UNIT 1

Sulphur

- Sulphur, also spelled as “sulfur” is a nonmetallic, odorless, tasteless chemical element, insoluble in water, having the Periodic Table atomic symbol of “S”.
- Sulphur may appear as a gas, liquid, or solid. As a mineral, sulphur appears as a pale yellow, brittle crystalline form
- Exists in 2 forms:
  - *Rhombic, mp :112.8°C*
  - *Monoclinic, mp:119°C*
- Boiling Point : 444.6°C
- Insoluble in water, soluble in organic solvents and liquid NH_3

SULFUR - USES

- The main use of sulphur is in the preparation of SO_2 which is used in the manufacture of sulphuric acid.
- Sulphur is used in the manufacture of carbon disulphate, sodium thiosulphate, gun powder, matches and in fireworks.
- Sulphur is used on vulcanization of rubber. Natural rubber is soft and sticky. Heating it with sulphur makes it hard non-sticky and more elastic. This process of heating of natural rubber with sulphur is known as vulcanization.
- Sulphur is used as fungicide and insecticide in agriculture and as a disinfectant in medicines.
- Sulphur is used in ointments for curing skin diseases.
- Sulphur is used in beauty parlors to give specific shapes to the hair.

Raw Materials Sources

- Elemental sulphur
- Pyrites (sulphide of iron)
- From Sour gas (Natural gas) containing H_2S

India :

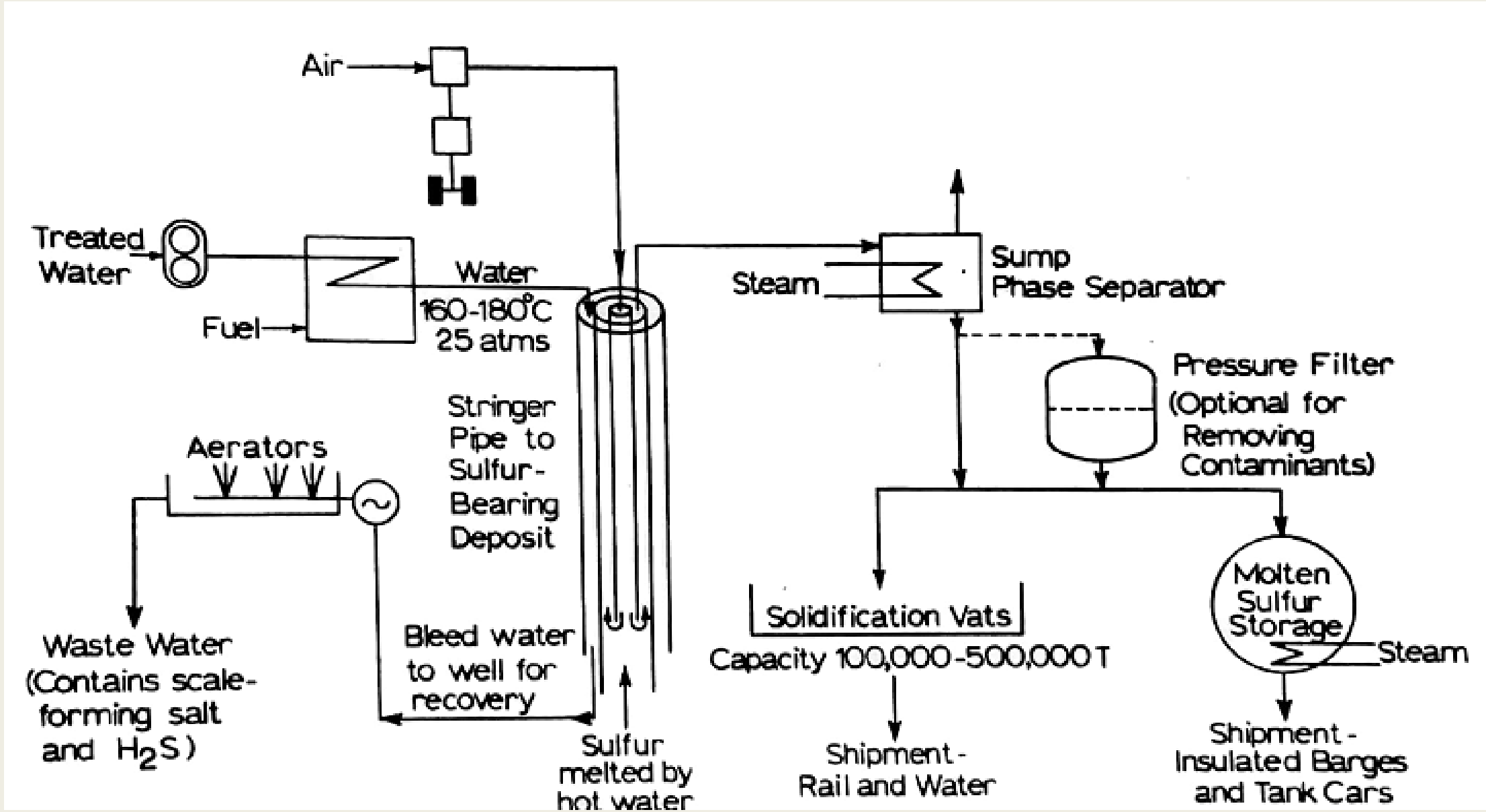
- Pyrite deposits in Amjhore Bihar
- Puga valley in Kashmir but difficult to mine due to terrain conditions

