

PULP AND PAPER INDUSTRY

CHEMICAL PROCESS TECHNOLOGY

CHE F419

INTRODUCTION

- The pulp and paper industry converts wood or recycled fibre into pulp and primary forms of paper.
- **Paper** production requires a disintegration of the bulky fibrous material to individual or small agglomerate fibers. This is called **Pulping**.
- India was first country to use bamboo as a basic raw material for making paper.
- Due to limited forest resources, other raw materials like bagasse, straw, jute etc. were identified and now extensively used.
- There is a large gap between demand (7-8 million ton/ A) and production (3-4 million ton/ A).
- Future growth requires
 - Raw material expansion with improved pulping process
 - Better reclamation and reuse of waste paper
 - Installation of newer, more efficient, continuous pulping process.

PULP

- Pulp is a commercial fibrous material obtained from bamboo, wood, bagasse (waste material) etc. by mechanical and chemical means.
 - Pulping means disintegration of bulky fibrous material to small fibres.
 - First mechanical and then chemical methods have been developed to produce pulp from wood.
 - There are mainly three modes of production of pulp:
 - a) Mechanical
 - b) Chemical
 - c) Semi chemical
- Kraft (68%)-Chemical
mechanical (22%)
semi-chemical (4%)
sulphite (4%) - Chemical
dissolving (2%).

Wood Composition

- **Cellulose (42-48 %)**
 - Main component of fiber.
 - It's a polymer of β -D-glucose; white in color
 - Insoluble and relatively stable in water or aqueous alkali.
 - Decomposes above 260-270°C and stable toward oxidation
- **Lignin (15-30 %)**
 - Important compound of wood, functions as interfiber bonding agent.
 - Heterogeneous structure composed of n-propylbenzene units joined by ether (C-O-C) and (C-C) links.
 - Brown in color; readily oxidized.
 - Soluble in hot aqueous base and hot aqueous bisulfite ion (HSO_3^-).
- **Hemicellulose (27%)**
 - Less dominant compound; soluble in aqueous alkali.
 - Important component of papermaking as it improve interfiber bonding.
- **Other non-cellulosic compounds (3-8%)**
 - Polymeric material-Pectin, strach, ash; soluble in cold water;
 - Fatty acids and resin acids formed from oxidized terpenes cause corrosion/foaming

Mechanical Process (Groundwood)

- Pulp produced rely solely on physical work on log to reduce the wood to a fiber suspension in water.
- Debarked wood is mechanically shredded to form fibers.
- Suitable where strength and ease of bleaching are not important :Low cost paper.
- Yield obtained in about 95%.
- Example :for the production of newsprint, toweling, toilet tissues and cheap paperback books

Chemical Process (Sulfate process , Sulfite Process)

- The cellulose from wood is freed from lignin and other non-cellulose ingredients by reaction with chemical reagents.
- The chemical employed operate at low or high pH; with higher ratios of chemical to wood, and cooking conditions are more severe than other processes.

Chemical Process (Continue...)

- Paper produced is of 'high strength' and 'fine texture'.
- Readily bleached to high brightness (whiteness) levels because they consists of almost pure cellulose.
- Due to loss of lignin and hemi-cellulose as well, yield is half that from the mechanical ground process (40-65%).

Semi-chemical Process

- Mild treatment of wood with dilute (chemical) mixture and softening to allow mechanical separation of fiber.
- Result in a good yield (65-80%) with better quality than groundwood pulp.
- Lower power input than mechanical pulping
- Intermediate intensity chemical treatment is achieved by
 - Decreased ratio of chemical to wood
 - Decreased cooking times and/or temperature
 - Use of chemicals which pulp at neutral pH conditions.

Comparison of Chemical Pulping Processes

Characteristic	Sulfate Process	Sulfite Process
Trade Name	Kraft : Can handle all types of wood and raw materials.	Sulfite; Magnifite : Bamboo and hardwoods preferable.
Digestion liquor	Alakaline [NaOH; Na ₂ S]	Acidic [Solution of SO ₂ in water]
Digester Conditions	Time [2-5 Hours for wood; 5-6 minutes for bagasse] Temperature : 150-180°C Pressure : 10 atm	Time [6-10 Hours for wood; 20-40 minutes for bagasse] Temperature : 120-150°C Pressure : 4-6 atm
Types of Pulp	Brown color; difficult to remove unless ClO ₂ used ad bleach agent. High strength and texture. Well tested chemical recovery system	Dull white color; easily bleached. Less than optimum paper strength properties . Expensive chemical process recovery
Typical paper product	Strong brown bags, Brow paper, paper board boxes; strong white paper via bleaching.	White grade bond paper; tissue paper for it's softer fibers.

Sulfate (*Kraft*) Pulp Process

- Most popularly used process. This is an alkaline process.
- In this process wood chips are cooked in a pulping liquor (consists of sodium hydroxide and sodium sulfide in water : so called white liquor).
- Na_2SO_4 is added to the cooking liquor. So its common name is sulfate process.
- The presence of sodium sulfide accelerates the pulping rate and makes bleaching of pulp easier .
- The sulfide also stabilizes the cellulose, so the paper produced has better strength.
- The digestion liquor from each batch of chips to be pulped is obtained from chemicals recovered from the spent liquor of previous digestions.

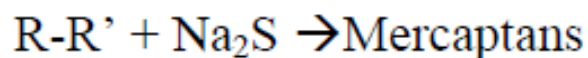
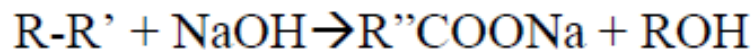
Raw material : Bamboo or wood

Lime make up

Salt cake Na_2SO_4 make up

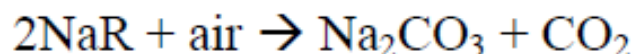
Chemical reactions involved

- (i) Digestion (hydrolysis and solubilization of lignin)

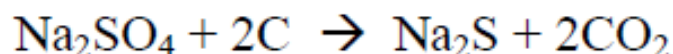


- (ii) Chemical recovery from black liquor

- (a) Smelting

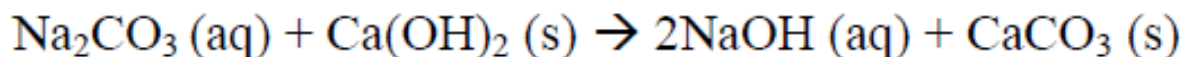


(lignin)



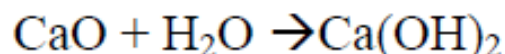
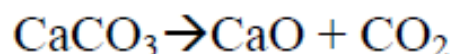
(from R) (white liquor)

