Lecture 2

Pulping And Bleaching
Paper industry uses wide variety raw materials employing different type of pulping and bleaching processes depending on the type of raw materials and requirement of pulp furnish for final paper making. Both unbleached and bleached pulp is produced to meet the requirement of paper. Requirement of bleaching chemicals are also varying depending on the quality of paper and brightness and environmental considerations for cleaner and greener paper. Various steps in pulping and bleaching process is given in Table M-III 2.1. Pulping and bleaching play important role in providing strength to paper depending on fibre length, cellulose content. Commonly used term in pulping is given in Table M-III 2.2.

Table M-III 2.1: Puling and Bleaching Process

- **Acquisition of Raw Material**: Hard wood, soft wood, bagasse, wheat and Rice straw, sabai grass etc.

- **Raw Material Preparation**: Debarking, Chipping, Cutting, Screening

- **Pulping**:  
  - Chemical: Sulphate (Kraft), Soda Pulping, Sulphite Pulping  
  - Semi Chemical: Neutral Sulphite Semi-chemical (NSSC)  
  - Mechanical Pulping: Stone Ground Wood (SGW)  
  - Thermo Mechanical Pulp (TMP)  
  - Refiner Mechanical Pulp (RMP)  
  - Cold Soda Refiner Mechanical Pulp (CRMP)  

- **Sulfite**:  
  - Acid Sulfite higher % of free SO₂ (Ca, Mg, Na, Ammonia base)  
  - Bisulfite: (little or no free SO₂ (Ca, Mg, Na, Ammonia base)

- **Washing and Screening**: 3-4 stage washing, screening and cenricleaning

- **Bleaching**: Bleaching chemicals: Oxygen, Ozone, Chlorine, caustic soda, chlorine dioxide, calcium hypochlorite  
  - Conventional bleaching sequence CEHH, CEH, CEHD, for chemical pulp  
  - Advance bleaching sequence  
  - Hydrogen peroxide, Sodium peroxide, Hydro sulfite for mechanical
## Table M-III 2.2: Commonly Used Terms in Pulping

<table>
<thead>
<tr>
<th>Terms</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>White liquor</td>
<td>Cooking Liquor obtained after causticising green liquor containing NaOH, Na₂S, and small quantity of Na₂CO₃</td>
</tr>
<tr>
<td>Black liquor</td>
<td>Liquor obtained after washing of pulp after cooking which is further concentrated for burning in furnace to recovered chemicals</td>
</tr>
<tr>
<td>Green liquor</td>
<td>Liquor obtained after dissolving smelt from furnace in weak liquor from causticising section</td>
</tr>
<tr>
<td>Active alkali</td>
<td>NaOH + Na₂S</td>
</tr>
<tr>
<td>Effective alkali</td>
<td>NaOH + 1/2 Na₂S</td>
</tr>
<tr>
<td>Total titratable alkai</td>
<td>NaOH + Na₂S + Na₂CO₃</td>
</tr>
<tr>
<td>Sulphidity</td>
<td>Na₂S / Titratable alkali</td>
</tr>
<tr>
<td>Causticity</td>
<td>NaOH / (NaOH + Na₂S)</td>
</tr>
<tr>
<td>Causticising Efficiency</td>
<td>(NaOH / (NaOH + Na₂S) ) x 100</td>
</tr>
<tr>
<td>Reduction</td>
<td>Na₂S / (Na₂SO₄ + Na₂S)</td>
</tr>
<tr>
<td>Over all recovery</td>
<td>Recovery ± black liquor stock / froth liquor consumed</td>
</tr>
<tr>
<td>K.No. (Permanganate numer)</td>
<td>No. of 0.1 N KMnO₄ consumed by 1 gm of moisture free pulp.</td>
</tr>
<tr>
<td>Dilution factor (D.F.)</td>
<td>DF = W – E</td>
</tr>
<tr>
<td></td>
<td>W= Water added per ton of mass</td>
</tr>
<tr>
<td></td>
<td>E=Water going in pulp per ton of pulp</td>
</tr>
<tr>
<td>Bath Ratio</td>
<td>Wood to liquor ratio</td>
</tr>
<tr>
<td>Consistency</td>
<td>B.D. pulp / total pulp weight (100gms ) i.e. wt of BD pulp in 100 gm of pulp + water mixture</td>
</tr>
<tr>
<td>Copper No:</td>
<td>No of milligrams of metallic copper which is reduced from cupric hydroxide to cuprous oxide in alkaline medium by 100 gm of pulp</td>
</tr>
<tr>
<td>Kappa No</td>
<td>837 + .0323 * 40 ml KMnO₄ No.</td>
</tr>
</tbody>
</table>
CHIPPING

