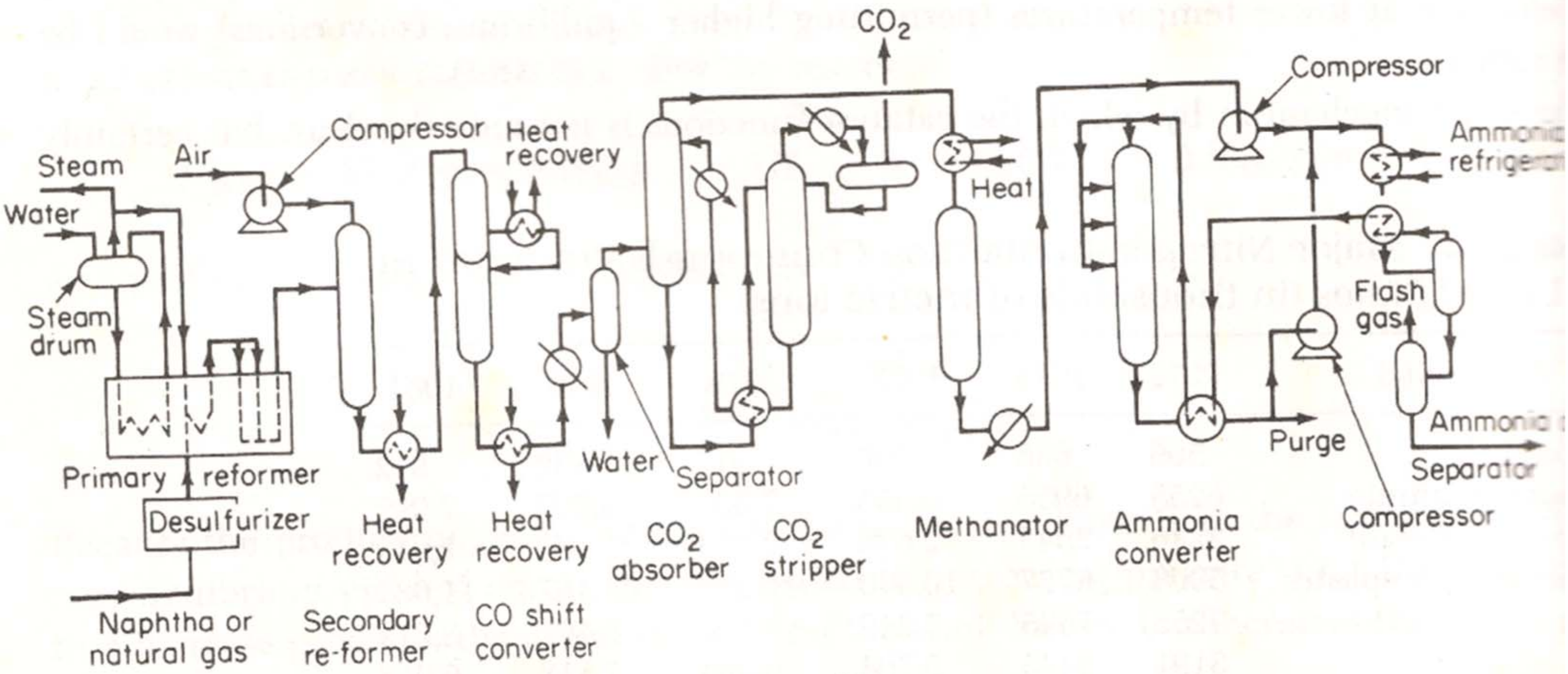
Catalyst : Iron Oxide (FeO) promoted by K_2O (1-2%) & alumina Al_2O_3 (2-5%)

Iron oxide is fused in an electric furnace when the promoters are added. It is then grounded to produce the desired particle size.

Typically $T > 600°C$, the iron-oxide catalyst fuses.



PFD for Production of Ammonia – Haber-Bosch process



CO2
Compressor
Steam
Air
Compressor
Heat recovery
Water
Steam drum
Heat
Ammonia refrigera
Flash gas
Primary reformer
Desulfurizer
Heat recovery
Heat recovery
Water
Separator
Purge
Ammonia
Separator
Compressor
CO2 absorber
CO2 stripper
Methanator
Ammonia converter
Naphtha or natural gas
Secondary re-former
CO shift converter