- (b) Causticizing

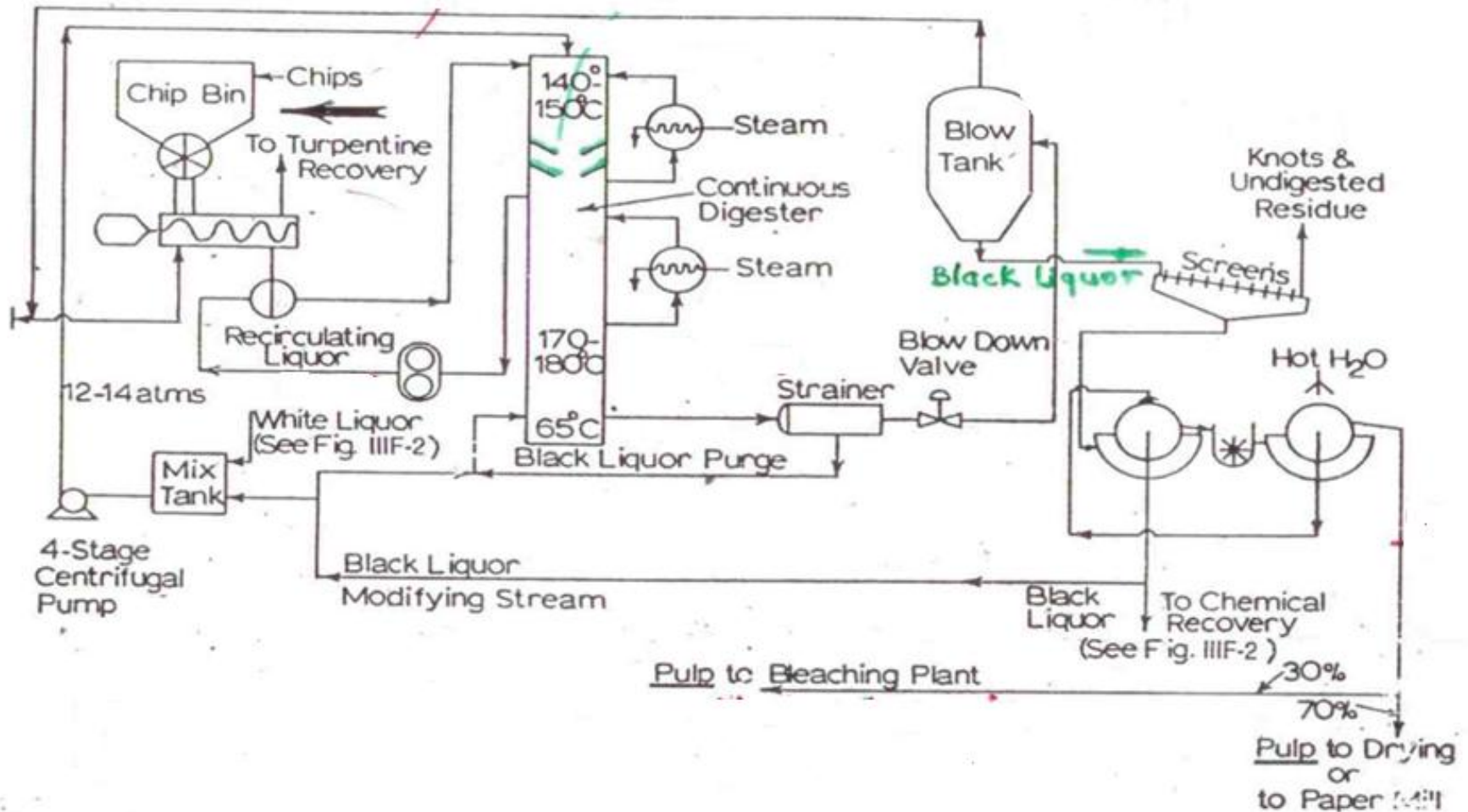


(green liquor)

(white liquor)



Preparation of wood pulp by Sulfate Process



Process Description

- **Wood Preparation**
 - Bark removal by tumbling and rubbing action. (as bark contribute an undesirable highly colored, non fibrous constituent to pulp).
 - Cut logs are conveyed to the chipper where rotary disks with heavy knives reduce the wood to size 2-5cm flat chips. Size reduction is done to maximize penetration of process chemicals.
- **Preheating**
 - Chips are preheated with volatilizing turpentine and non-condensable gases.
- **Digestion**
 - Cook is carried out in digester. Steam is blown to the opening of digester, displaces much of air. It aids in liquor penetration into the chip from its air displacement, warming and wetting.
 - At the time of white liquor addition, sufficient “weak black liquor” is also added to control solid-liquid concentration and temperature.
- **Blow tank**
 - After the digestion is complete, a valve is open, causing a very rapid discharge of the content of the digester into a blow tank. The fast pressure drop experienced by the pulp on discharge blows the fiber bundles apart, aiding in the production of pulp from the chips.

- **Screening**

- Cooked pulp plus weak black liquor (spent white liquor) has picked up lignin and some hydrolyzed cellulose and hemicellulose; proceed to screens; which serve to remove any uncooked fragments and knots from the pulp.

- **Filtration**

- Pulp is filtered to separate black liquor for chemical recovery plant. Black liquor is also recycled back to digester for cooling the digested chips. Hot water is added to second filter for better filtration.
- At this stage the separated product is fairly clean pulp; still dark brown in color; because of residual lignin.

- **Bleaching of pulp**

- To produce white paper, the pulp is bleached. The chemicals used to bleach pulp must be environment friendly. Bleaching with chlorine produces dioxins and other undesirable products. So, nowadays pulp is bleached with hydrogen peroxide, ozone, chlorine dioxide, oxygen etc. The objective of bleaching is to remove small fractions of lignin that remains after digestion.

Recovery of Chemicals

There are three objectives of chemical recovery from weak black liquor separated from the pulp after kraft pulping.

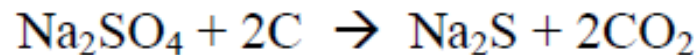
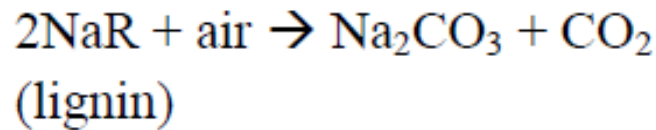
- 1) Recovery and regeneration of most of the chemical employed in the original digestion liquor are primary objective.
- 2) Next is to generate a significant fraction of steam requirement of pulp mill from combustion of the dissolved lignin residues and other organic constituents contained in a weak liquor.
- 3) Burning the organic constituent in the spent liquor also accomplished the third objective , which is to avoid the significant polluting potential of un-reacted discharge of spent pulping liquor.

It is accomplished in following steps:

- Initially the weak liquor is oxidized, by sparging air to decrease the volatility and losses of foul-smelling volatile sulfur compounds.
- After oxidation of the weak liquor, of about 15-18% total solids content by weight, it is concentrated. Concentration before combustion is necessary to increase the energy recovery from combustion of the organic constituents.
- Evaporation to 50-55 % solids is carried out in 3-6 stages of multiple-effect evaporators. The last stage of evaporation, from 50-55% solids to about 65-70% solids, is by direct contact of the black liquor with hot flue gases from the recovery boiler.

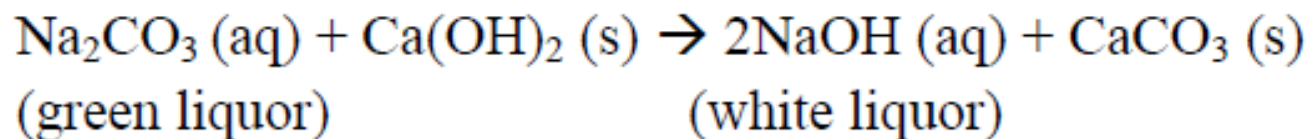
- Next is combustion of black liquor in furnace to reduce sodium(/thio) sulfate to sodium sulfide and any remaining sodium hydroxide to sodium carbonate. This mixture called smelt, trickles out.

(a) Smelting

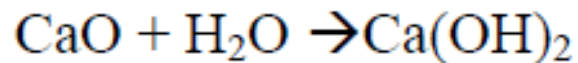
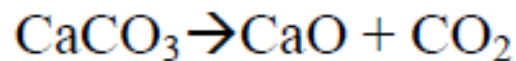


- The smelt is immediately dissolved in lime mud wash water for the first stage in fresh liquor preparation known as green liquor.
- For white liquor preparation, clarified green liquor is fed to caustisizer (Carbonating tower), which form sodium hydroxide on addition of slaked lime, leaving sodium sulfide unchanged.