Chipping quality plays important role in the overall quality of pulp. Efficiency of debarking process, chip size- length, thickness, uniformity of size, removal of dust and fines are important factors affecting pulping efficiency and quality of pulp. In case of bagasse depithing is very important in overall quality of pulp and paper. In case of agricultural residue size of the straw and removal of dust also is important. In chipping of bamboo and wood drum chipper and disc chipper are used

KRAFT PULPING PROCESS

Kraft pulping involves Pulping, Washing, Screening, Bleaching. Pulping involves separation of fibre for chemical or mechanical pulping, removal of knots, washing of pulp for recovery of chemical, rejects uncooked material, sand and other foreign material. Bleaching of pulp involves bleaching of washed and screened pulp with bleaching chemicals – chlorine, caustic, hypochlorite, chlorine dioxide, ozone, hydrogen peroxide, sodium hydrosulfite. Conventional used bleaching sequences were (CEHH, CEH, CEHDED, CEDED). Many of the mills in India have also gone for oxygen delignification and newer bleaching sequences.

Cooking of raw material is done batch digester, continuous digester. Spherical batch digester is commonly used for cooking agricultural residues. Cooking liquor used in kraft pulping process is sodium sulphide, sodium carbonate. Cooking cycle may be around 3-5 hr depending of raw material and extend of cooking in batch digester. Typical continuous digester consists of Upper heating zone, upper cooking zone, lower cooking zone, and washing zone. Sequence of operation in coking in digester are chip filling, presetting, liquor charging, heating up and pressure up period, cooking and blowing

- Bulk density: 130-150 kg/m³.
- Bath ratio: 1:3, Sulphidity 15%
- Cooking temp: 170-175 ℃.
- Pressure: 7-7.5 kg/cm²
- Temp to rise: 135 ℃ 2 hr.
- Time at: 135-140 ℃ 2 hr.
**DEVELOPMENT IN PULPING AND BLEACHING:**

Driving force in pulping and bleaching technology has been to produce pulp with lower possible lignin content while preserving the yield and strength of pulp. Lowering the bleaching requirements has been instrumental in making it possible to find alternatives to the traditional chlorine based bleaching [Pulliam,1997]. Some of the development has in pulping has been Pre-impregnation of chips with lower caustic, high sulphidity liquor, split addition of alkali charge as cook progresses, longer milder, lower temperature cooking. Another development has been oxygen delignification prior to bleaching to produce stronger pulp with higher strength and low bleaching requirements. Use of additives like anthraquinone and polysulphide has been also implemented. Major development in bleaching has been to go for either elemental chlorine or chlorine from bleaching. Oxygen delignification and ozone bleaching has been introduced chlorine free bleaching. Other development has been use of peroxide, peroxy acids, enzyme etc. Process flow diagram of Kraft puling and bleaching process is shown in Figure M-III 2.1.

