Module-3
Nitrogen Industries

Ammonia, Urea, Nitric Acid, and Ammonium Nitrate

Arnab Karmakar

BIT Mesra, Ranchi

Nitrogen Industries

- Nitrogen Fertilizers in the form of liquid and aqueous NH_3 solutions, ammonium salts, and urea.
- Nitric acid (HNO_3).
- Most Nitrogen chemical compound.

⇒ 90 % of NH_3 Production is used in India as fertilizer. Producttution of N, P, K fertilizer.

Ammonia

Ammonia

Grades: Anhydrous or Liquified ammonia,
(Stored at 80°F and 175 psig.)
Aqueous grade (28 wt%, NH_3, ammonia)

uses:
Direct application as fertilizer 25%
urea (fertilizer & plastic) 21%
Ammonium phosphate 16%
Nitric acid 12%
Ammonium nitrate 8%
" sulfate 3%

Mixed fertilizer: It contains tree principal elements (Nitrogen, phosphorus, and potassium) The composition is expressed as wt% of total N, available P_2O_5 and Soluble K_2O.
(e.g. 5-10-5 is 5% N, 10% P_2O_5, 5% K_2O)
These are generally granular Solid.

NH_3 Production Process.

It is based on prssure-catalytic reaction of N_2 and H_2. The principal variation is operating pressure.

chemical reaction.

$$N_2 + 3H_2 \overset{Fe}{\rightleftharpoons} 2NH_3 \; ; \Delta H = -22.00 \text{kcal}$$

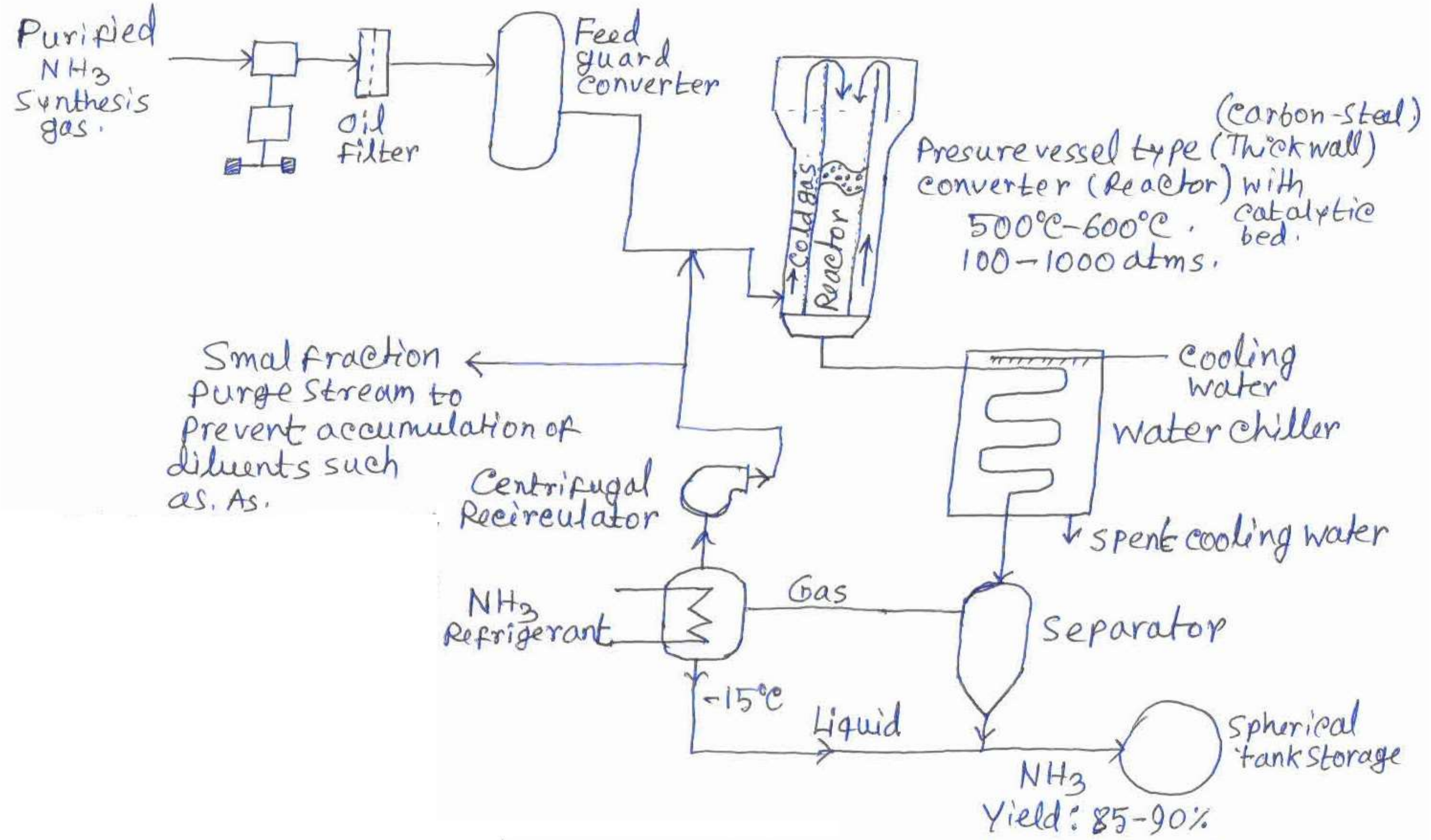
Raw materials: i) H_2 from synthesis gas.
ii) N_2 from air; It is added synthesis gas process, or liquefaction process.

