The Paper & Pulp Industry
Trees are classified into 2 categories:
- **Hardwoods** (angiosperms or dicotyledonous angiosperms of which there are 30 000 – 35 000 species)
- **Softwoods** (gymnosperms of which there are about 1000 species)

Wood has unique structural and chemical characteristics which make it suitable for a number of different end uses and as such commercial exploitation of its growth and characteristics have been attempted to maximize its use.
What is Wood Made of?

- **Structural components:**
  - Carbohydrates (polysaccharides such as *cellulose* and *hemicelluloses*)
  - Lignin

- **Nonstructural components:**
  - Extractives
  - Water soluble organics and inorganics

Low molar mass compounds, as well as trace amounts of nitrogen containing compounds eg., alkaloids and proteins
Middle lamella - found between the cells & is the glue that holds the cells together. Contains lignin to give it mechanical strength.

Inner warty layer - thin amorphous layer with wart like deposits.

Secondary wall - S1 & S3 are thin outer and inner layers and S2 is a thick middle layer - they all contain lignin & hemicellulose.

Primary wall - first layer that forms during cell development. It is a thin layer and consists of cellulose, hemicellulose, pectin & protein embedded between lignin.

Simplified structure of a woody cell.
Florescence imaging of wood cells

www.cb.uu.se/annual_report/AR07html/node19.html
Cellulose is the world’s most abundant biopolymer. It consists of repeating glucose units linked by (1→4)-glycosidic bonds. Cellulose has a strong tendency for intra- and intermolecular hydrogen bonds and is very inert during chemical treatments, making it insoluble in most solvents.

Note: Every alternating repeat unit is rotated 180°.
Cellulose structure

intra

inter
Hemicellulose

- its building units are
  - Hexoses
  - Pentoses
  - Deoxyhexoses
  - Hexuronic acids

- hardwoods and softwoods differ in the total content of hemicellulose as well as in the percentages of the individual hemicellulose constituents

- hemicelluloses have a lower thermal stability than cellulose
Lignin

* are natural polymers based on \( C_6 - C_3 \) building blocks

4-hydroxycinnamyl alcohol (\( p \)-coumaryl alcohol)  
coniferyl alcohol  
sinapyl alcohol

* the building blocks are joined together by ether linkages (\( C-O-C \)) and carbon-carbon bonds (\( C-C \))
A proposed possible structure of lignin showing the types of bonding
Extractives

- include the terpenes, esters of fatty acids, fatty acids and alcohols, stilbenes, condensed tannins etc
- responsible for the wood’s colour, odour and taste and may be a source of energy for the biological functions of the wood cell
- resins protect against insect attack or microbiological damage

Inorganic compounds

- presence of various metals such as Mn, Fe, Ca, Mg, P, K, Na, Si, Cu, etc → affects the bleaching process and may lead to scaling of process equipment
Pulping Process

- First writing “paper” made from papyrus in Egypt in 2500 - 2000 BC.
- Chinese were the first to invent processes for paper manufacture in 105 AD.

As printing and education increased, the demand for paper increased → development of a number of methods for producing various grades of pulp.

Pulp not only required for paper manufacture but also found use in textiles, plastics and explosives industries.

www.earlham.edu/~seidti/iam/tc_pap66.html
Pulping Methods

- process of separating individual fibers from wood to make paper
- the main aim is to remove as much of the lignin whilst keeping the cellulose and hemicellulose intact to increase the yield of the fibers
- fibers are naturally coloured → therefore bleached to remove colour with minimum loss and degradation
- 4 general methods:
  - Mechanical pulping - block of wood is pressed against a grinding stone to separate the fibres
    - eg., stone groundwood (SGW), thermo mechanical pulp (TMP) & refiner mechanical pulp (RMP)
    - high yields (90-95 %) but low pulp strength
  - Chemical pulping - wood chips are treated with both acids and bases at high temperatures (~ 170 °C) and high pressures
    - eg., Kraft pulping, acid sulfite pulping and bisulfite pulping
    - low yields (40-50 %) but high quality pulp
- **Semi-chemical pulping** – wood chips are softened with chemicals and disc refiners are used to mechanically convert chips into fibres
  - e.g., neutral sulfite semi-chemical pulping (NSSC)
  - high yields (70-80 %)

