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Chemical processing of wood

Kateřina Hájková

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Introduction

- Wood – a natural renewable material
- The use of wood by human civilization in many times and countries and across industries
- A versatile material from a technological point of view
- Environmental friendliness

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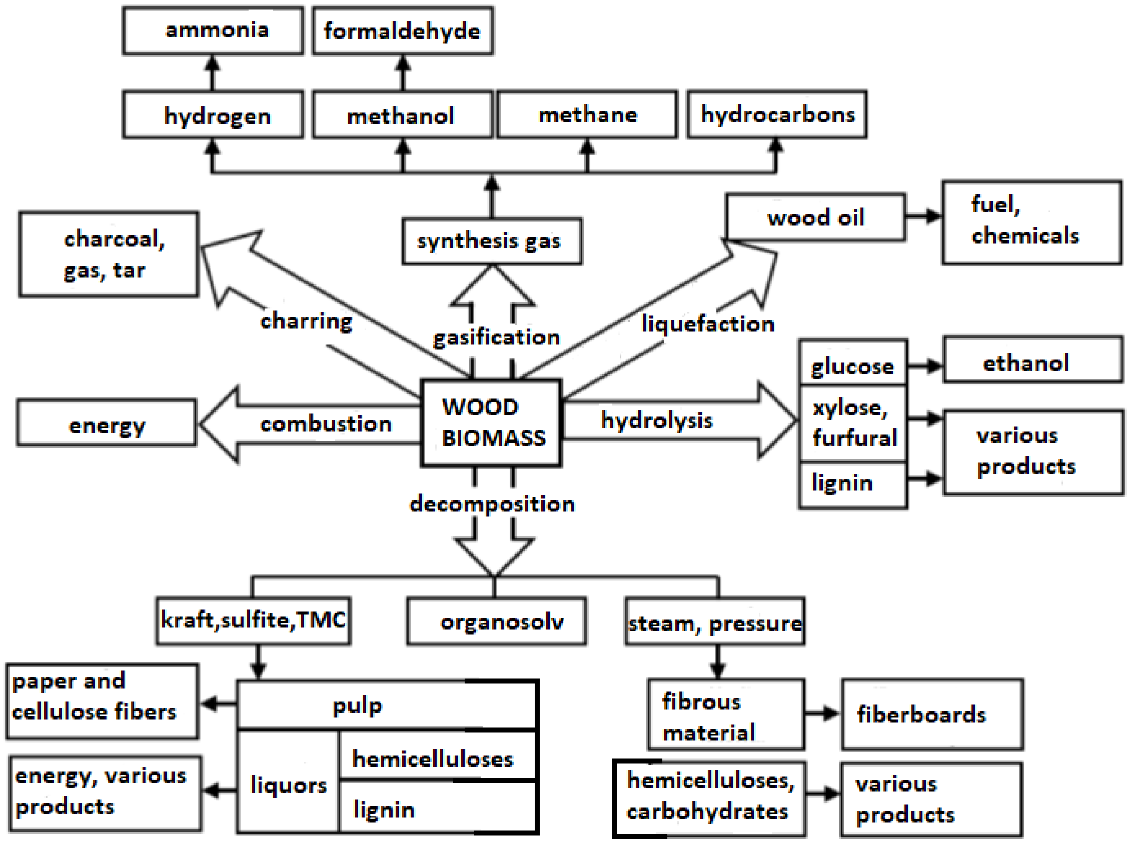
Thermal and chemical conversion of wood and biomass into energy and a range of products



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Combustion and thermal energy gain

- Great possibilities of use in the field of energy
- Since ancient times, one of the most important sources of heat for heating and cooking
- Energy from wood is used in industry (49%) and in households (34%)
- The calorific value of wood: ≈15–18 MJ/kg
- The moisture content of wood has a significant influence on its calorific value
- Differentiation of firewood according to hardness:
  - hardwood (hard) - stable, long-lasting heat
  - conifers (soft) - better kindling, rapid increase in heat

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Charring

- Conversion of wood into charcoal
- One of the oldest applied chemical changes of wood raw material
- Coal made from wood has a higher calorific value, is not subject to biodegradation, and its reducing ability enables the melting of metals
- Two types of wood burning:
  - With access to air (burning, formation of ash) - production of lye from ash, so-called potash (K_2CO_3)
    - Use for textile, soap, and glass production
  - Without air access (subdued heating, exclusion of H_2O, charring) – in hearths and pits, later until the middle of the 20th century. in charcoil piles (up to 350 °C)
    - Use in smelters and hammer mills, large kitchens
    - Production of black gunpowder
    - Tar (a waste product) – gluing, unguent making and wound dressing (antiseptic)

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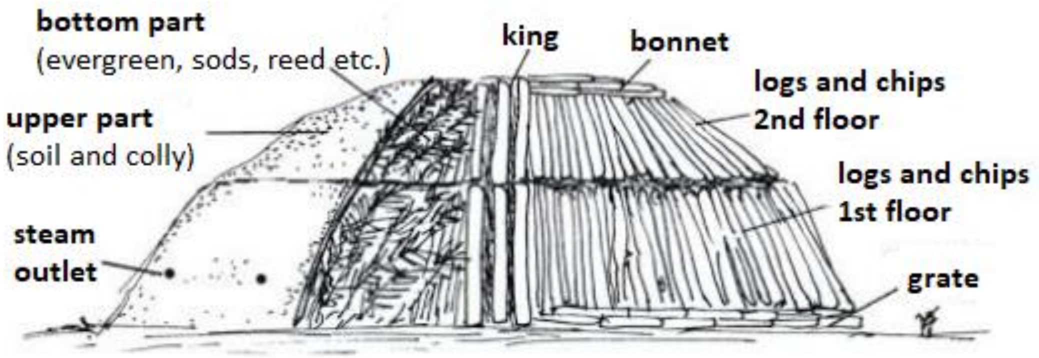
Charring

- Charcoil pile



- Carbonizer

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Gasification

- Thermochemical transformation of wood at higher temperatures (800–900 °C) with the supply of a limited amount of oxygen
- Wood gas only developed, not burned
- When using O_2 as an oxidizer - a low calorific value (4–6 MJ/m^3)
- Composition: approx. 20% CO, 20% H_2, 3% CH_4 + CO_2, N_2, tars, phenols, solid particles
- Applications: internal combustion engines, turbines, fuel cells (in the future)
- Development:
  - During World War II - in transport (lack of petroleum fuels), catalytic processing into methanol
  - Current technologies: gasification in fixed bed generators, gasification in fluidized bed generators at atmospheric pressure