<table>
<thead>
<tr>
<th>Year</th>
<th>Bleaching Sequences</th>
</tr>
</thead>
<tbody>
<tr>
<td>1950-1975</td>
<td>CEH, CEHH</td>
</tr>
<tr>
<td>1975-1990</td>
<td>CE(DC),O(ED) EOP (EP), DEDED</td>
</tr>
<tr>
<td>1990 onwards</td>
<td>(DZ)DED;</td>
</tr>
<tr>
<td></td>
<td>(ZD)EDED</td>
</tr>
<tr>
<td></td>
<td>APDED</td>
</tr>
<tr>
<td></td>
<td>QPDED</td>
</tr>
<tr>
<td></td>
<td>D (DC)CO(EO)(EOP)</td>
</tr>
<tr>
<td></td>
<td>P(PO)OZPAAP,X</td>
</tr>
</tbody>
</table>

C: chlorination, E: alkaline extraction, H: hyochlorite, D: chlorine dioxide, DC; Combination of chlorine dioxide and chlorine, O: oxygen, EO: alkaline extraction under mild condition, EOP alkaline extraction under both under hydrogen peroxide a, P: peroxide, PO: peroxide under oxygen pressure, Q: chelating, Z: ozone, PAA: peroxy acetic acid, Px: peroxymono sulohonic acid X: enzymes, AQ; Antroquinone pulping, PS : poloy sulphide

Source: [Chirat & Lachenal,1997]
Figure M-III 2.1: Kraft Puling and Bleaching Process
PULPING OF RICE STRAW, WHEAT STRAW, GRASSES JUTE STICKS

Pulping of agricultural residues require mild cooking condition as compared to hard wood and soft wood pulping. Various steps involved are.

- Cutting and dusting.
- Cooking batch or rotary spherical or tumbler digester.
  - Bulk density: 130-150 kg/m³
  - Bath ratio: 1:6, % alkali: 8-10%
  - Cooking temp: 135-140 °C.
  - Temp to rise: 135 °C 1hr.
  - Time at: 135-140 °C 2hr.
- Blowing
- Washing and screening, centricleaning,
- Bleaching
- Recovery of chemicals

Problems in Utilization of Agricultural Residues

- Higher % of silica
- Problem in washing due to slow drainage, high dilution
- Higher % silica create problem in evaporator
- Longer wire parts due to poor drainage
- Lower strength of pulp
- Low bulk density, seasonal availability, higher pollution load.

BAGASSE PULPLING

Due to availability of bagasse from sugar mills number of agro based paper mills are using bagasse. About 10% of the bagasse is available from sugar mills.

Bagasse 60% fibre and 30% pith, 60% good quality fibre, 30% pitch, 10% water

- 0.25 ton of bagasse (dry) per tonne of sugarcane.
- 3 tons of bagasse per ton of unbleached pulp

Bagasse with 50% moisture & about 2-2.5% sucrose & water soluble material
**PROCESS:** Process of bagasse pulping involves depithing and pulping of depethed bagasse. Depithing—Removal pith is necessary before pulping as pith has high ash, difficult to bleach and has little value in paper making. Various depithing processes are dry depthing, wet depthing, and combined depthing. Figure M-III 2.2 illustrates the agro residue, pulping and bleaching process. Pulping washing and screening: cooking of bagasse can be done in batch or continuous digester. Typical cooking conditions for bagasse pulping are: Batch cooking 10-12% NaOH, 160 °C, 6-7 kg/ash, 2 hrs, bleaching requirement 5-6%3-stage Brown stock washing is done which is followed by screening and centri-cleaning.

![Diagram of Agro Residue, Pulping and Bleaching](image)

**Figure M-III 2.2: Agro Residue, Pulping and Bleaching**

Detail pulp digesting process is illustrated in Figure M-III 2.3.
Figure M-III 2.3: Pulp Digesting Process
MECHANICAL PULPING

Mechanical pulping has significant importance in paper making because of the high yield and its requirement in Newsprint. Conventional method of mechanical pulping was ground wood stone pulping which is being still used by many mills. However many new generation mills has gone for refiner mechanical pulping or thermo mechanical pulping. Process flow diagram for mechanical pulping is shown in Figure M-III 2.4.

STONEGROUND WOOD (SGW)

Primary action in grinding zone involves compression and release of wood as the grit projecting from the pulp stone surface passes of the underneath of the wood. The function of wood as wood, as it is deformed, friction of wood and pulp stone and friction of fluid generates heat which causes softening of the lignins, and resins binding the fibres and also generate vapour pressure which assist in separating the fibre from the wood wall. The act of compression and release of wood fibre flushes fluid in and out of the wood wall thus dividing some of the binding agents and assisting in the release of the fibre from wood. Pulp stone manufacture supply their basic abrasives, silicon carbide, aluminum oxide and modified aluminum oxide. The grinding surface of the pulp stone will be maintained as near constants possible to ensure uniform quality of the pulp.

