Unit-5

Industrial Chemicals

&

Explosives n Propellants

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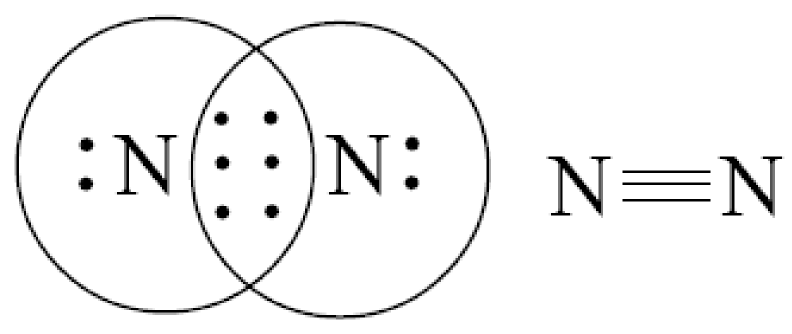
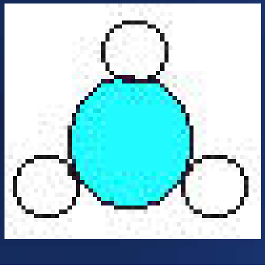
- The nitrogen bond can be represented as
- follows:

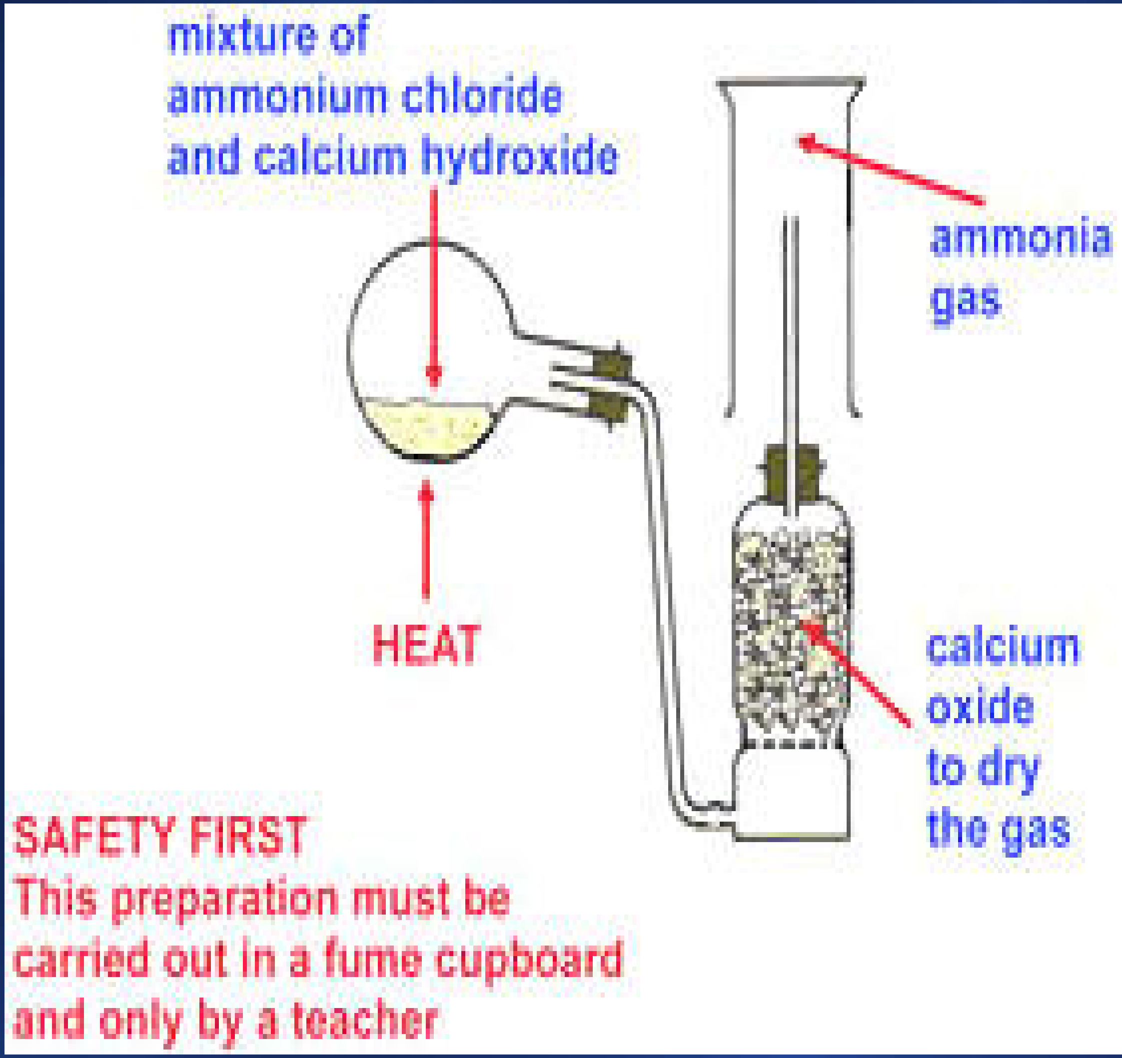


- Did you observe the triple bond between
- the two nitrogen atoms? What type of chemical
- bonding is this? **High energy is required to**
- **break this triple bond.** Now you can explain
- **why nitrogen is inert under normal conditions.**

- **ammonia** NH_3
- **Heating together ammonium chloride and calcium hydroxide.**

- **The ammonia gas is dried by passing it through calcium oxide granules** before it is collected by upward delivery.





SAFETY FIRST
This preparation must be carried out in a fume cupboard and only by a teacher

L-41-- NH_4Cl, $NH_4NO_{3,}$ $(NH_4)SO_4$

AMMONIUM CHLORIDE:--

Manufacture :-- **From**

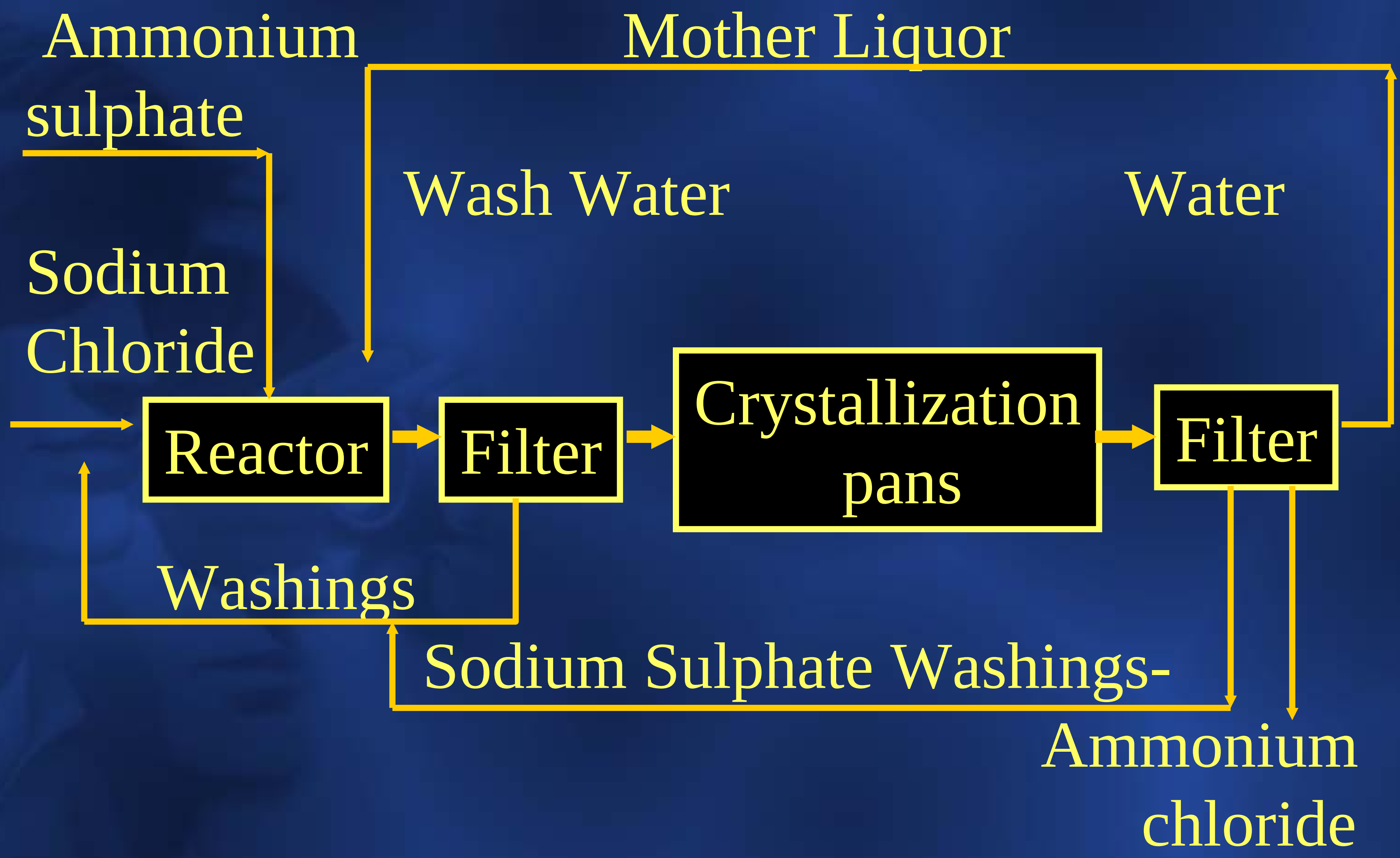
Ammonium Sulphate And Sodium Chloride :--

- NH_4Cl is manufactured by the reaction of

- **ammonium sulphate and sodium chloride solutions.**

- The NH_4Cl is recovered by crystallization. (fig.------).

Flow Diagram for Manufacturing of NH_4Cl,



Ammonium sulphate

Mother Liquor

Wash Water

Water

Sodium Chloride

Reactor

Filter

Crystallization pans

Filter

Washings

Sodium Sulphate Washings-

Ammonium chloride

L-41-- NH_4Cl, NH_4NO_3, $(NH_4)SO_4$

- 1.Ammonium sulphate and sodium chloride (in 5% excess) are
- added to a residual NH_4Cl solution.
- 2. The mixture is heated to **100^0C while it is violently agitated.**

L-41-- NH_4Cl, NH_4NO_3, $(NH_4)SO_4$

- 3. Resulting mixture **(containing only sufficient water to hold the** NH_4Cl **in solution)** is
- almost paste like because of the comparatively low solubility of sodium sulphate.

L-41-- NH_4Cl, NH_4NO_3, $(NH_4)SO_4$

- **4. This pasty mixture is vacuum-filtered,** and the precipitated sulphate is washed free of NH_4Cl and

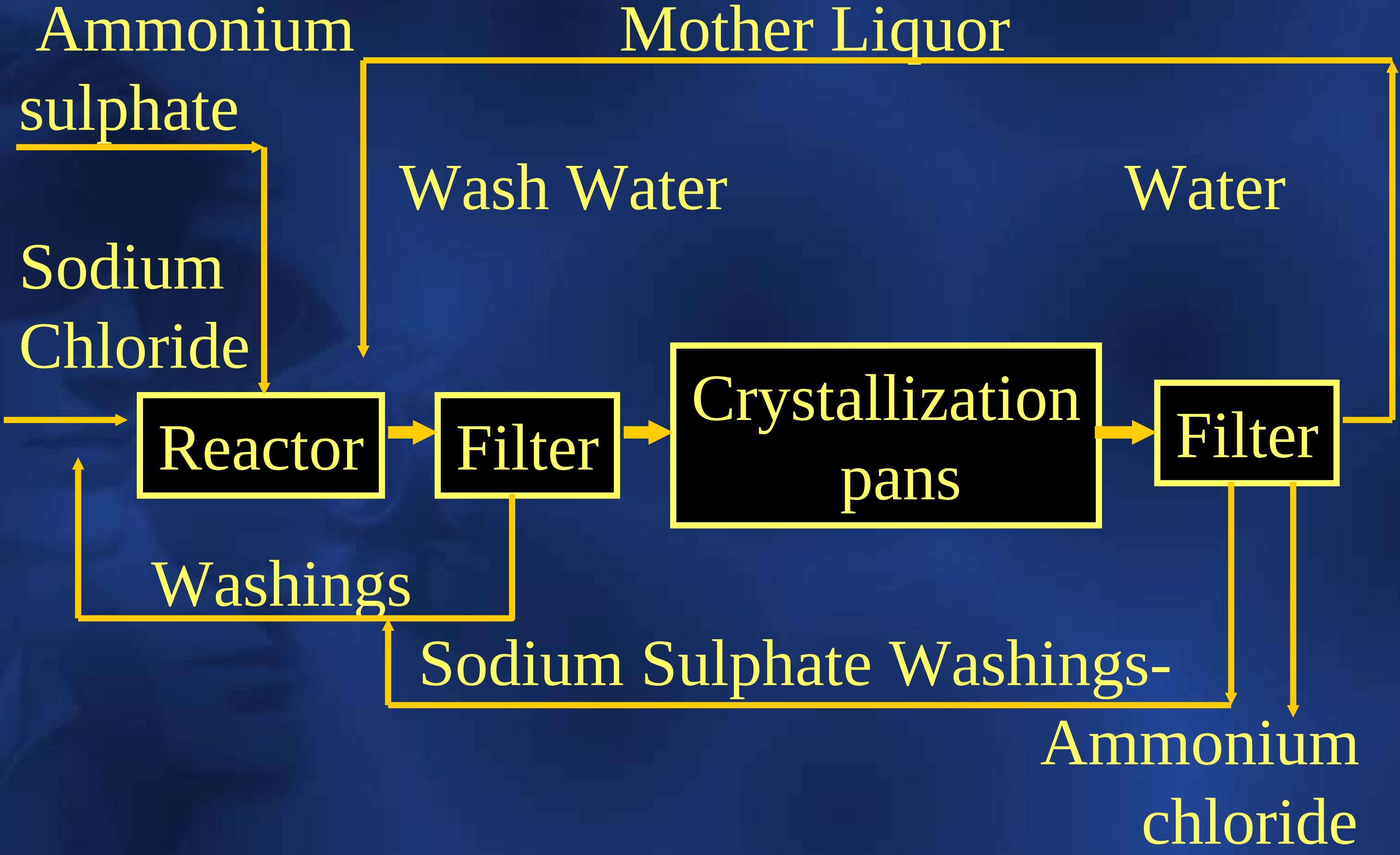
  - The wash water is returned to process.
  - The filtrate is sent to acid - resistant concentrating pans.
  - Where it is concentrated and cooled.

L-41-- NH_4Cl, $NH_4NO_{3,}$ $(NH_4)SO_4$

5. **Ammonium chloride crystallises** and is recovered by filtration or centrifugation, washing and drying.

- The mother liquor is returned to the next batch as indicated.
- The by -product, **sodium sulphate,** may be discarded or converted to **Glauber's salt.**

Flow Diagram for Manufacturing of NH_4Cl,



Ammonium sulphate

Mother Liquor

Wash Water

Water

Sodium Chloride

Reactor

Filter

Crystallization pans

Filter

Washings

Sodium Sulphate Washings-

Ammonium chloride

L-41-- NH_4Cl, NH_4NO_3, $(NH_4)SO_4$

Properties:

White to greyish lumps, crystals, or powder:

Formula wt	**53:49;**
Sp gr.	**1.53**
m. p.	**17^0C;**
Decomposes at	
b. p.	**350^0C;**

L-41-- NH_4Cl, NH_4NO_3, $(NH_4)SO_4$

- Sublimes at **520^0C.**
- Soluble in water
- **(29.4 g/100g at 0^0C;**
- **77.3g/100 g at 100^0C)** and in ammonia.
- Slightly soluble in ethanol.
- Threshold limit value,

fume in air (mg/m^3) 10.