- **Chemi-mechanical pulping** – wood chips are treated with chemicals (NaOH) at low temperatures (~ 20 °C) followed by a final refiner defibration
  - e.g.s., chemithermomechanical pulping (CTMP) & chemigroundwood pulping (CGWP)
  - good yields (85-90 %)
Why is wood debarked?
- it is not fibrous
- it is difficult to bleach

2 methods for debarking of wood

a) Rotate logs where friction between logs causes the bark to abrade off & a stream of water carries the bark away

b) Use of a high-pressure jet of water directed at an angle that strips the bark off and breaks it up

The bark is normally burned but some companies may extract wax and a type of cork material from the bark
Kraft Pulping (Sulfate Pulping)

**Black liquor recovery**

Chemicals are recovered and organics are burnt for energy.

**Digestion**

Wood chips pre-steamed at 100 kPa and then steam impregnation at 900 kPa where they are cooked with “white liquor” (Na$_2$S, NaOH and Na$_2$CO$_3$) for 1.5 hrs at 170 °C.

**Pulp washing**

Pulp is washed to separate the pulp fibers from the “black spent liquor”.

**Bleaching**

Multi-stage bleaching process using oxidative bleaches, eg., ozone, Na$_2$O$_2$, H$_2$O$_2$, ClO$_2$ & Cl$_2$.

**Preparation to be rolled into sheets/bundles**
Digestion

- fibers are separated by breaking down the chemical structure of lignin → delignification
- pulping liquor (white liquor) is made up of NaOH and Na$_2$S & Na$_2$CO$_3$
- wood chips are presteamed at 100 kPa to volatilize the turpentine and noncondensable gases and then are cooked with white liquor at 170 °C and 900 kPa for ~ 1½ hours
- can have continuous or batch digesters
once the cooking stops, the pulp and the black liquor is discharged into the blow tank, the steam from the digester is recovered and the black liquor is removed and undergoes recycling back into the cooking process

- pulp yield is expressed as the amount of material recovered compared to starting amount

\[
Pulp \text{ yield (\%)} = \frac{\text{dry mass of material out}}{\text{dry mass of material in}} \times 100\%
\]

- the pulp is washed countercurrent and screened to remove any knots and unreacted chips which is sent back to the digestor
- during digestion blowing gases from the black liquor are allowed to escape
- mainly $H_2S$, methyl mercaptan ($CH_3SH$) together with smaller amounts of dimethylsulfide ($CH_3SCH_3$) and dimethyl disulfide ($CH_3S_2CH_3$)
- a lot of effort is being made to reduce these emissions by incineration, absorption into the white liquor or scrubbing of black liquor
- other waste liquor are black liquor & **green liquor**
- black liquor - contains inorganic elements, dissolved hemicellulloses and lignin and carboxylic acids
- **green liquor** contains chemicals recovered by combustion of black liquor
### Typical black liquor analysis

<table>
<thead>
<tr>
<th>Agent</th>
<th>Content [g/kg dry solid]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>19.3</td>
</tr>
<tr>
<td>K</td>
<td>3.34</td>
</tr>
<tr>
<td>S\textsubscript{tot}</td>
<td>5.50</td>
</tr>
<tr>
<td>Cl\textsubscript{tot}</td>
<td>0.41</td>
</tr>
<tr>
<td>S\textsuperscript{2-}</td>
<td>1.93</td>
</tr>
<tr>
<td>NaOH</td>
<td>1.1</td>
</tr>
<tr>
<td>CO\textsubscript{3}\textsuperscript{2-}</td>
<td>6.2</td>
</tr>
<tr>
<td>Na\textsubscript{2}SO\textsubscript{3}</td>
<td>0.1</td>
</tr>
<tr>
<td>Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}</td>
<td>2.13</td>
</tr>
<tr>
<td>Na\textsubscript{2}SO\textsubscript{4}</td>
<td>1.23</td>
</tr>
<tr>
<td>C</td>
<td>31.9</td>
</tr>
<tr>
<td>H</td>
<td>3.33</td>
</tr>
<tr>
<td>N</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Calorimetric heat value, HHV 12.74 (MJ/kg dry solids)
Bleaching of Pulp