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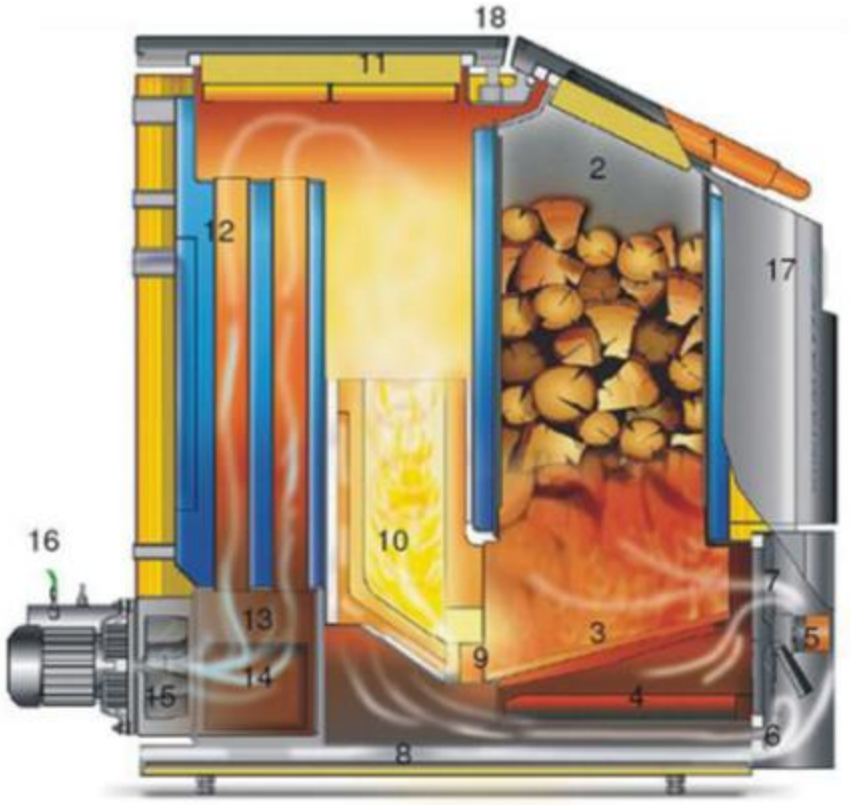
Gasification

- Gasification boiler for lump wood and briquettes



1. Chamber lid with extraction channel
2. Filling chamber with protective layer
3. Hot cast iron grate
4. Ashtray
5.Primary and secondary air motor
6. Secondary air
7.Primary air
8. Bottom air preheat
9. Secondary air nozzle
10. High temperature combustion chamber
11. Cleaning lid
12. Tubular heat exchanger
13. Dust extraction zone
14. Cleaning opening
15. Exhaust fan
16. Smoke sensor
17. Microprocessor control
18. Transport fitting

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Liquefaction

- A low temperature (300–350 °C) high pressure (12–20 MPa) thermochemical conversion process taking place in an aqueous environment requiring a catalyst (NaOH) or high partial pressure H_2
- Hydrogenolysis
- Polyols are formed from polysaccharides and phenols from lignin
  - Primary product: organic liquid (bio-oil) with reduced O_2 content (10%)
  - By-product: H_2O containing soluble organic matter, mainly fural

Hydrolysis

- Conversion to simpler cleavage products - monomeric carbohydrates
- Hydrolysis options:
  - **In an aqueous environment** – under ↑T water autoprotolysis and the influence of H_3O^+ ions
  - **Acid hydrolysis** – rather drastic reaction conditions, many complex reactions, conversion of polysaccharides to sugars, also their undesirable degradation
  - **Enzymatic hydrolysis** – cellulase, hemicellulase enzymes, etc. Slower, more expensive, but more gentle. The necessity of pre-hydrolytic treatments
  - **Bimimetic catalysts** – based on polyalcohols, under development

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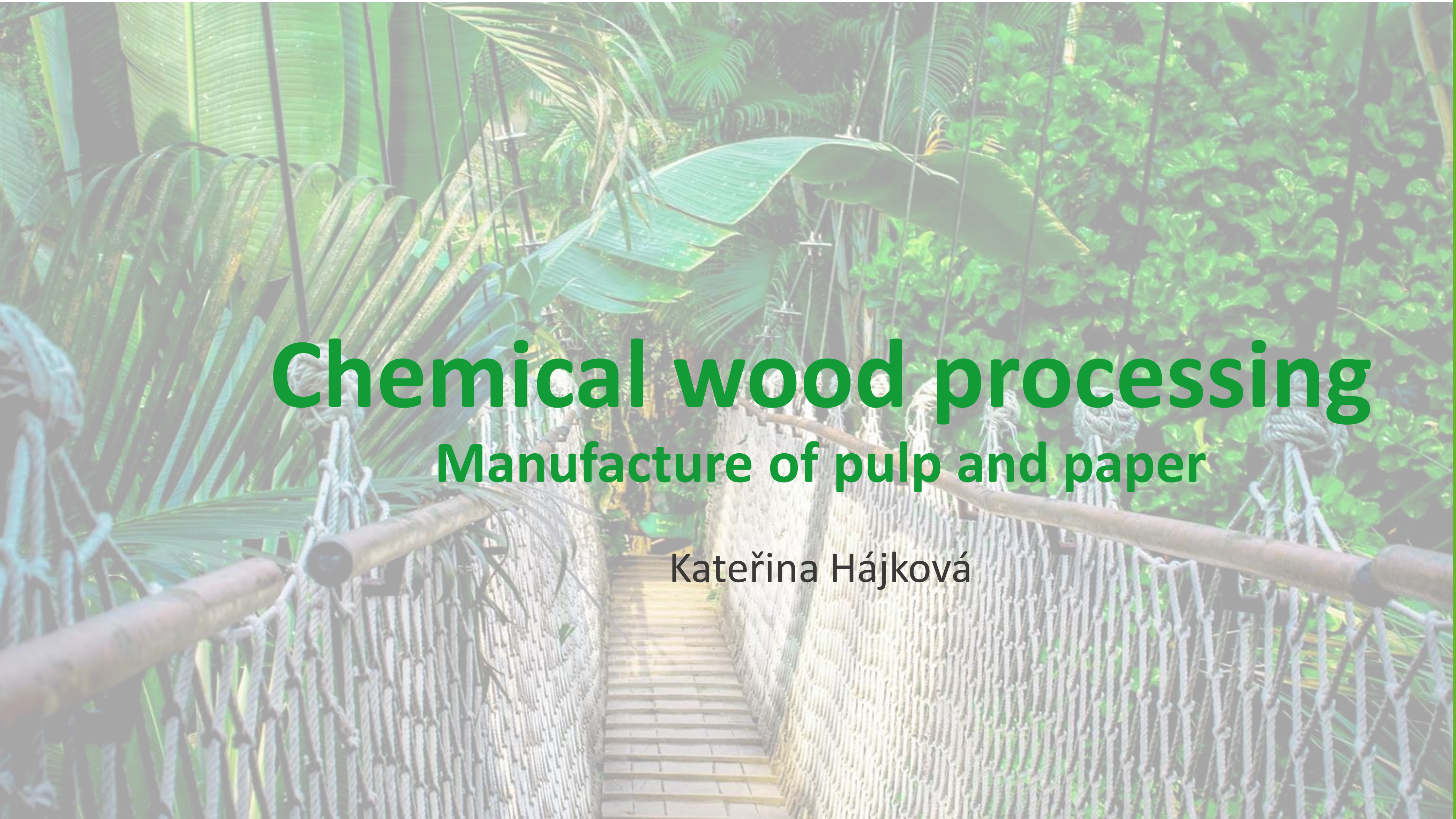