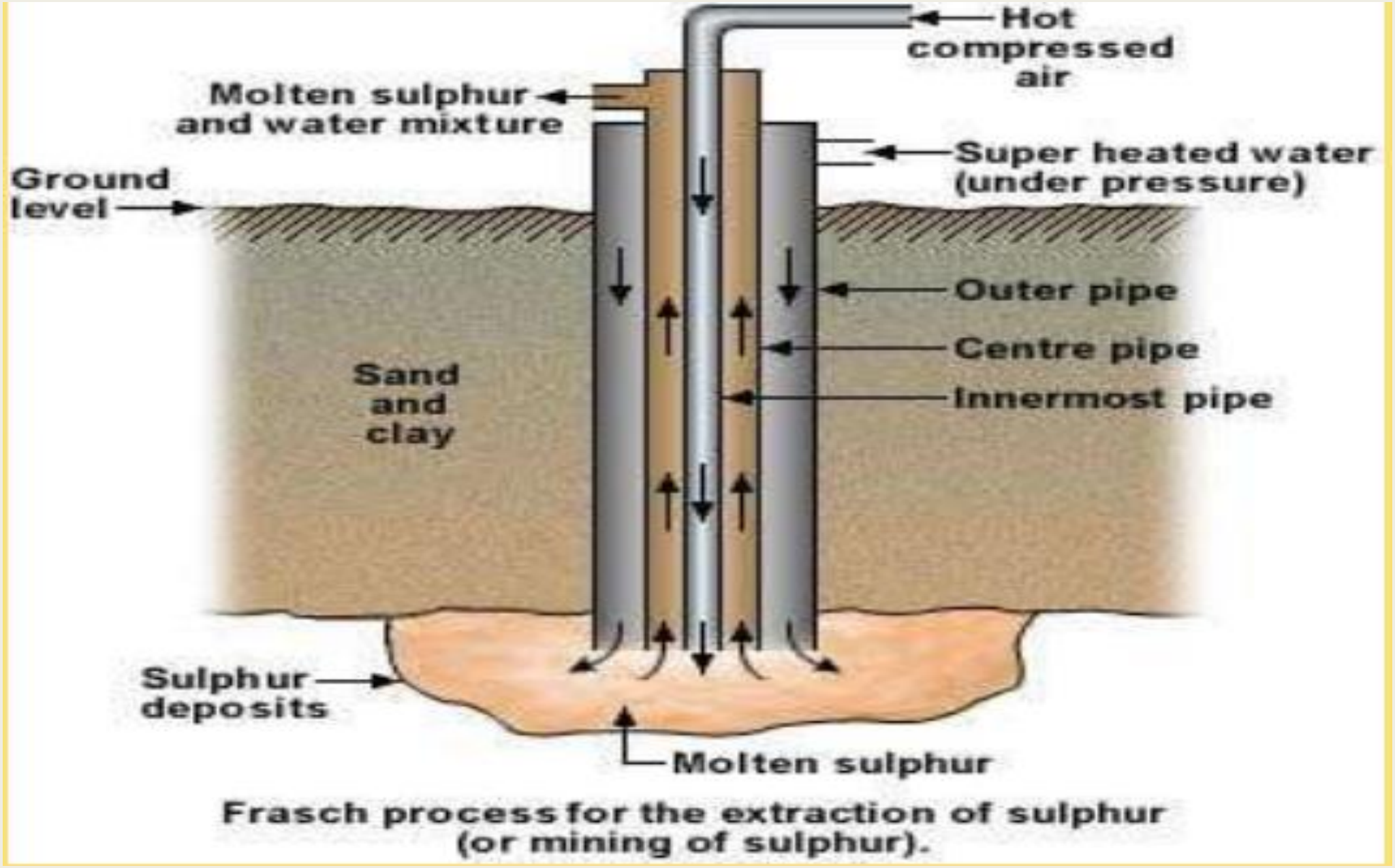
Classification of processes

Recovery of sulphur is done in three basic ways:

- Elemental sulfur mining from salt domes (USA)
- Hydrogen sulfide conversion from natural gas and industrial gases (Indian refineries and many U S refineries)
- Iron pyrites from Amjhore in Bihar

Elemental sulphur mining by Frasch process





Frasch process for the extraction of sulphur (or mining of sulphur).

Recovered sulphur from Natural gas

Raw Materials:

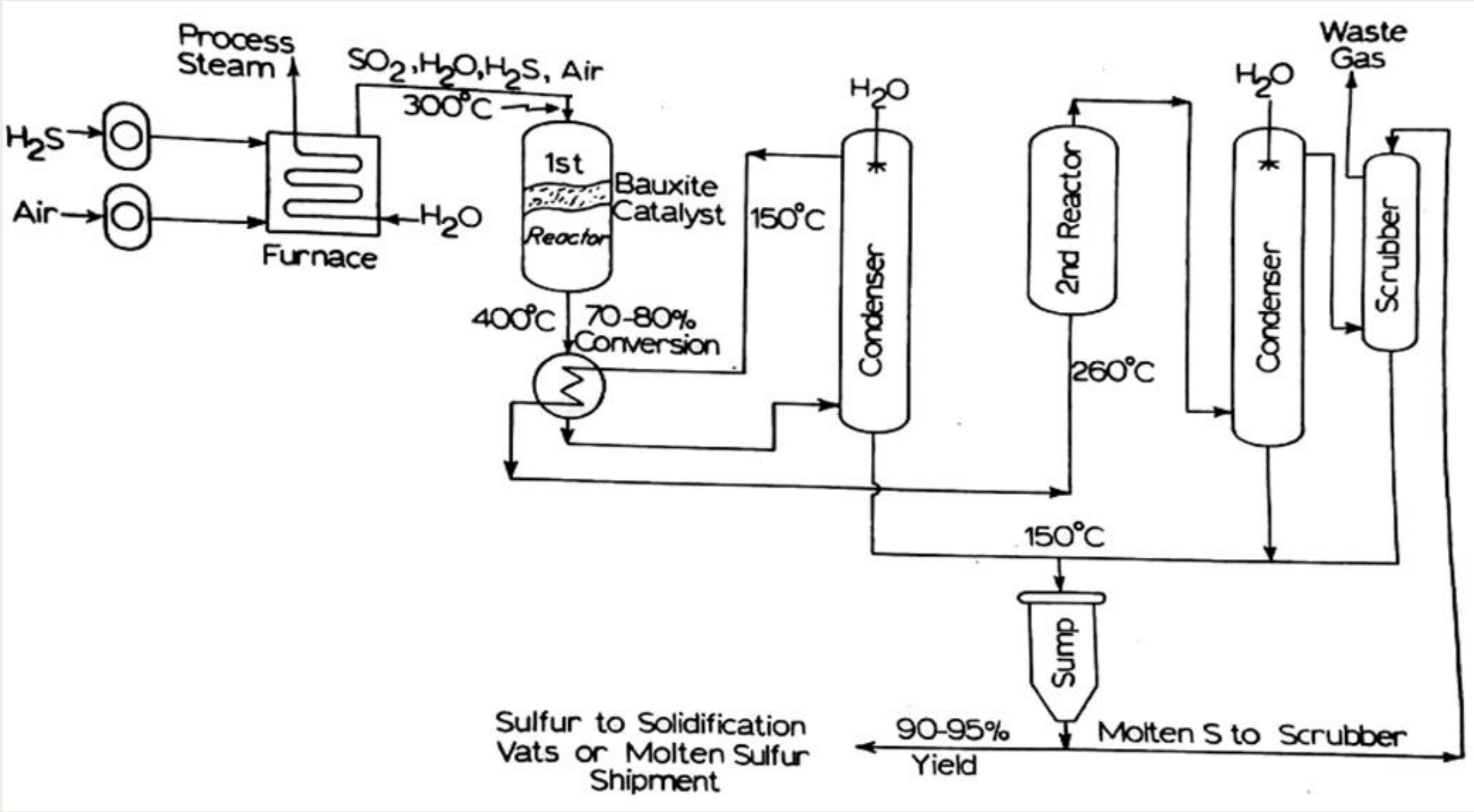
H_2S from natural (sour) gas and petroleum refinery streams, air

Chemical Reactions

Chemical reactions

(a) $2H_2S + 3O_2 \xrightarrow[Al_2O_3]{} 2SO_2 + 2H_2O;$ $\quad \Delta H^\circ = -247.89$ Kcal

(b) $4H_2S + 2SO_2 \rightarrow S_6(g) + 4H_2O;$ $\quad \Delta H^\circ = -42.24$ Kcal


Process Steam
SO_2, H_2O, H_2S, Air
300°C
H_2S
Air
H_2O
Furnace
1st
Bauxite Catalyst
Reactor
400°C
70-80% Conversion
150°C
H_2O
Condenser
2nd Reactor
260°C
H_2O
Condenser
Waste Gas
Scrubber
150°C
Sump
Sulfur to Solidification Vats or Molten Sulfur Shipment
90-95% Yield
Molten S to Scrubber

Elemental sulphur from Pyrites (Finnish Process)

Chemical reactions

(a) Thermal dissociation

$$FeS_2 \xrightarrow[1{,}300^\circ C]{1\ atm.} \tfrac{1}{2}S_2(g) + FeS(1); \qquad \Delta H = +15.98\ Kcal$$