Motor 5000 h/s – 10000 h/s, Speed of the pulp stone is 35-40 m/sec, 360 rpm

Purpose of grinding is to fibre the wood with a minimum damage to fibres and to develop quality required for the end wood, thereby lowest consumption of energy and grinding material and higher production for grinding and desired to minimize the products as the cost the following variables are important.

Wood-species, shape of bolts manufacture of wood.
Stone-Type of abrasives, size of grit, type of pattern, depth of grooves, extent of wear.
Grinder-Type of grinder, specific grinding pressure which is inter related to the load and the rate of wood advance, length of grinding zone, width of stone-grinding area, tangential speed of stone, pulp temp, pulp consistency, shower temperature, depth of emersion of stone in pil.

5-10 ton/day
50-1000 h/sec
20 ton/day 5000 h/sec
Silicon carbide, Aluminium oxide sintered together.

Figure M-III 2.4: Mechanical Pulping

REFINERY MECHANICAL PULPING

This involves mechanical reduction of chips in a double rotating disc refiner with the use of two refiners in series and gave pulp much stronger than SGW in tensile burst and tear strength. Although soft wood does need any treatment but hardwood need light chemical soak with about 1-1.5%NaOH + 0.7-1.0 Na₂SO₃ at a temp of 75-80 °c.

Refining

Fiberising of chips was earlier done by rod mill. The chips were fed in a rotating drum at one end, the defilation was achieved by the crushing action of a number of steel rods and the fibres were collected at the opposite end of the drum. The variables in refining: are Speed of rotation, Disk inter distance, load, temperature and consistency
**Refiner Mechanical Pulp (RMP):** RMP involves mechanical reduction of chips in a precision double rotating disc refiner with use of two refiners in series. Stronger pulp than SWD in tensile, burst and tear strength and permitted reduction of chemical pulp.

**Thermo Mechanical Pulping (TMP):** Thermo mechanical pulping consists of refining of chips in pressurized environment with steam and chemicals in gas phase, following by washing, screening, refining, bleaching, Short steaming period with a duration 2-3 min at about 110-120 °C, at refining pressure of 10-25 psi in the first stage with second stage refining under atmospheric conditions. Refining is done at temperature of 100-130 °C improved pulp quality long fibre fraction is increased because of softening of the lignin at elevated temperature which losses the bond between the fibres in the wood structure. The usage of small amount of chemical either swelling (NaOH) and or brighter NaHSO₃ increase giving high strength and brighter pulp, During TMP less damage to pulp. Various variables are chip quality chip washing, pre-steaming, solute pattern, plate size, speed, consistency.

Power 100-200 HPD/T

SWPG-65-85 HPD/T

Some of the advantage of thermo-mechanical pulping are

- Complete utilization of the trees.
- Greater flexibility of raw material utilization enabling utilization of cheaper raw materials, as wood stacks, edgings, sawdust, shaving, and other refuse.
- No or very little consumption of chemicals.
- Pulp with good bonding properties and high content of long fibres, improved strength characteristics, improved paper machine runnability, higher production, lower costs.
- Lower shive content and simplified cleaning.
- Good bulk, improved quality and printability.
- Minimum labour cost.
- High yield and high strength resulting in either reduced or eliminated costly chemical pulp, improved quality and lower cost/ton.
- More and better utilization of the available raw material.
- No air-atmospheric pollution, little water pollution and reduced environmental damage.
- Adaptability to easier control automatic and computer control.
- Good bulk, improved quality and printability.
  1300 KWH/TON : stone ground
  1475 KWH/TON : RMP
  1475 KWH/TON : TMP

In chemical pulping substances if the middle lamellas chemically dissolved to an extent that makes fiberising possible as that mechanical treatment is more elaborate machinery.