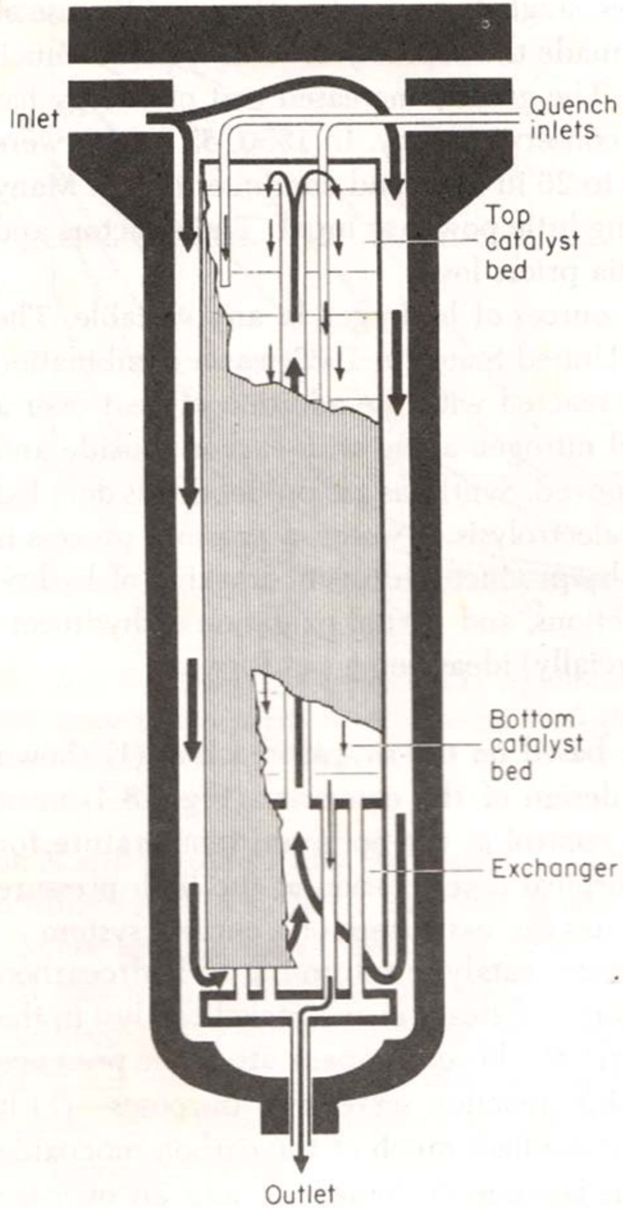


Fig. 18.4. Ammonia-synthesis converter. The converter consists of a high-pressure shell containing a catalyst section and a heat exchanger. The catalyst section is a cylindrical shell which fits inside the pressure shell, leaving an annular space between the two. The catalyst section contains several beds supported on screened grids. To maintain the catalyst at optimum temperature for maximum yield, cold feed-gas quench is injected before each catalyst bed. The top bed contains the smallest quantity of catalyst. Since the temperature gradient is flatter in succeeding beds, bed sizes are graduated, with the largest bed at the bottom. Beneath the catalyst section is the heat exchanger. This preheats fresh inlet gas against hot reacted gas from the last catalyst bed. The top quench point permits the introduction of feed gas without preheating and provides temperature control to the first catalyst bed.

The feed gas enters at the top of the converter and flows downward between the pressure shell and the wall of the catalyst section. The gas cools the shell and is heated. The gas then enters the exchanger at the bottom of the converter and, by circulating around the exchanger tubes, is further preheated against hot effluent. Some feed gas is introduced directly to the top of the first bed, where it meets the preheated feed. The combined stream at a temperature of 370 to 425°C is then introduced into the top catalyst bed. The gas passes downward through the catalyst, with a rapid temperature rise as the ammonia reaction proceeds, and then through the catalyst supporting grid into a space between the first and second beds. Here the temperature is reduced and the ammonia content diluted by injection of cold feed gas. This permits control throughout the catalyst beds to obtain optimum temperatures for maximum yields. In a like manner, the gas flows downward through the lower catalyst beds. *(M. W. Kellogg Co.)*

UREA production

Ammonia and Carbon-dioxide are compressed and reacted at 100-200 atm., and 170-190 °C in a pressure vessel to produce ammonium carbamate. Urea is formed by dehydration in low-pressure flash drums.