- is a multi-stage process
- “brightness” - measured as reflectance in the blue portion of the visible spectrum & depends on the amount of residual lignin in the pulp
- brown paper bags have a brightness of 20-30
- newspaper has a brightness of ~ 55
- bleached kraft pulp has a brightness of 86-94
- dark pulps are due to lignin and lignin degradation products and specific compounds that absorb light called chromophores

www.sfk.ca/EN/Mill_Saint-Felicien/Product.php
if only remove chromophores and not lignin from the pulp → pulp brightening
this is not permanent as UV light and oxygen will create more chromophores resulting in yellowing
classical bleaching processes aim to remove the lignin → more permanent brightness improvement

Is it better to remove only the chromophores or both the chromophores & lignin?
• **Aim of bleaching**: to remove residual lignin or convert and stabilize chromophoric groups in mechanical pulps without loss of pulp strength

• $Cl_2$ was the traditional chemical used

• $O_2$, ozone, $H_2O_2$, $ClO_2$ and $NaOCl$ have replaced $Cl_2$

• processes that have replaced $Cl_2$ are called **elemental chlorine free (ECF)** bleaching

• processes that have removed chlorine and chlorine based bleaches completely from their process are called **totally chlorine free (TCF)**
<table>
<thead>
<tr>
<th>Oxidizing chemical</th>
<th>Stage</th>
<th>Main function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine ($Cl_2$)</td>
<td>C</td>
<td>Chlorinates &amp; oxidizes lignin (forms polychlorinated aromatics which are toxic)</td>
</tr>
<tr>
<td>NaOH</td>
<td>E</td>
<td>Dissolves &amp; extracts lignin</td>
</tr>
<tr>
<td>$ClO_2$</td>
<td>D</td>
<td>Selective for lignin &amp; solubilizes lignin for the next stage, forms carboxylic acids</td>
</tr>
<tr>
<td>$O_2$</td>
<td>O</td>
<td>Together with NaOH, it removes some hemicellulose, 30-50 % lignin &amp; low m.m. cellulose, effluent is easily disposed</td>
</tr>
<tr>
<td>NaOCl</td>
<td>H</td>
<td>Oxidizes lignin, whitens pulp &amp; removes small amount of hemicellulose</td>
</tr>
<tr>
<td>$H_2O_2$</td>
<td>P</td>
<td>Modifies chromophores without dissolution of lignin. Sensitive to the presence of trace metals, therefore inorganics must be removed before P-stage</td>
</tr>
<tr>
<td>Ozone</td>
<td>Z</td>
<td>Oxidizes lignin &amp; acts similar to $Cl_2$</td>
</tr>
<tr>
<td>Xylanase</td>
<td>X</td>
<td>Enzyme that hydrolyzes lignin &amp; breaks up xylan for removal in subsequent bleaching stages → biobleaching</td>
</tr>
</tbody>
</table>
C stage bleaching:
- Cl\(_2\) is generally made at the mill site via electrolysis of NaCl

\[
2 \text{NaCl} + e^- + 2 \text{H}_2\text{O} \rightarrow 2 \text{NaOH} + \text{Cl}_2 + 2 \text{H}_2
\]

- C-stage bleaching is based on substitution & oxidation reactions
- At low pH, substitution dominates → polychlorinated aromatics
- At high pH oxidation reactions dominate → polysaccharide degradation
- This type of bleaching results in eventual degradation of cotton material
D-stage bleaching

- ClO$_2$ is prepared from sodium chlorate & sulfuric acid

\[ 2 \text{NaClO}_3 + \text{SO}_2 \rightarrow 2 \text{ClO}_2 + \text{Na}_2\text{SO}_4 \]

(used in white liquor)

- Unlike the C-stage, ClO$_2$ is selective for lignin degradation and polysaccharides are stable
- Results in breakdown of the aromatic ring to form carboxylic acids