(b) Causticizing

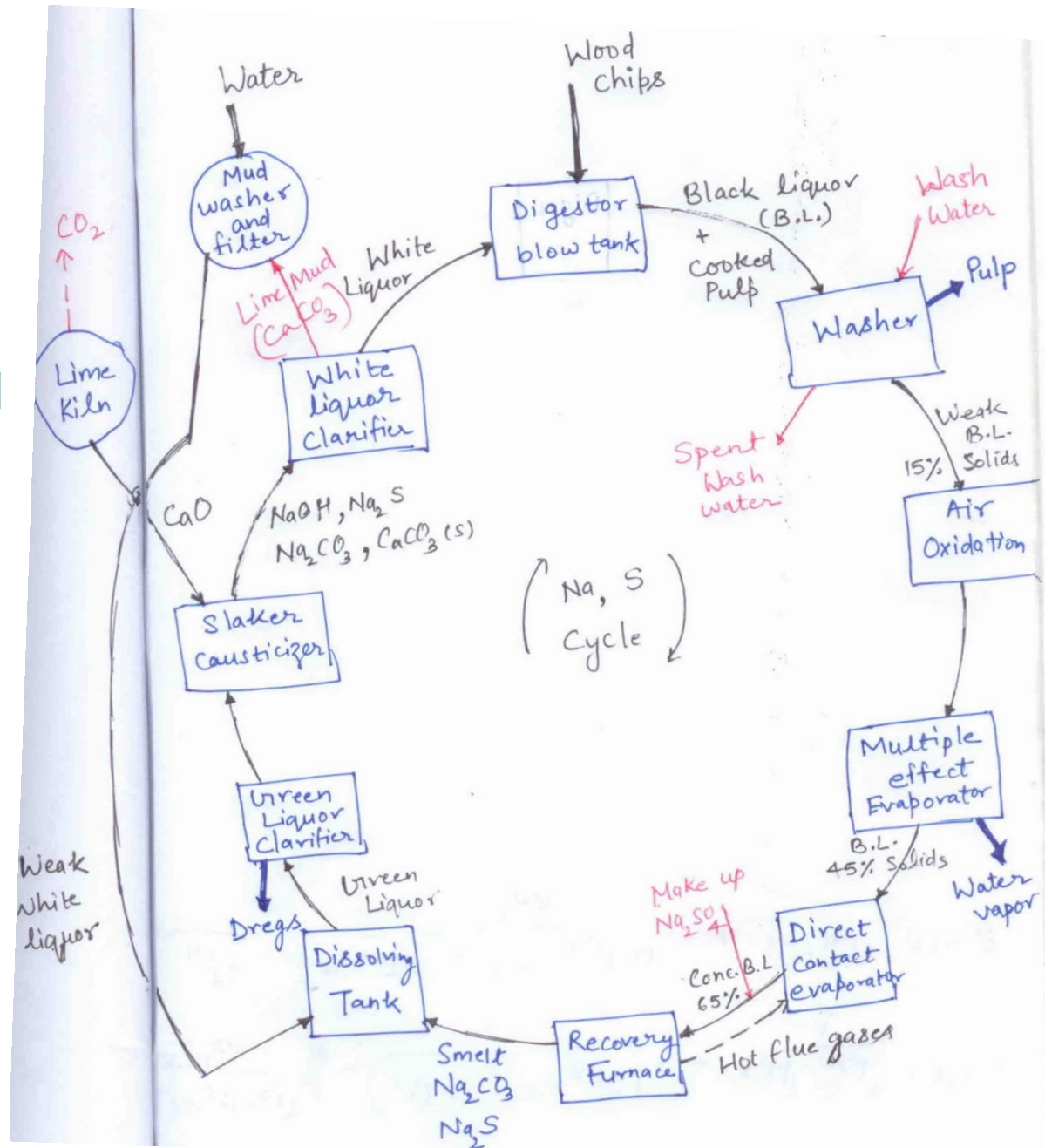


- The insoluble calcium carbonate mud is settled out from this mixture, filtered and rinsed with water. Calcium carbonate in the lime mud is recycled by first calcining to decarbonate, followed by slaking to regenerate the calcium hydroxide required for subsequent causticization.



- Several by products are recovered from kraft pulping operations, among them kraft turpentine, tall oil, and dimethyl sulfoxide. Turpentine is condensed from digester relief gas and recovered by washing and fractional distillation of crude product.
- Dimethyl sulfoxide $(\text{CH}_3)_2\text{SO}$ is made from dimethyl sulfide recovered by condensation from kraft digester relief gases. It is polar, and water-miscible industrial solvent.

Cyclic Process for recovery of chemicals and energy from the spent pulp liquor of the kraft process



Major Engineering problems

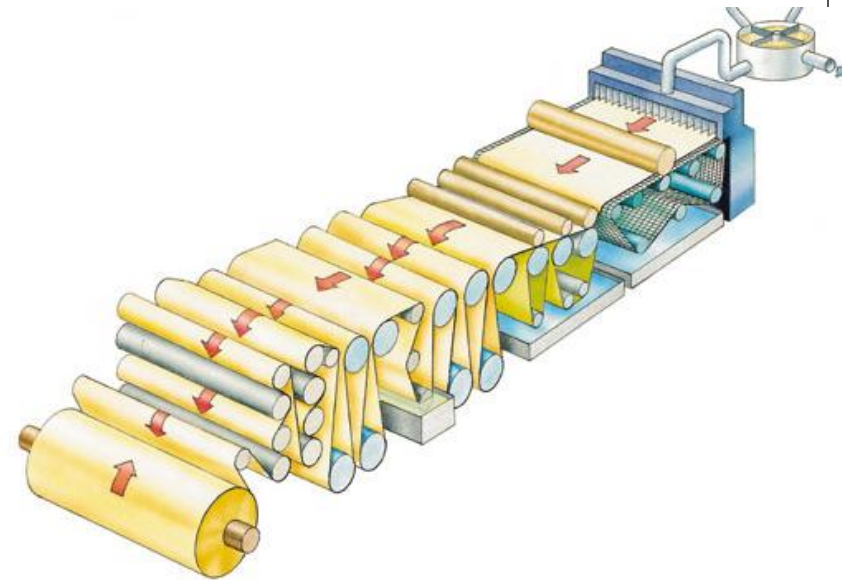
1. Choice of process
2. Use of soda process
3. Pollution and waste disposal
4. By product utilization

Paper industry

- Paper is matted or felted sheet of cellulosic fibers which are held together by hydrogen bonds.
- Mechanical and other properties of paper depend on nature of fiber distribution and bonding between them.
- Bleached or unbleached pulp, from different pulping processes (mechanical/chemical), are fed in diluted form (wet process) on paper mill.
- In wet process, fiber suspension in water is made and it is then made into sheet and dried.
- Paper making process is generally done on **Fourdrinier machine**.
- Raw material —
 1. Fibrous : Paper Pulp, Reuse Pulp (from recycle paper)
 2. Non- fibrous : Filler(Clay, talc) ; Color; Latex; additives

Almost all types of paper and board-making processes have the following basic units:

- Stock preparation
- Approach flow system
- A paper and board machine consisting of
 - **Head box** introduces the suspension of fibres to the wire and creates a uniform dispersion of fibres across the total width of the wire belt
 - A **wire section** drains paper web to around 12 - 20% solids
 - A **press section** removes more water out of the web by pressing down to about 50% moisture content
 - A **drying section** removes rest of moisture by heating the web with drying cylinders
 - A **reeler** reels the paper web into a roll



Stock Preparation/Preparation of fiber suspension

- Stock preparation is conducted to convert raw stock into finished stock (furnish) for the paper machine.
- The pulp is prepared for the paper machine including the blending of different pulps, dilution and the addition of chemicals.
- The raw stocks used are the various types of chemical pulp, mechanical pulp, and recovered paper and their mixtures. The quality of the finished stock essentially determines the properties of the paper produced.
- Stock preparation consists of several process steps that are adapted to one another as fiber disintegration, cleaning, fiber modification and storage and mixing.