(b) General combustion reaction

$$C + H + S + O_2 \rightarrow SO_2, H_2S, CO, H_2CO_2, H_2O$$

(c) Sulfur recovery from gases—Hot stage

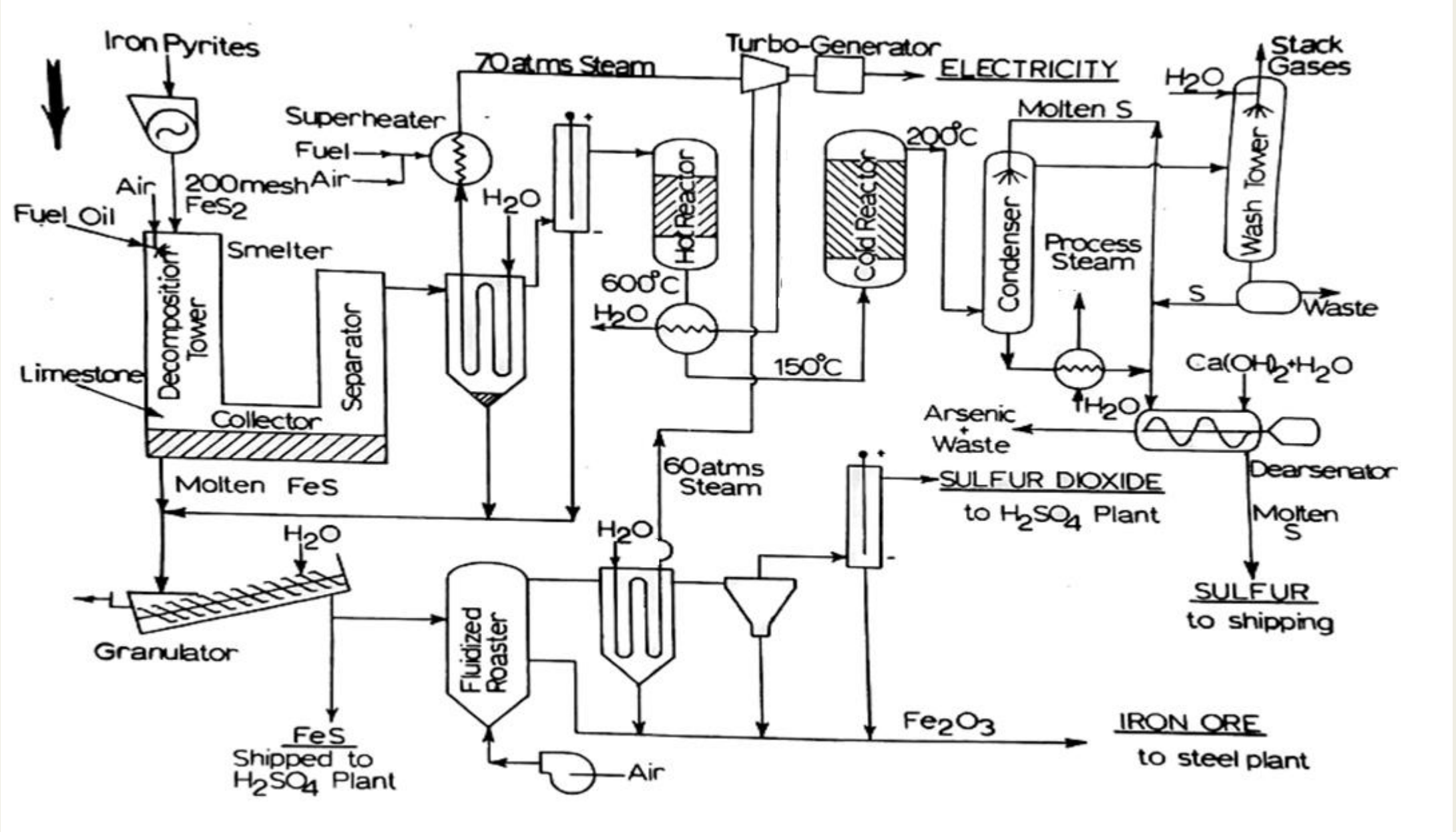
$$2COS + CS_2 + 2SO_2 \xrightarrow[600^\circ C]{catalyst} S_6 + 3CO_2$$

(d) Sulfur recovery from gases—Cold stage

$$4H_2S + 2SO_2 \xrightarrow[280^\circ C]{Al_2O_3} 4H_2O + S_6$$

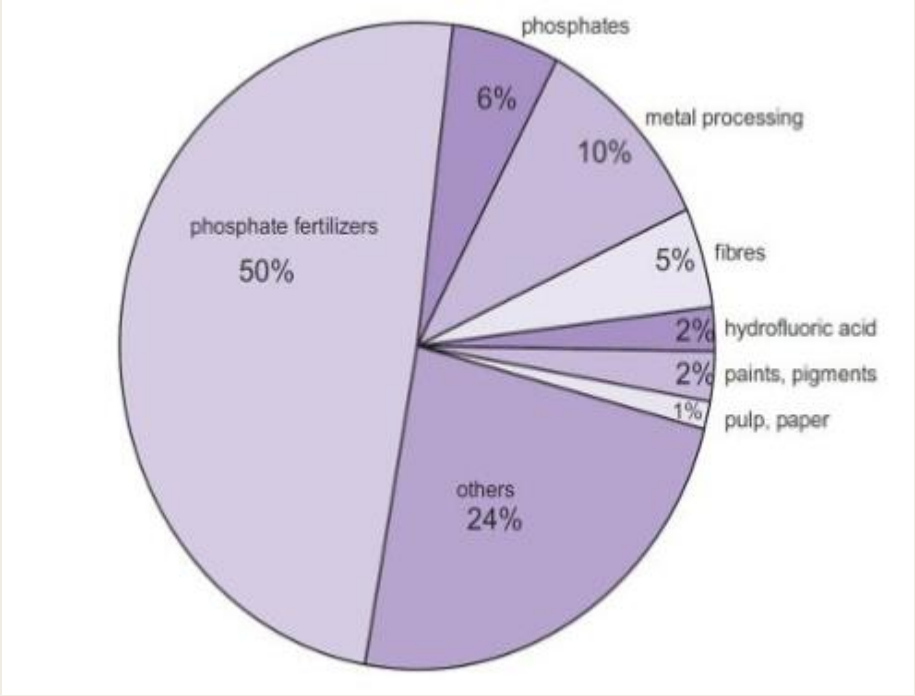
(e) Roasting of FeS (pyrrhotite) for SO_2 recovery

$$2FeS + 3\tfrac{1}{2}O_2 \xrightarrow[1{,}000^\circ C]{1\ atm.} Fe_2O_3 + 2SO_2; \quad \Delta H = -295.02\ Kcal$$


Iron Pyrites
70 atms Steam
Turbo-Generator
ELECTRICITY
Stack Gases
H_2O
Molten S
Superheater
Fuel
Air
200 mesh FeS_2
Air
H_2O
Hot Reactor
Cold Reactor
200°C
Condenser
Wash Tower
Fuel Oil
Smelter
Decomposition Tower
Separator
Process Steam
600°C
H_2O
S
Waste
Limestone
Collector
150°C
$Ca(OH)_2+H_2O$
H_2O
Arsenic + Waste
Dearsenator
60 atms Steam
SULFUR DIOXIDE
to H_2SO_4 Plant
Molten S
Molten FeS
H_2O
H_2O
Granulator
Fluidized Roaster
SULFUR
to shipping
Fe_2O_3
IRON ORE
to steel plant
FeS
Shipped to H_2SO_4 Plant
Air

Sulphuric acid

- Sulfuric acid is perhaps the most fundamentally important, in that it has a number of large -scale uses within the chemical industry
- By far the most important user is the phosphate fertilizer industry.
- Applications of sulfuric acid are found in metal processing, petroleum refining, pigment production, steel pickling, nonferrous metals extraction, and the manufacture of explosives, detergents, plastics, and man-made fibers.