Why is this stage more environmentally friendly than the C-stage?
Reaction of $\text{Cl}_2$ & $\text{ClO}_2$ with lignin
- O-stage bleaching
  - Developed to move away from chlorine bleaching
  - Degradation products are similar to that of ClO₂ bleaching
  - Can remove 30 - 50% of lignin but not any higher as polysaccharides are then degraded

Why is O-stage bleaching environmentally friendly?
Reactions of lignin with oxygen

where $R_1 = H, CH_3$

$R_2 = H, OCH_3$

Reactions of lignin with oxygen
Advantages & Disadvantages of Kraft Pulping

- capable of pulping low quality woods and any combination of hardwoods and softwoods including wood with high extractive contents
- short cooking times
- well established procedure which has recovery of valuable by-products such as tall oil & turpentine & cooking chemicals
- disadvantage - low yields (45 - 50 %) and lower quality of unbleached pulps which results in more intense & expensive bleaching process
- installation of a new mill is expensive
Acid Bisulfite Pulping

Simplified diagram of the acid bisulfite pulping process
- Digestion

- cooking chemicals were traditionally calcium bisulfite, & more recently magnesium bisulfite

\[
\begin{align*}
\text{MgO} & \quad \text{Mg(HSO}_3\text{)}_2 \\
& \quad (\text{Mg bisulphite}) \\
+ \text{ SO}_2 & \quad \text{Ca(HSO}_3\text{)}_2 \\
& \quad (\text{Ca bisulphite}) \\
\text{CaCO}_3 & \quad + \quad \text{free SO}_2
\end{align*}
\]

- wood chips are digested with cooking chemicals in an excess of SO\textsubscript{2} at temperatures of \(~ 125 - 140 \, ^0\text{C}\) and pressures of \(~ 480 - 1013\) kPa for \(~ 6 - 12\) hrs
2 major reactions occurring in the digester:
- Sulfonation and solublization of lignin with the bisulfite
- Hydrolytic splitting of the cellulose-lignin complex

Problem: - large amount of waste liquor produced which contains large amounts of organics and calcium sulfite, CaSO₃ which is not recoverable

Use Mg(HSO₃)₂ as cooking chemical - can be burnt & chemicals recovered
burning of $\text{Mg(HSO}_3\text{)}_2$ waste results in $\text{MgO}$ and $\text{SO}_2$ forming

Reactions during recovery:

$$\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2$$

$$\text{Mg(OH)}_2 + 2 \text{SO}_2 \rightarrow \text{Mg(HSO}_3\text{)}_2$$

Sent to digester to be used as cooking chemical
- after digestion, pulp is washed & screened to remove black liquor & knots
- bleaching step similar to Kraft process but each mill has optimized process for their end product
- Sappi Saiccor (acid bisulfite process) uses a 5 - step bleaching process

- **O stage** - \( (O_2 & NaOH) \) removes lignin (delignification), hemicellulose & low m.m. cellulose
- **D\(_1\) stage** - \( (ClO_2) \) solublizes remaining lignin for the next stage
- **E stage** - \( (NaOH) \) dissolves lignin and removes small amounts of hemicellulose
- **D\(_2\) stage** - \( (ClO_2) \) whitens pulp & breaks down remaining lignin residues
- **H stage** - \( (NaOCl) \) whitens pulp, chemically alters the molecular size of cellulose & remove small amounts of hemicellulose
Environmental Concerns

- large amounts of effluent produced previously dumped in a river or pumped out to sea
- effluent found to affect aquatic life (deformed fish)
- large amounts of $SO_2$ emission to the atmosphere
- government environmental legislation requires industry to be more responsible in the handling of their waste

http://2.bp.blogspot.com/_jqLzRML3_tM/SBZuxLXR1MI/AAAAAAAABFA/9lkpBZqw1W0/s800/DSCN3893.JPG
So how have acid bisulfite mills reduced their waste?

1) introduced $\text{Mg(HSO}_3\text{)}_2$ that is recovered thus reducing effluent
2) calcium spent liquor forms a large amount of lignosulfonates that is removed before wasted is disposed

- Lignosulphonates are formed by the reaction of $SO_2$ or $HSO_3^-$ with lignin forming a sulfonated form of the lignin
- Lignosulfonates are soluble in the aqueous phase of the effluent and extracted to be used as a tanning agent for leather tanning, ore binder & binder in animal feed and coal briquettes.