• Forming the Sheet

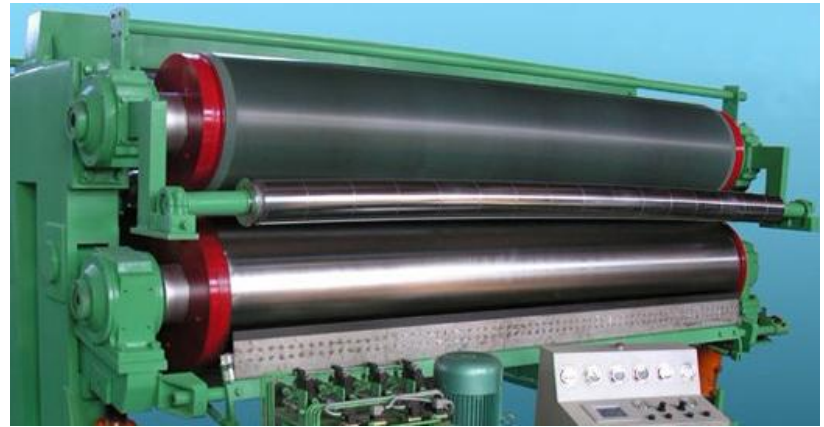
- The "furnish"(from stock preparation) containing 99% water or more, is pumped into the headbox of the paper machine. The task of the head box is to create a uniform dispersion of fibers across the total width of the wire belt, in order to achieve uniform paper formation.
- From the headbox, the furnish is dispensed through a long, narrow "slice" onto the "wire", a moving continuous belt of wire or plastic mesh.
- As it travels down the wire, much of the water drains away or is pulled away by suction from underneath. The cellulose fibers, trapped on the wire as the water drains away, adhere to one another to form the paper web.
- By the time the paper web has drained to around 10 - 20% solids on the wire the web is self-supporting and can be led away from the mesh onto subsequent pressing and drying stages. From the wire, the newly formed sheet of paper is transferred onto a cloth belt (or "felt") in the press section, where rollers squeeze out much of the remaining water

Drying

- After leaving the press section, the sheet encounters the drying cylinders. These are large hollow metal cylinders, heated internally with steam, which dry the paper as it passes over them.
- The sheet will be wound up and down over many cylinders in the drying process. Between dryer sections, the paper may be coated with pigments, latex mixtures, or many other substances to give it a higher gloss or to impart some other desirable characteristic.
- In the dryer section the web is dried to the final dry content of 90 - 95%.
- Practically all the heat used for drying ends up in the hood exhaust air.
- The temperature of the exhaust air is normally 80 - 85 °C and humidity 140 - 160gH₂O/kgdry air.
- For economic reasons, all paper mills have installed heat recovery systems.

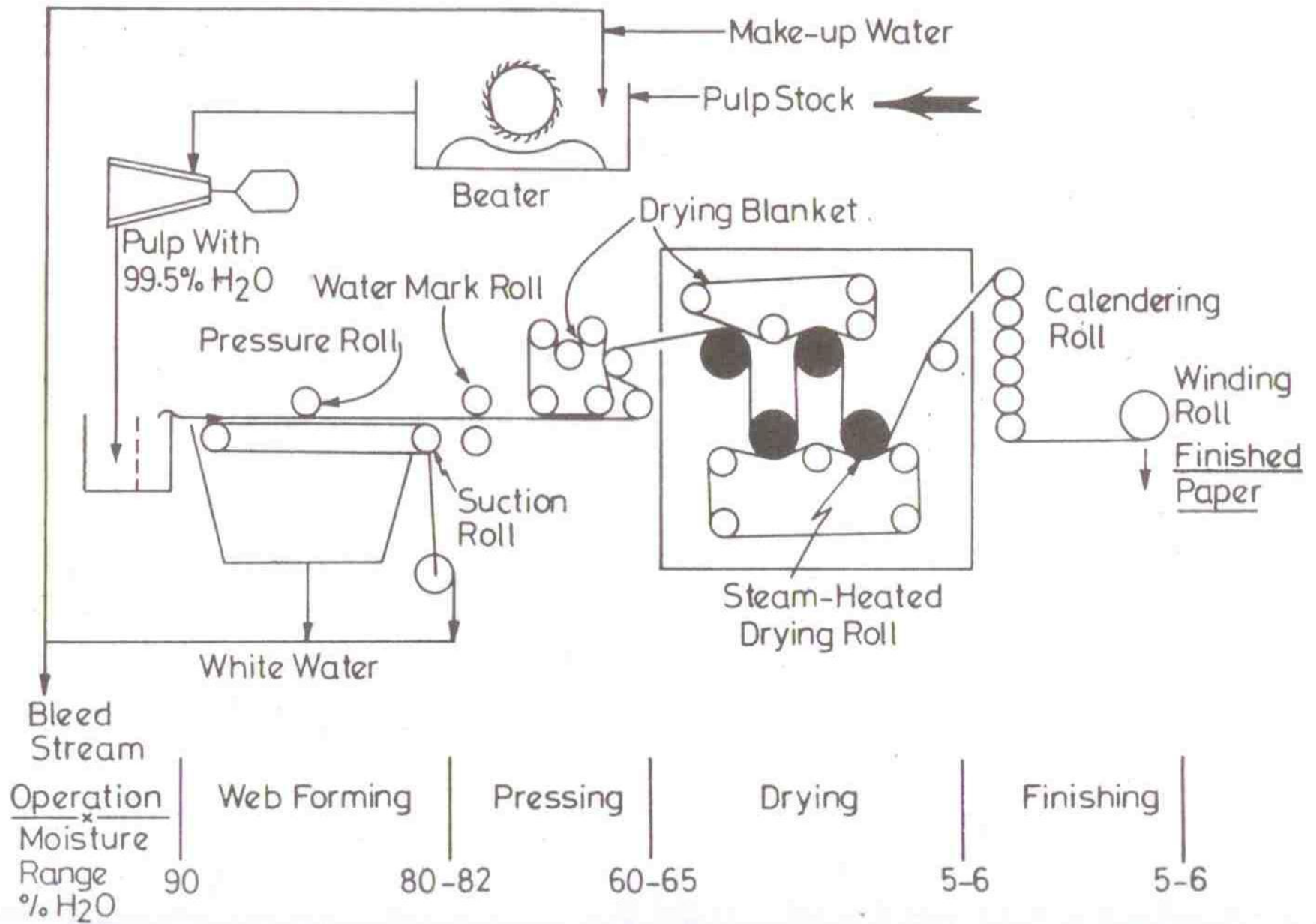
- **Calendering**

- After another round of drying, the paper sheet is passed through a series of polished, close-stacked metal rollers known as a "calender" where it is pressed smooth. Finally, the sheet is collected on a take-up roll and removed from the paper machine.



- **Sizing (optional)**

- Usually sizing means wet end sizing where starch or synthetic sizing agents are added direct to furnish to reduce the natural suction capacity of the paper.
 - In sizing, starch or other sizing agents are applied to the fiber matrix to increase the strength of the base paper web and to modify the surface properties with respect to liquid uptake during writing, printing or coating.
 - Wet end sizing is applied for instance to fine paper (copy paper) and some special paper grades.



Class Assignment

Paper Recycling

- Suggest a conceptual paper recycling process : starting from the paper collection from your campus up-to finished paper product .
- What can be made from recovered paper?

COAL AND COAL CHEMICALS

Introduction

- **Coal as Energy Source**

- Coal is used as fuel for electric power generation, industrial heating and steam generation, domestic heating, rail roads and for coal processing.
- Major raw material for organic synthesis. Many of the products made by hydrogenation, oxidation, hydrolysis or fluorination are important for industrial use.