Basis: 1 ton Ammonia — 85% yield.

H_2 : 0.21 ton
N_2 : 0.96 ton
synthetis catalyst : 0.2 kg
Power: 850 KWH
Fuel gas for compressor: 3,800 kcal.
cooling water: 12.5 tons.
plant capacities : 100 – 1,500 tons/day of NH_3

Process description

- Synthesis gas (mole ratio H_2 and N_2, 3:1) is compressed to operating pressure (100-1000 atms depending on conversion) and sent through a filter to remove compression oil. Temperature guard converter then converts CO and CO_2 to methane and removes traces of moisture, H_2S, P, and As.
- The cool gas is fed along the outside annulus of the tubular converter that provides cooling of the exothermic catalytic reactor bed at center of the converter. The preheated gas flows next through the inside (center) the tubular packed bed containing porous iron catalyst at 500-550^oC.
- Produced ammonia gas with 8-30% conversion (depending on the process) is recovered by condensation with cooled water first then with ammonia refrigerant.
- The unconverted hydrogen and nitrogen gases are recycled back to the reactor for 85-90% yield.



Ammonia synthesis process

Major engineering problems

- Thermodynamic and kinetic considerations: Highest equilibrium yield of the catalyst reaction (ammonia synthesis) is obtained at high pressure and low temperature. Yield of ammonia, $Y_{NH_3} = \left(K_p Y_{N_2} Y_{H_2}^3 P_T\right)^{1/2}$ and equilibrium constant K_p is inverse function of temperature as it is an exothermic reversible reaction. Like SO_2 oxidation the ammonia synthesis reaction is favoured by low temperature, but to compromise reaction kinetics it is carried out at higher temperature 500-550°C.
- The multistage reactor is not feasible economically due to the high cost of high-pressure reactor vessels.
- The mole fraction of ammonia in exit gas *x* decreases with increase in space velocity *V*. The relation is, $x = fV^{-n}$; $n < 1$, if bed is at correct temperature and $n > 1$, when bed is at too low temperature due to high space velocity.
- Space time yield $Y = Vx = V^{1-n}$ *(m^3 product/hr m^3 catalyst)*
- High space velocity *V* results a) increase in cost of ammonia recovery because *x* is lower. b) Increase of pumping cost

