Pulping Fundamentals

Lecture 2
Category of Pulping Process

- Chemical Pulping
  - Sulphate (Kraft) process
  - Sulphite process
  - Neutal
- Semi-chemical
- Chemi-mechanical
- Mechanical pulping
Table 3-1. Summary of pulping processes.\(^1\)

<table>
<thead>
<tr>
<th>Process</th>
<th>Chemicals</th>
<th>Species</th>
<th>Pulp Properties</th>
<th>Uses</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical pulping</td>
<td>none; grindstones for logs; disk refiners for chips</td>
<td>Hardwoods like poplar or light-colored softwoods like spruce, balsam fir, hemlock, true firs</td>
<td>High opacity, softness, bulk. Low strength and brightness.</td>
<td>Newsprint, books, magazines.</td>
<td>92-96%</td>
</tr>
<tr>
<td>Chemimechanical pulping</td>
<td>CTMP; mild action; NaOH or NaHSO₃</td>
<td></td>
<td>Moderate strength</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kraft process, pH 13-14</td>
<td>NaOH + Na₂S (15-25% on wood); unlined digester, high recovery of pulping chemicals, sulfur odor</td>
<td>All woods</td>
<td>High strength, brown pulps unless bleached</td>
<td>Bag, wrapping, linerboard, bleached pulps for white papers</td>
<td>65-70% for brown papers, 47-50% for bleachable pulp; 43-45% after bleaching</td>
</tr>
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<tr>
<td>Sulfite, acid or bisulfite</td>
<td>$\text{H}_2\text{SO}_3 + \text{HSO}_3^-$ with $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Na}^+$, or $\text{NH}_4^+$ base; $\text{Ca}^{2+}$ is traditional but outdated since no recovery process; lined digesters</td>
<td>hardwoods-poplar and birch and non-resinous softwoods; Douglas-fir is unsuitable</td>
<td>light brown pulp if un-bleached, easily bleached to high brightness, weaker than kraft pulp, but higher yield</td>
<td>Fine paper, tissue, glassine, strength reinforcement in newsprint</td>
<td>48-51% for bleachable pulp; 46-48% after bleaching</td>
</tr>
<tr>
<td>pH 1.5-5</td>
<td>Mg$^{2+}$ base</td>
<td>almost all species-spruce and true firs preferred</td>
<td>Same as above but lighter color and slightly stronger</td>
<td>Newsprint, fine papers, etc.</td>
<td>50-51% for bleachable pulp 48-50% after bleaching</td>
</tr>
<tr>
<td>Neutral sulfite semi-chemical</td>
<td>$\text{Na}_2\text{SO}_3 + \text{Na}_2\text{CO}_3$ about 50% of the chemical recovered as $\text{Na}_2\text{SO}_4$</td>
<td>Hardwoods (preferred) aspen, oak, alder elm, birch; softwoods Douglas-fir sawdust and chips</td>
<td>Good stiffness and moldability</td>
<td>Corrugating medium</td>
<td>70-80%</td>
</tr>
<tr>
<td>(NSSC) pH 7-10</td>
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</tbody>
</table>
Mechanical Pulping

- Stone Groundwood (SGW) – wood logs
- Thermo-mechanical pulp (TMP)
- Chemi-thermo-mechanical pulp (CTMP)
- Bleached CTMP (BCTMP)
- Pressure Groundwood (PGW)
Stone Groundwood (SGW)

Wood

Wood Storage

Grinders

Coarse Screens

Rejects

Refiner

Rejects

Fine Screens

Rejects

Cleaners

Deckers

Pulp Storage

Bleach Plant

Paper Machines

White Water

White Water Tank

1300 KW/ton

Yields: 93 – 95%
Sharpening must be done after 50 – 150 hr.

Fig. 3-4. Burr patterns used for sharpening pulp stones for stone groundwood production.
The important grinding variables are:

- Wood species and other wood variables.
- Type of pulpstone.
- The use (or not) of a water-filled grinding pit.
- Type of burr pattern on the stone.
- Stone surface speed.
- Hours on the stone since last burring.
- Pressure of wood against the stone.
- Temperature of grinding surface, 130-180°C
- Amount of water used (and, therefore, the final pulp consistency).
1900 A.D.