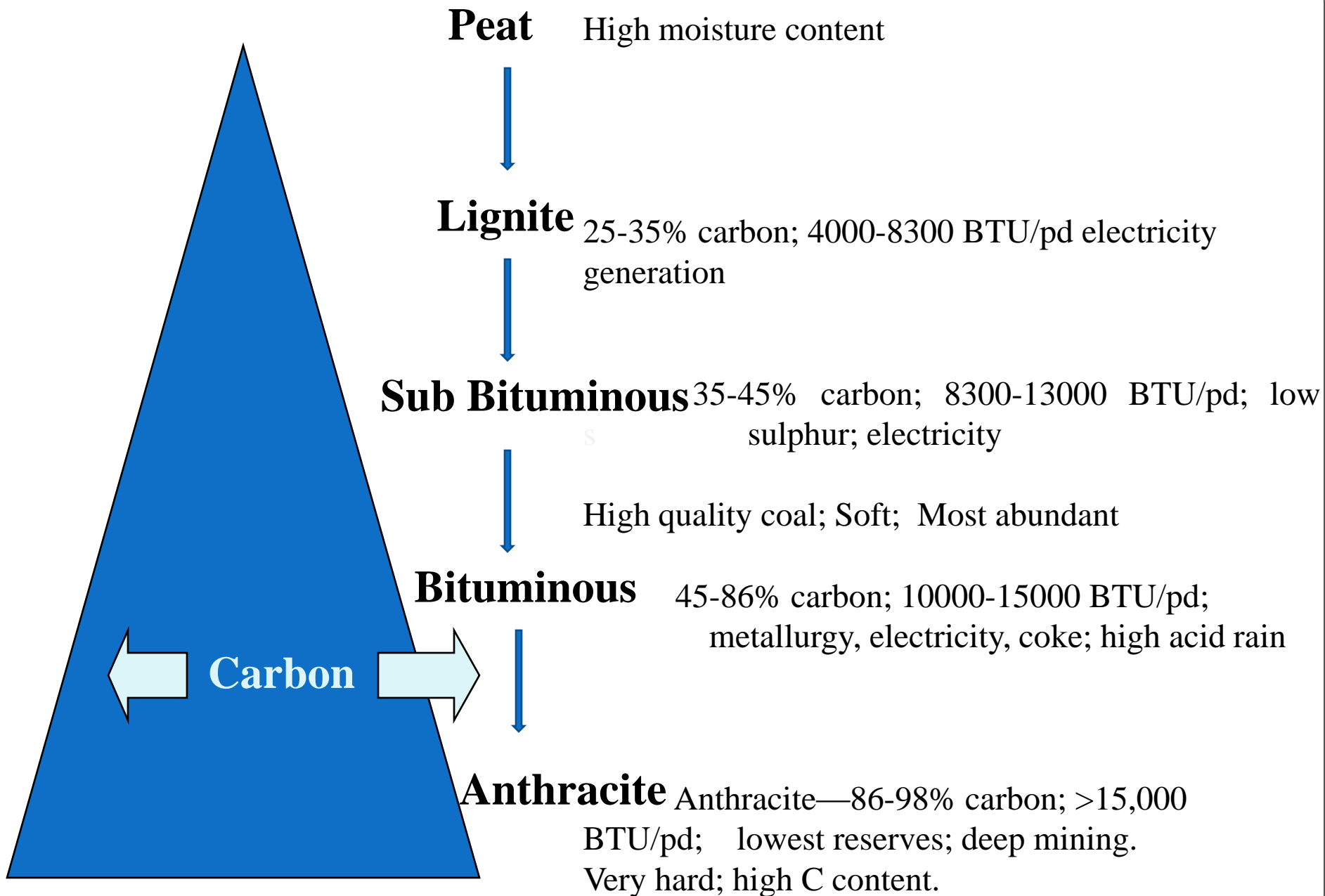
Production Picture for India

- In India coal is the critical input for major infrastructure industries like Power, Steel and Cement.
- Coal is the most dominant energy source in India's energy scenario.
- Coal meets around 52% of primary commercial energy needs in India against 29% the world over.
- Around 66% of India's power generation is coal based.
- India is the 3rd largest coal producing country in the world after China and USA.

• Nature of Coal

- Coal is *sedimentary* rock usually found in layers with other sedimentary rocks such as shale, limestone and sandstone
- Fossil fuel formed millions of years ago by the anaerobic decay of living plants.
- Complex mixture of many compounds.
- The chemical formula of coal has been approximated as $(C_3H_4)_nO_9NS$
- This translates to a material with 60-95% C (which is the energy producing component).
- In addition coal content appreciable amount of minerals, which forms ash during combustion and gasification.
- Major part of coal is built up of complex polycyclic aromatic rings.
- C/H atomic ratio : 1 to 2.75.

Coal Quality Pyramid



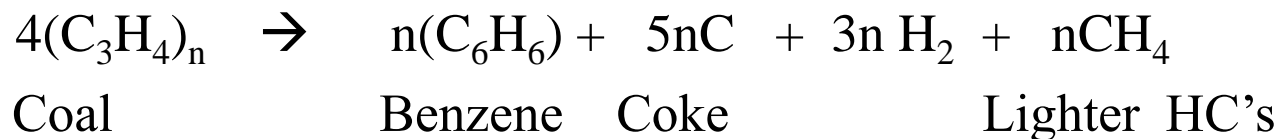
COKING OF COAL

- **Raw material**

Bituminous coal. It appears to have specific internal surfaces in the range of 30 to 100 m²/g. Generally one ton of bituminous coal produces

- 1400 lb of coke.
- 10 gallons of tar.

- **Chemical reaction**



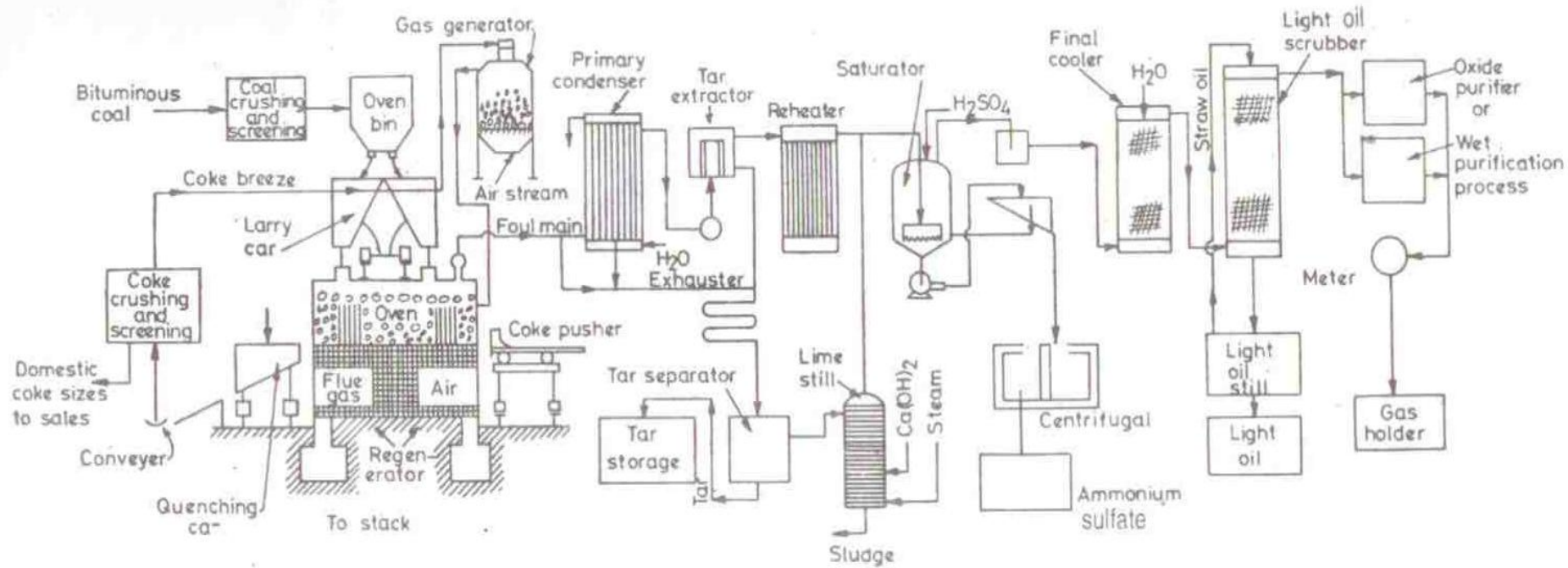
- **Process Variables –**

Temp: 900 – 1150°C, vertical ceramic chambers : 13 feet height, 38 – 40 feet long, 10 -100 oven to form battery. 16 -24 tons of coal in one oven , time : 17-20 hours