Chemical wood processing

Manufacture of pulp and paper

Kateřina Hájková

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Primary fiber raw material

- Fibrous raw materials for paper production
- Many suitable raw materials in nature - technical and economic requirements:
  - large quantities available
  - cheap
  - high yield
  - fibre long enough
  - easy to unravel
  - fibre well felted
  - good bleachability
  - processing costs low
- Suitable: wood, recovered paper

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Breakdown of primary fiber raw materials

- By origin:
  - Plant raw materials - wood, straw, cotton, flax, hemp, reeds, bagasse, bamboo, rags, textile waste, waste paper, etc.
  - Animal raw materials - wool, hair, natural silk, leather waste
  - Mineral raw materials - glass, basalt, asbestos, ceramic, metal fibers
  - Polymeric raw materials - polyamide, polyester, aramid fibers, artificial silk, etc.

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Plant raw materials

- Fibres suitable for papermaking are obtained from:
  - wood from the trunks or branches of conifers and some deciduous trees - spruce, fir, pine, beech, poplar, aspen, chestnut, linden, birch
  - hazel - flax, hemp, mulberry
  - seeds – cotton
  - stalks and stems - straw, esparto, sunflower, corn, nettle, rapeseed, bamboo, sugar cane
  - leaves - sisal, manila, pineapple, aloe
  - fruit - coconut

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Animal raw materials

- Made up of proteins built from amino acids
- The division of fibers according to their amino acid content and origin into:
  - Keratin - forms the hair covering of vertebrates
  - Fibroin - the secretions of the caterpillars of storms
- Preparation: cutting, combing, washing, dyeing, spinning
- Use mainly in the textile industry

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Non-plant fibrous raw materials (mineral, polymeric)

- Not entirely suitable for the production of paper in the usual way
- They do not have fibres suitable for conventional felting (they cannot fibrillate and form bonds with H-bridges or -OH groups)
- Use only for special types of paper produced in small quantities under special purpose

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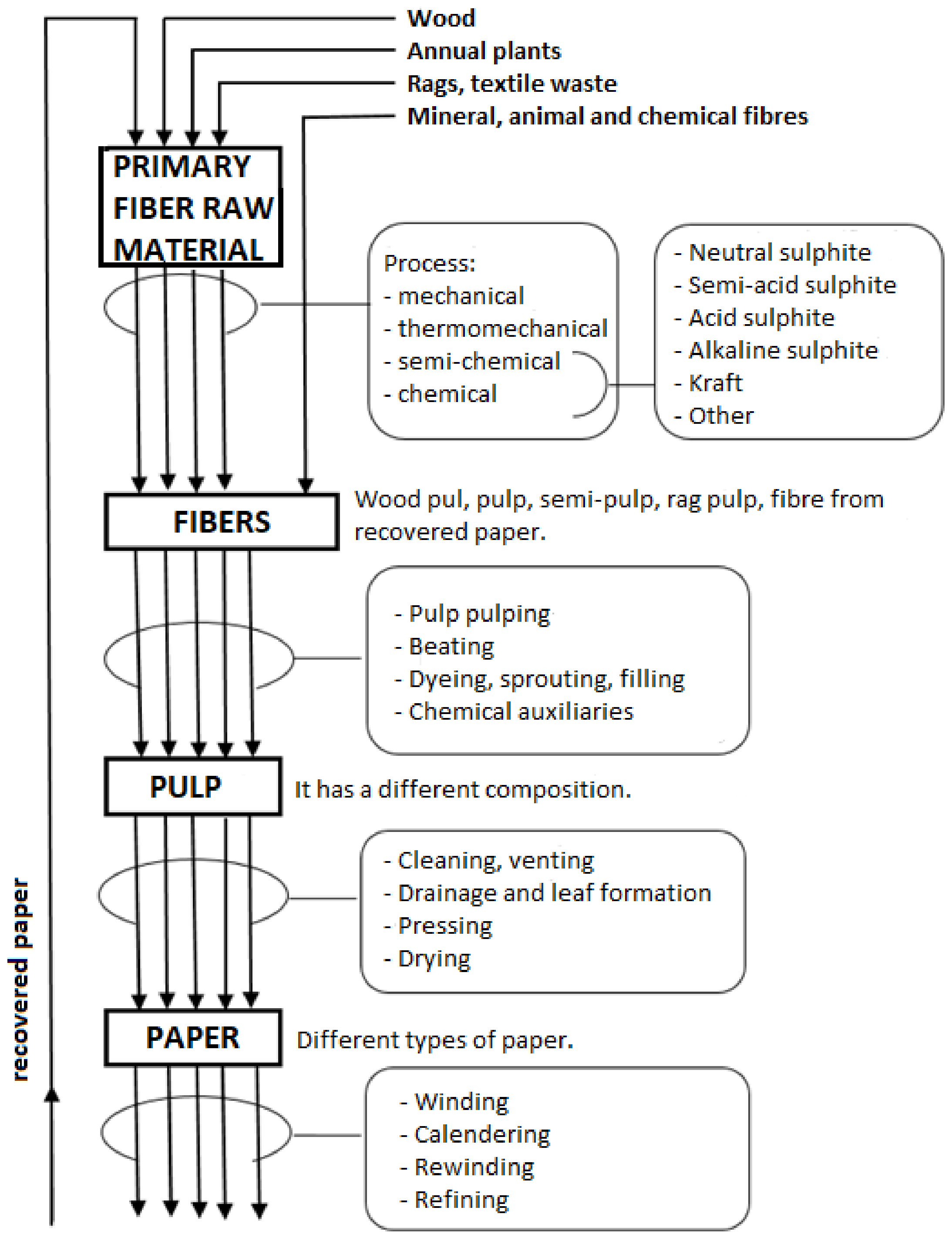
Fibers