Properties

- Pure sulfuric acid H_2SO_4, Mw 98.08, is a colorless, water-white, slightly viscous liquid, melting point 10.4 °C, boiling point 279.6 ° C, and density 1.8356.
- It can be mixed with water in any ratio.
- Aqueous sulfuric acid solutions are defined by their H_2SO_4 content in weight-percent terms.
- Sulfuric acid will dissolve any quantity of SO_3, forming Oleum (“fuming sulfuric acid”).

Manufacturing Process

The manufacture of Sulphuric acid is carried out by two processes:

1. The Lead Chamber process
2. The Contact process.

- Both processes are based on SO_2
- Chamber process was developed first (1746) but produced acid of concentration less than 80%. It is less efficient than the contact process. Contact process yields 98% H_2SO_4 and higher which can be diluted, if necessary.
- The main principle of the chamber process is that the moist sulphur dioxide is oxidized by the oxygen of the air into sulphur trioxide in the presence of gaseous nitrogen oxide acting as catalyst. These large chambers are lined with sheets of lead. Sulphur trioxide combined with water to form sulphuric acid.

Contact Process

Sources of raw material

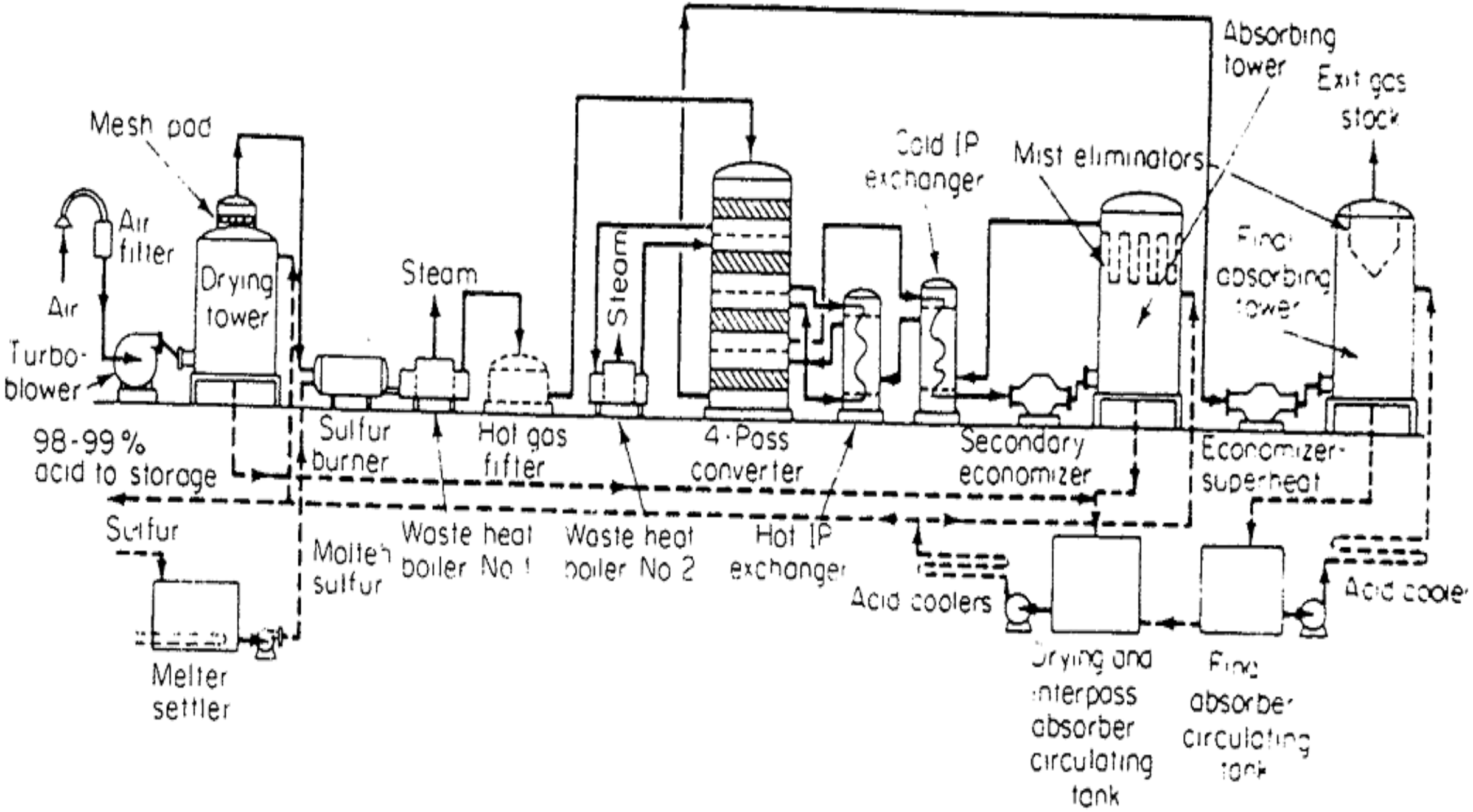
The sources of sulfur and sulfur dioxide are as follows