Three Pocket Hydraulic Grinder

Water

Wood Magazine

Cylinder

Pressure Foot

Shower

Sharpening Lathe

Stone

Pit

Dam

Ditch
Roberts Ring Grinder
Pressure Grindwood (PGW)

Similar as SGW:

- By pressurizing the wood with steam at temperatures of 105-125°C, the wood is heated and softened prior to the grinding process.
- This gives better separation of fibers with less cutting action and lower fines generation.
- This process yields a pulp that has higher tear strength and freeness and is brighter than SGW.
- Lower power requirements.
Refiner Mechanical Pulp (RMP)

- Chips are used.
- Power requirements are 1600-1800 kWh/ton.
- Disk refiners are up to 1.5 m in diameter and rotate at 1800 rpm with 60 Hz power; this gives a velocity at the periphery of up to 140 m/s.
- The plates containing the metal bars must be replaced every 300-700 hours or low quality pulp is produced and energy use increases.
- Refining is usually carried out in two stages. The first is at 20-30% consistency to separate the fibers, while the second is at 10-20% consistency to alter the surface of the fibers for improved fiber bonding in the final paper.
Thermo-Mechanical Pulp (TMP)

- Most important mechanical pulping method.
- The TMP process is very similar to the RMP process except that pulp is made in special refiners that are pressurized with steam in the first stage of refining. First stage: Elevated T (110-130°C, just below the glass transition temperature of lignin 140°C, enhance fibrillation) & P. second stage: Ambient T, P
- Higher pulp strength. Energy req. 1900-2900 kWh/ton
- An even consistency of 20-30% is ideal
- The pulp yield is 91-95%
Chemi-Mechanical Pulping (CMP)

- C before SGW, PGW, RMP or TMP.
- The grinding requirements were about half that required without pretreatment and the CSF was 300-350 ml.
- 2 stage: Chemical Pretreatment + Mechanical pulping
- Chemical Pretreatments:
  - Hot sulfite: brighter, low strength
  - Cold soda: drains faster, coarse fiber,
Fig. 3-9. Liquor impregnation using the pressure-expansion technique. Courtesy of Sunds Defibrator.
Alkaline Peroxide Mechanical Pulping (APMP)

• APMP is alternative Bleaching CMP process which requires 30-40% less energy than with sulfite pretreatment for BCTMP pulp.
• Chemical impregnation is used prior to RMP.
Semi – Chemical Pulping

Vapor phase pulping:
• After impregnation by chemicals, chips are further cooked in steam atmosphere.

Semi-chemical pulping:
• High yield chemical pulping (60-80%)
• Similar to any of the commercial chemical pulping methods (to be described), except that the temperature, cooking time, or chemical charge is reduced. NSSC and Kraft semi-chemical methods
Neutral Sulfite Semi-Chemical (NSSC)

- High pulp yields are obtained (75-85%).
- Cooking liquors contain Na$_2$SO$_3$ plus Na$_2$CO$_3$ (10-15%, act as a buffer); the liquor pH is 7-10.
- Cooking time is 0.5-2 h at 160-185°C.
- The residual lignin (15-20%) makes paper from this pulp very stiff.
- Subsequent refining energy of the pulp is 200-400 kWh/ton

Kraft green liquor semi-chemical process
General Chemical Pulping

- Delignification
- Kappa number or Permanganate (K) number
- Pulp viscosity: degree of polymerization (DP)
- Fiber liberation point
- Full chemical pulps, unbleached, bleached
- Dissolving pulp
- Digester: Batch, continuous
Batch digester

- 70-350 m³, 6-8 digester in a plant.
- Direct or indirect heating
- Time to, at temperature
Sequence of events in batch digester

1. The digester is first opened and filled with chips, white liquor, and black liquor.
2. After initial circulation of the liquor additional chips are added as the contents settle.
3. The digester is then sealed and heating with steam begins. The temperature rises for about 90 minutes until the cooking temperature is achieved.
4. The cooking temperature is maintained for about 20-45 minutes for the kraft process. During the heating time, air and other noncondensable gases from the digester are vented.
5. When the cook is completed, as determined by the kappa of pulp from the digester, the contents of the digester are discharged to the blow tank.
6. The digester is opened and the sequence is repeated.
Continuous Digester

• A continuous digester is a *tube-shaped* digester where chips are moved through a course that may contain elements of *presteaming*, *liquor impregnation*, *heating*, *cooking*, and *washing*.

• Continuous digesters tend to be more *space efficient*, *easier to control* giving *increased yields* and *reduced chemical demand*, *labor-saving*, and *more energy efficient* than batch digesters.

• Special feeders is needed e.g., Screw feeder, Rotary valve
Fig. 3-16. The M&D continuous digester. The inserts show various aspects of the rotary valve. Courtesy of Andritz Sprout-Bauer, Inc.
Blow tank

- Up to 1000 kg of steam per ton of pulp is generated by batch digesters and some continuous digesters and must be condensed.
- Condensation of the blow gases also decreases pollution by recovering most of the volatile reduced sulfur compounds, organic compounds such as methanol, and related materials known together as foul condensate.
Delignification selectivity

- Delignification selectivity is the ratio of lignin removal to carbohydrate removal during the delignification process.