- Schematic diagram of the processing of fibre materials into fibers, pulp and paper



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The basic methods of obtaining fibre

- Mechanical method
- Combined chemical-mechanical method
- Chemical method

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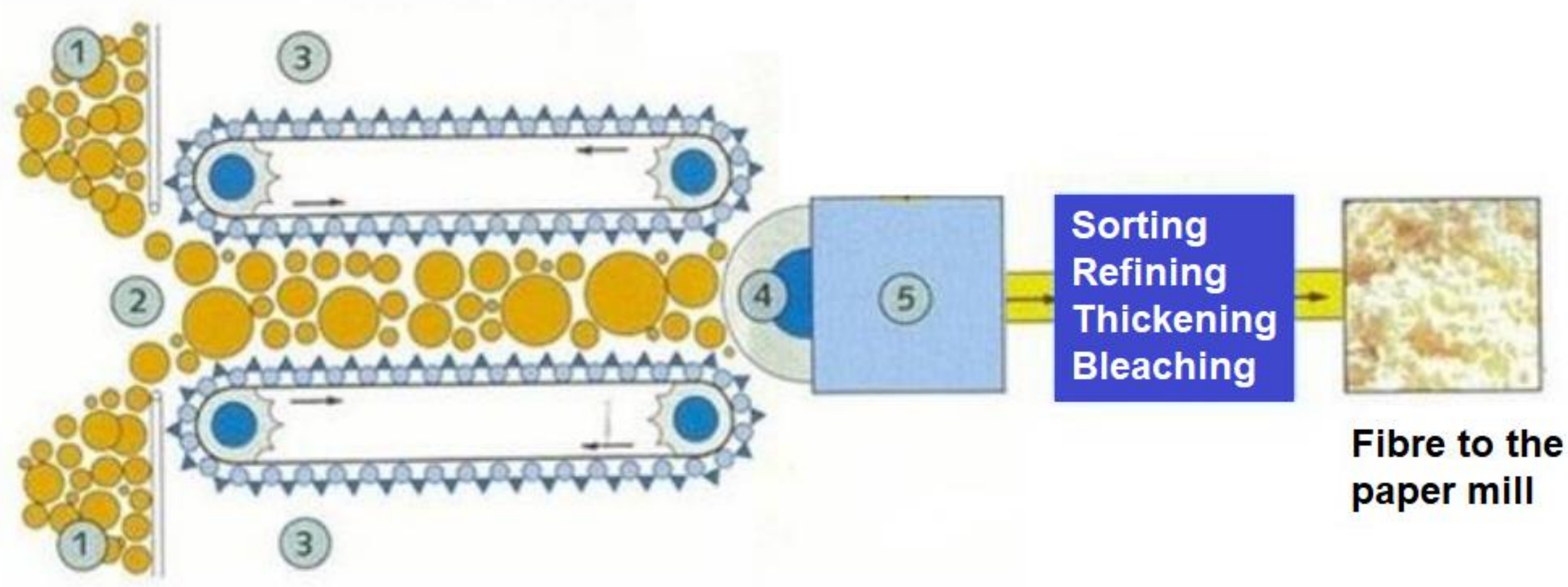
Mechanical method



1 Logs of wood

2 Carrying chamber

3 Guide chains

4 Grinding stone

5 Fibre tank

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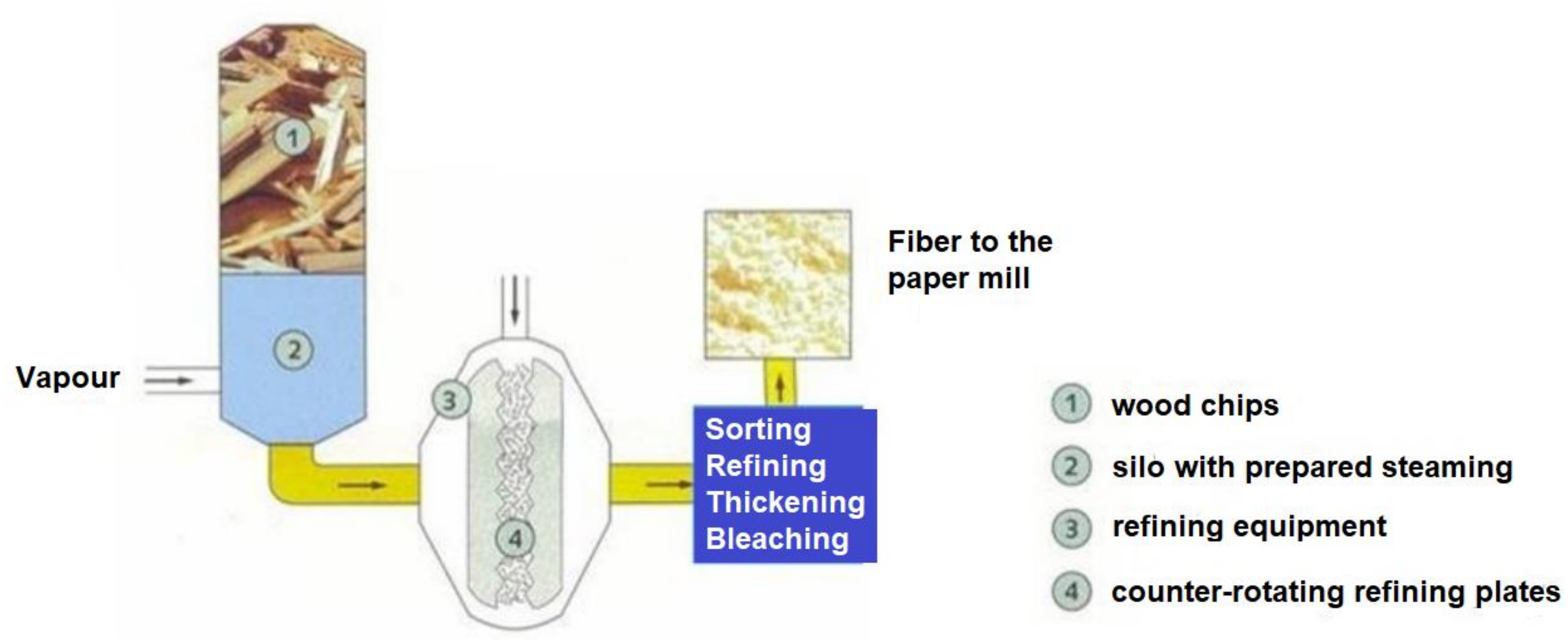
Combined chemical-mechanical method