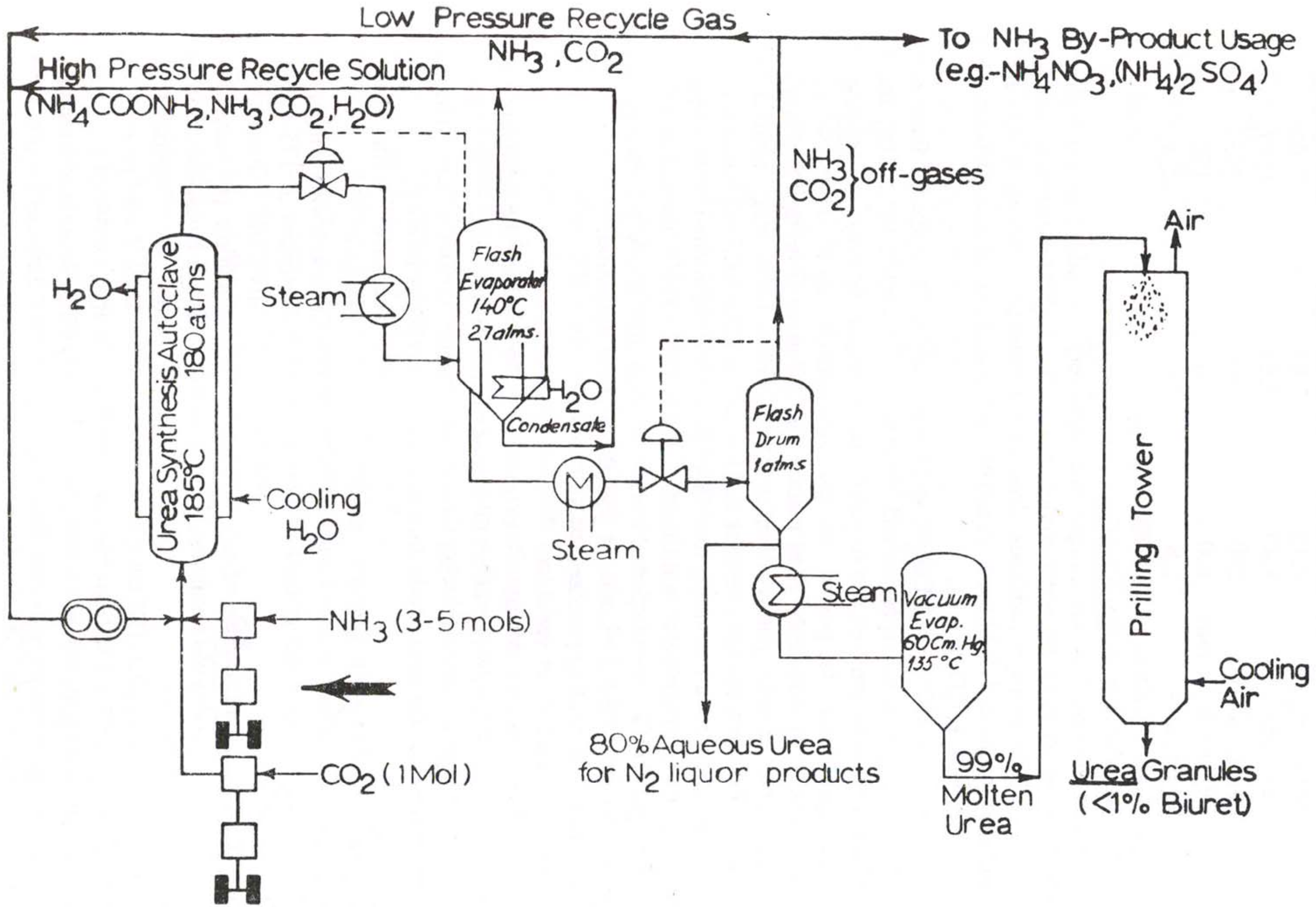
Chemical rxns:

$$CO_2 + 2NH_3 \longrightarrow NH_4(COO)NH_2 \qquad \Delta H = -157 \text{ kJ}$$

$$NH_4(COO)NH_2 \longrightarrow NH_2(CO)NH_2 + H_2O \qquad \Delta H = +26.5 \text{ kJ}$$

(Undesired side rxns)

$$2NH_2(CO)NH_2 \rightarrow NH_2CONHCONH_2 + NH_3$$



Process flow diagram for production of urea

Major engineering challenges

- Pressure vessel parameters
- Carbamate decomposition and recycle
- Production of granular urea
- Heat transfer / dissipation in the autoclave
- Corrosion
- Process design modifications in the treatment of the off-gas and their effect on the process economics

Ammonium nitrate

Usage : as a chemical fertilizer. In rice-paddy field the ammonical form of nitrogen is preferred over the nitrate form, so this is also converted to nitrolime in the Indian context.

other use : explosives (15-20% of ~~total~~ amt. of Amm. nitrate produced)

Chemical reaction

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3 \qquad \Delta H = -85 \text{ kJ}$$

Liq. form

55-60% pure

clay such as diatomaceous earth is used for coating the final product to prevent explosion.