- Sulfur from mines
- Sulfur or hydrogen sulfide recovered from petroleum desulfurization
- Recovery of sulfur dioxide from the smelting of metal sulfide ores

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

- Isolation of SO_2 from pyrite
- Recovery of sulfur dioxide from coal or oil-burning public utility stack gases

Burning of sulphur	$S + O_2 \longrightarrow SO_2$	$\Delta H = -71.2$kcals
Catalytic oxidation of SO_2	$2SO_2 + O_2 \rightleftharpoons 2SO_3$	$\Delta H = -46.3$kcals
Hydration of SO_3	$SO_3 + H_2O \longrightarrow H_2SO_4$	$\Delta H = -31.1$kcals


Mesh pad
Air filter
Air
Turbo-blower
Drying tower
98-99 % acid to storage
Sulfur
Melter settler
Molten sulfur
Sulfur burner
Steam
Hot gas filter
Waste heat boiler No 1
Steam
Waste heat boiler No 2
4-Pass converter
Cold IP exchanger
Hot IP exchanger
Mist eliminators
Secondary economizer
Absorbing tower
Exit gas stack
Final absorbing tower
Economizer-superheat
Acid coolers
Drying and interpass absorber circulating tank
Final absorber circulating tank
Acid cooler

Comparison of vanadium and platinum catalyst

Aspect	Vanadium catalyst	Platinum catalyst
Conversion	Higher	Lower and decrease with use
Investment	Initially less, 5% replacement is required per year	High, Lower life and highly fragile
Catalyst poisoning	Relatively immune to poison	Poisoned, especially by arsenic
Handling of SO_2	Less (7-8%)	High (8-10%)
Requirement per 1000kg (100% acid)/day	14kg catalyst mass containing 7-8%V_2O_5	189gms

Industrial Gases

- **Industrial gases** are the gaseous materials that are manufactured for use in industry.
- These industries include chemicals, power, medicine, electronics, aerospace, and even food.
- As useful as these gases are, they may be flammable and come with other dangers.
- Examples : acetylene, hydrogen, carbon dioxide, nitrogen, oxygen

Carbon Dioxide (CO_2)

It is a trace gas with a concentration of 0.039% by volume in atmospheric air.

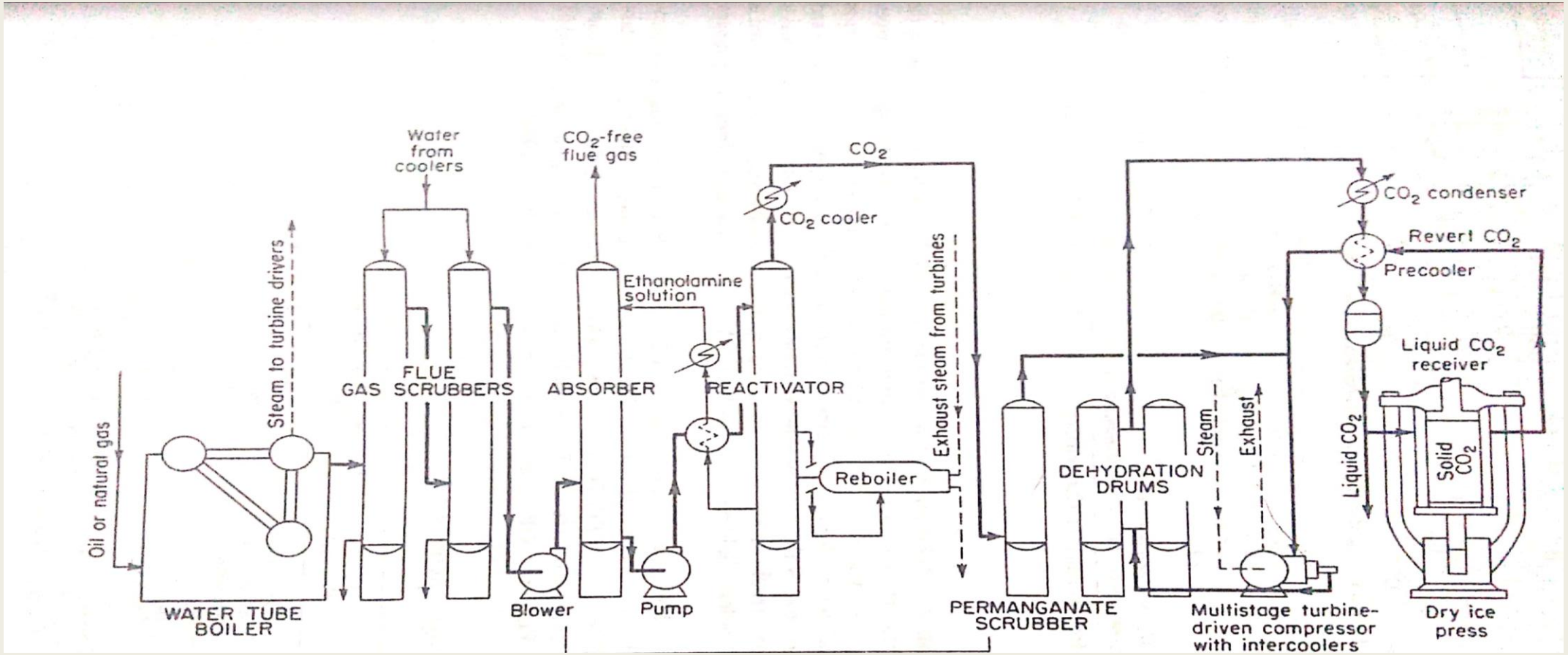
PROPERTIES

- Molecular formula : CO_2
- Molecular weight : 44.01gm/mole
- Appearance : Colourless gas
- Odour : Odourless gas
- Boiling point : -57^0C
- Melting point : -78^0C
- Density : 1. 977kg/m^3 @ 1atm and 0^0C
- Solubility : Soluble in water