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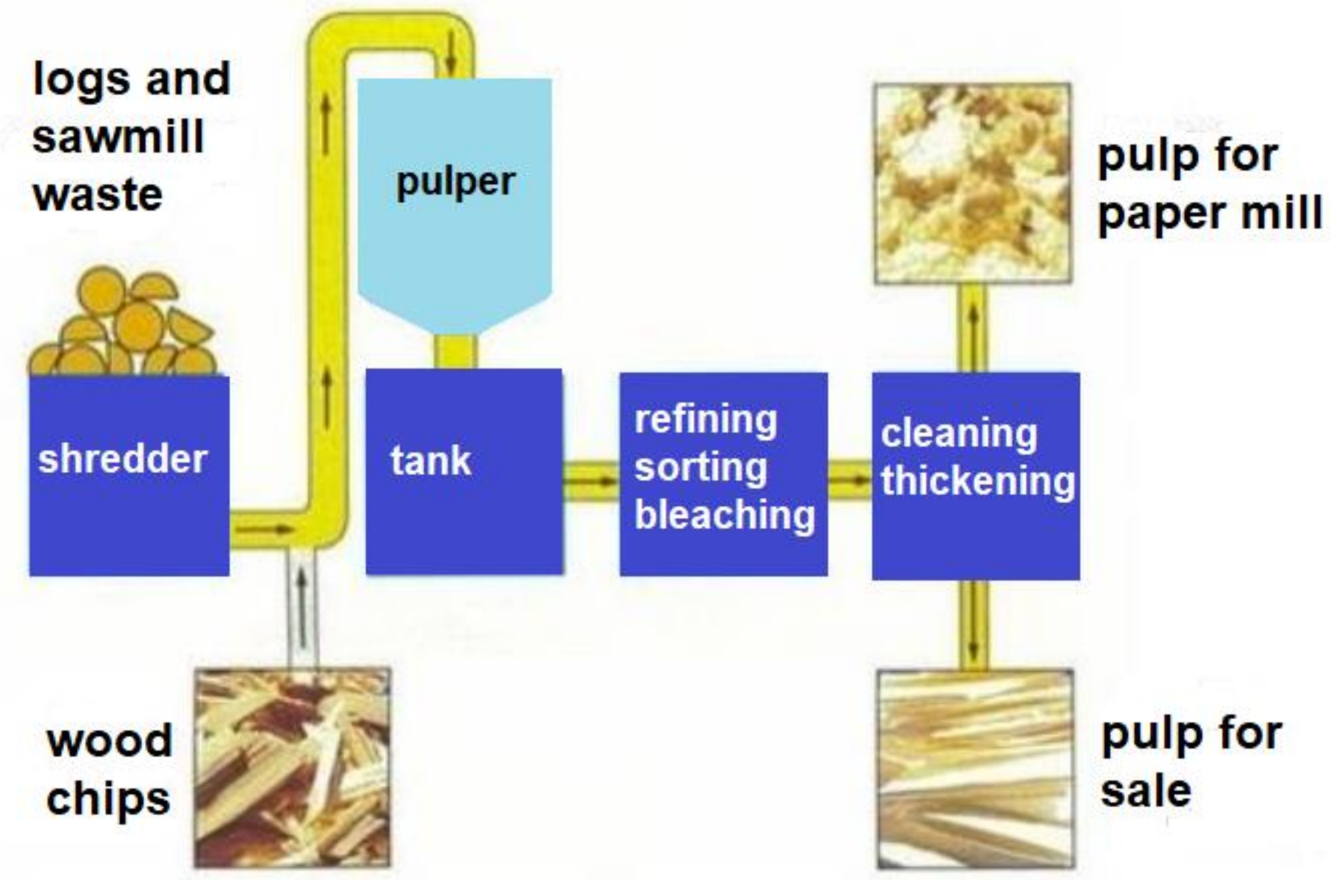
Chemical method



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Chemical method

- Kraft method (alkaline)
  - cooking liquor (solution of NaOH and Na_2S)
  - cook approx. 5 hours at a temperature of up to 180 °C

- Sulphite method (acidic)
  - cooking acid (solution of $Ca(HSO_3)_2$ and H_2SO_3)
  - the cooking process takes several hours at a temperature of about 110-140 °C

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Summary

- Chemical, mechanical and chemical-mechanical fibres belong to the group of so-called commercial fibres, sometimes referred to as primary fibres
- Approximately 75 % of all commercial fibre production is bleached kraft pulp
- A special group consists of rag pulp used for the production of special types of paper in limited quantities and recycled fibre

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Experiments of students at FFWS

- Nitrate-alkaline cooking
- Determination of kappa number
- Rheosedimentation of pulp
- Analysis of liquors
- General paper properties

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Nitrate-alkaline cooking

- The chemical method for pulp making can be the very nitrate-alkaline process where the cellulose-lignin bond is hydrolytically released during the cooking in the acid
- The lignin is being nitrated and partly oxidizes into nitro-lignin which is soluble in alkali

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Nitrate-alkaline cooking – separation of rejects

$$x_R = \frac{m_R}{m_{OD}}$$

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Nitrate-alkaline cooking – total yield

$$Y = \frac{m_P + m_R}{m_{OD}}$$

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Determination of kappa number

- The degree of pulp delignification is proportional to the degree of delignification of the wood, i.e., it gives information about the amount of lignin contained in the pulp
- A number of auxiliary variables are used for this determination, one of the most widely used of which is the so-called Kappa number

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Determination of kappa number

- The Kappa number expresses the volume of potassium permanganate used to oxidise the substances contained in 1 g of absolute dry pulp under the conditions of determination
- The Kappa number thus determined is used to express the degree of delignification, the bleachability or the relative hardness of the pulp

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Determination of kappa number
- determination of the thiosulphate factor

$$f = \frac{5V_d c_a}{V_b c_b}$$

Determination of kappa number – determination of kappa number

$$V_a = \frac{(V_b - V_c)c_b f}{5c_a}$$

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Determination of kappa number – determination of kappa number