L-41-- NH_4Cl, NH_4NO_3, $(NH_4)SO_4$

Uses

- In Dry cells;
- Soldering and galvanising flux;
- Leather; Food; Chemical.

2.AMMONIUM NITRATE

- ***From Ammonia and Nitric Acid:-*** Ammonia and nitric acid are reacted to yield **ammonium nitrate either in solution or in a molten form.**
- It is then further processed to crystal or granular form.
- Concentration of the **nitric acid is typically 57 to 60% but may range from 40 to 65%**

L-41-- NH_4Cl, $NH_4NO_{3,}$ $(NH_4)SO_4$

Properties

- White **hygroscopic crystals,**
- which are relatively unstable,
- forming **explosive mixtures with combustible materials**
- or when contaminated with certain organic compounds.

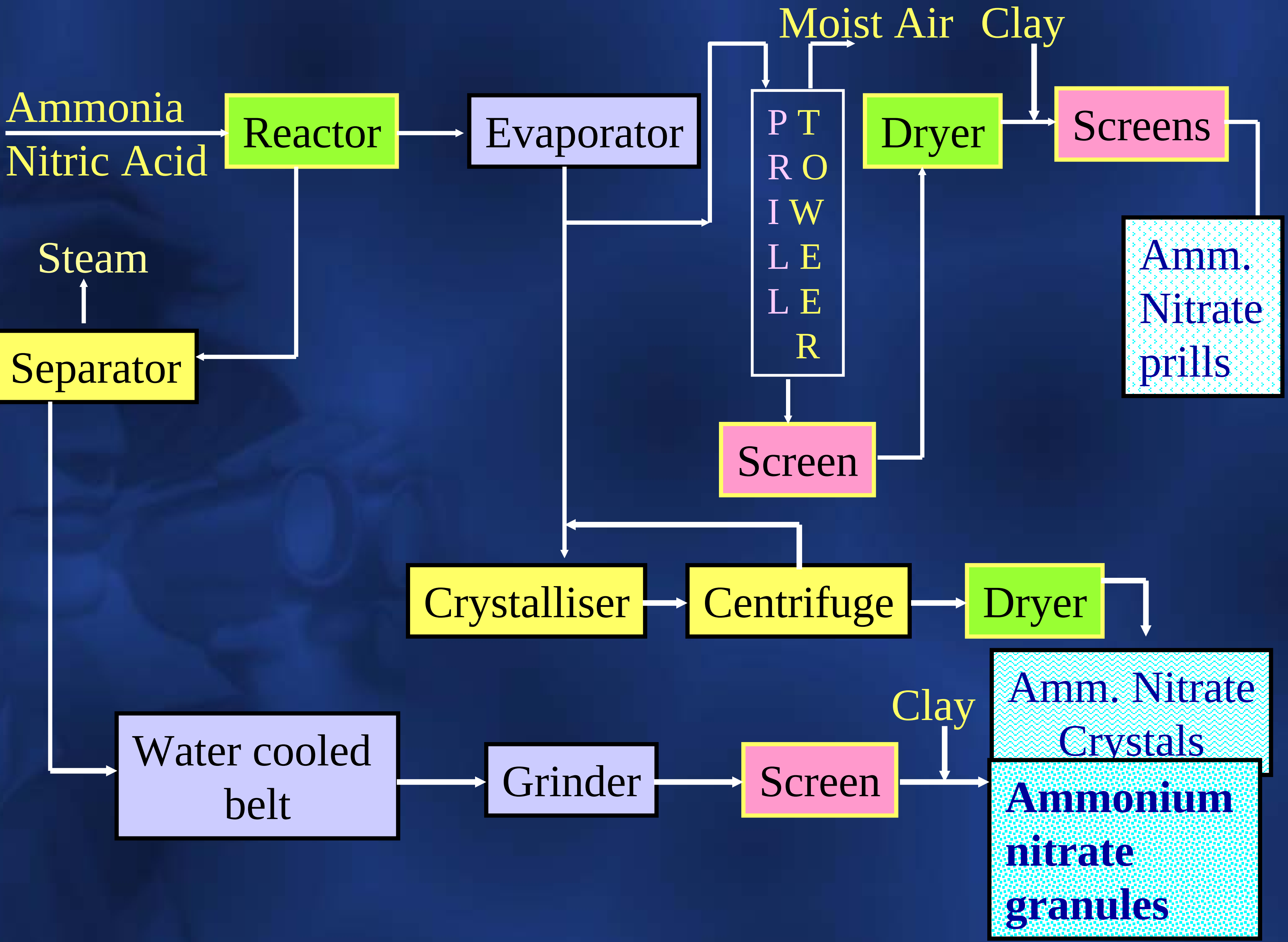
L-41-- NH_4Cl, $NH_4NO_{3,}$ $(NH_4)SO_4$

Formula wt. **80.04;**

Sp gr (α) **1.66**

mp 25^{0}C/4;
bp 169.6^{0}C;

Slowly decomposes at **210^{0}C.**



Ammonia

Nitric Acid

Reactor

Evaporator

Moist Air

Clay

PRILL TOWER

Dryer

Screens

Amm. Nitrate prills

Steam

Separator

Screen

Crystalliser

Centrifuge

Dryer

Amm. Nitrate Crystals

Clay

Water cooled belt

Grinder

Screen

Ammonium nitrate granules

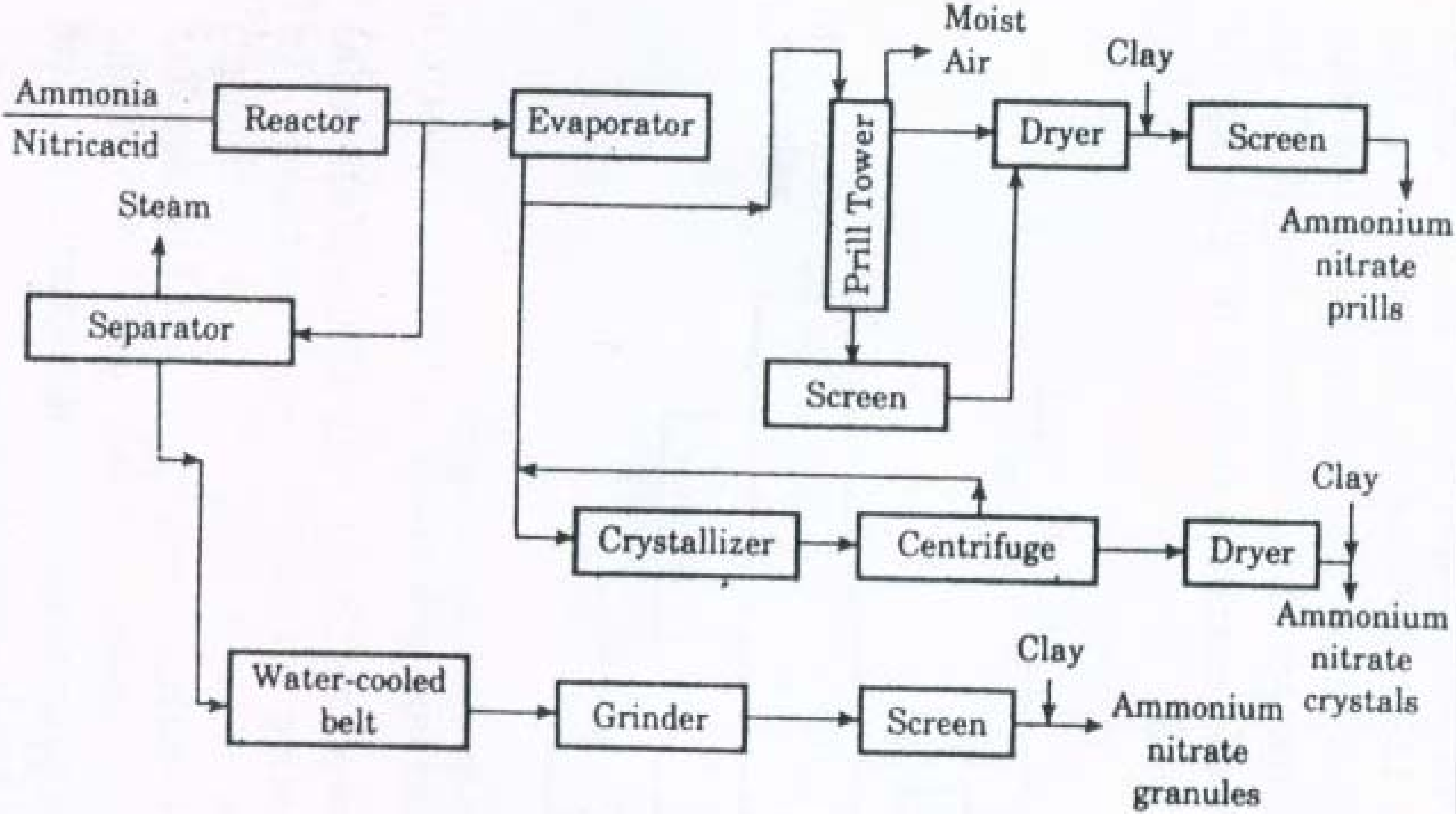


Fig. [illegible] .. Flow diagram for manu facturing of ammonium nitrate from ammonia and nitric acid.

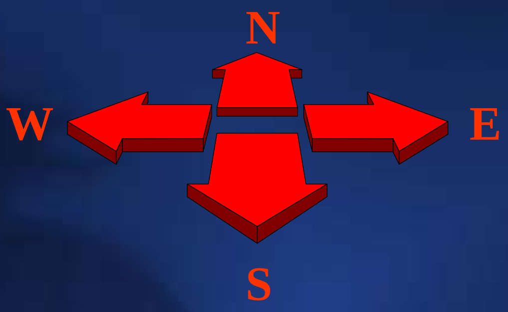
L-41-- NH_4Cl, NH_4NO_3, $(NH_4)SO_4$

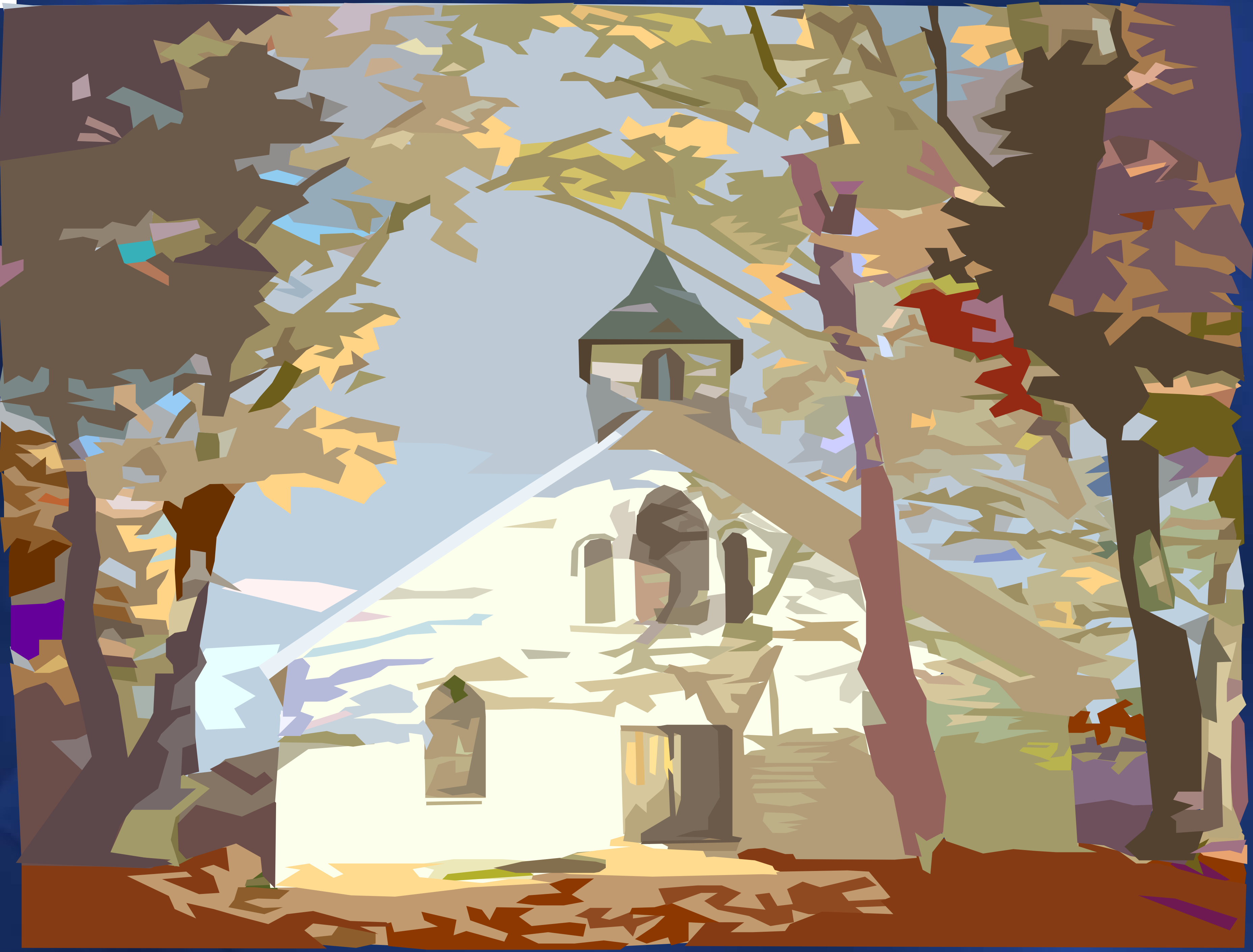
- **Uses:- Fertiliser, Explosive.**
- Ammonium nitrate may exist in four crystalline forms, depending on temperature.
- Very soluble in water

(55% at 0^0C, 90% at 100^0C),

- **ethanol** (3.7% at 20^0C),
- **methanol** (14.6% at 20^0C),
- **and ammonia.**

L-41-- NH_4Cl, NH_4NO_3, $(NH_4)SO_4$





3. Ammonium Sulphate $(NH_4)_2\ SO_4$

1. From Coal Gas

2. From Synthetic Ammonia and Sulphuric Acid

L-41-- NH_4Cl, NH_4NO3, $(NH_4)_2SO_4$

1. From coal gas

- **$(NH_4)_2$ SO_4** is produced as a **by product** during the production of coke from coal

- **ammonia in the coal gas is made to react with sulphuric acid.**

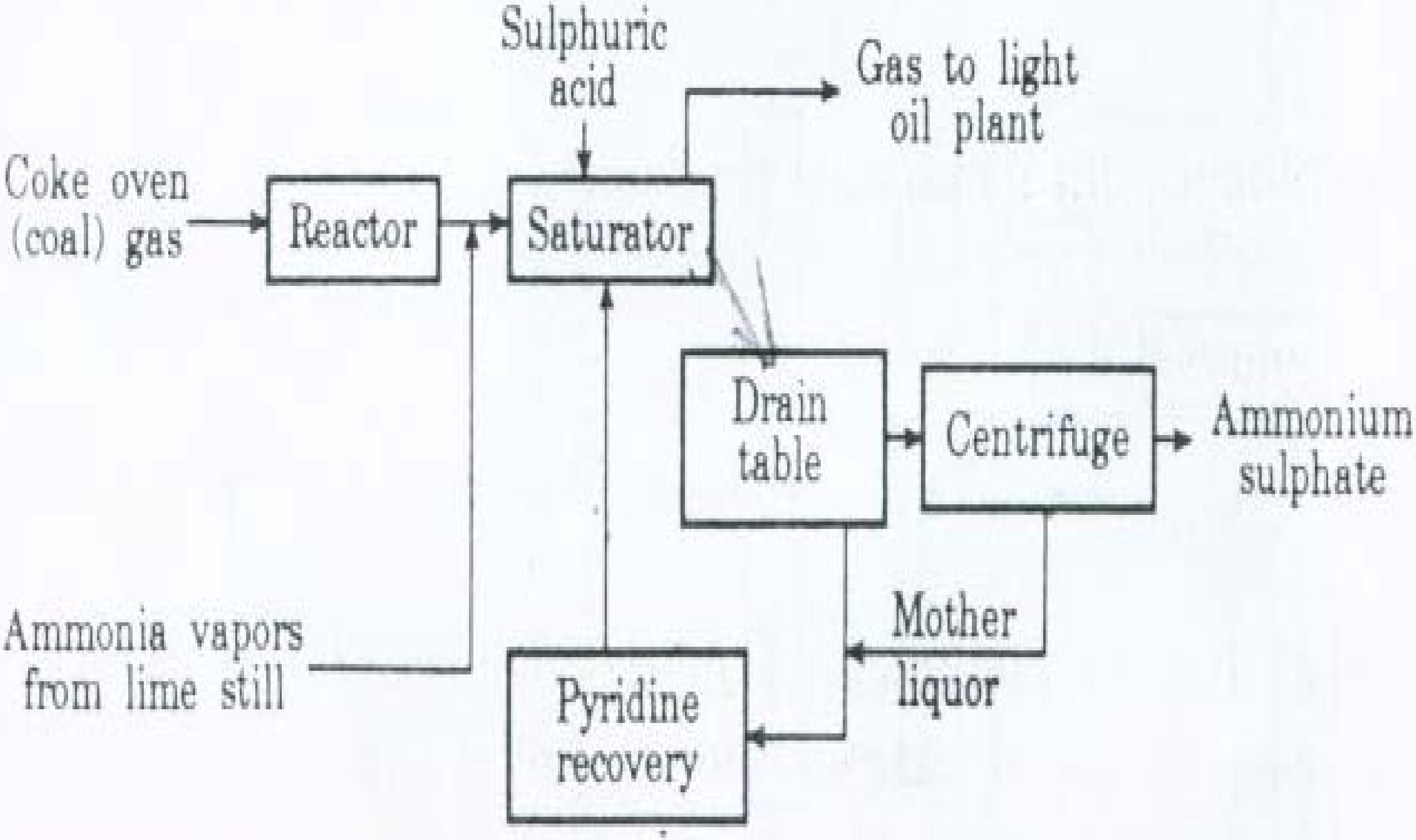


Fig Flow diagram for manufacturing of ammonium sulphate from coal gas.