USES

- As solid CO_2 in refrigeration process
- Liquid CO_2 is needed in carbonated.
- Used in creating inert atmosphere.
- As fire extinguisher
- Gaseous CO_2 used as a neutralizing agent
- Gaseous CO_2 is the basic raw material for production of Na_2CO_3, $NaHCO_3$

CO_2 from fuel oil or natural gas



Acetylene (C_2H_2)

- Acetylene is a colorless, combustible gas with a distinctive odor.
- When acetylene is liquefied, compressed, heated, or mixed with air , it becomes highly explosive. As a result special precautions are required during its production and handling.
- The most common use of acetylene is as a raw material for the production of various organic chemicals including 1,4-butanediol, which is widely used in the preparation of polyurethane and polyester plastics. It is used in the synthesis of certain vitamins like Vitamin A and E.
- Another common use is as the fuel component in oxy-acetylene welding and metal cutting.

Acetylene from partial or stage wise combustion of hydrocarbons

Chemical reactions

- Exothermic heat supply

  (a) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$; $\Delta H^\circ = -212.798$ Kcal

- Endothermic production reaction

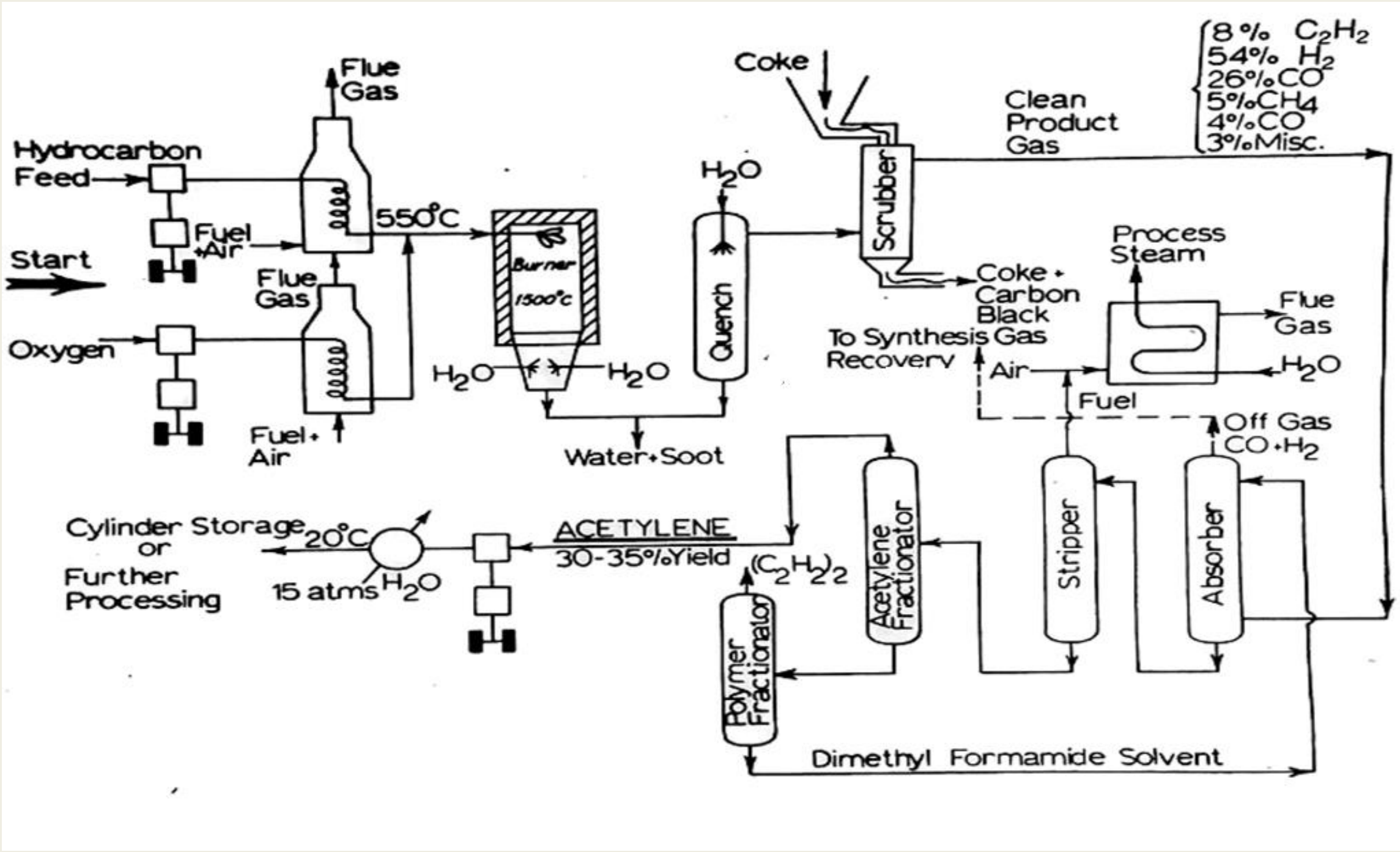
  (b) $2CH_4 \rightarrow C_2H_2 + 3H_2$; $\Delta H^\circ = +89.97$ Kcal