Coking

- Coke is a solid carbon fuel and carbon source produced from coal that is used to melt and reduce iron ore.
- Coke production begins with pulverized, bituminous coal.
- In current operations, coal itself cannot be used in place of the central placement of coke in a blast furnace because it would not form a permeable bed of sufficient strength and porosity to support the weight of material in the blast furnace.
- Coal is fed into a coke oven which is sealed and heated for 14 to 36 hours to about 1100 C. Coke is produced by heating particulate coals of very specific properties in a refractory oven in the absence of oxygen.
- As temperature increases inside the coal mass, it melts or becomes plastic, fusing together as devolatilization occurs, and ultimately resolidifies and condenses into particles large enough for blast furnace use. During this process, much of the hydrogen, oxygen, nitrogen, and sulfur are released as volatile by-products, leaving behind a partially crystalline and porous carbon product.

COKE OVEN PROCEDURE

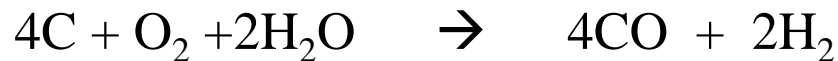


- **Major engineering problem-**

- a. Maintenance of refractory and brickwork at high temperatures
- b. Maintenance of uniform coking temperature by proper heating and waste gas recirculation

COAL GASIFICATION

- Conversion of coal into gas; which happen to predominantly contain CO + H₂ (synthesis gas).
- Gasification advantages
 - Easier transport of gas compare to solids.
 - Second advantage is coal contains many pollutants, which are released on heating. When coal is transformed in gas, cleaning is relatively easy.
- **Gasification Reactions :**



Reaction	ΔH_{800}^0 (kJ/mol)
<i>Heterogeneous reactions</i>	
$\text{C} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2$	136
$\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$	173
$2\text{C} + \text{O}_2 \rightleftharpoons 2\text{CO}$	-222
$\text{C} + \text{O}_2 \rightleftharpoons \text{CO}_2$	-394
$\text{C} + 2\text{H}_2 \rightleftharpoons \text{CH}_4$	-87
<i>Homogeneous reactions</i>	
$2\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2$	- 572
$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	- 37

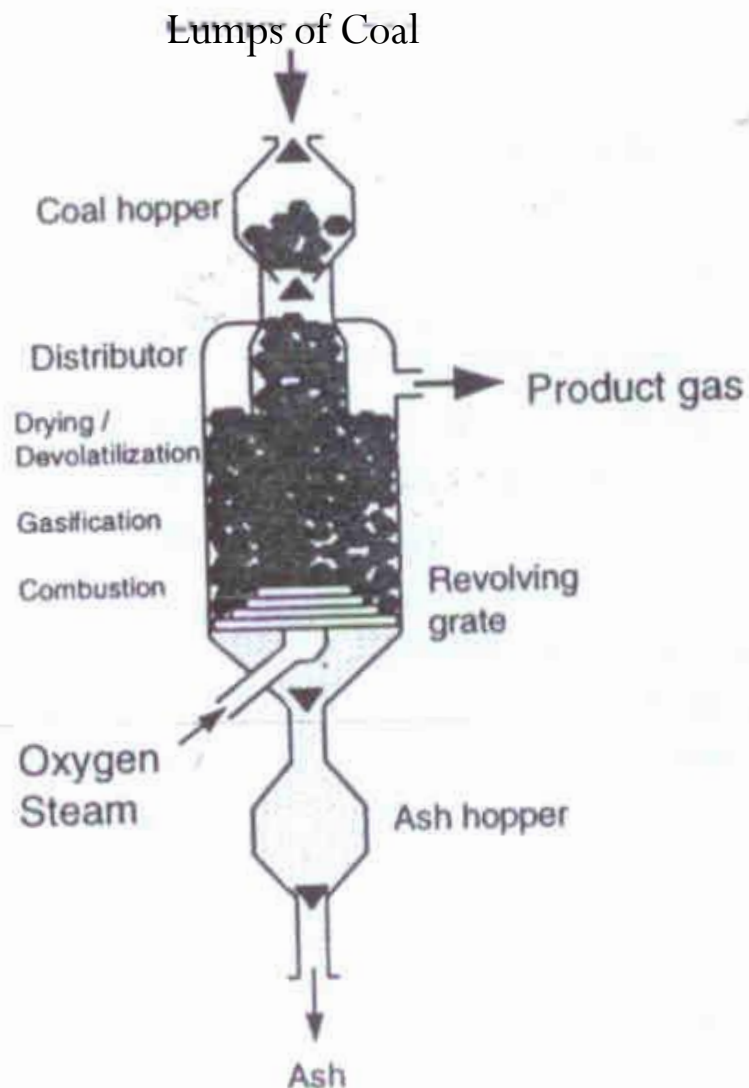
- The first two reactions are endothermic, where as other are exothermic. So it is practice to carry out coal gasification in an 'autothermic' way.
- The reaction is carried out with a mixture of O₂ and H₂O; so the combustion provides the heat needed for endothermica reactions.

Coal Gasification Processes

- Coal gasification processes differ widely.
- Three different reactor technologies are:
 - Moving bed gasifier (Lurgi)
 - Fluidized bed
 - Entrained flow gasifier (Koppers-Totzek)

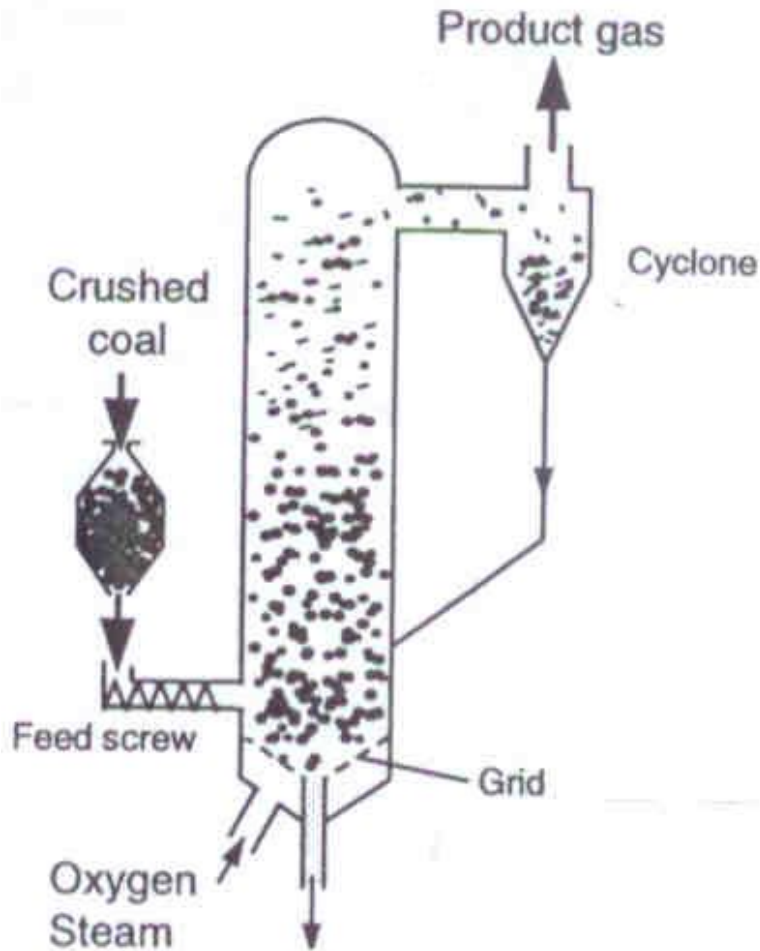
Reactor Type	T _{reactor} [K]	O ₂ Cons. (kg/kg coal)	D _p (mm)	Coal Type
Moving bed	1250-1350	0.5	20	Non-caking
Fluidized bed	1250-1400	0.7	2	Reactive
Entrained Flow	1600-2000	0.9	<0.1	All