Nitric acid

Important info: Forms azeotropic (const. boiling) mixture at 110 C and 1 atm for 68% w/w HNO_3

Ammonia – Oxidation process

1. Oxidation of NH_3 to NO

$$NH_3 + \frac{5}{4}O_2 \rightleftharpoons NO + \frac{3}{4}H_2O \qquad \Delta H = -226.8\ KJ$$

2. Oxidation of NO to NO_2

$$2NO + O_2 \rightleftharpoons 2NO_2 \qquad \Delta H = -114.2\ KJ$$

3. Absorption of NO_2 in water

$$3NO_2(g) + H_2O\ (l) \rightleftharpoons 2HNO_3(aq.) + NO \qquad \Delta H = -135\ KJ$$

$$2NO_2 + H_2O \rightleftharpoons HNO_3\ (aq.) + HNO_2$$

$$2HNO_2 \rightleftharpoons H_2O + NO + NO_2$$

Side reactions

$$NH_3 + \frac{3}{4}O_2 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2O\ (g)$$

$$NH_3 + O_2 \rightleftharpoons \frac{1}{2}N_2O + \frac{3}{2}H_2O\ (g)$$

$$NH_3 + \frac{3}{2}NO \rightleftharpoons \frac{5}{4}N_2 + \frac{3}{2}H_2O\ (g)$$