V_a, ml	0	1	2	3	4	5	6	7	8	9
30	0,958	0,960	0,962	0,964	0,966	0,968	0,970	0,973	0,975	0,977
40	0,979	0,981	0,983	0,985	0,987	0,989	0,991	0,994	0,996	0,998
50	1,000	1,002	1,004	1,006	1,009	1,011	1,013	1,015	1,017	1,019
60	1,022	1,024	1,026	1,028	1,030	1,033	1,035	1,037	1,039	1,042
70	1,044	–	–	–	–	–	–	–	–	–

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Determination of kappa number – determination of kappa number

$$\kappa = \frac{V_a d}{m_{OD}}$$

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Rheosedimentation of pulp

- Rheosedimentation is a specific type of disturbed sedimentation
- The method is based on the observation and description of the kinetics of the spontaneous movement of the formed mesh of fibrous suspension components during sedimentation or flotation
- It can therefore also be classified as a rheological method

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Rheosedimentation of pulp

- However, here we are not concerned with the rheology of the flow of suspensions, but with the spontaneous movement of the netting formed from the individual components of the paper pulp
- A mesh is defined as a compact phase permeating a liquid and characterized by a distinct interface between the formed mesh and the liquid
- The mesh is formed only after a certain concentration of suspended matter, typically 1 kg-m^{-3}, has been reached

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Rheosedimentation of pulp

$$\rho_P = \frac{h_\infty \cdot \rho}{h_0}$$

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Rheosedimentation of pulp

$$z = t(h_0 - h)$$

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Rheosedimentation of pulp

$$\rho_K = \rho \cdot \frac{h_\infty}{h_0 - \frac{1}{\beta}}$$

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Rheosedimentation of pulp

$$v_0{}^s = \frac{1}{\alpha} \cdot \frac{\rho_P{}^2 \cdot (\rho_K - \rho_P)^2}{1 \cdot (\rho_K - \rho_P)^2}$$

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Analysis of liquors

- Before preparing the cooking liquor for the kraft cooking, it is necessary to determine the composition of the white liquor, specifically: the concentrations of Na_2S, $NaOH$, Na_2CO_3, the concentration of active alkali and sulphidite

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Analysis of liquors

- The analysis of the black liquor is carried out for environmental reasons. In order to be able to compare the variables that enter production and those that exit production. Therefore, the analysis of physical quantities such as density, viscosity or interfacial tension is carried out

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Analysis of white liquors – Sodium sulfide concentration

$$c_{Na_2S} = 12,4(V_B - V_A)$$

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Analysis of white liquors – Sodium hydroxide concentration

$$c_{NaOH} = 6{,}2(2V_A - V_B)$$

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Analysis of white liquors
– Sodium carbonate concentration

$$c_{Na_2CO_3} = 6{,}2(V_C - V_B)$$

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Analysis of white liquors
– Active alkali concentration

$$c_{AA} = c_{Na_2S} + c_{NaOH}$$

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Analysis of white liquors – Effective alkali concentration

$$c_{EA} = \frac{1}{2} c_{Na_2S} + c_{NaOH}$$

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Analysis of white liquors – Total alkali concentration

$$c_{CA} = c_{Na_2S} + c_{NaOH} + c_{Na_2CO_3}$$

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Analysis of white liquors - Sulfidite

$$S = \frac{c_{Na_2S}}{c_{Na_2S} + c_{NaOH}} . 100$$

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Analysis of black liquors – liquor density

$$\rho = \frac{m_2 - m_1}{m_3 - m_1} \cdot \rho_V$$

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Analysis of black liquors – dynamic viscosity

$$\mu = \frac{\mu_V}{\rho_V t_V} \rho t$$

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Analysis of black liquors – interfacial tension

$$\gamma = \gamma_V \frac{m}{m_V}$$

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General properties of paper

- Basis weight is defined as the ratio of the weight of the material under examination to the area concerned
- The thickness of paper means the vertical distance between their opposite surfaces. It is measured with respect to the compressibility of the fibrous structures at the specified measuring pressure and is given in mm or µm

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General properties of paper

- The bulk density of paper is defined as the ratio of the weight of a given material to the volume that the material occupies. The bulk density indirectly expresses porosity, i.e. it shows to what extent a bulk unit of paper is filled with fibrous and non-fibrous components and what part of this volume remains filled with air

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General properties of paper – basis weight

$$BW = \frac{m}{S}10^4$$

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General properties of paper - thickness

$$t = \frac{\sum t_i}{i}$$

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General properties of paper – bulk density

$$\rho_V = \frac{BW}{t}$$

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General properties of paper – air volume in the paper sheet

$$V = \left(1 - \frac{\rho_V}{1600}\right) \cdot 100$$

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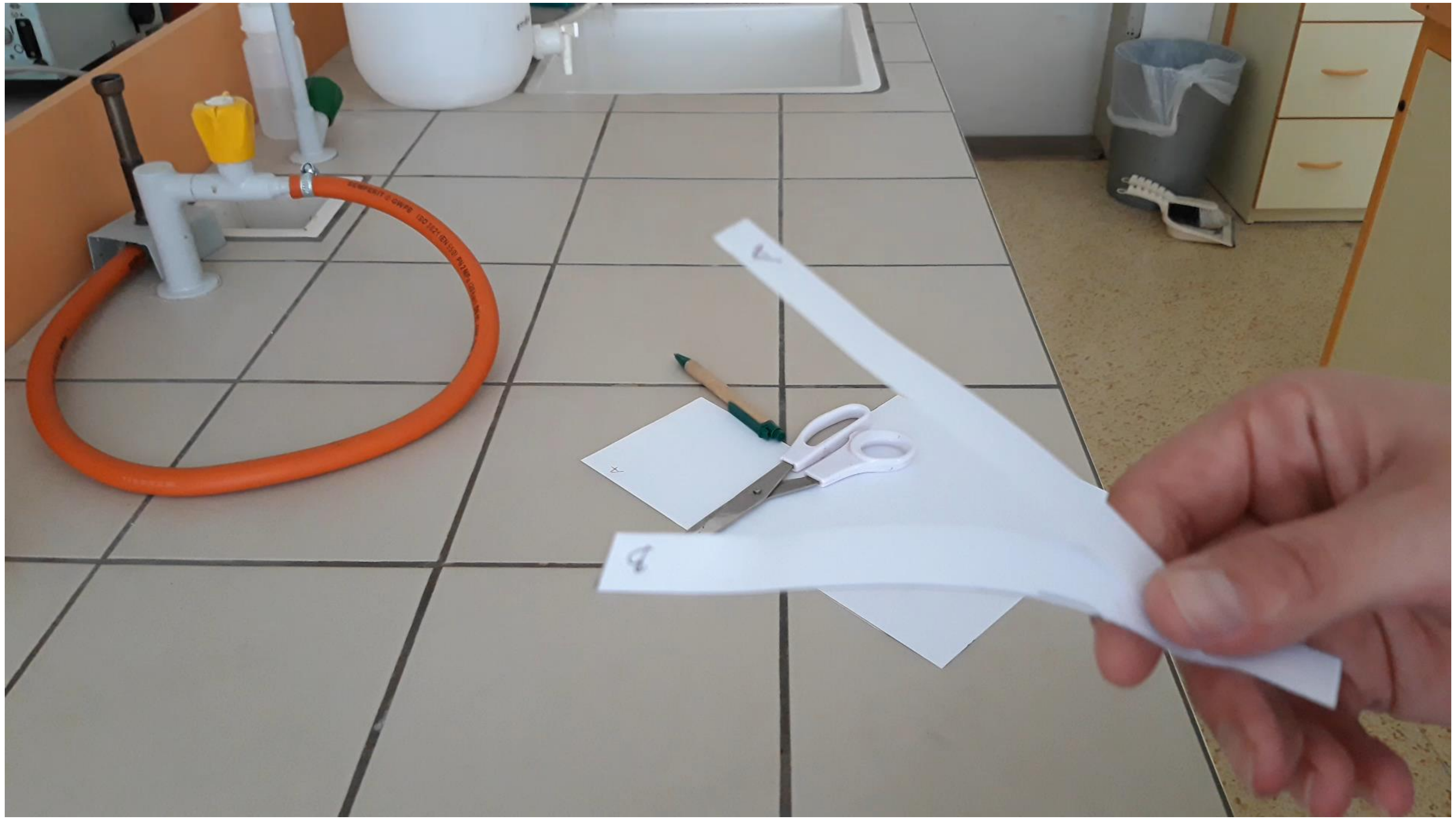
General properties of paper – direction of production