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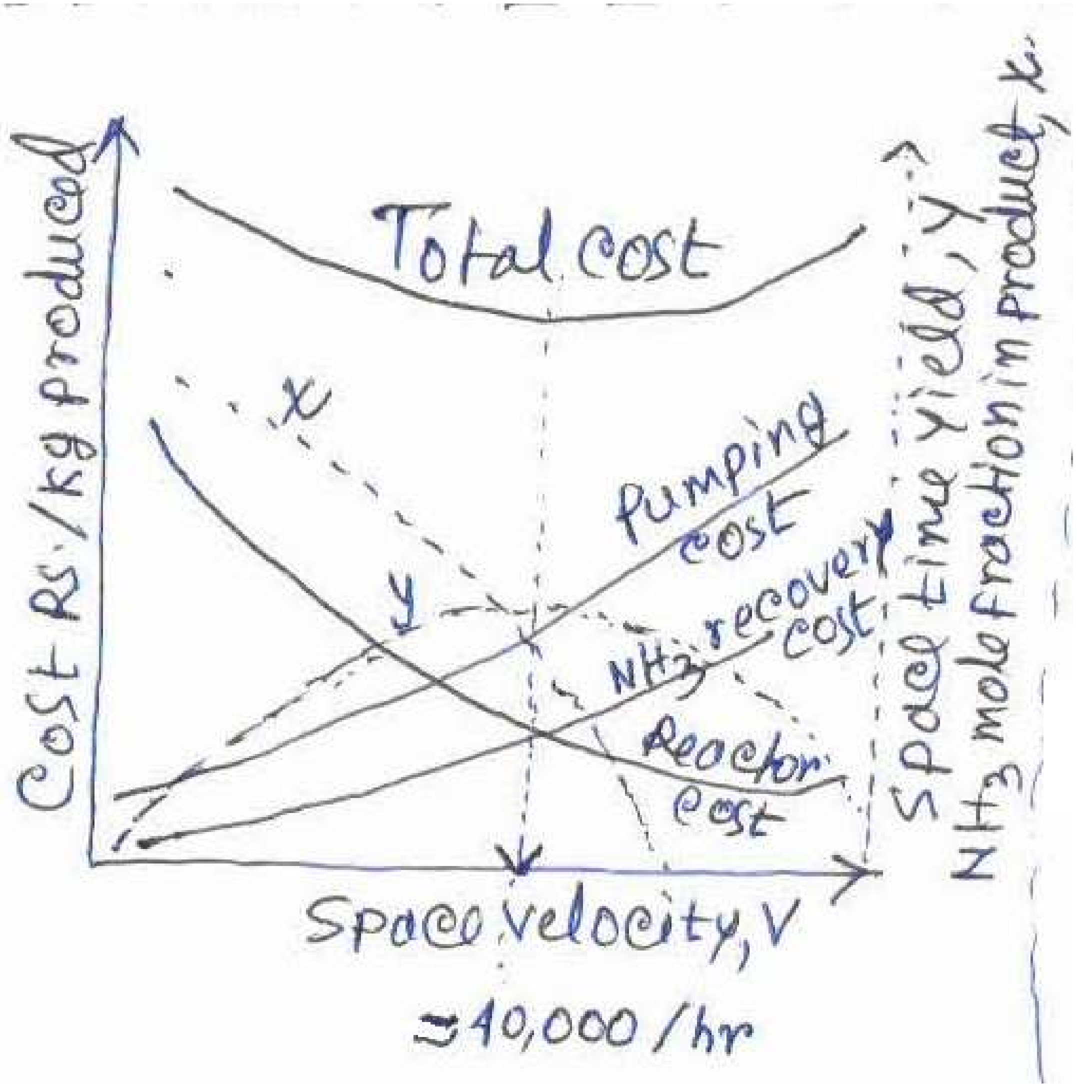
Cost Rs./kg produced
Total cost
x
Pumping cost
y
NH3 recovery cost
Reactor cost
Space velocity, V
≃40,000 /hr
Space time yield, Y
NH3 mole fraction in product, x

- Catalyst development: Objective of the catalyst is to improve yields at lower temperature and pressure. It is based on iron oxide promoted by alkali or non-ferrous metal oxide like, K_2O (1-2%) and Al_2O_3 (2-5%). Iron oxide is fused in an electric furnace and promoters are added. Solidified mass is grounded to desired particle size. A promoted iron catalyst is developed in Europe (Mont Cenis process) that allows lower temperature of 400 ^oC and pressure of 100 atms.
- Process design modifications: The modifications for the ammonia process are:

1. Very high pressure (900-1000 atms., 500-600^oC, 40-80% conversion)– Claude, Dupont, L' Air Liquide.
2. High pressure (600 atms., 5000^oC, 15-25% conversion)– Casale
3. Moderate pressure (200-300 atms., 500-550^oC, 10-30% conversion)– Haber-Bosch, Kellog, Fauser, Nitrogen engineering corporation.
4. Low pressure (100 atms., 400-425^oC, 8-20% conversion)

   Modern trend is to lower pressure and increased recirculation rate. It promote lesser cost of reactor vessel. Nowadays centrifugal compressor is used, and the plant produces near about 1000 ton/day ammonia from a single reactor at low production cost.

Urea Production process.

urea ($NH_2 \cdot CO \cdot NH_2$)

Grades: **C.P** technical (46% N)

Fertilizer: Granular-coated with non-hygrscopic dust such as, phosphate rock or limestone (40–42% N)

Liquor –: Mixture of urea in NH solution (45% N, 30% Free NH_3, 15% urea).

slowrelease: low m.w urea polymer.

uses: Solid fertilizers (53%), liquid fertilizer (31%)

· animalfeed, formaldihyde resins, melamine and adhesives.

Melamine formaldihyde resins are used as a dinnerware or extra hard surface (Formica).

Method of production.

NH_3 and CO_2 are compressed and reacted at 100-200 atms, 170°C - 190°C in an autoclave to form ammonium carbamate ($NH_4 \cdot COO \cdot NH_2$). Urea is formed by dehydration of ammonium carbamate in a low- pressure stripping operation.

Chemical reaction

a) $CO_2 + 2NH_3 \longrightarrow NH_4 \cdot COO \cdot NH_2 + \Delta H^0 = -37.4$ kcal

b) $NH_4 \cdot COO \cdot NH_2 \longrightarrow NH_2 \cdot CO \cdot NH_2 + H_2O$
(urea) $\Delta H^0 = +6.3$ kcal

Undesirable side reaction

$2NH_2 \cdot CO \cdot NH_2 \longrightarrow NH_2 \cdot CO \cdot NH \cdot CO \cdot NH_2 + NH_3$
(biuret).

basis: 1 ton of prilled urea (99+%)

	once-through	Partial recycle	Total recycle
NH_3 ton	1.15	0.88	0.6
CO_2 ton	1.47	0.91	0.77
Power kWH	210	165	145
cooling H_2O tons	120	70	110
Steam, tons	1.8	2	2.4

Process description

- Ammonia and carbon dioxide gases are compressed and added to the high-pressure autoclave reactor that is cooled by external water jacket. The residence time of the reactor is 1.5 to 2 hrs on continuous basis. A mixture of urea, ammonium carbamate, water, and unreacted gases (ammonia+CO_2) is produced.
- The liquid effluent is fed to flash-evaporator with gas-liquid separator and condenser at 27 atms pressure, where unreacted gases and water are separated as top product or high pressure recycle to be sent at the reactor inlet. The aqueous urea-carbamate solution at the bottom product is sent to atmospheric flash drum where further decomposition of carbamate takes place. The off gases from this stage is recycled to reactor and few percent of it is purged to fertilizer making process.
- The bottom product of the atmospheric flash drum is 80% aqueous urea solution which can be used as urea fertilizer or sent so vacuum evaporator to obtain molten urea containing less than 1% biuret. The molten urea is sprayed at the top of prilling tower or granulation tower dispersed in cooling air from bottom.