Mechanical pulping give nearly quantitative yield but causes rupture of the fiber walls on fiberising and gives pulp which contain pulping by pressing wood against a revolving grindstone in the presence of water to cool the stone, which become heated by friction.

Stone surface is burred to a certain pattern of grooves before the stone is engaged in production.

Production refiner mechanical pulp involves two basic steps.

- Fiberisation (defibration)- center original wood structure to single structure.
- Fibrillation- reduces the portion

**Chemi Thermo Mechanical Pulping:** This involves short cooking with 1-2 % caustic and sodium sulphate which facilitate the separation maintaining maximum strength characteristic. It gives better strength and bright pulp.

Advantage: Power Shaving, Superior quality of Pulp and Finished Product, permits utilization higher % of mechanical pulp, power shires, minimum labor, high yield, less pollution.

Power Consumptions

<table>
<thead>
<tr>
<th></th>
<th>kWh/Ton</th>
<th>SWW</th>
</tr>
</thead>
<tbody>
<tr>
<td>1300-1400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1475</td>
<td>kWh/Tin</td>
<td>RMP</td>
</tr>
<tr>
<td>1475</td>
<td>kWh/Ton</td>
<td>TMP</td>
</tr>
</tbody>
</table>
Bleaching of Mechanical Pulp

Hydrosulphite

Zinc hydrosulphite and sodium hydrosulphite are commonly used for ground wood pulp and refiner pulp. Zinc hydrosulphite is prepared by reacting zinc dust with sulphuric acid. Sodium hydrosulphite can be generated by reacting sodium borohydride and bisulfite.

Peroxide: Hydrogen peroxide and sodium peroxide are recognized as effective economical bleaching agents, they don’t form chlorinated organic derivatives. They are particularly used in the bleaching of high lignin wood pulp and as a final stage in chemical pulp bleaching.

News Print: News print one of the major portion of paper produced and playing important role in information, cultural, economic growth. News print typical contains 70% chemi-mechanical pulp from eucalyptus and 30% chemical pulp from reed and bamboo. Eucalyptus wood is chipped screened and the chips are washed. The washed chips are treated with steam and caustic soda solution. The impregnated chips are pressed to remove spent liquor in refined in two stages. Then pulp is washed on brown pulp washer and bleached by two step hypochlorite treatment. The bleached pulp is again refined in a third step refiner, screened, center cleared and dewatered in a thickener drum and stored. Process flow diagram of news print manufacture is given in Figure M-III 2.5. Newsprint is a paper of printing category embossing in itself the qualities like runnability, opacity and low cost.

Advantage of Ground wood pulp in news print furnish are

- Higher bulk-improves calendar action.
- Improve formation because of time fraction
- Decreased far-sidedness
- Better and improved opacity inhibits show through.
- Better ink absorptivity
- Absence of print through.
- Improved surface
QUALITY OF GOOD NEWS PRINT

Runnability, good print ability, minimum two side uniformity. Pulp formation should need following requirements:

- Low freeness 50csf.
- Specially good screening
- Good pulp strength property
- Uniform pulp quality
- Controlled bleaching system to maintain required brightness

Mechanical pulp has to have good wet end strength, good bonding

Chemical pulp used in newsprint hard wood pulp, Bagasse pulp chemical

Bagasse TMP, CTMP

**BAGASSE NEWSPRINT:** Bagasse newsprint is made for 50% bagasse having good printing quality, run-ability, opacity, rapid absorption
BAGASSE PULPLING: Due to availability of bagasse from sugar mills number of agro-based paper mills are using bagasse. About 10% of the bagasse is available from sugar mills.