Raw materials

Ammonia from Haber's process

Filtered air

Platinum rhodium catalyst

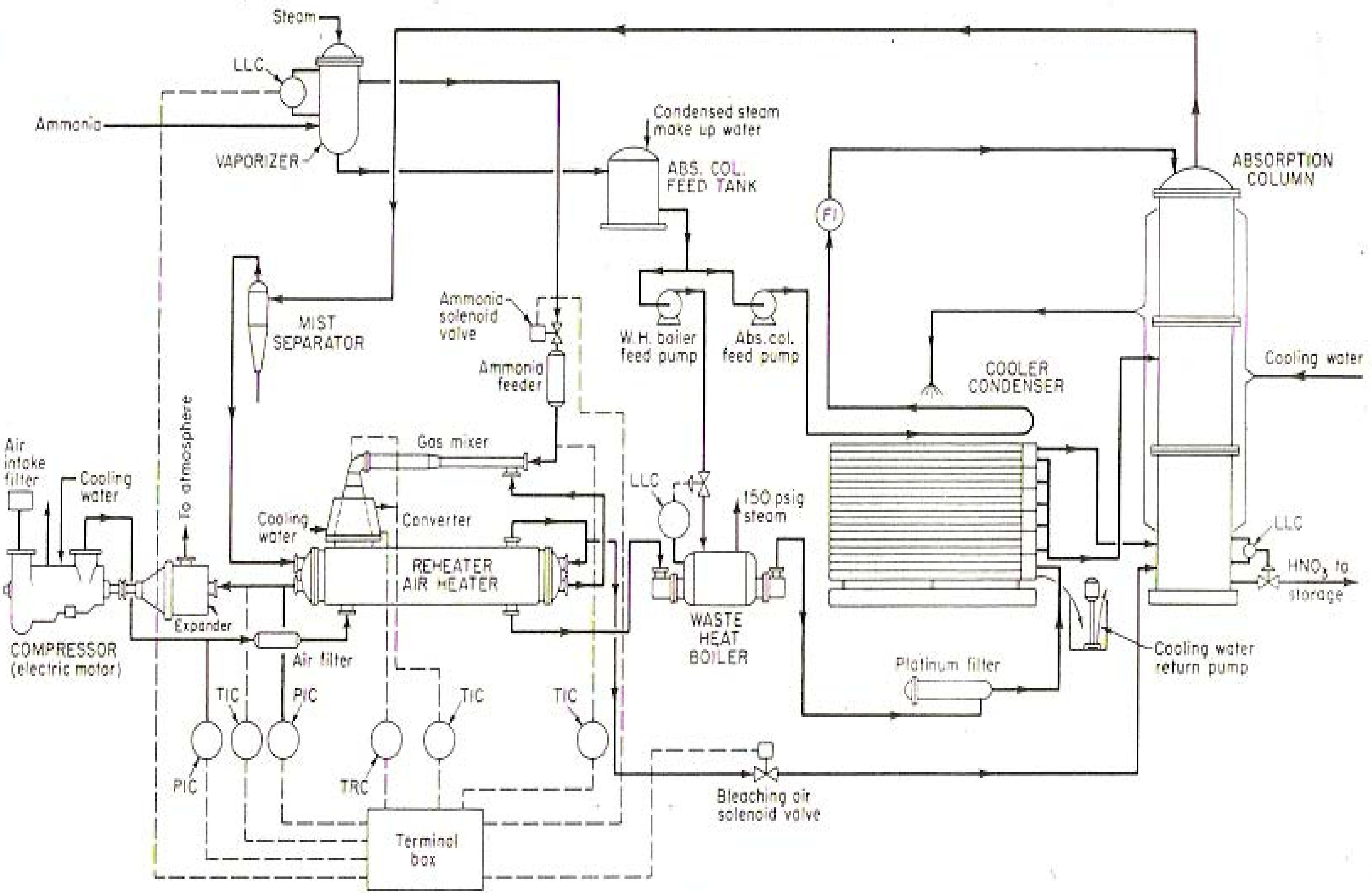
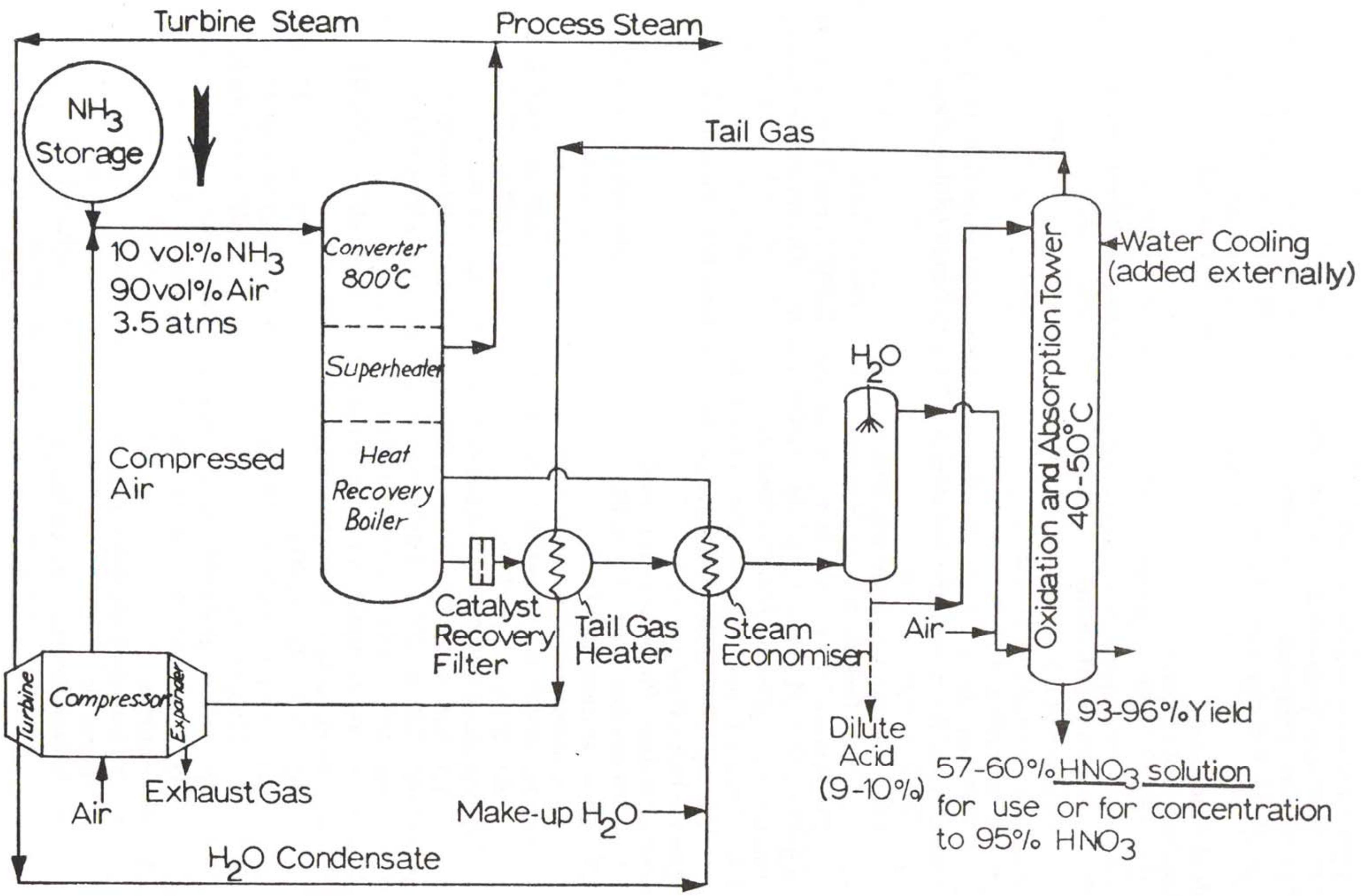