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General properties of paper – sieve and face side

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Chemical processing of wood

Modification of wood

Kateřina Hájková

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Modification of wood

- A modification is a term that generally refers to a change, modification or other variation of a thing
- Modification is also a special term, change or transformation, for example, in chemistry it means a change in a chemical substance, in manufacturing a version or modification of a product standard, in metallurgy a melt is modified
- The modification may be only simple and marginal, or it may be a total change

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Purpose of modification

- Change material parameters
  - Wood properties
    - Physical properties of wood
    - Mechanical properties of wood

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The principle of modification

- Modification is a method of modifying wood so as to preserve or improve its positive properties while reducing or eliminating its unfavourable properties

- Positive effects of modification
  - hygroscopicity of wood
- Negative effect of modification
  - hardness vs. toughness

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Modification usability

- Usability depends on many parameters that enter into the modification process:
  - Input material
  - The modification method
  - Duration of the modification process
  - Proper use of the modified material
  - Economic return on the process
  - Environmental impact
  - Technological complexity on an industrial scale
  - Resulting product cost

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Modification usability

- Factors that influence the selection of input material:
  - The price of the input material
  - Availability of raw material on the market
  - Logistical availability
  - Quality of raw material
  - Environmental impact of the raw material
  - Seasonal availability
  - Shelf life in storage
  - Technological processability

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Method of modification

- Thermal modification
- Chemical modification
- Impregnation
- Modification by pressure
- Modification by microwave radiation

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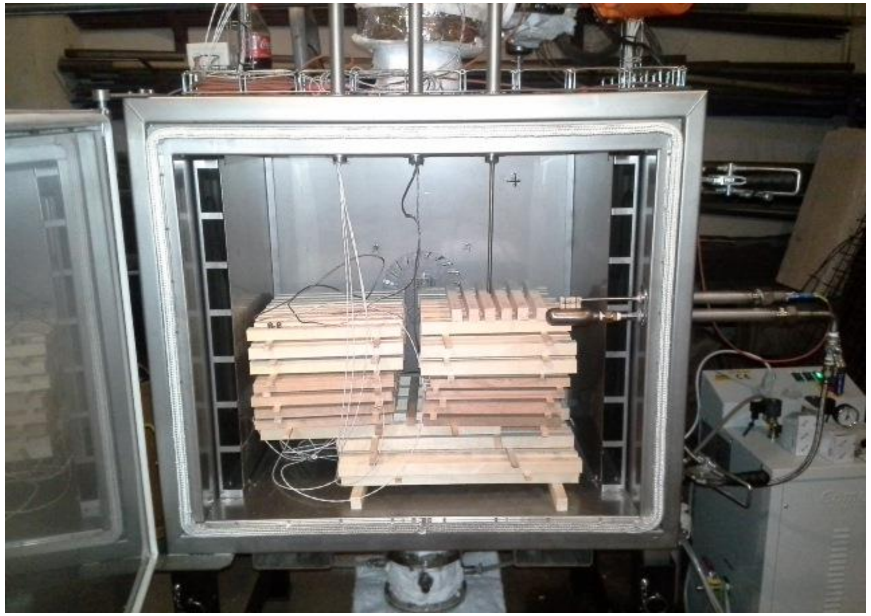
Thermal modification



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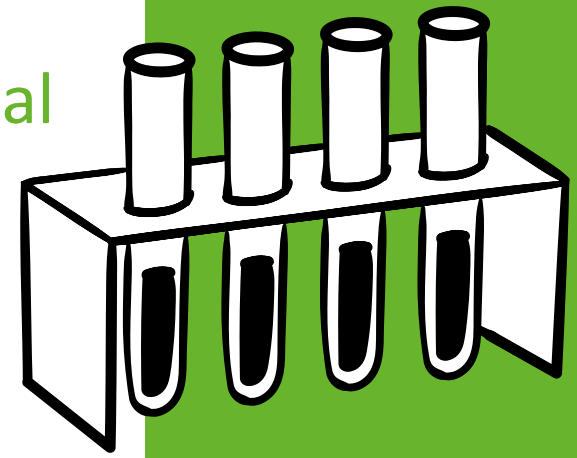
Thermal modification

https://www.youtube.com/watch?v=BUCShKLyhig

Chemical modification

- The progress and effectiveness of the chemical modification is evaluated by:
  - Uptake and distribution of the modifying agent in the wood
  - Dimensional stabilization of the wood
  - Change in mechanical properties of the wood
  - Change in durability of the wood
  - Overall efficiency - effectiveness of the modification process