L-41-- NH4Cl, NH4NO3, $(NH_4)_2SO_4$

In high – temperature coking

process, (Carbonization)

15 to 20% of the N_2

in the coal appears in the

crude coal gas as ammonia.

L-41-- NH_4Cl, NH_4NO_3, $(NH_4)_2SO_4$

- This gas, contains in an average
- **about 8 kg NH_3 /m^3 gas**

(1.1% by volume),

- corresponding to
- **2.8 kg of NH_3 /metric ton of coal**

- there are mainly **three methods**
- of **ammonia recovery,**

L-41-- NH_4Cl, NH_4NO_3, $(NH_4)_2SO_4$

Mostly the hot gases from the ovens are

precooled in the
collecting mains,
and then

the gases are passed through an
acid bath (saturator).

L-41-- NH_4Cl, NH_4NO3, $(NH_4)_2SO_4$

2. From Synthetic Ammonia and Sulphuric Acid

- About 75% of **$(NH_4)_2$ SO_4**
- Is produced from the direct reaction between
- **ammonia and sulphuric acid.**

L-41-- NH4Cl, NH4NO3, $(NH_4)_2SO_4$

- **Ammonia is directly neutralized with sulphuric acid,**

- water is removed.
- The **$(NH_4)_2$ SO_4** product is recovered by crystallization,

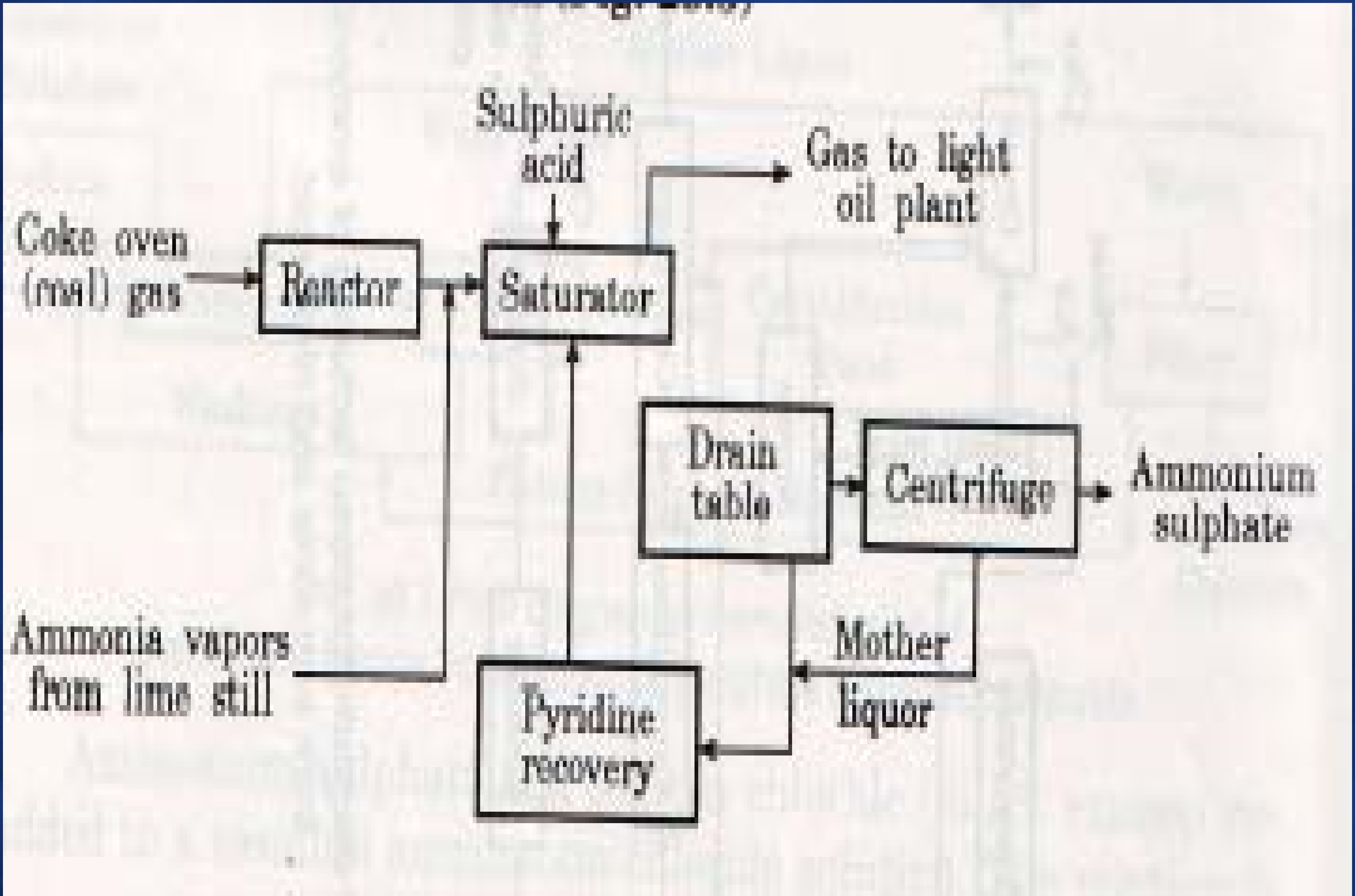
- Producing large uniformly sized particles.
- **The yield is practically 100%.**

L-41-- NH4Cl, NH4NO3, $(NH_4)_2SO_4$

- Ammonium sulphate may also be produced, using **gypsum** instead of sulphuric acid,

- $2NH_3 + CO_2 + H_2O \rightarrow$ **$(NH_4)_2\ CO_3$;**
- **$(NH_4)_2\ CO_3 + CaSO_4 . 2H_2O$** $\rightarrow$

  $(NH_4)_2SO_4$ $+ CaCO_3 + 2H_2O$.


Sulphuric acid
Gas to light oil plant
Coke oven (coal) gas
Reactor
Saturator
Drain table
Centrifuge
Ammonium sulphate
Ammonia vapors from lime still
Mother liquor
Pyridine recovery

L-41-- NH4Cl, NH4NO3, $(NH_4)_2SO_4$

Finely ground gypsum **$(CaSO_4.2H_2O)$ or anhydride (CaSO4)**

is mixed with about

twice its weight of water.

Ammonia and carbon dioxide

are passed in to the mixture, forming **ammonium carbonate,** …….

L-41-- NH4Cl, NH4NO3, $(NH_4)_2SO_4$

Ammonia and carbon dioxide

are passed in to the mixture, forming

ammonium carbonate,

which then react with the calcium sulphate (gypsum) forming

calcium –carbonate and

ammonium sulphate,

the latter dissolving in the water.

L-41-- NH4Cl, NH4NO3, $(NH_4)_2SO_4$

The reaction end by **6 to 9 Hours.**

the $(NH_4)_2$ SO_4 solution (**25%)** is filtered and

the insoluble calcium carbonate is removed.

The clear solution is concentrated in evaporators to crystallize out the **ammonium sulphate** .

L-41-- NH4Cl, NH4NO3, $(NH_4)_2SO_4$

The crystals are **centrifuged** and
dried in a rotary dryer,
the mother liquor
is returned to the reactor
for
subsequent batches.

L-41-- NH_4Cl, NH_4NO_3, $(NH_4)_2SO_4$

$(NH_4)_2$ SO_4 is also a by-product of several chemical processes.

The production of

acrylates ,

carpolactam etc.

L-41-- NH4Cl, NH4NO3, $(NH_4)_2SO_4$

Properties:-

White to brownish gray crystals.

Formula wt **132:14;**

Sp gr. **1.769** (at20^0C);

mp 513^{0}C

with decomposition.

L-41-- NH4Cl, NH4NO3, $(NH_4)_2SO_4$

Properties:-

Soluble in water

(70.6 g/100 ml at 0^0C,

103.8 g/100 ml at 100^0C),

very slightly soluble in ethanol.

Insoluble in acetone.

L-41-- NH4Cl, NH4NO3, $(NH_4)_2SO_4$

- **Uses:-**
- **Fertilizer;**
- **Industrial**

(water treatment, fermentation, Fireproofing & tanning).

L - 42 Bromine,

** BROMINE **

Manufacture:--

- ***From Natural Brines*** :-- All commercial processes for the production of bromine start with a solution of bromide ion. Four basic steps are involved.

1. **Oxidation** of bromide to bromine,
2. **Separation** of bromine vapour,
3. **Condensation** of the vapour and
4. **Purification.**

L - 42 Bromine,

- The economic sources of bromide ion contain various concentrations of the ion **65 to 75 ppm. in sea water** (no longer a commercial source).
- **Fresh brine,** which may be **preheated**
  - by one or more heat exchangers,
  - is introduced at the top of tower, and
  - **steam and chlorine** are injected
    - at the bottom .

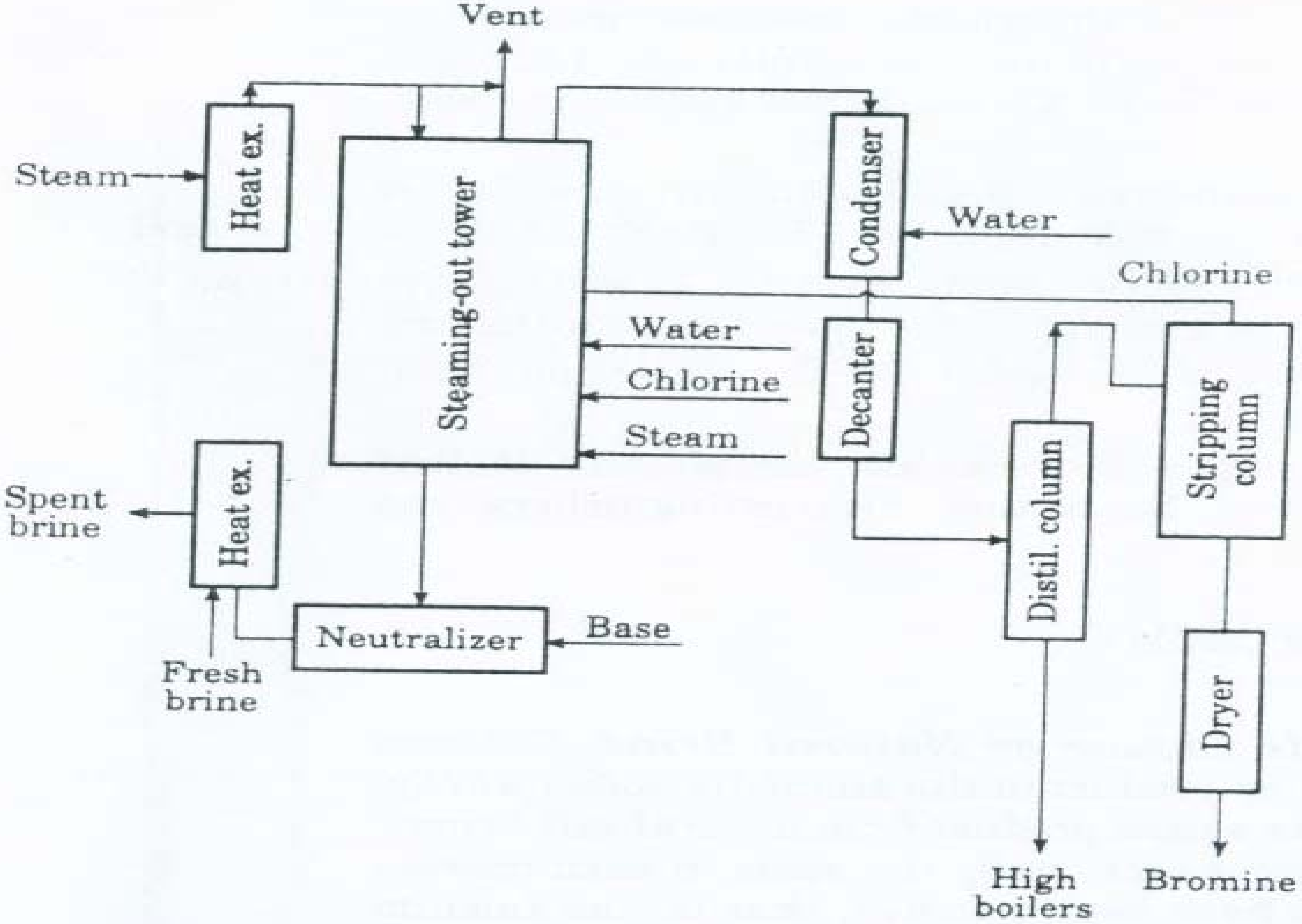


Fig. Flow diagram for manufacturing of bromine from natural brines.

L - 42 Bromine,

- **The spent acidic brine** (pH approx.1)
- from the bottom of tower is neutralized,
- the hot, neutralized brine may be used
- to heat fresh brine before
- being disposed off,
- or
- used for recovery of other components.

L - 42 Bromine,

- **A mixture of bromine, chlorine and water** vapour from the top of the tower is condensed,
- and the condensate is separated into
- Crude bromine and
- the aqueous phase in a decanter.
- The aqueous phase, containing
- significant amounts of bromine and chlorine,
- is returned to the tower.

L - 42 Bromine,

- The **crude bromine sent to a distillation column,**
- where it is separated from high boiling impurities,
- The **bromine vapours** are condensed and
- **fed to a stripping column,**
- where the remaining **traces of chlorine** are
- **distilled off** for return to the tower,
- **refined bromine is removed from**
- **the bottom of the coloumn, dried, and packaged.**

L - 42 Bromine,

- Although theoretically **1 part of chlorine releases 2.25 parts** of bromine,
- in practice more chlorine is required,
- the excess is used in oxidising other components of the brine,
- especially organic and hydrogen sulphide. Recoveries of **about 95%**
- **of the bromine content of**
- **the fresh brine** are achieved.