Fig. 18.8 Flowchart for the manufacture of 60% nitric acid from ammonia: Du Pont high-pressure (100-psi) self-sustaining 250 tons/day unit. The "expander" turbine operates on "waste heats" of tail gas (essentially N_2). For platinum filter, the very efficient Brink filter of Monsanto is now recommended. LLC, Liquid-level controller; LG, liquid gauge; FI, feed intake; LIC, liquid indicating controller; PIC, pressure indicating controller; TIC, temperature recording controller; WH, waste heat; abs. col., absorption column. (*E. A. Rass, Chemical & Industrial Corp.*)



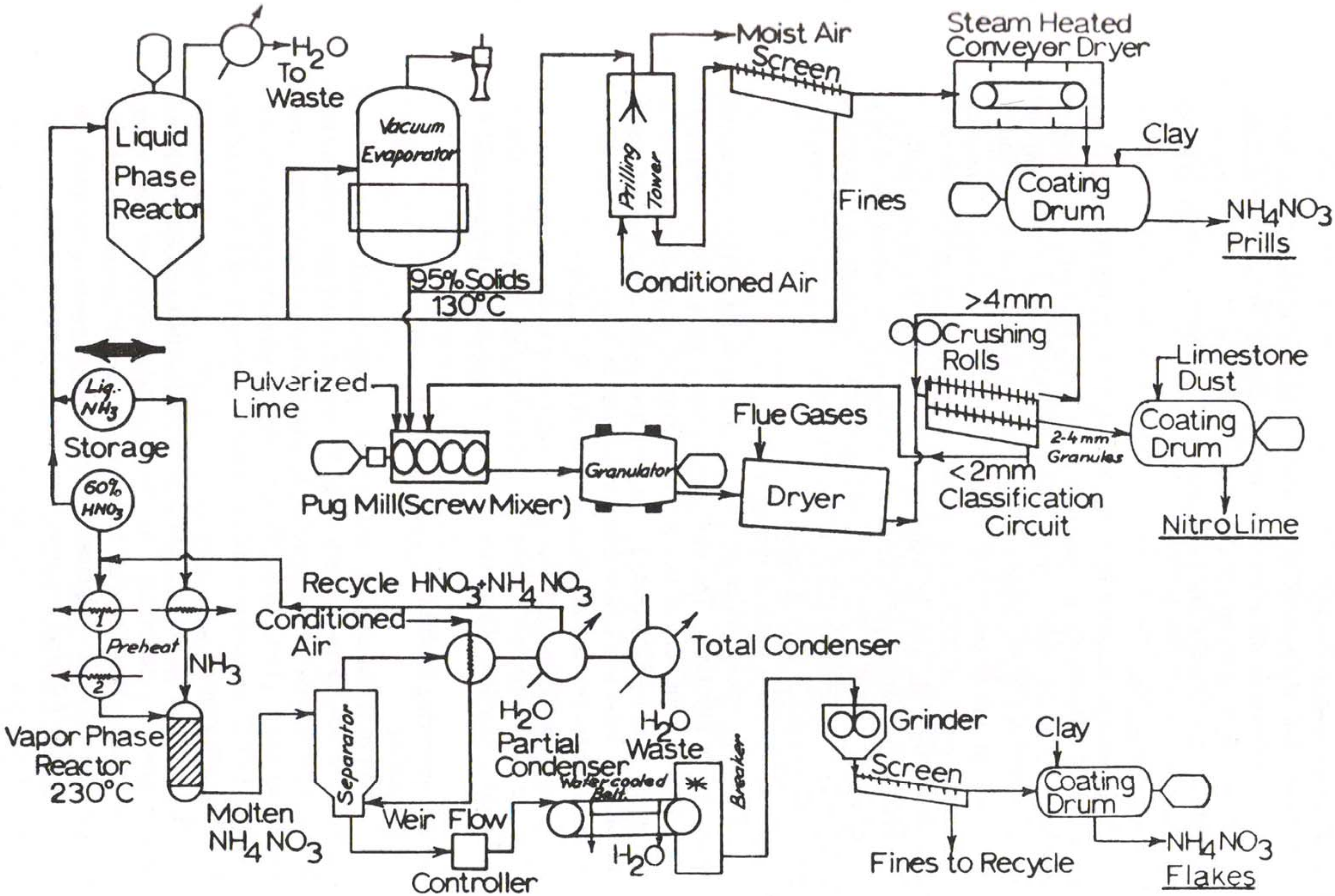
Process flow diagram for nitric acid production by oxidation of ammonia

Concentration of nitric acid

- Rectification by 90–95% H_2SO_4 in silicon-iron or stoneware towers produces HNO_3 upto 90% conc. and 70% H_2SO_4 which can be revaporated & recycled.