Rejects, knotter or screener and pulp screener

Brown stock washers

Fig. 3-21. Pulping selectivity curve.
Fig. 3-24. Brown stock washers showing countercurrent flow.
Soda Pulping

• Invented in England by Burgess and Watts in 1851, but was not popular.
• The soda process still has limited use for easily pulped materials like straws and some hardwoods, but is not a major process.
• Anthraquinone may be used as a pulping additive to decrease carbohydrate degradation.
Kraft pulping (Sulfate)

• In 1879, Dahl, a German chemist
• Much faster delignification and stronger pulps, since shorter cooking times are used resulting in less carbohydrate degradation.
• Kraft pulping is a full chemical pulping method using sodium hydroxide and sodium sulfide at pH above 12, at 160-180°C, corresponding to about 800 kPa (120 psi) steam pressure, for 0.5-3 hours to dissolve much of the lignin of wood fibers.
• **H-factor:** combines cooking temperature and time into a single variable that indicates the extent of reaction (Kraft process only). The rate of delignification approximately doubles for an increase in reaction temperature of 8°C.

• **White liquor:** $\text{NaOH} + \text{Na}_2\text{S} + \text{low Na}_2\text{CO}_3$

• **Black liquor:** Waste liquor from cooking. About 7 tons of black liquor at 15% solids are produced per ton of pulp. This liquid is burnt at 65-70% solid content.
• **Green liquor, chemical recovery:** Green liquor is produced by dissolving the smelt from the recovery boiler (Na$_2$S, Na$_2$CO$_3$, and any impurities) in water. Further processing of the green liquor converts to white liquor.

• **Total chemical or total alkali (TA)**

\[
\text{TA} = \text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{S}_x\text{O}_y
\]

• **Total titratable alkali (TTA)**

\[
\text{TTA} = \text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 \quad \text{(as Na}_2\text{O)}
\]
• **Active Alkali (AA)**

\[
AA = NaOH + Na_2S \quad (as \ Na_2O)
\]

• **Effective alkali (EA)**

\[
EA = NaOH + \frac{1}{2} Na_2S \quad (as \ Na_2O).
\]

• **Sulfidity**

\[
sulfidity = \frac{Na_2S}{NaOH + Na_2S} \times 100\%.
\]

• **Causticity**

\[
causticity = \frac{NaOH}{NaOH + Na_2S} \times 100\%.
\]

• **Causticizing efficiency**

\[
causticizing\ eff. = \frac{NaOH}{NaOH + Na_2CO_3} \times 100\%.
\]
• **Reduction efficiency**

\[
\text{reduction eff.} = \frac{\text{Na}_2\text{S}}{\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4} \times 100\%
\]

• **Dead load: NaCl**

• **Residual Alkali: NaOH present after cooking**
Sulfite Pulping

• Using mixtures of sulfurous acid and/or its alkali salts (Na$^{+2}$, NH$_3^+$, Mg$^{+2}$, K$^+$ or Ca$^{+2}$) to solubilize lignin through the formation of sulfonate functionalities and cleavage of lignin bonds.

• Advantages: Bright, easily bleached pulps, relatively easily refined pulps, pulp that forms a less porous sheet that holds more water than kraft pulps (for use in grease-resistant papers), and pulps with higher yield than kraft.

• Disadvantages: Weaker than kraft, not all species of wood can be pulped easily, cooking cycles are long, and chemical recovery is complicated.

• Treats the wood chips with cooking liquor at 120-150°C from 500-700 kPa.
• **Sulfite Liquor preparation**
  \[ S + O_2 \rightarrow SO_2 \]
  \[ SO_2 + H_2O \rightleftharpoons H_2SO_3 \]
  \[ H_2SO_3 + MOH \rightleftharpoons MHSO_3 + H_2O \]
  \[ MHSO_3 + MOH \rightleftharpoons M_2SO_3 + H_2O \]

• **Brown (or red) liquor**

• **Sulfite pulping base metals**
  - Calcium, Magnesium, Sodium, Ammonia

• **Chemical recovery:**
  1. Washing of the spent sulfite liquor from the pulp.
  2. Concentration of the spent sulfite liquor.
  3. Burning of the concentrated liquor.
  5. Pulping chemical regeneration.
  6. By-product recovery (mostly in Ca\(^{+2}\) based system).
Class test 3

Date & Time:
18 September, Saturday @ 11:AM

Syllabus:
Pulp and paper covered till now