1) Moving-bed Gasifier (Lurgi)



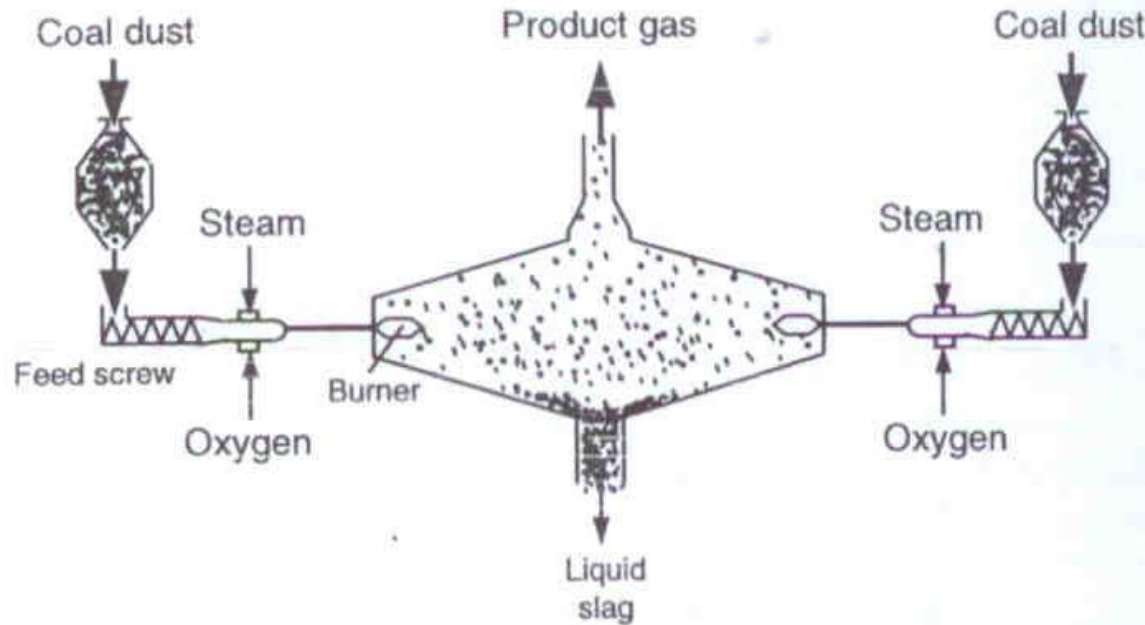
- Operate counter currently : Coal enters the gasifier at the top, slowly heated and dried (partial pyrolysis) on its way down while cooling the product gas as it exits the reactor.
- The coal is further heated and devolatilized as it descends. In the gasification zone part of the coal is gasified in steam and CO_2 , which is formed in the combustion zone upon burning of the remaining part of the coal.
- The highest temperature (1300 K) are reached near the bottom of the reactor. All that remains of the original coal is ash. For most coal 1300 K is below the 'slagging' temperature (the temperature at which the mineral matter becomes sticky or even melts) of the ash, so ash leaving the reaction zone is dry.
- The coal is supported on rotating grate where the ash is cooled by releasing heat to the entering steam and oxygen. In this type of reactor the temperature has to be kept low in order to protect the internal of reactor. The consequence is that large excess of steam has to be fed to the gasifier, which reduces the efficiency.

2) Fluidized-bed gasifier (Winkler)



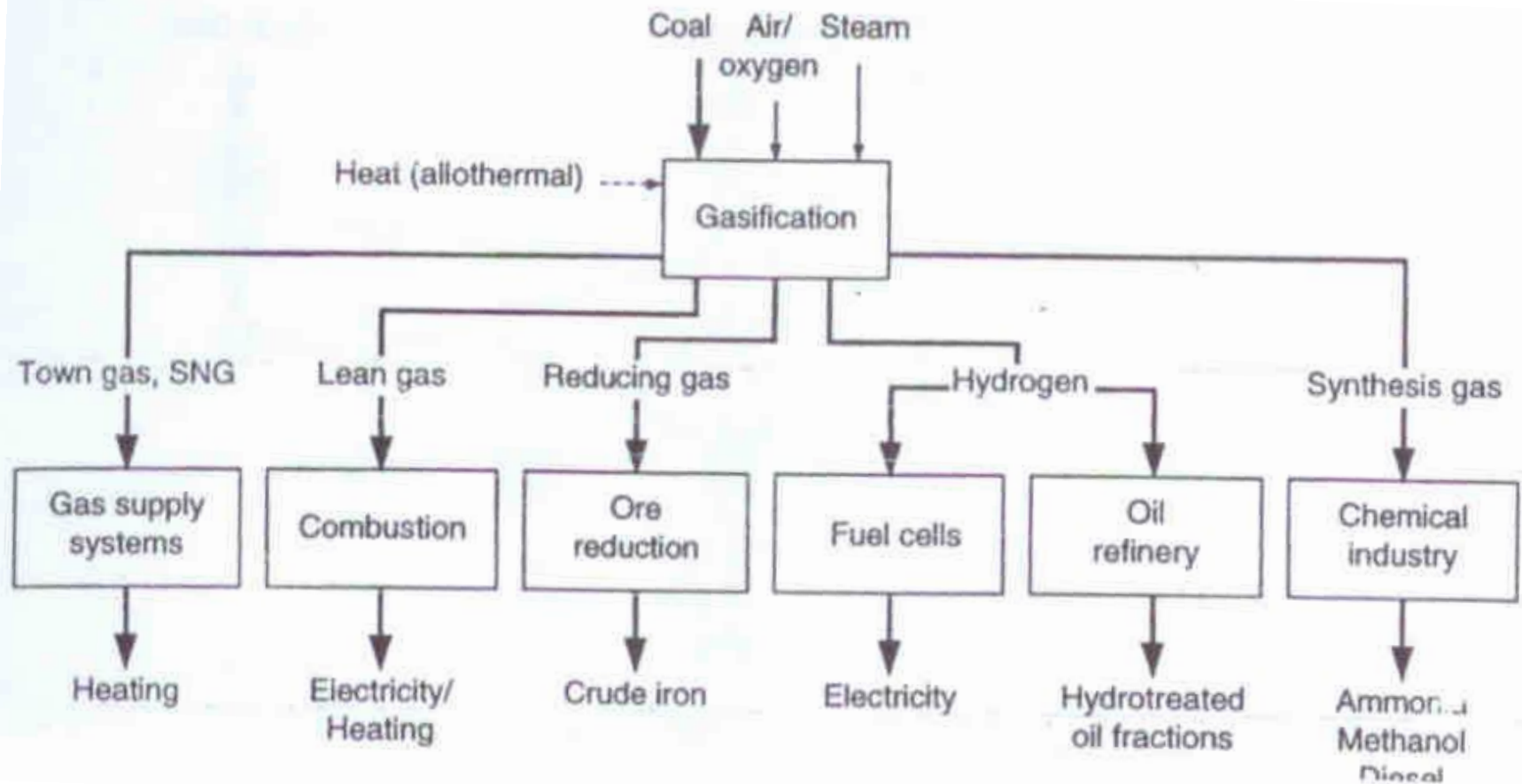
- A fluidized bed gasifier is a back mixed reactor in which coal particles in the feed are well mixed with coal particles already undergoing gasification. The gasifier operates at atmospheric pressure and moderate, uniform temperature.
- Char particles that leave the reactor with the product gas are recovered in cyclone and recycled to reactor. Dry ash leaves the reactor at bottom.
- As a result of back mixing, significant amount of unreacted carbon is removed with the product ash, which lowers the conversion.
- The preferred feed for this gasifier is a highly reactive coal. Due to higher operating temperature Winkler gasifier produces much less impurities than the Lurgi gasifier.