L - 42 Bromine,

- When the brines contain less than about 1000 ppm. Bromide, or
- when seawater is use,
- the steaming out process is uneconomic, and
- **air is used to sweep out the bromine** vapours following chlorination.

L - 42 Bromine,

- Varius methods can be used to recover the bromine from the air stream.
- It may be **scrubbed through sodium carbonate solution,**
- forming a **mixture of sodium bromide and sodium bromate,**
- or
- the bromine may be reduced to
- hydrobromic acid
- with sulphur dioxide.

L - 42 Bromine,

- In the first case, acidification of the solution releases bromine,
- in the second, additional chlorine is used to oxidize the hydrogen bromide to bromine.
- In either case, the remaining steps of purification are as described.

L - 42 Bromine,

- **Properties:--** Dark reddish-brown liquid with irritating fume which burn the skin on contact.
- Mol. wt. 159.81,
- sp gr. 3.119 (20^0C),
- m . p. 7.2^0C,
- b. p. 58.80^0C,
- soluble in water (4.22g / 100 ml at 0^0C, 3.13g / 100 ml. at 30^0C),
- ethanol, ether, alkalies and carbon bisulphide,
- vapour density 7.59 mg / ml (20^0C),
- threshold limit value (ppm. by volume) 0.1 .

L - 42 Bromine,

- **Uses:--**
- Ethylene dibromide,
- bromine and compounds,
- Methyl bromide,
- Gasoline additive,
- Sanitation,
- Fire exitinguishers and
- flame retardants.

L - 42 **CALCIUM PHOSPHATE (MONOCALCIUM PHOSPHATE, SUPERPHOSPHATE) $CaH_4(PO_4)_2$**

MANUFACTURE :----

- ***From Phosphate Rock And Sulphuric Acid :--***
- Normal Super Phosphate, primarily the monocalcium salt of phosphoric acid, is made by the reaction of sulphuric acid

- with phosphate rock, which is fluoroapatite or calcium fluophosphate.

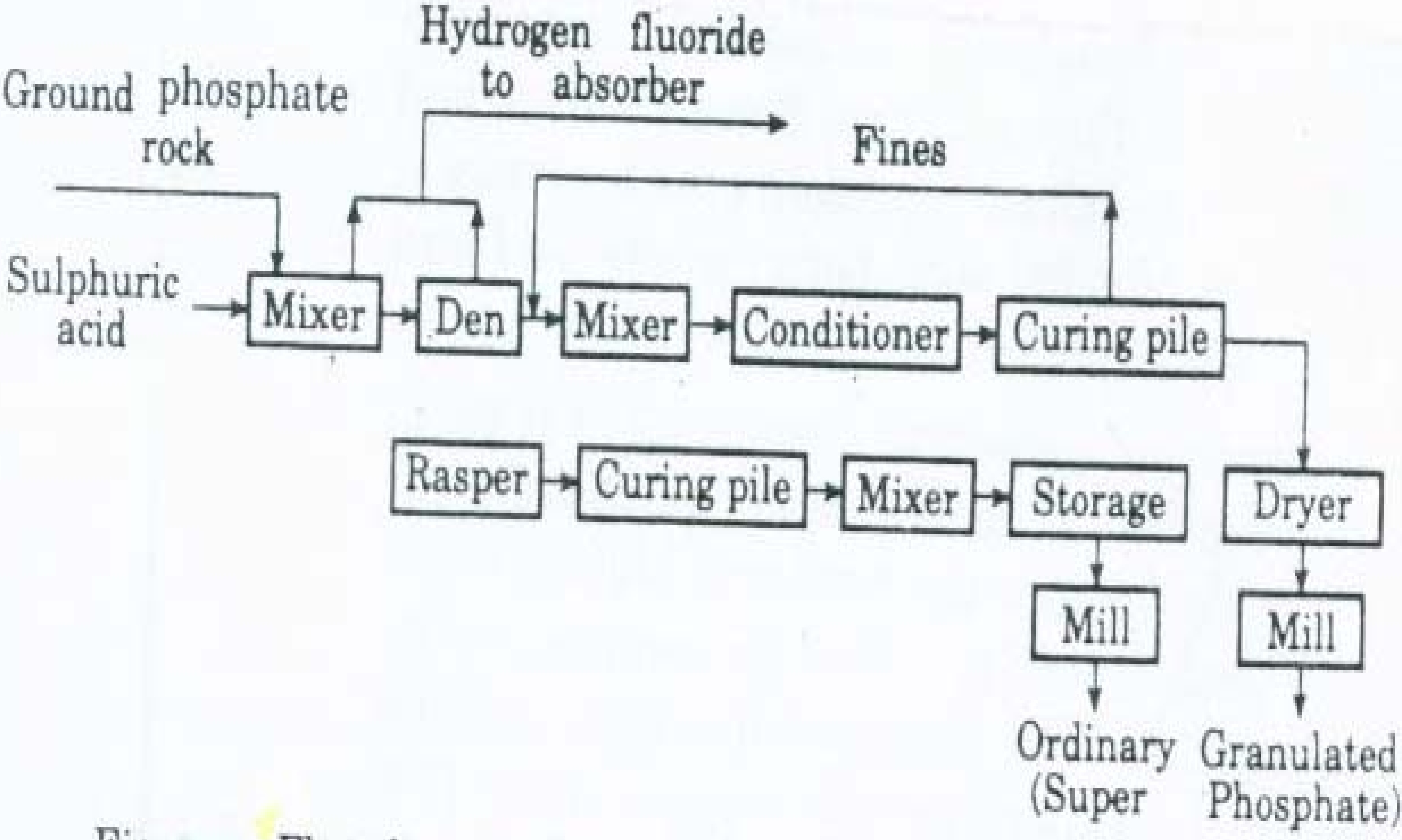


Fig. Flow diagram for manufacturing of calcium phosphate from phosphate rock and sulphuric acid.

L - 42 CALCIUM PHOSPHATE (MONOCALCIUM PHOSPHATE, SUPERPHOSPHATE) $CaH_4(PO_4)_2$

L - 42 **CALCIUM PHOSPHATE (MONOCALCIUM PHOSPHATE, SUPERPHOSPHATE) $CaH_4(PO_4)_2$**

L - 42 **Chromic Acid (Chromium Trioxide, Chromic Anhydride) CrO3**

Manufacture :--

From Sodium Dichromate:--

Chromium trioxide or chromic anhydride (CrO_3) is **commercially, though erroneously, called chromic acid.**

it is produced by the action of concentrated **sulphuric acid on a solution of chromate or Dichromate.** (Fig.----)

L - 42 **Chromic Acid CrO3**

Manufacture :--

From Sodium Dichromate:--

(Fig.----)

- Sodium dichromate and water are charged in to an acidulator
- **in a weight ratio of**
- **3:2 to 1:1,**
- at room temperature.

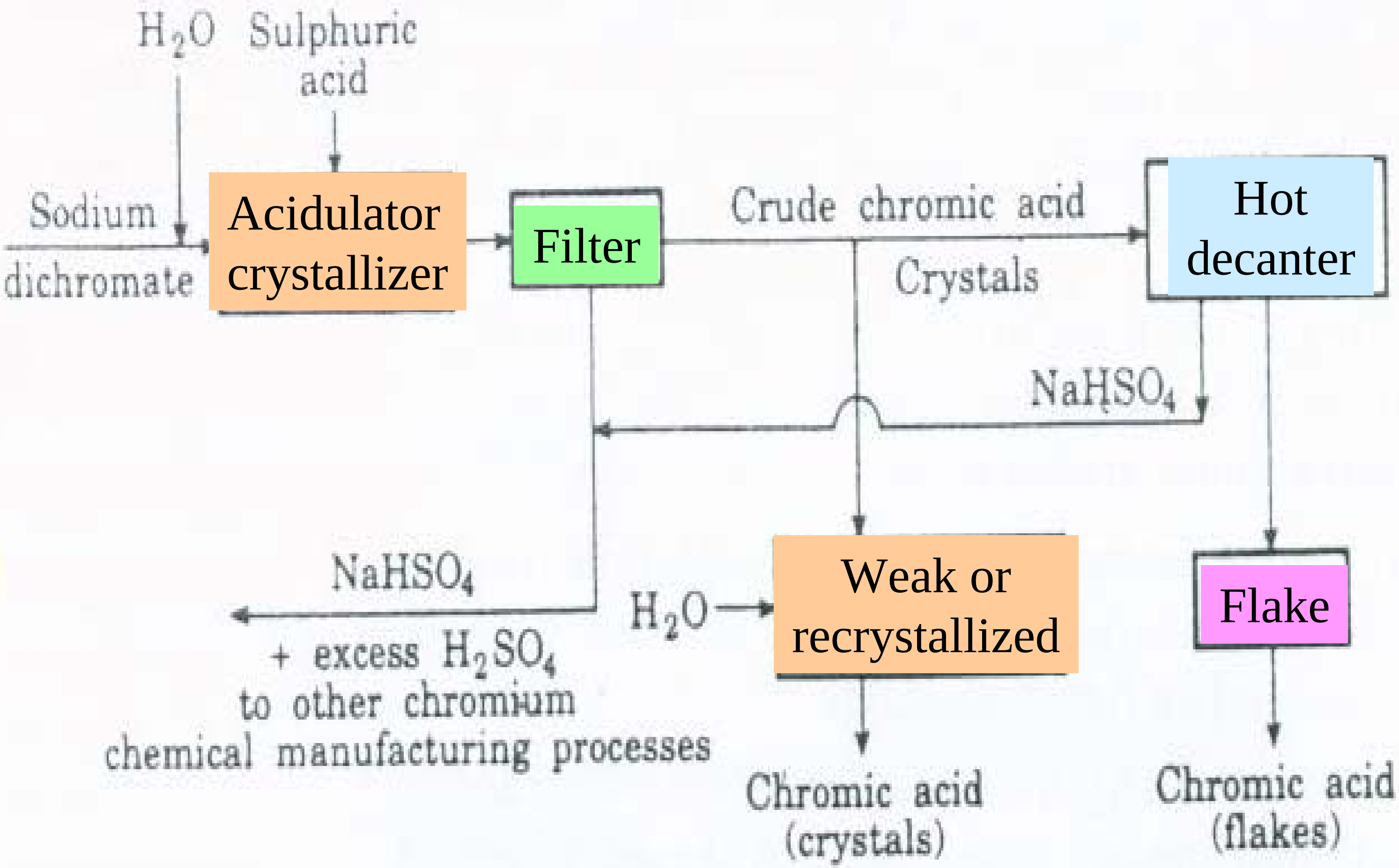


Fig. . Flow diagram for manufacturing of chromic acid from sodium dichromate

L - 42 Chromic Acid CrO3

Alternatively,

- a saturated solution of **sodium dichromate**
- from the evaporator or crystalliser
- in the dichromate plant may be used.
- **Concentrated sulphuric acid**
- **(sp.gr.- 1.8354)** is
- slowly added to **the dichromate** solution with cooling and good agitation.

L - 42 **Chromic Acid CrO3**

- **About 1 part of sulphuric acid** is
- required for **0.85 to 1.25 parts of sodium dichromate.**
- the dichromate is converted to
- **chromium trioxide,**
- and
- **sodium bisulphate.**
- the chromic acid crystallises out
- during the acidification.

(Fig.- 28.11)

L - 42 **Chromic Acid CrO3**

- Then filtered to **remove**
- **precipitated chromic acid,**
- and the filterate returned to
- recover acid and chromium values,
- with the **preparation of**
- **sodium sulphate by- product.**

L - 42 **Chromic Acid CrO3**

- ❐ **the crystals must be washed**
- ❐ or
- ❐ preferably **recrystallized to remove inpurities.**

L - 42 **Chromic Acid CrO_3**

- In some plants the sodium dichromate - sulphuric acid process is carried out.

- the raw materials are

- or anhydrous dichromate and concentrated sulphuric acid .

L - 42 **Chromic Acid (Chromium Trioxide, Chromic Anhydride) CrO3**

- Chromic acid, used as
- an oxidizing agent in the preparation of organic compounds,
- may be regenerated by electrolytic oxidation.
- In the oxi- dation of organic compounds,
- chromic acid
- in a solution of sulphuric acid
- is reduced and
- forms chromium sulphate.

L - 42 **Chromic Acid (Chromium Trioxide, Chromic Anhydride) CrO3**

- A typical solution, after oxidation,
- may contain about
- 1 part of chromic acid as chromium sulphate and
- 3.5 parts of sulphuric acid.
- this solution is electrolysed between lead electrodes
- in a lead lime- tank divided by a diaphragm.
- the anodes become covered with lead oxide, while
- chromic acid is formed in the analyte.

L - 42 **Chromic Acid (Chromium Trioxide, Chromic Anhydride) CrO3**

- True chromic acid (H_2CrO_4) is reputed to be formed by heating the anhydride with a small amount of water and cooling.
- However, if it does exist it very unstable and is not isolated commercially.
- Aqeuos solution of chromium trioxide are strongly acidic and are believed to contain
- several polychromic acids such as dichromic ($H_2Cr_2O_4$) and trichromic acid ($H_2Cr_3O_{10}$), although chromic acid (H_2CrO_4) is also no doubt present.

L - 42 **Chromic Acid CrO3**

- **Properties :--** Deep red to reddish-brown.
  - very deliquescent rhombic crystals. volatilizes at about 100^0 C,
    - formula wt. 99.993,
      - sp. gr. 2.70
  - mp. 197^0 C with decomposition,

L - 42 **Chromic Acid CrO3**

- **Properties :--**
- soluble in water
- (161.0g/100g at 0^0 C,
- 206.7g/100 at 100^0 C),
- Soluble in sulphuric acid and ethanol.
- slow decomposition starts at 197^0 C,
- the rate of decomposition increases with temperature.

L - 42 **Chromic Acid CrO3**

Uses :---

1. Used for metal Treatment.
2. Also used as an oxidising agent
3. Used for chromium plating ceramic glaze and colored glass.

L - 42 **Chromic Acid (Chromium Trioxide, Chromic Anhydride) CrO3**

L- 43 Acrylonitrile, Benzene, Butyl acetate

L-44 Caprolactum, CCl_{4}, Cellulose Acetate

** CARPOLACTAM **

Manufacture :- *From Cyclohexanone:---*

Cyclohexanone is a key intermediate
in the most of
carpolactam processes.

Cyclohexanone is derived either
from phenol or, from cyclohexane.