- Undesirable side reaction

  (c) $C_2H_2 \rightarrow 2C + H_2$; $\Delta H^\circ = -54.194$ Kcal

Raw materials

- Low purity natural gas or higher mol. wt. hydrocarbons


Flue Gas
Hydrocarbon Feed
Fuel + Air
Start
Oxygen
Flue Gas
Fuel + Air
550°C
Burner 1500°C
H_2O
H_2O
Quench
H_2O
Water + Soot
Coke
Scrubber
Clean Product Gas
8% C_2H_2
54% H_2
26% CO
5% CH_4
4% CO
3% Misc.
Process Steam
Coke + Carbon Black
To Synthesis Gas Recovery
Air
Flue Gas
H_2O
Fuel
Off Gas CO + H_2
Cylinder Storage or Further Processing
20°C
15 atms
H_2O
ACETYLENE
30-35% Yield
$(C_2H_2)_2$
Polymer Fractionator
Acetylene Fractionator
Stripper
Absorber
Dimethyl Formamide Solvent

Hydrogen Gas (H_2)

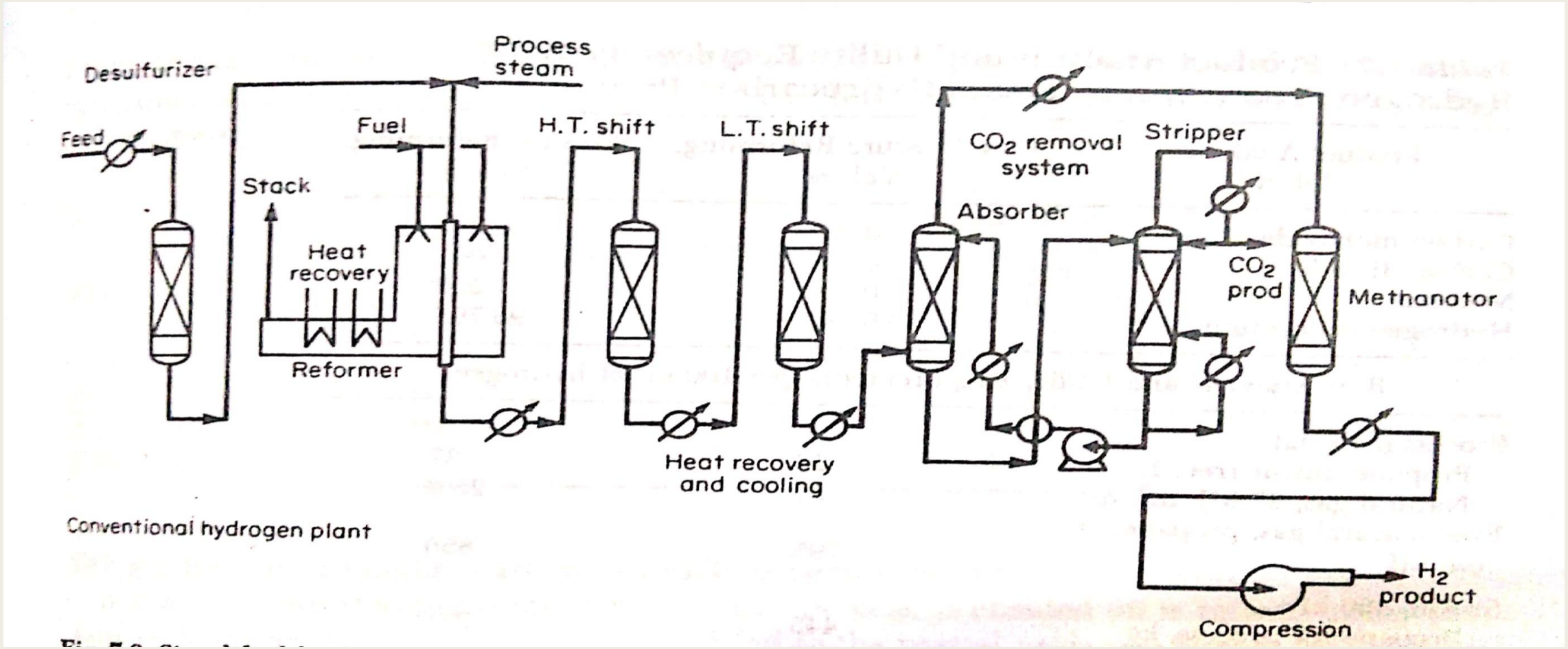
- Hydrogen is the most common element in the universe, but it takes a lot of processing to extract and contain pure hydrogen.
- Hydrogen is the lightest element and will explode at concentrations ranging from 4-75% by volume in the presence of sunlight, a flame, or a spark.
- melting point = -259.14 °C
- boiling point = -252.87 °C.
- Hydrogen has a density of 0.08988 g/L, making it less dense than air.
- This gas can be liquefied, compressed, or mixed with other gases for various uses.
- Hydrogen fuels space rockets, helps the steel welding process, powers alternative energy cars, refines crude oil, aids in the production of common household chemicals, and more.

Steam Reforming for Hydrogen Production

The principal process for converting hydrocarbons into hydrogen is steam reforming, which involves the following reactions:

$$C_nH_m + nH_2O = nCO + \left(\frac{m+2n}{2}\right) H_2$$

$$CO + H_2O = CO_2 + H_2$$



Conventional hydrogen plant