[3]Entrained-flow Gasifier (Kopper Totzek)



- The entrained flow gasifier is a plug flow system in which the coal particles react co-currently with steam and oxygen at atmospheric pressure. The temperature is high in order to maximize coal conversion.
- At this high temperature only CO and H₂ are formed. Ash is removed as molten slag.
- If mixing is poor considerable amounts of volatiles, coke etc. will be formed. So the process design should be such that this does not lead to lowered efficiency and problems downstream of the reactor.

Coal gasification Applications

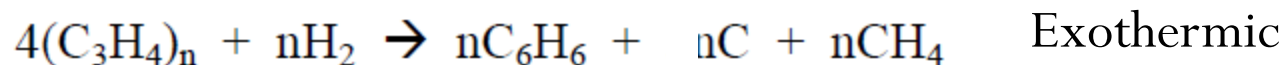


Hydrogenation of Coal

- The process of coal hydrogenation is becoming attractive due to the price of oil and the continuously dwindling crude oil reserves. Unlike crude oil, current coal reserves are sufficient for well into the coming centuries.
- Coal or hydrogenation of coal involves raising the atomic hydrogen to carbon ratio.
- Coal can be converted to liquid and gaseous fuels by direct and indirect processing.
- Hydrogenation of coal is also called liquefaction of coal. The source of coal is from various coal mines.

Direct hydrogenation method :

- **Reaction**



Powdered coal

Aromatic liquid

Hydrocarbon

Temperature : 400 to 1000 °C,

Pressure : 500 to 3000 psi

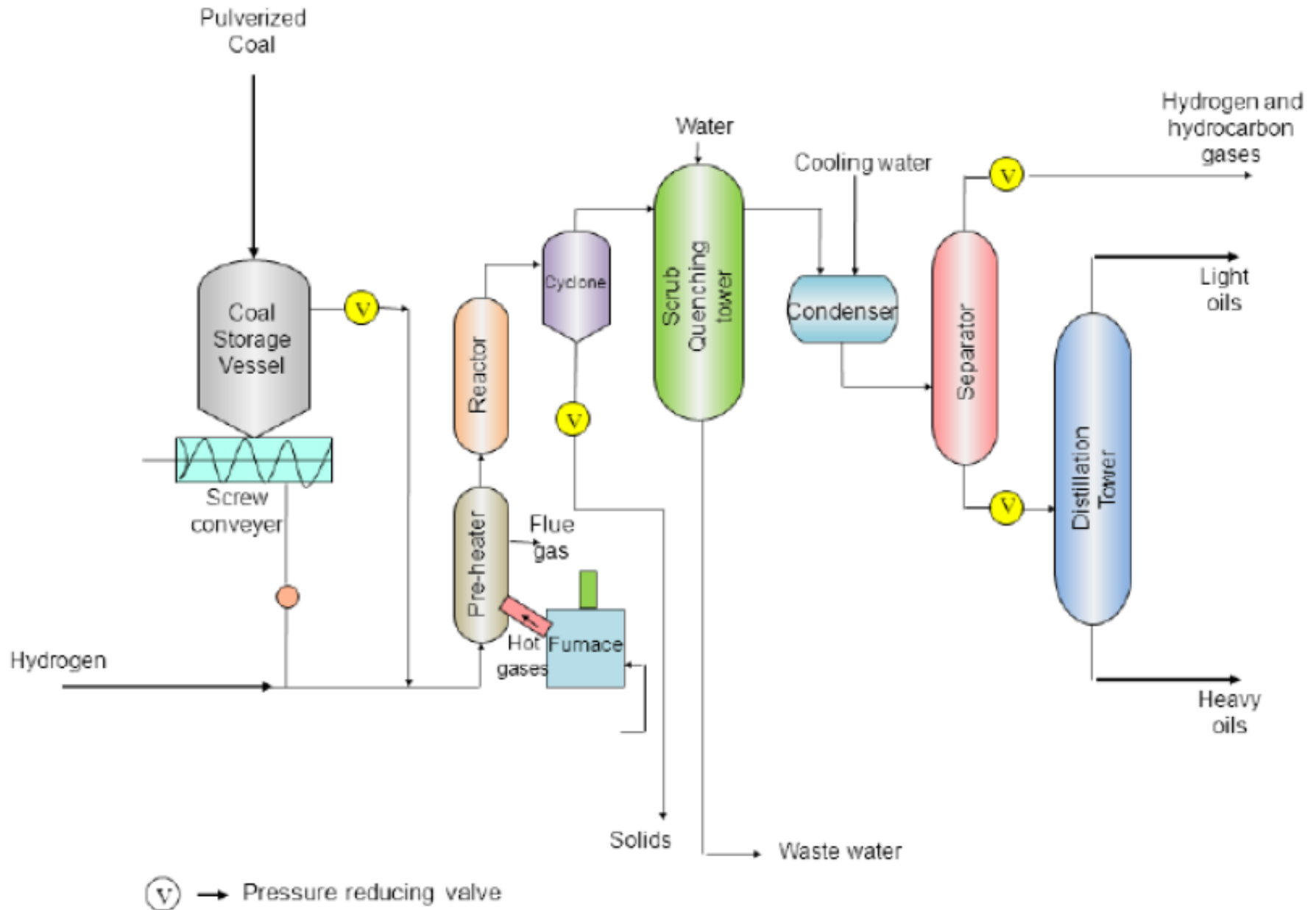
Reaction time : 1 to 10 minutes

- **Catalyst** – 1% Tungsten / Molybdenum oxide. [A few amphoteric sulfides-namely, molybdenum and tungsten disulfides and stannous sulfide-are the most active of the metal sulfide catalysts.]

Raw material Preparation

- Solvent (Tetrahydro naphthalene, phenol, naphthalene) extraction of powdered coal followed with hydrogenation of the extract.
- Treatment of a paste formed with pulverized coal and heavy oil in a hydrogenation reactor (Bergius Process).
- Hydrogenation of powdered coal + hydrogen in a reactor.

Process Flow Sheet



Light Oil : Benzene, Toluene, Paraffin, Naphtha (C_5 - C_{30}).

Heavy oil is asphaltic. It is "heavy" (dense and viscous) due to the high ratio of aromatics and naphthenes to linear alkanes and high amounts of NSO's (nitrogen, sulfur, oxygen and heavy metals). Heavy oil has a higher percentage of compounds with over 60 carbon atoms and hence a high boiling point and molecular weight.

Major engineering problems –

- a. Hydrogen embrittlement of reactor steel
- b. Complex separation process
- c. Coal slurry and the hydrogen used in the process are flammable substances. Require process control and monitoring using a reliable and dependable automation system design