- Bagasse 60% fibre and 30% pith
  - 60% good quality fibre
  - 30% pitch
  - 10% water
- 0.25 ton of bagasse (dry) per tonne of sugarcane.
- 3 tons of bagasse per ton of unbleached pulp

Bagasse with 50% moisture & about 2-2.5% sucrose & water soluble material

PROCESS:

DEPITHING- Dry depthing, wet depthing, combined depthing

Pith has high ash, difficult to bleach and has little value in paper making

Pulping: batch cooking10-12% NaOH, 160° C, 6-7 kg/ash, 2 hrs, bleaching requirement 5-6%

Problems in Utilization of Hard Wood

1. Debarking
2. Chipping problem – high density chips difficult to chip
3. Higher reject
4. Problem in washing due to more fines and foam
5. Bleaching of mixed hardwood and bamboo pulp creates problem due to varying bleach Requirement
6. Shade variation, darker shade
7. Problem in evaporator
8. Higher percentage of hard wood affects runnability of machine lower strength

News Prints Pulp: News print pulp furnish consist of Kraft pulp and mechanical pulp

Furnish:

25-30% Kraft Pulp
70-75% Mechanical Pulp

Raw Material: Bamboo, Hardwood, Bagasse,

Advantage of ground wood pulp:

- Higher Bulk – Improves Calendarizing Action.
• Improve Formation because fine fraction.
• Better and Improved capacity, inhibits show through better ink absorbency.
• Absence of print through good bonding.

In Bleaching of Mechanical Pulp, Zinc Hydrosulfide 1%, Hydrogen Peroxide.

**SULPHITE PROCESS**

Sulphite process was earlier used for pulping, however it has been replaced with Kraft pulping. Table M-III 2.3 gives details of important terms used in sulphite process.

**Acid Sulphite:** The process in which the cooking acid contains a high % of free SO₂ pH 1.2-1.5. Not suitable for resinous wood.

\[ \text{NaHSO}_3 + \text{SO}_2 \]

**Bisulphate:** The process in which the cooking liquor contains a predominance of bisulphate ion in the 3.6 pH ranges with no free SO₂.

\[ \text{NaHSO}_3 \]

**Neutral Sulfite:** \( \text{Na}_2\text{SO}_3 + \text{Na}_2\text{SO}_3 \text{pH } = 7-9 \)

\[ \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 \]

\[ \text{CaCO}_3 + 2\text{H}_2\text{SO}_3 \rightarrow \text{Ca (HSO}_3) + \text{CO}_2 + \text{H}_2\text{O} \]

\[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca (OH)}_2 \]

\[ \text{Ca (OH)}_2 + \text{H}_2\text{SO}_3 \rightarrow \text{Ca (HSO}_3)_2 + 2\text{H}_2\text{O} \]

\[ \text{Mg (OH)}_2 + \text{H}_2\text{SO}_3 \rightarrow \text{Mg (HSO}_3) + 2\text{H}_2\text{O} \]

\[ \text{Na}_2\text{CO}_3 + 2\text{H}_2\text{SO}_3 \rightarrow \text{NaHSO}_3 + \text{H}_2\text{O} \]

\[ \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH} \]

\[ \text{NH}_4\text{OH} + \text{H}_2\text{SO}_3 \rightarrow \text{NH}_4\text{HSO}_3 + \text{H}_2\text{O} \]

Rate of pulping: \( \text{NH}_3 > \text{Mg} > \text{Na} \)


Total cooking time 6-12 hr.

Cooking acid 7% - 8% of total SO₂.
1 ton of pulp  175- 220 kg of SO\textsubscript{2} 55 -68 kg MgO

### Table M-III 2.3: Important terms in Sulphite Process

<table>
<thead>
<tr>
<th>Terms</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total sulfur dioxide:</strong></td>
<td>Total SO\textsubscript{2} as determined by an iodometric titration and expressed as % total SO\textsubscript{2}</td>
</tr>
<tr>
<td><strong>Free sulfur dioxide</strong></td>
<td>Free SO\textsubscript{2} is the actual free SO\textsubscript{2} plus half of the SO\textsubscript{2} in the bisulfite of the base. It is also called available SO\textsubscript{2}.</td>
</tr>
<tr>
<td><strong>Combined SO\textsubscript{2}</strong></td>
<td>Difference between total SO\textsubscript{2} and free SO\textsubscript{2}</td>
</tr>
</tbody>
</table>

**References**