- Their dispersive property allows them to be used in drilling oil wells to maintain the flow of the oil and drilling at high temperatures.

- Used as concrete additives when mixing cements → results in the concrete requiring less water thus increasing the concretes compressive strength, density & uniformity.

- Sprayed onto roads to make the surface hard & durable and also forms an impermeable layer with the natural clays in the soil keeping the road free of surface water.
3) Research also carried out to recover lignin from effluent
- Oxidation of lignin found to produce vanillin which has a unique taste to natural or synthetic vanillin
- Oxidation reactions of lignin also found to produce syringaldehyde and other aceto-phenolic compounds that have a variety of uses.
Advantages & Disadvantages of Acid Bisulfite Pulping

- higher yields at a given kappa number, resulting in lower wood consumption
- higher brightness of unbleached pulp $\rightarrow$ not as intense bleaching process required resulting in lower bleaching cost
- higher flexibility of bleaching & bleaching without chlorine
- lower installation capital costs
- higher flexibility in pulp yields & grades
- disadvantage - large volumes of waste and use of $\text{Ca(HSO}_3\text{)}_2$ is not recoverable
Uses of Cellulose

- mostly used for paper or paperboard but its derivatives have different properties → used to make many other products
- structure of cellulose has many hydroxyl groups linked by hydrogen bonds which react to form derivatives such as:
  - cellulose nitrates
  - cellulose acetate
  - cellulose xanthate
**Cellulose acetate**

- Prepared by reacting cellulose with acetic anhydride

- The acetate group replaces an available hydroxyl group with the percentage of hydroxyls derivatized depending on the amount of acetic acid added

- 3 hydroxyls allow for degree of substitution of 3
* As **degree of substitution (DS)** increases, the melting point increases & vapour permeability decreases.

* As **degree of polymerization (DP)** decreases, its solubility in polar solvents increases & moisture resistance increases.

**Uses**
- Textiles & fibers
- Plastics
- Frames for spectacles
- Osmotic membranes

Cellulose nitrates

- Was the first synthetic plastic
- Depending on the level of nitration, it has a variety of uses
  - 11% nitrated is used for plastics
  - 12% nitrogen for lacquers
  - 13% nitrated used for explosives (smokeless powder & dynamite)
- Nitrating agent is HNO₃ together with H₂SO₄, H₃PO₄ & acetic anhydride, CH₃CO(O)COCH₃
- main disadvantage: burns easily; discolours & becomes brittle on aging
Step 1: generate the nitronium ion, $\text{NO}_2^-$

$$\text{HONO}_2 + 2 \text{H}_2\text{SO}_4 \rightleftharpoons \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2 \text{HSO}_4^-$$

Step 2: electrophilic nitronium ion attacking the hydroxyl of the cellulose

$$\text{NO}_2^+ + \text{HO-cell} \rightleftharpoons \text{NO}_2\text{O}^+\text{Cell} \rightleftharpoons \text{NO}_2\text{O}^-\text{Cell} + \text{H}^+$$

Industrial scale uses chemical grade pulps or cotton linters which are torn up and then are mixed with acid. Cellulose nitrate is separated from residual nitrate acid using a centrifuge.
Cellulose xanthate

- Produced by first treating cellulose with 18% NaOH at 15 – 30 °C
- Excess NaOH is removed & pressing down on the fibers allows the fibers to be shredded & alkaline ripened to bring the DP down to 200 – 400.
- Xanthation is achieved by exposure to carbon disulfide at 25 – 30 °C for ~ 3 hours → DS = 0.5

\[
\text{Cell} - O + C\equiv S \rightleftharpoons \text{Cell} - O - C\equiv S^- \\
\text{cellulose xanthate}
\]
Dissolution of cellulose xanthate in NaOH results in an orange coloured viscous liquid called viscose.

After ripening, the viscose solution is filtered and forced through a spinneret into an acid bath (H₂SO₄ & salts) → regeneration of cellulose as fine filaments resulting in rayon fibers.

If the viscose is pressed through a narrow slit into an acid bath to form thin sheets we get cellophane forming...