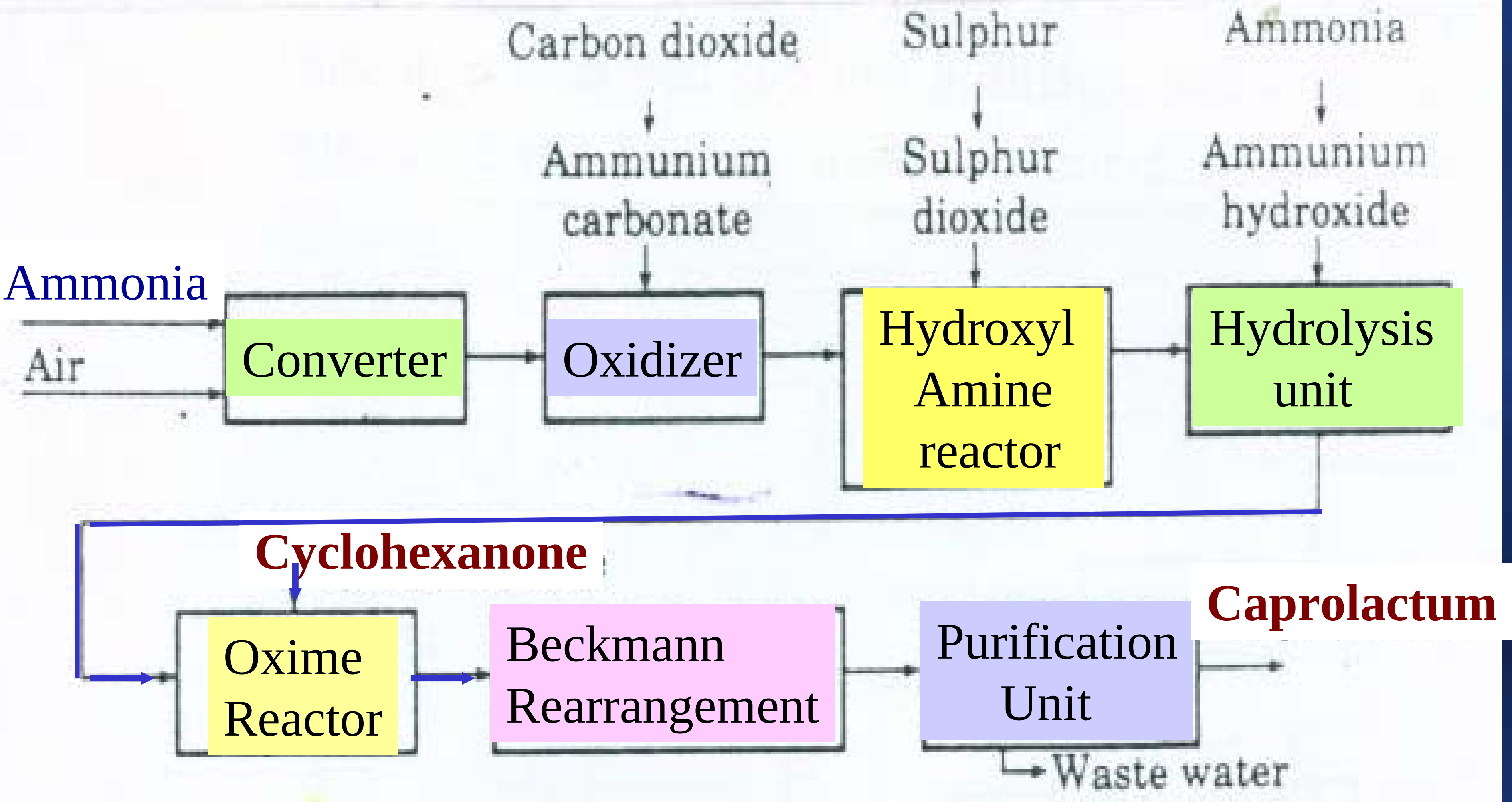
L-44 Caprolactum,

**** CARPOLACTAM ****

Manufacture :--

From Cyclohexanone:---

Carpolactam is produced by
the addition of hydroxylamine sulphate
to cyclohexanone.



Carbon dioxide

Ammunium carbonate

Sulphur

Sulphur dioxide

Ammonia

Ammunium hydroxide

Ammonia

Air

Converter

Oxidizer

Hydroxyl Amine reactor

Hydrolysis unit

Cyclohexanone

Oxime Reactor

Beckmann Rearrangement

Purification Unit

Caprolactum

Waste water

Fig . Manufacture of caprolactam from cyclohexanone

L-44 Caprolactum,

- **Properties :---**

- White flakes or fused.
- Mol. wt. 113.16,
- Sp. gr. 1.05
- (70% solution),

- mp. 68 to 69^{0}C,
- bp. 139^{0}C/ 12 mL.

L-44 Caprolactum,

- **Properties :---**
- soluble in - water,
- chlorinated solvents,
-
- petroleum distillates,

And

cyclohexane.

L-44 Caprolactum,

Uses :---

- **Nylon 6 fibres, Nylon 6 plastics and film; And Nylon 6 resins (65-70% of total global consumption).**

Used in brush bristles,

textile softeners,

Film coatings, synthetic leather,

Plastics, plasticizers,

paint vehicles etc.

Benzene

- **Manufacture :--**

1. From petroleum by catalytic Reforming :-- Benzene may be produced by

- dehydrogenation of petroleum stocks
- rich in naphthene hydrocarbons
- in the presence of hydrogen - rich recycle gas
- (to suppress coke formation) and so
- known as hydroforming

Benzene

- the charge stock is usually a specially treatred virgin naptha, different catalysts are used.
- special facilities are required to recover pure aromatic hydrocarbons from the “Reformate”.
- A typical process is, Fig.--------- is shown in flowsheet.

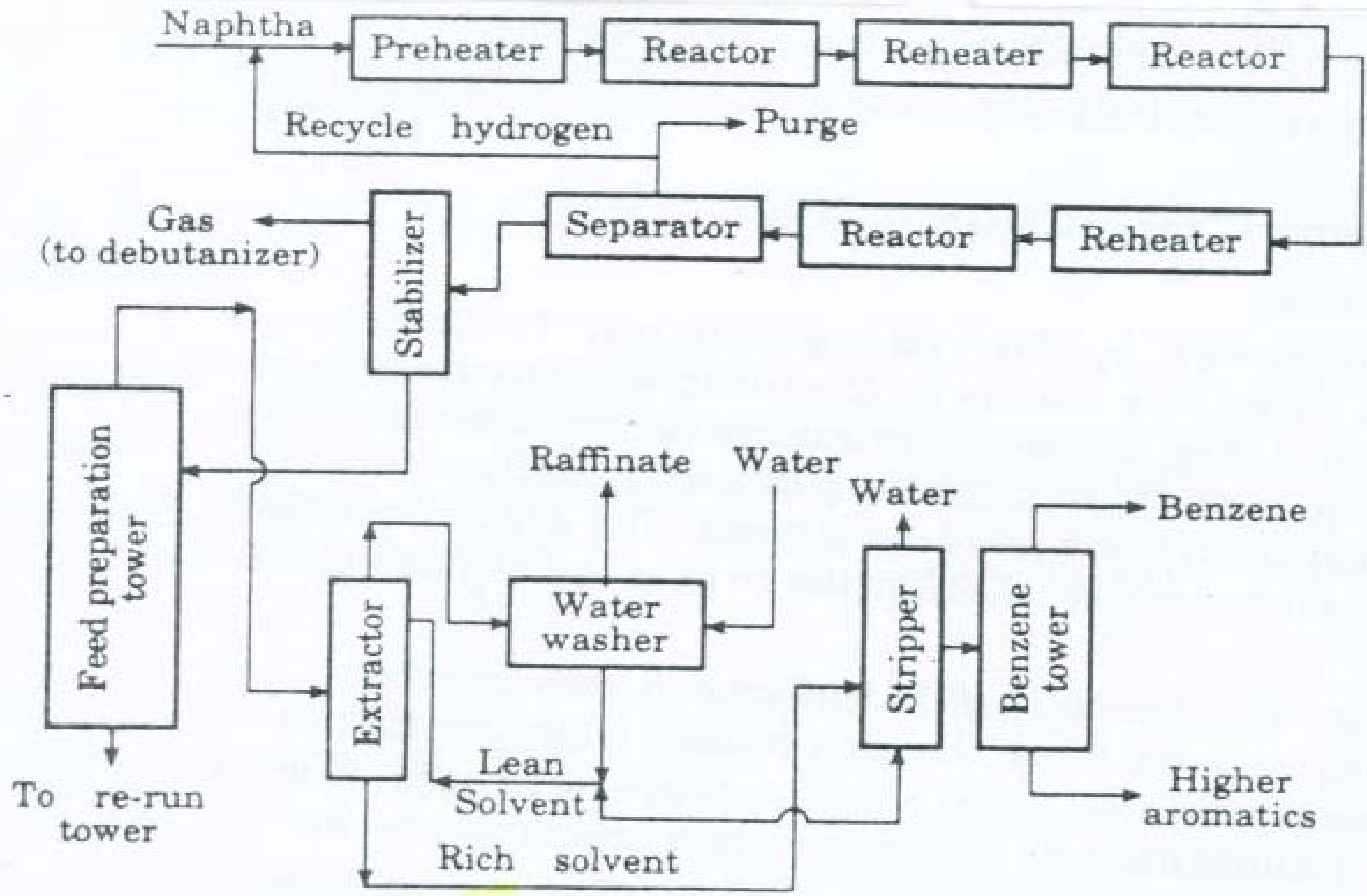


Fig. Manufacture of benzene from petroleum by catalytic reforming.

Benzene

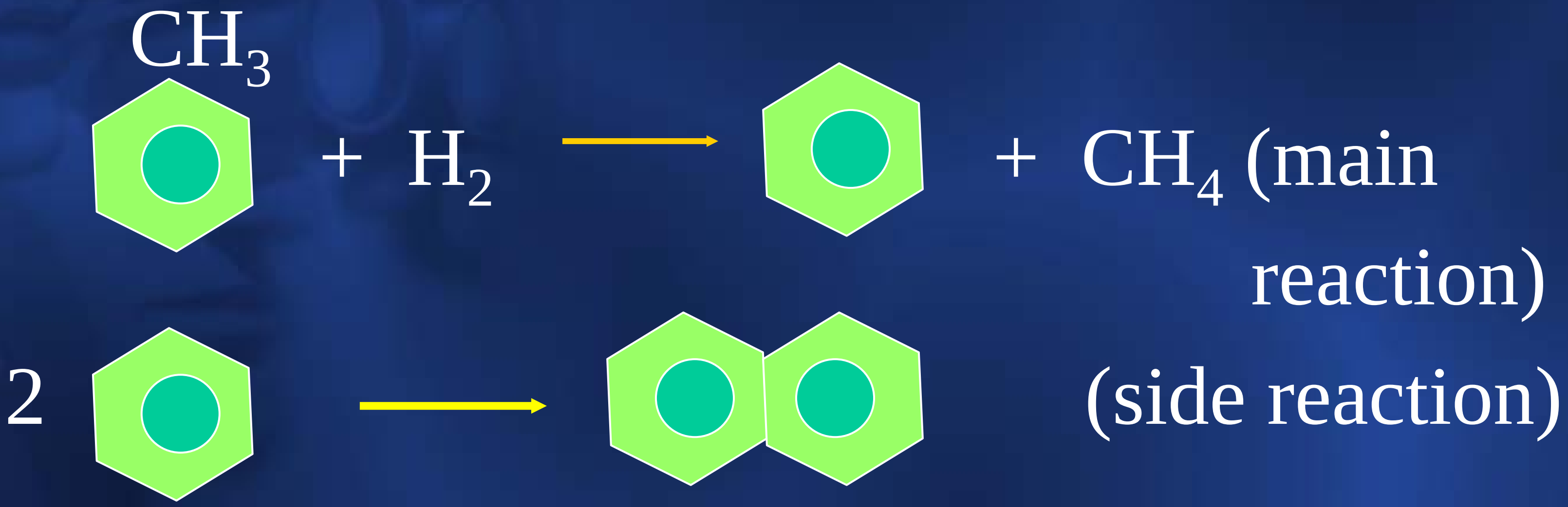
2. From Toluene by Hydro- de- alkylation :--- Benzene may be produced by the de-alkylation of toluene or toluene containing stocks

- such as heavy catalytic reformats, catalytic cycle oils etc.

- Several processes, both catalytic and thermal, are available.

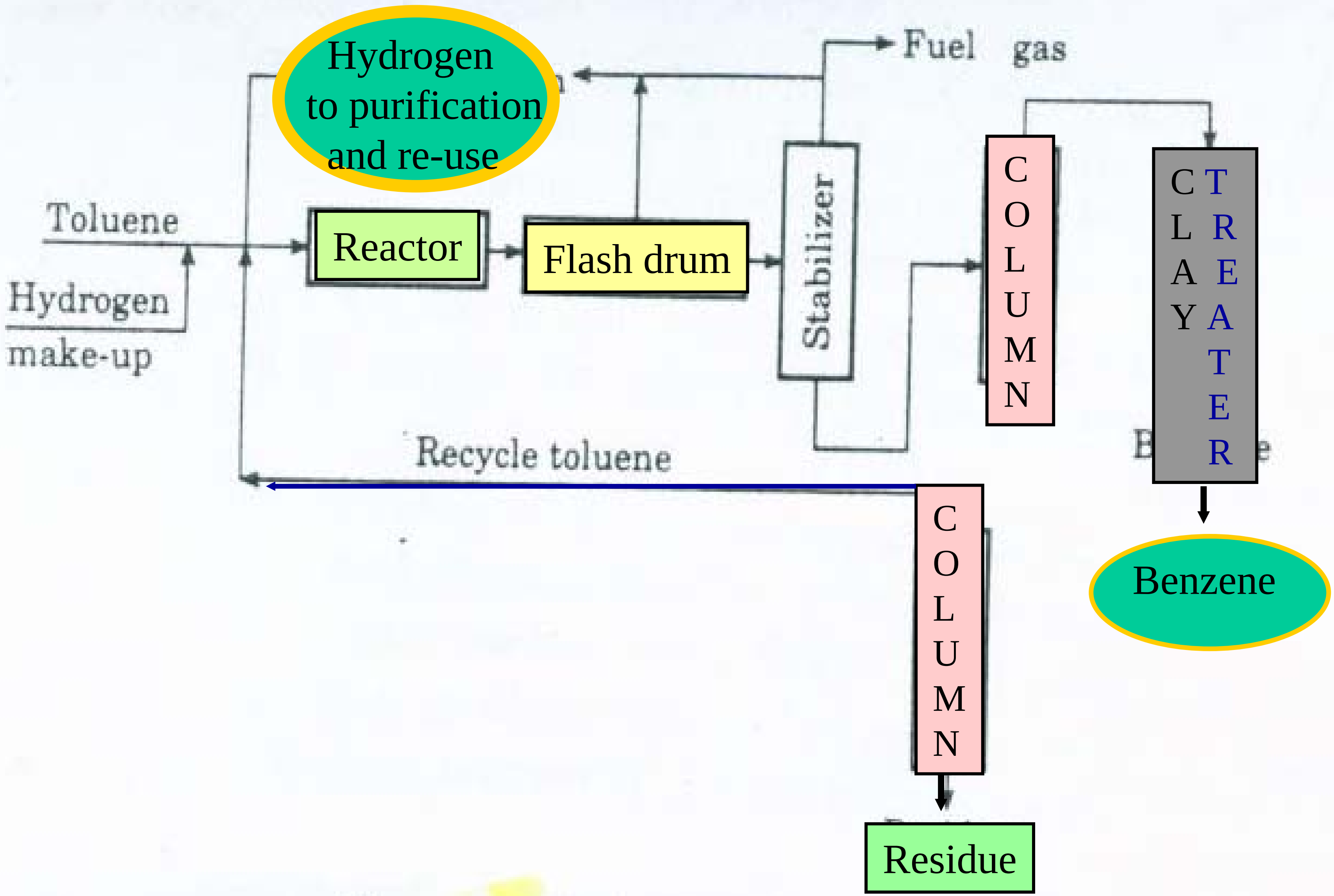
Benzene

- Fig. --------.
- the De-alkylation is carried out in the presence of hydrogen,
- often catalytic reformer hydrogen.



CH_3 + H_2 → + CH_4 (main reaction)

2 → (side reaction)



Hydrogen to purification and re-use

Fuel gas

Toluene

Hydrogen make-up

Reactor

Flash drum

Stabilizer

COLUMN

CLAY TREATER

Recycle toluene

COLUMN

Benzene

Residue

Fig. Manufacture of benzene from toluene by hydrodealkylation.

Benzene

- **Properties :---** Clear, colourless, flammable liquid with a pleasant characteristic odour. Liquid is highly refractive and the vapours burn
- with smoky flame. mol. wt. 78.11, Sp. gr. 0.879, 20’C / 4, mp. 5.56’C, bp. 80.1’C, weight per gallon 7.32 Ib.

Benzene

- Soluble in ethanol and ether,slightly soluble in water (0.07 at 22’C), flash point (closed cup)- 11.1’C, Ignition temperature 538’C, vapour-
- density (fair = 1) 2.77, Explosive limits (% by voluim in air) Lower 1.5, Upper 8.0, Threshold limit value (ppm.) 25.