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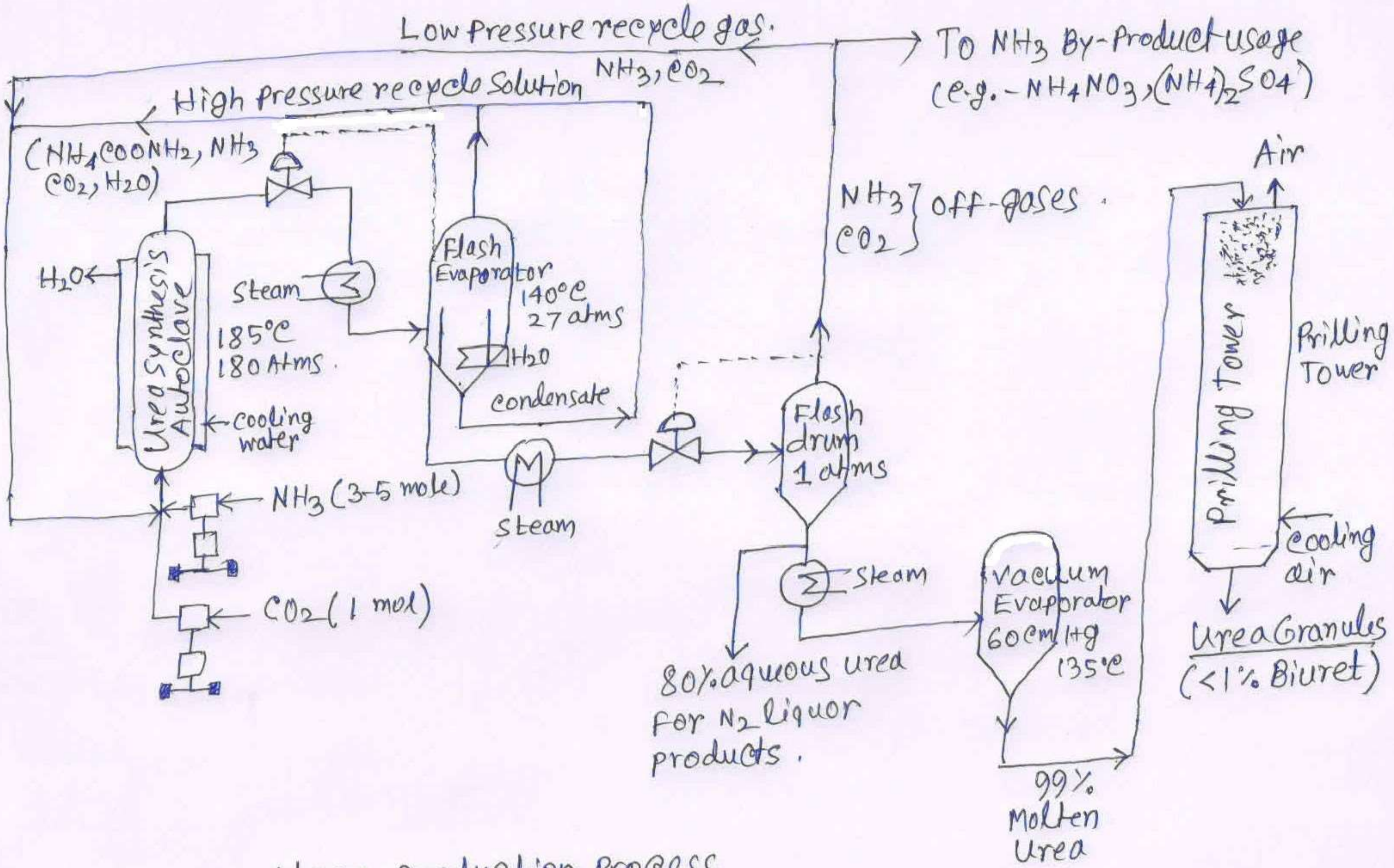

Urea production process.

- To prevent the formation of biuret (>1%) the temperature of the urea is kept just above the melting point and processing time is limited to 1-2 sec in this prilling operation.

Major engineering problems

- For the optimum economic yield of urea production, operating conditions of an autoclave reactor such as, temperature, pressure, flowrates and ratio of feed gases must be controlled.
- Urea production rate increases with pressure and temperature up to 170-180 ^{o}C. Above the temperature production rate reduces sharply. The operating pressure should be above the dissociation pressure of carbamate. (e.g., dissociation pressure is 180 atms at 190 ^{o}C.
- Urea production is not carried out at maximum temperature, pressure and with excess ammonia because of the following reasons:
  1. Operating pressure increases capital (material inventory of reactor) and operating cost (compression).
  2. Increased temperature accelerates decomposition of urea to biuret that is detrimental to germinating seeds and toxic to animals.
  3. Above conditions increases corrosion rate that gives higher design cost.