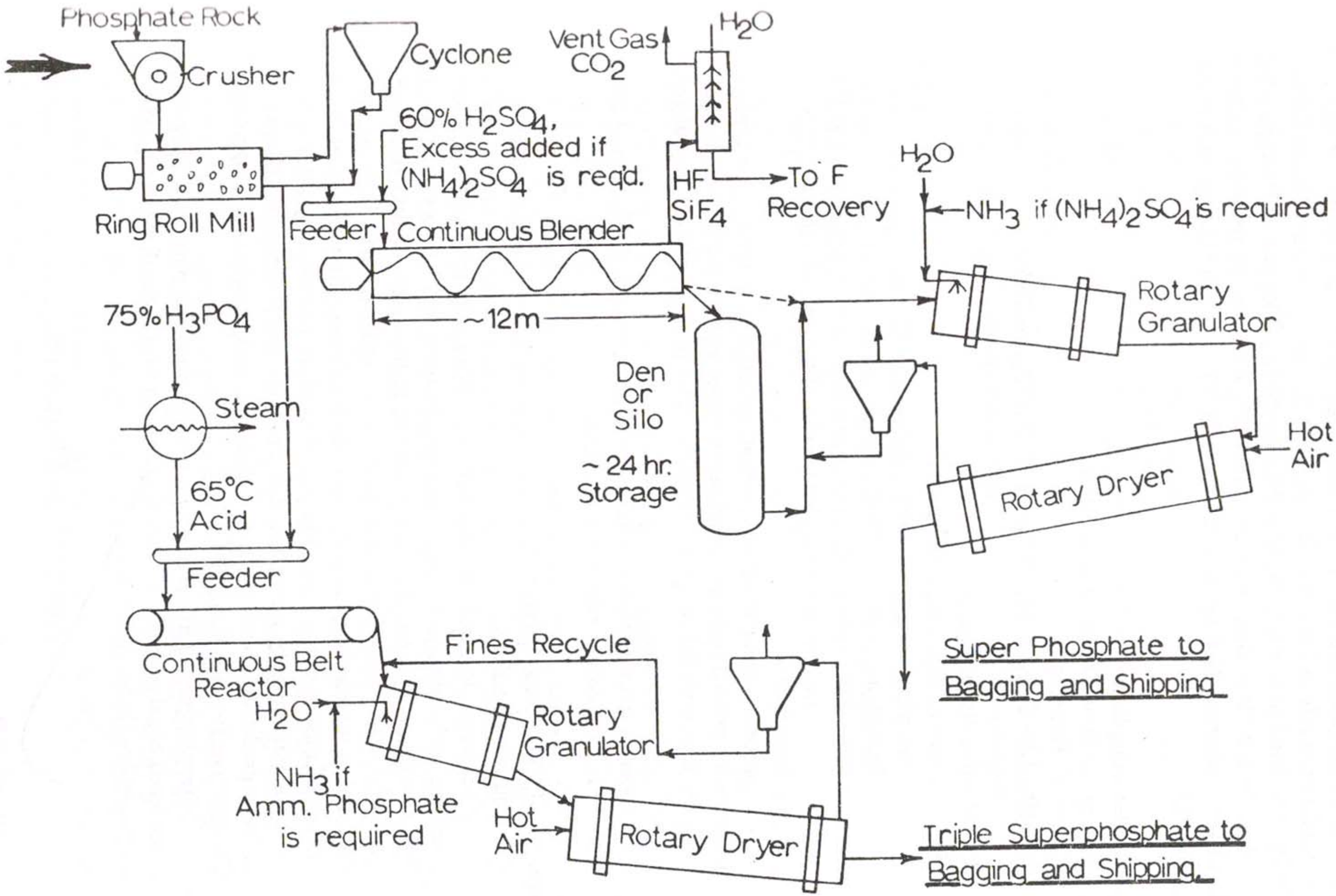
- Conc. by $Mg(NO_3)_2$

$Mg(NO_3)$ solⁿ containing 70–75% is fed to a dehydrating tray tower along with dil. HNO_3 from the absorption process. The Mg salt acts as an entrainer, removing water at 100°c or higher without forming azeotrope. The diluted $Mg(NO_3)$ can be evaporated and recycled.