Benzene

- **Uses :---** For the preparation of:
  - Styrene,
  - phenol,
  - Cyclohexene,
  - Nitrobenzene,
  - Maleic Anhydride etc.

Benzene

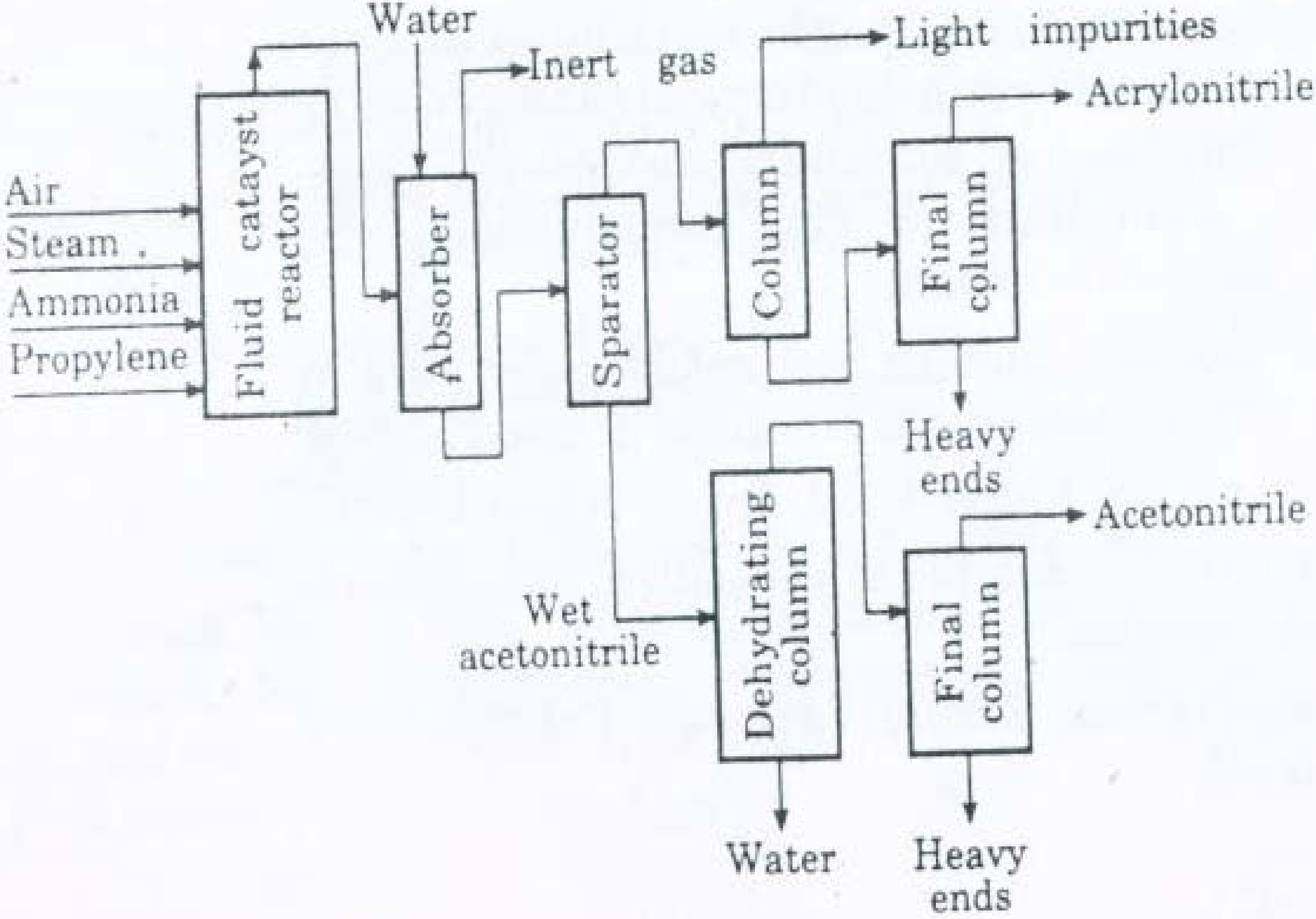


Fig Manufacture of acrylonitrile from propylene.

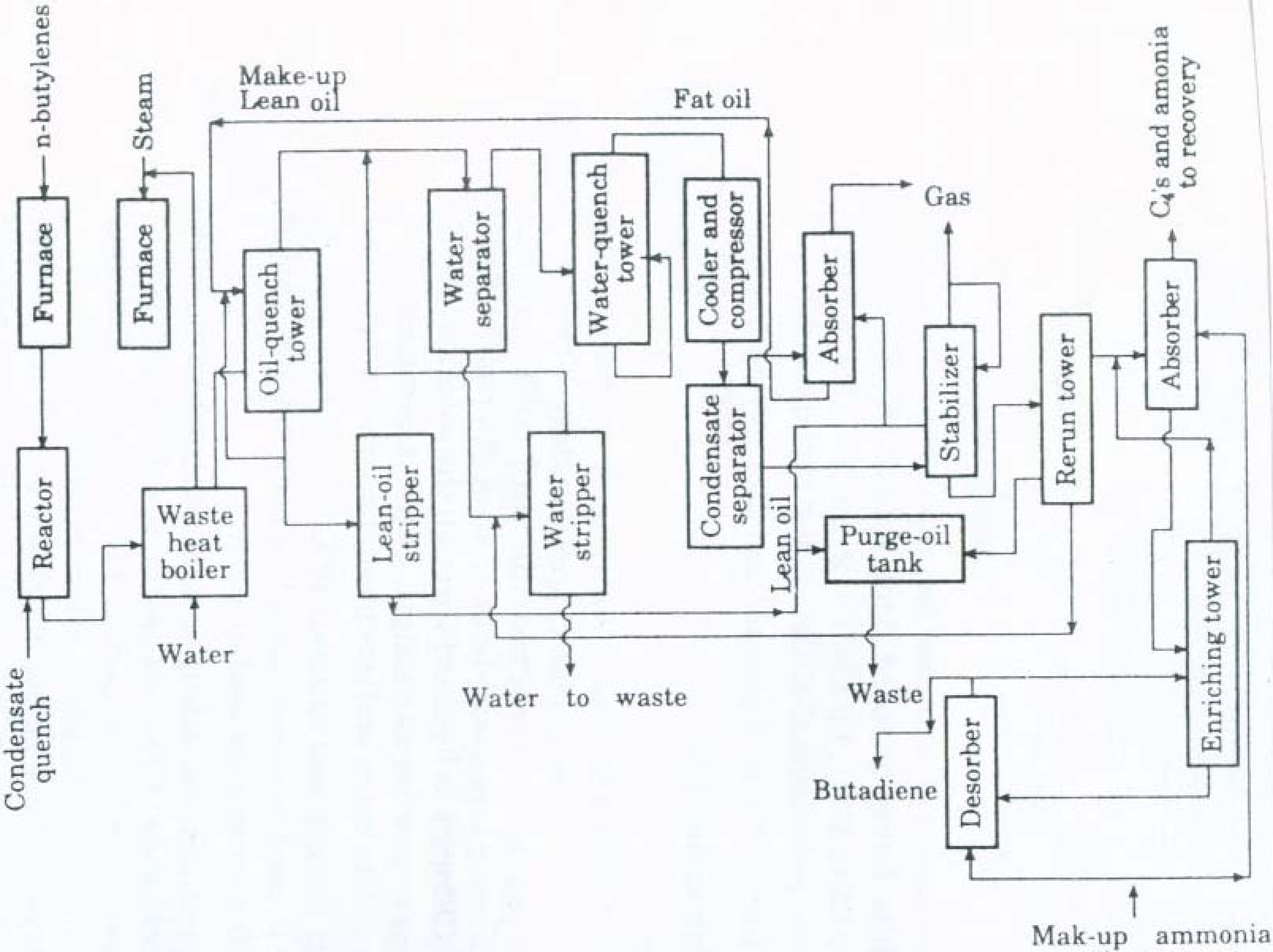


Fig. - Manufacture of butadiene from butylenes by dehydrogenation

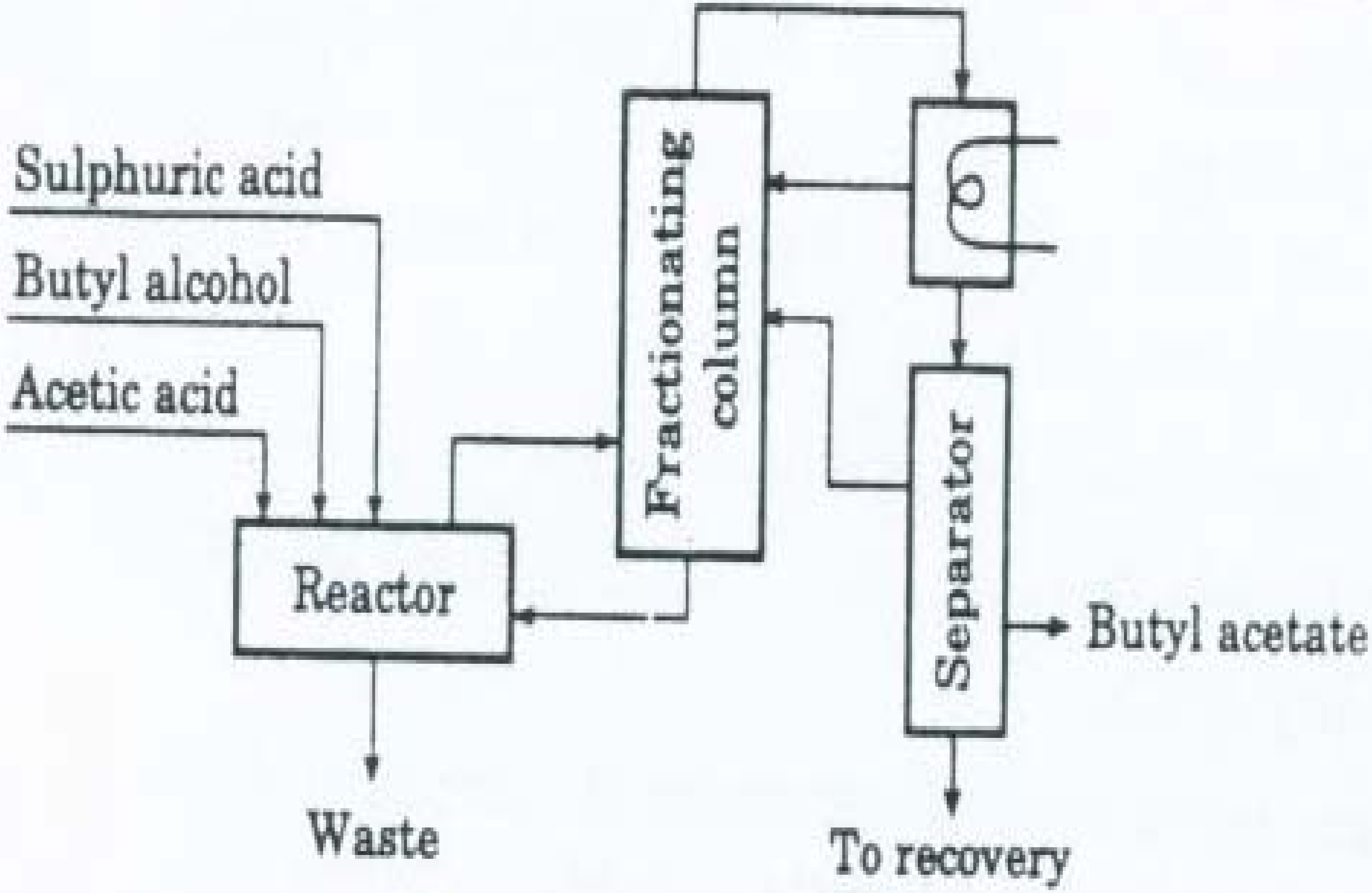


Fig. Manufacture of butyl acetate from butyl alcohol and acidic acid by esterification.

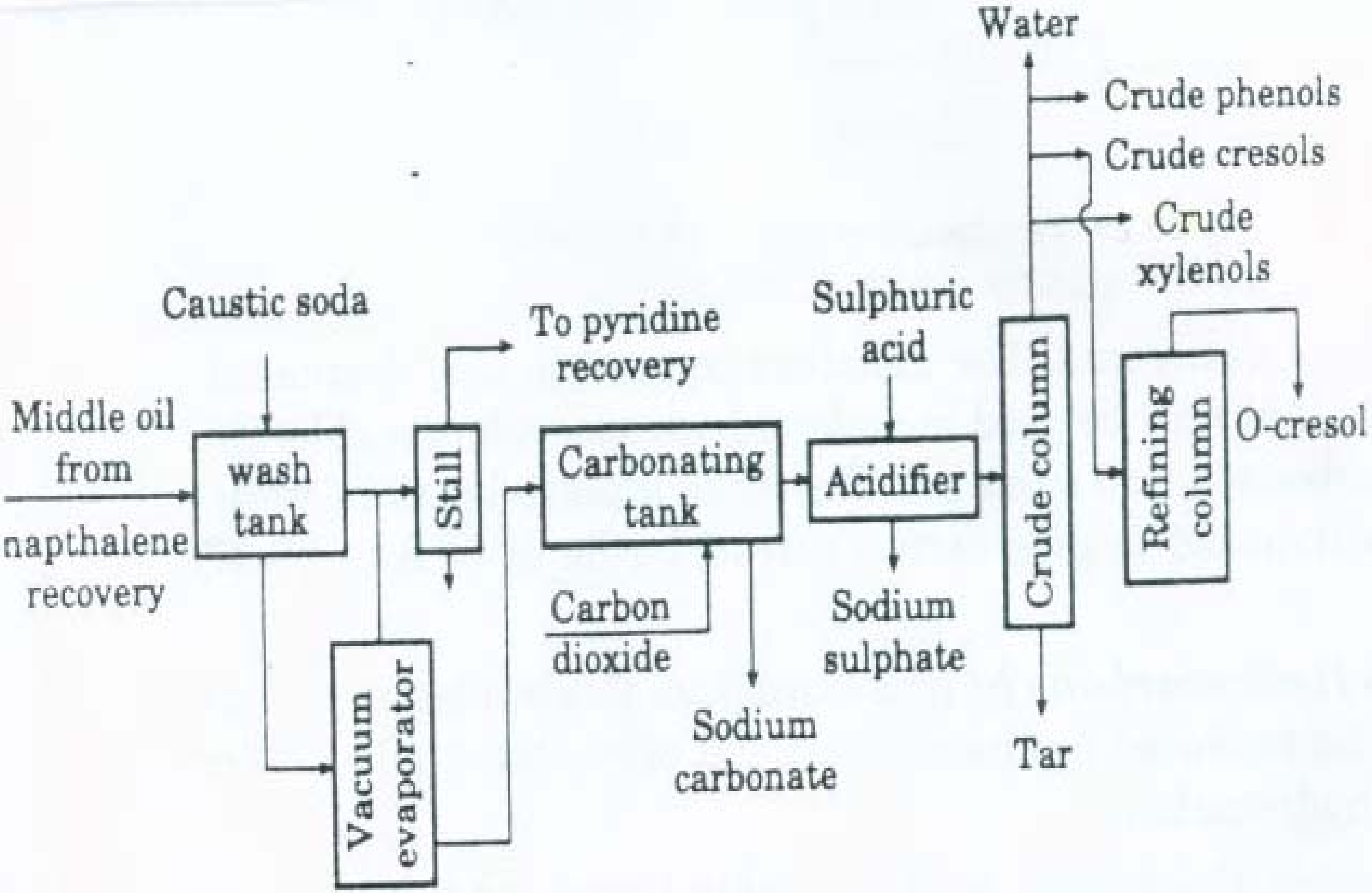


Fig. Manufacture of cresol from coal tar.