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- Ammonium carbamate stripping operation in the flash evaporator is favorable at low pressure, and temperature should be below 110^{o}C if hold-up time exceeds 1-2 sec to avoid biuret formation.
- Recompression of off gases is problematic because of corrosion and formation of solid carbamate in compressors. Unreacted off gas must be recycled by pump after forming solution. Few portion of it is purged and used economically.
- To prevent formation of biuret vacuum drying of 80% urea solution and granulation operation (Prilling) must be carried out just above the melting point of urea with minimum residence time of several seconds.
- The exothermic reaction in the autoclave is cooled by coils, wall cooling, or by increasing reactants flowrate to absorb heat.
- To prevent corrosion in high pressure NH_3-CO_2 process, high-cost silver or tantalum liners are used in the autoclave with Hastelloy C, titanium, SS 321, aluminium alloys used in the other parts. Minimum temperature and pressure with excess NH_3 are required to avoid corrosion in stainless steel autoclave.

- **Process modifications**
  1. **Once-through process**: Off gasses are used elsewhere. Expensive ammonia is recovered by neutralization with acid to produce ammonium salts.
  2. **Hot-recycle process**: Off gases are heated, compressed and recycled with precise temperature control to prevent solidification of carbamate in the compressor. The recycled hot gases increase the cooling load of the reactor.
  3. **'Inventa' process**: Unconverted ammonia is absorbed in aqueous urea nitrate solution, stripped and returned to the autoclave. It provides better temperature control and reduces cooling load.
  4. **'Chemico' process**: Carbon dioxide from off gases is stripped by monoethanolamine (MEA) solvent provides better temperature control. It is then recompressed and recycled.
  5. **Solution recycle (Montecatini)**: Recycle gases are absorbed in reaction product water to make a solution and pumped back to the reactor. It provides better temperature control in the autoclave but requires higher T, P and excess ammonia for good conversion.
  6. **Allied chemical high pressure process**: This process is operated in Visakhapatnam, India at 275 atms and 400 ^oC with high conversion of 75% per pass and does not recycle carbamate. A zirconium-lined reactor is used to minimize corrosion.
  7. **Toyo Katasu process**: Carbon dioxide formed in the shift reaction of ammonia process is absorbed by a mixture of hot carbamate solution (urea plant) and ammonia (ammonia synthesis process) and fed to the urea reactor. Indian Explosives Ltd. in Uttar Pradesh employed the process with total recycle.

Nitric Acid (HNO_3)

completely miscible with H_2O, Forms constant boiling mixture at 110°C and 760mm Hg containing 68 wt % HNO_3.

Grades: concentrated (95%) as technical.
commercial (52–68%).
Fuming (>86%).
Red Fuming (>95% with 10-15% excess dissolved oxide of N).
Nitrating or mixed acid (80% HNO_3 – 15 H_2SO_4 to 50% HNO_3 – 48% H_2SO_4).

uses
76%. For ammonium nitrate as fertilizer, explosive, N_2O.
9%. For adipic acid.
3.5%. for dinitrotoluene.
3.5%. " Nitrobenzene.
2%. , Ca, Na, K nitrates.
1%. other nitro compounds.

Production

i) Ammonia oxidation process.
Ostwald process (1902).
- Oxidation of NH_3 to NO
- Oxidation of NO to NO_2
- Absorption of NO_2 in water.
- Concentration of HNO_3.

ii) $NaNO_3$ + H_2SO_4 process.
Oldest process.

iii) N_2 fixation from air (Wisconsin process).

Production of NO & NO_2 by high temperature (2,200°C) reaction using air in a gas-fired pebble bed reactor followed by quick quench.