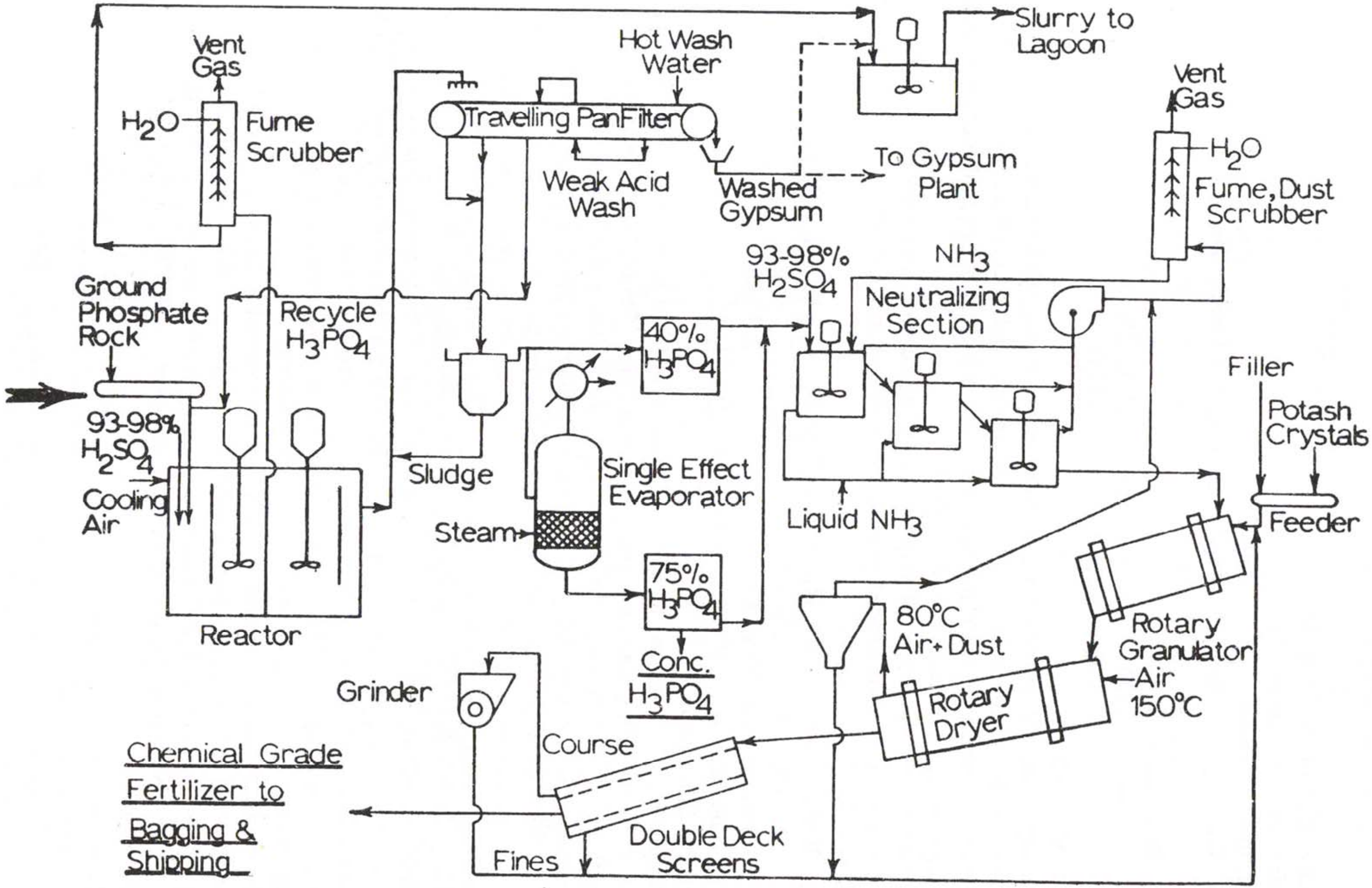
Process flow diagram of production of ammonium nitrate and nitrolime

Calcium phosphates



PFD for production of calcium phosphates: Superphosphate and triple phosphate

Ammonium phosphate



PFD for production of ammonium phosphate from phosphate rock by strong acid process