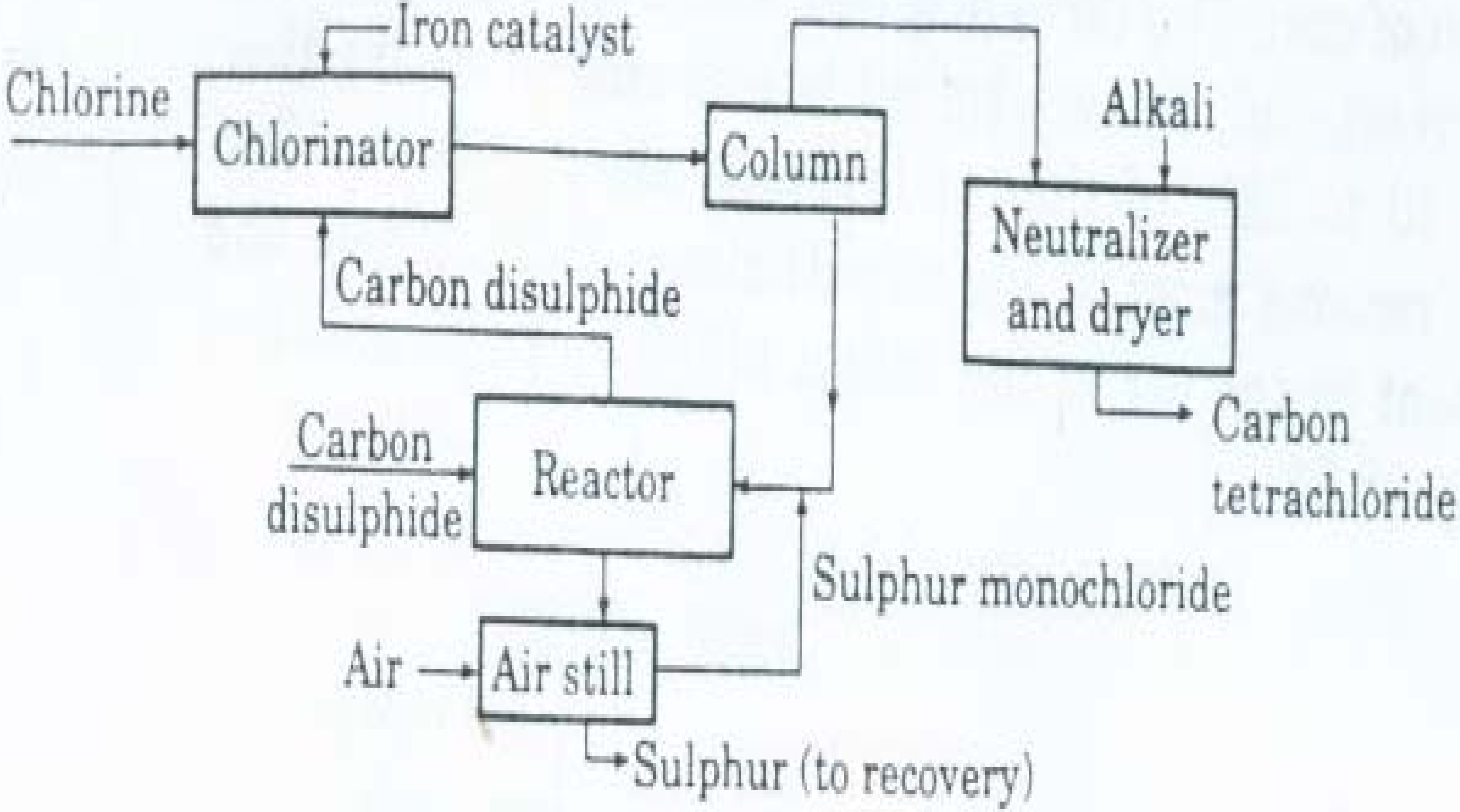


Fig. Manufacture of carbon tetrachloride from carbon disulphide and chlorine.

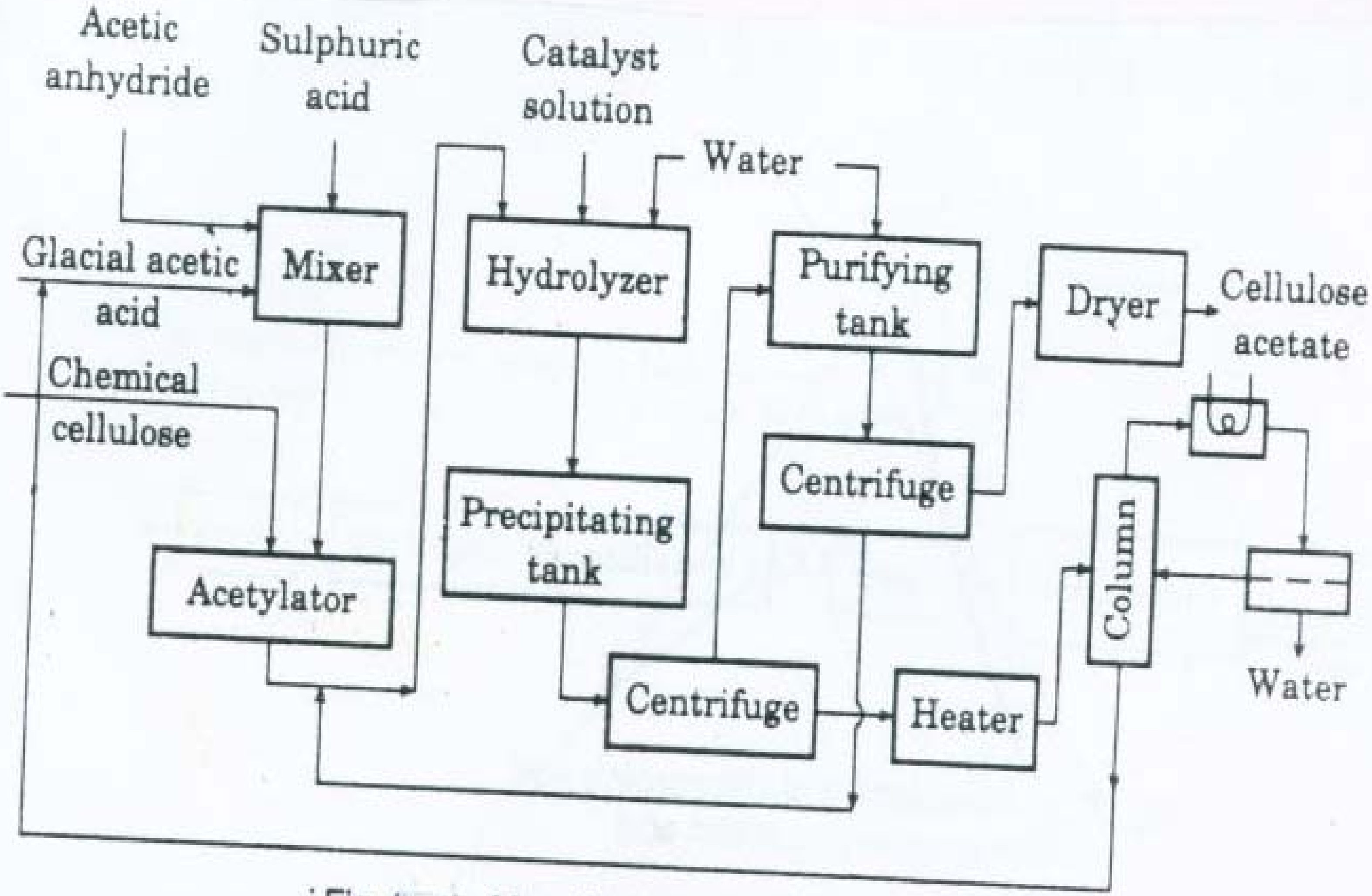


Fig. Manufacture of cellulose acetate from cellulose by acetylation

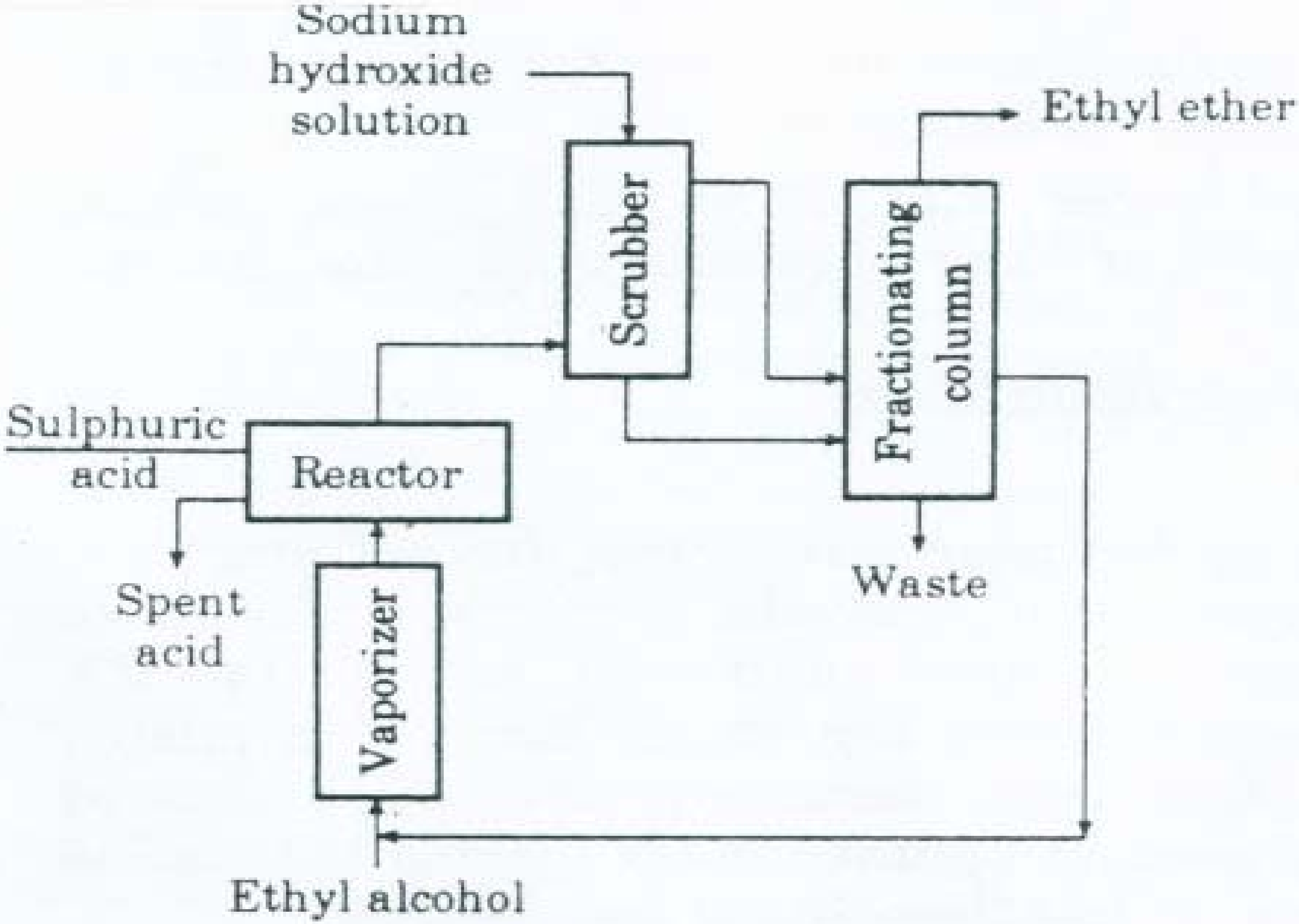


Fig. Manufacture of ether from ethyl alcohol by dehydration.

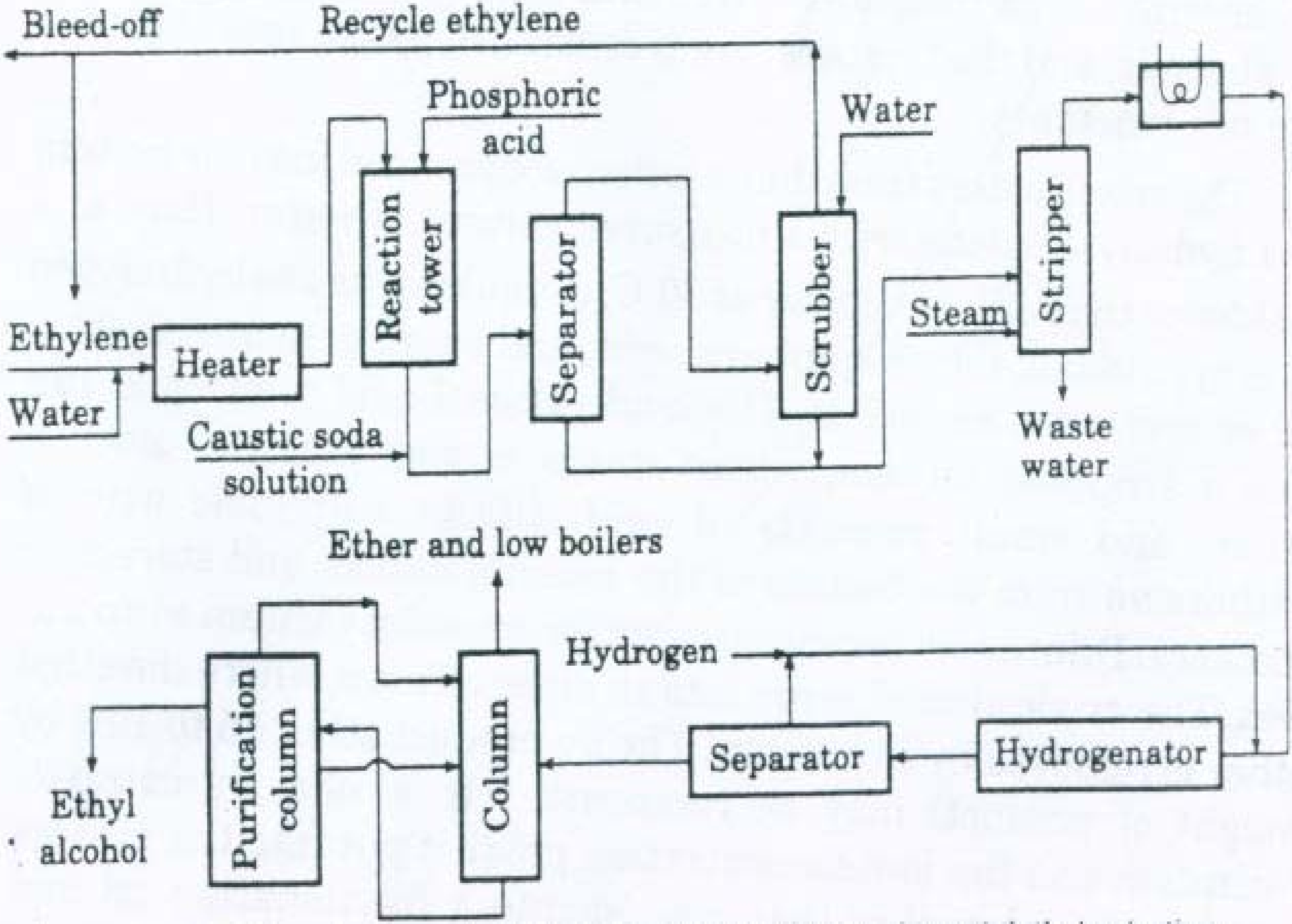


Fig. - Manufacture of ethyl alcohol from ethylene by catalytic hydration.