NH_3 oxidation method.

chemical reactions.

a) $NH_3 + \frac{5}{4}O_2 \rightleftharpoons NO + \frac{3}{2}H_2O$ $\Delta H = -54$ kcal

b) $2NO + O_2 \rightleftharpoons 2NO_2$ $\Delta H = -27.2$ kcal

Sidereactinos

$4NH_3 + 3O_2 \rightleftharpoons 2N_2 + 6H_2O$ $\Delta H = -75$ kcal

$NH_3 \rightleftharpoons \frac{1}{2}N_2 + 3/2\, H_2$;

$NH_3 + O_2 \rightleftharpoons \frac{1}{2}N_2O + 3/2\, H_2O$

$NH_3 + 3/2\, NO \rightleftharpoons 5/4\, N_2 + 3/2\, H_2O$ $\Delta H = -107.9$ kcal

Oxidation & absorption

$2NO + O_2 \rightleftharpoons 2NO_2$ $\Delta H - 27.2$ kcal

$3NO_2^{(g)} + H_2O^{(l)} \rightleftharpoons 2HNO_3^{(aq)} + NO$

$\Delta H = -32.2$ kcal

$2NO_2 \rightleftharpoons N_2O_4$ .. $\Delta H = -11.46$ kcal

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

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

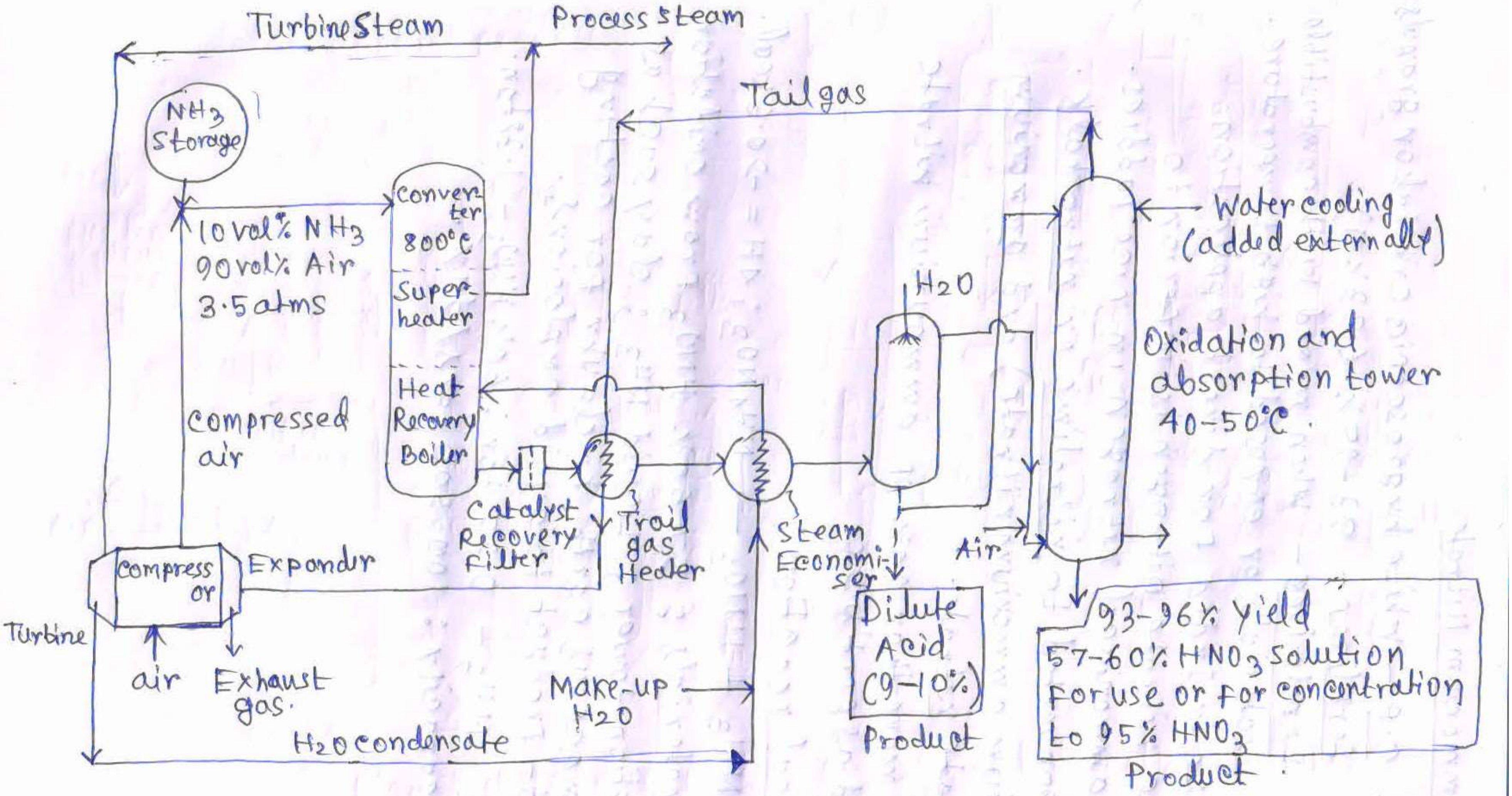
Basis: 1 ton HNO_3 (100%)