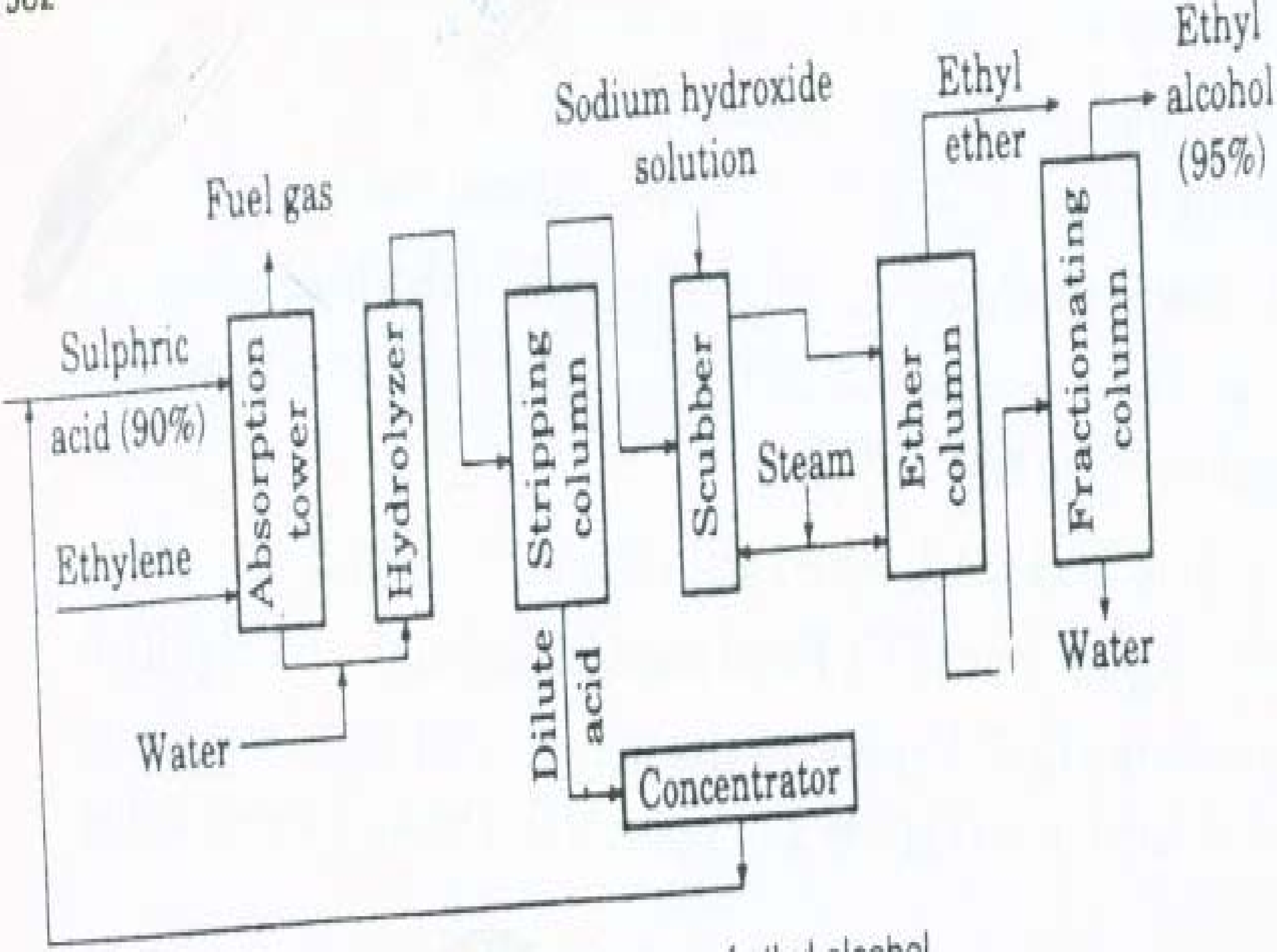
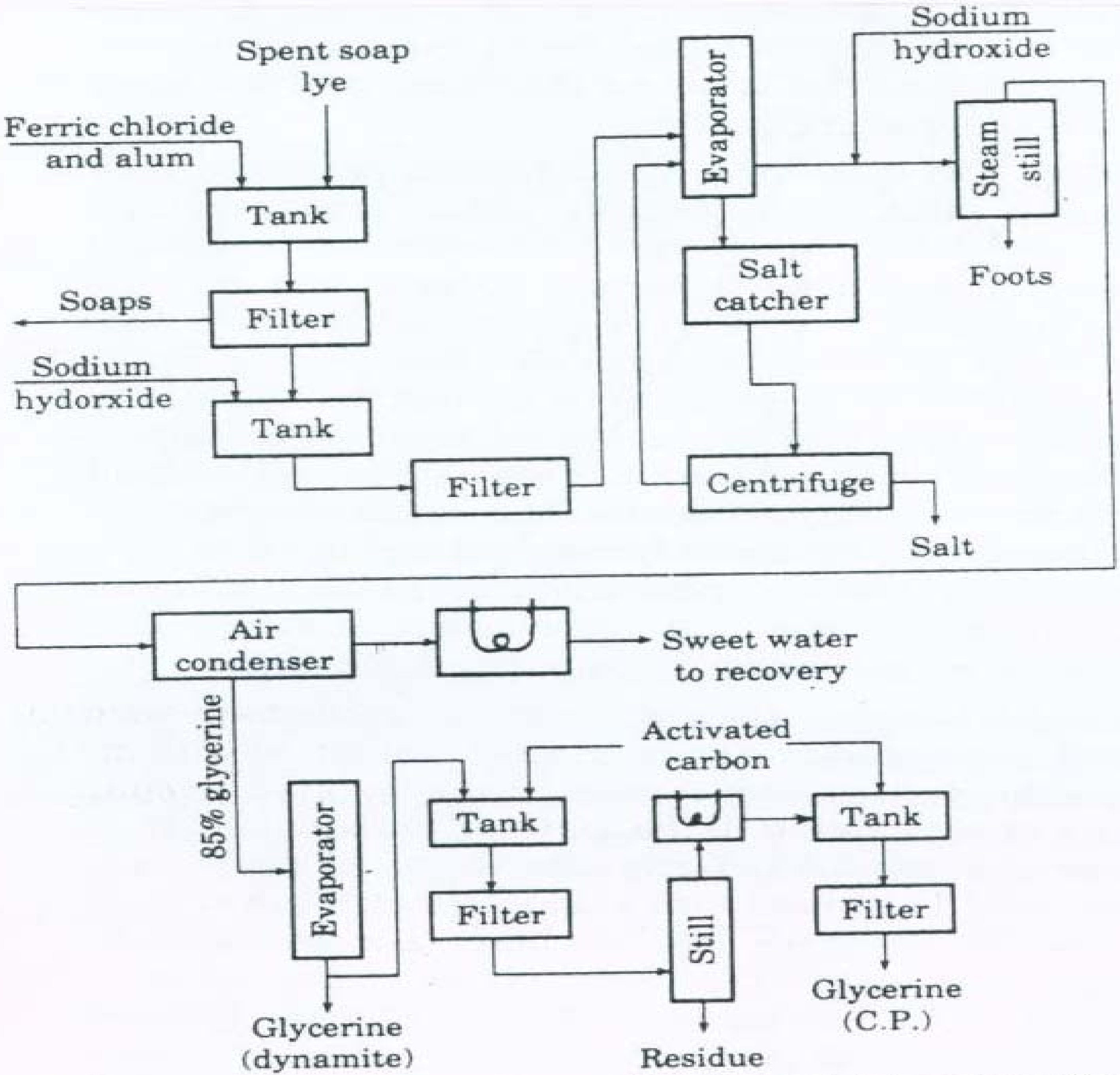


Fig. [illegible] Manufacture of ethyl alcohol.



ig. Manufacture of glycerine (glycerol)from by-product from soap manufacture.

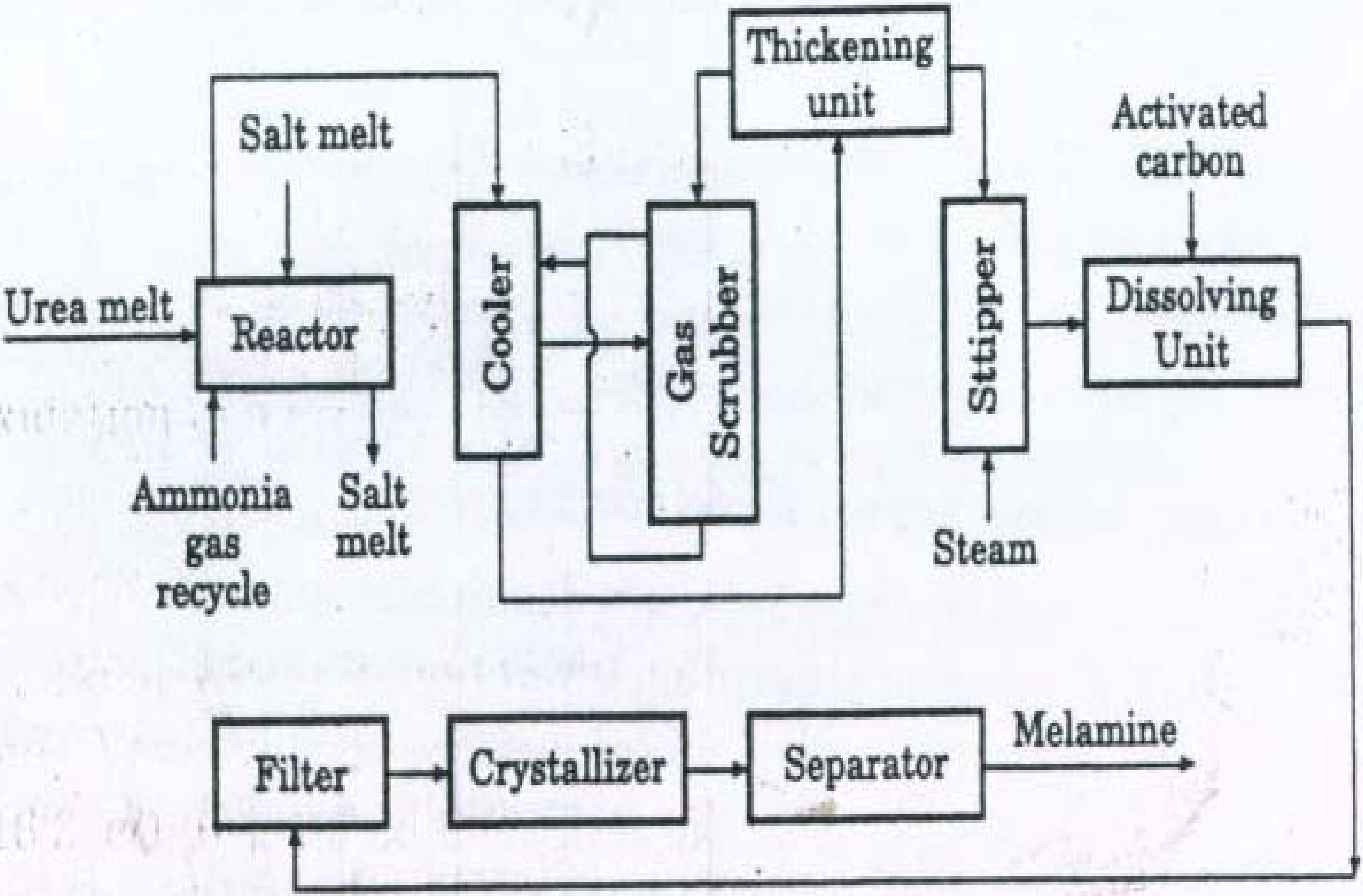


Fig. Manufacture of melamine from urea.

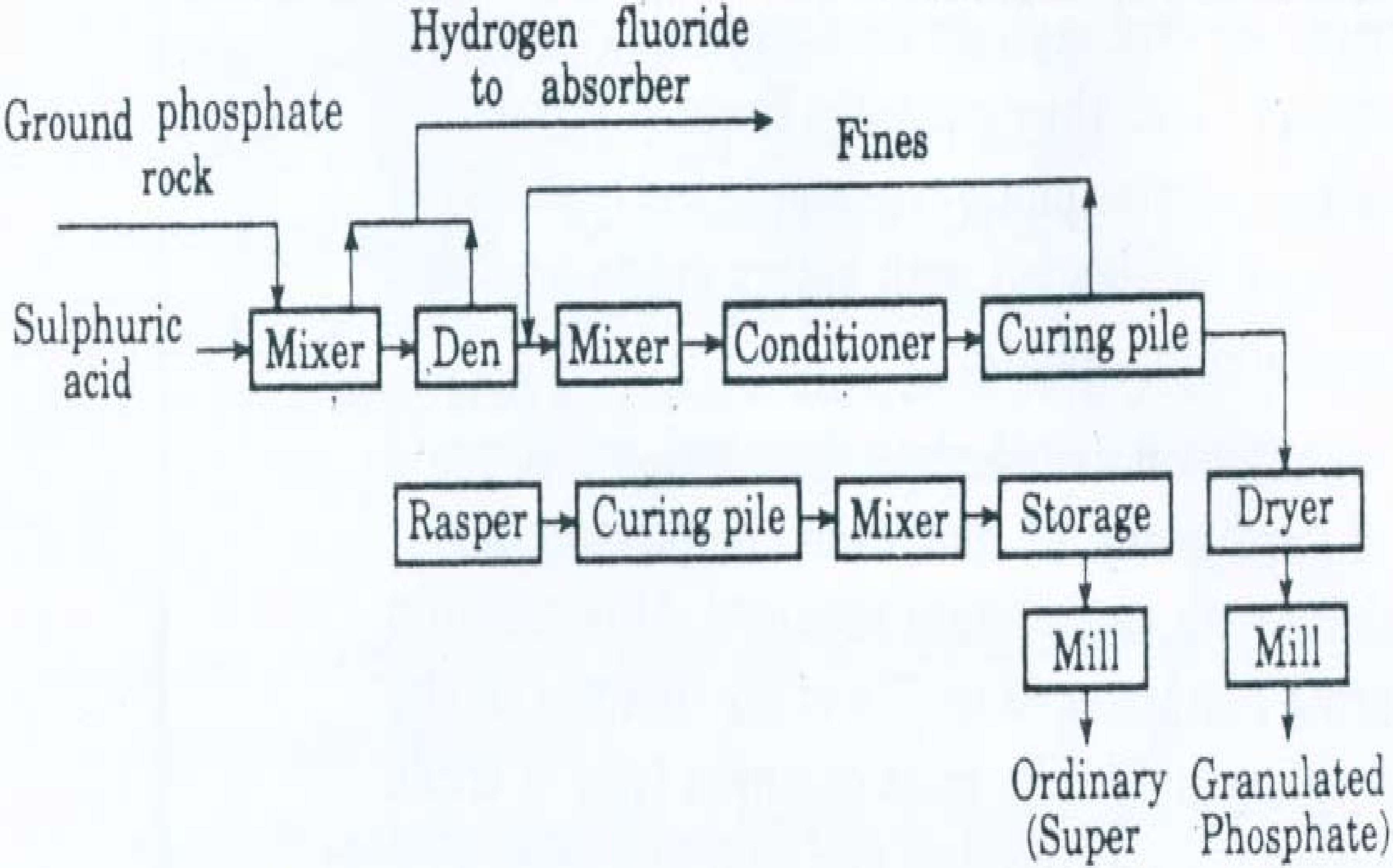
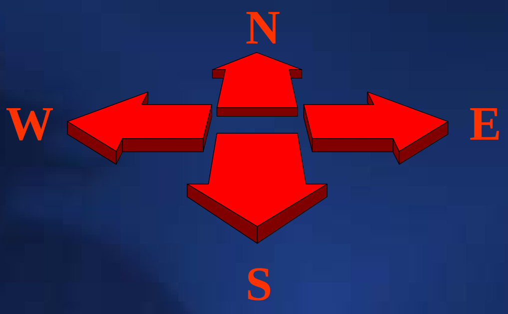


Fig. Flow diagram for manufacturing of calcium phosphate from phosphate rock and sulphuric acid.

L-41-- NH_4Cl, NH_4NO_3, $(NH_4)SO_4$



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