Anhydrous NH_3 —	0.287 – 0.290 ton
Air – – – – –	3000 Nm^3
Platinum (2-10% Rh promoted)	0.1 gm.
Process water	120 ton
Steam credit	1 ton @ 200 psig.
power	10–30 KWH.

Plant capacity 50 - 250 tons/day.

Process description: compressed air is mixed with anhydrous ammonia and fed to a shell and tube type converter that consists of converter section, with preheater, steam heat recovery boiler-superheater in the same reactor shell. It consists of 10–30 sheets of Pt–Rh alloy in the form of 60–80 mesh wire gage packed in layers inside the tube to host the catalytic reaction. Gas flows downward with a velocity conrresponds contact time 2-5 × 10^{-4} sec through the catalyst tube.

Product gases from the reactor containing 10–12% NO are sent through heat recovery units, a quench unit and into oxidizer-absorber system. Here air is added to convert NO to NO_2 at the temperature of 40-50°C. and simultaniously absrorbed with dilute HNO_3 to form 57-60% HNO_3 at the bottom.



Nitric Acid by Ammonia absorption process

Concentration of nitric acid to 95% is obtained by following methods:

1. By concentrated H_2SO_4: Rectification by 93% H_2SO_4 in silicon-iron or stoneware packed towers produces concentrated nitric acid (>70%) and 70% H_2SO_4 that can be distilled to higher concentrations.
2. By $Mg(NO_3)_2$ (developed by Hercules powder company, 1958): Magnesium nitrate solution (70-75% $Mg(NO_3)_2$) is fed to a dehydrating tray tower with dilute nitric acid (57-60%). The salt solution removes water at 100^oC or higher to cross the azeotropic concentration (68%), allowing rectification of dilute nitric to concentrated one.
   The dilute $Mg(NO_3)_2$ can be reevaporate to concentrate.

Operating costs of $Mg(NO_3)_2$ process are half of the costs that by H_2SO_4. Capital costs are onle 70%. It gives improved quality and yield of acid produced.

Major engineering problems

- High temperature one step converters at intermediate pressure favour the increased conversion. Optimum temperature increases with gas velocity.
- Platinum-Rhodium alloy catalytic surface improves yield.
- Lower temperature favours operation efficiency of the absorber.
- Increasing pressure favours physical absorption rate and shifts chemical equilibrium to produce higher strength acid.
- Rate of absorption depends on concentration of NO_2 in gas phase.

Ammonium Nitrate

Grades: C.P – white hygroscopic crystals or granuls:
fertilizer – 93-95% (33% N).
Expolosive – when mixed with combustible materials or exposed to high temperature.

Little use in India for direct application beause nitrate nitrogen is inferior to ~~amo~~ ammoniacal nitrogen in rice paddies. It is converted to nitrolime or nitrochalk. (calcium ammonium nitrate) and ammonium sulfate nitrate.

India more than 90% of ammounium nitrate is used as fertilizer.

Chemical reaction

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 ; \Delta H = -20.6 \text{ kcal.}$$

Raw materials: 57-60% HNO_3 from oxidation absorption tower; Liquid NH_3; clay such as diatomaceous earth, kiselguhr for coating on end-product to avoid explosions.

Basis NH_3 – 0.22 ton; 60% HNO_3 – 1.38 ton.

plant capacity: 100-500 tons/day.

Reference

- Dryden’s Outlines of Chemical Technology, M. Gopala Rao, M. Sittig, 3rd Edition, East West Press.