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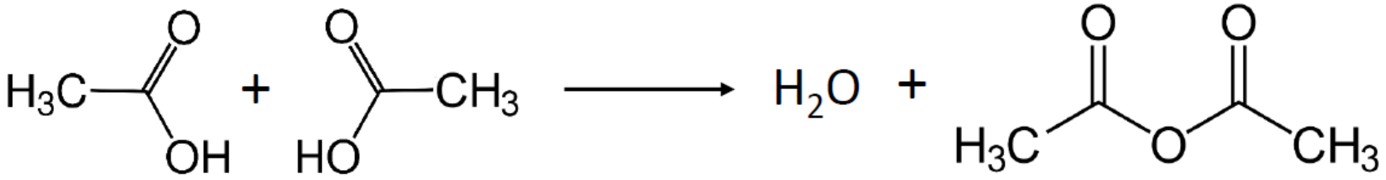
Chemical modification

- anhydrides of carboxylic acids (acetic anhydride) and dicarboxylic acids
- acyclic and cyclic anhydrides
- ketenes
- carboxylic acids
- carboxylic acid halides (acyl chloride)
- isocyanates
- aldehydes
- alkyloxides and epoxides
- acrylonitrile



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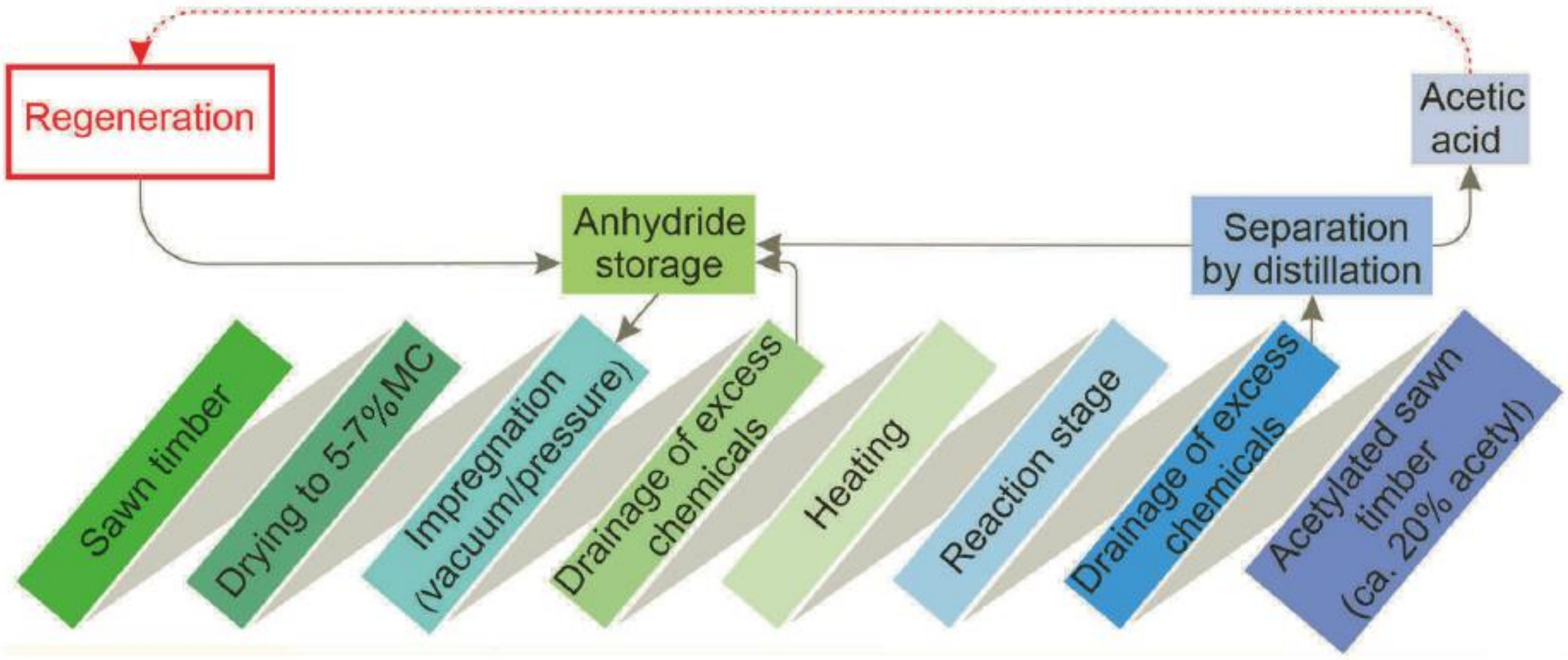
Acetylation of wood (Accoya wood)



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Acetylation of wood (Accoya wood)

https://www.youtube.com/watch?v=_PnpznfyVcE

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Impregnation




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Furfurylation of wood (Kebony wood)

https://www.youtube.com/watch?v=wUFl6ClB-WU

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Modification by pressure

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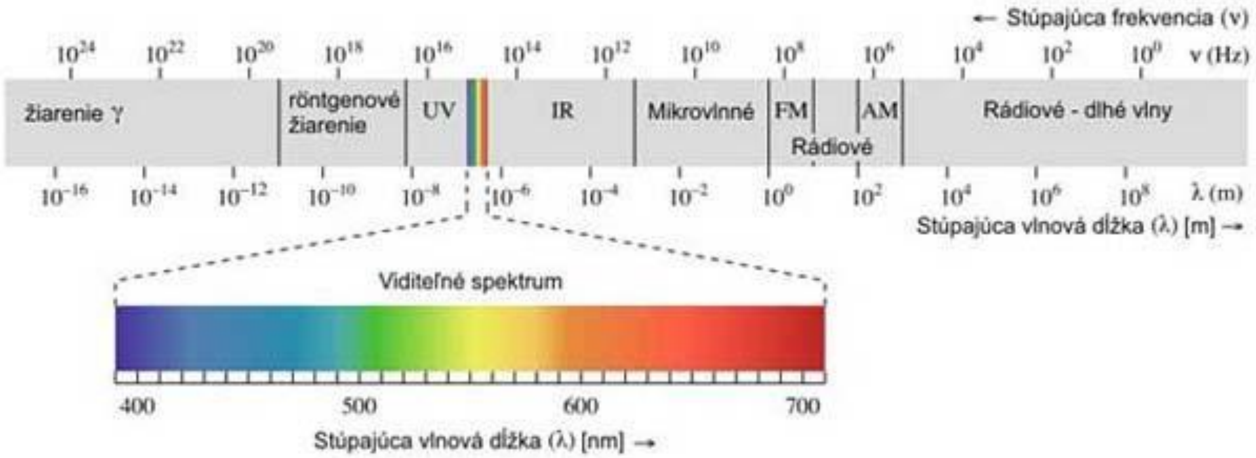
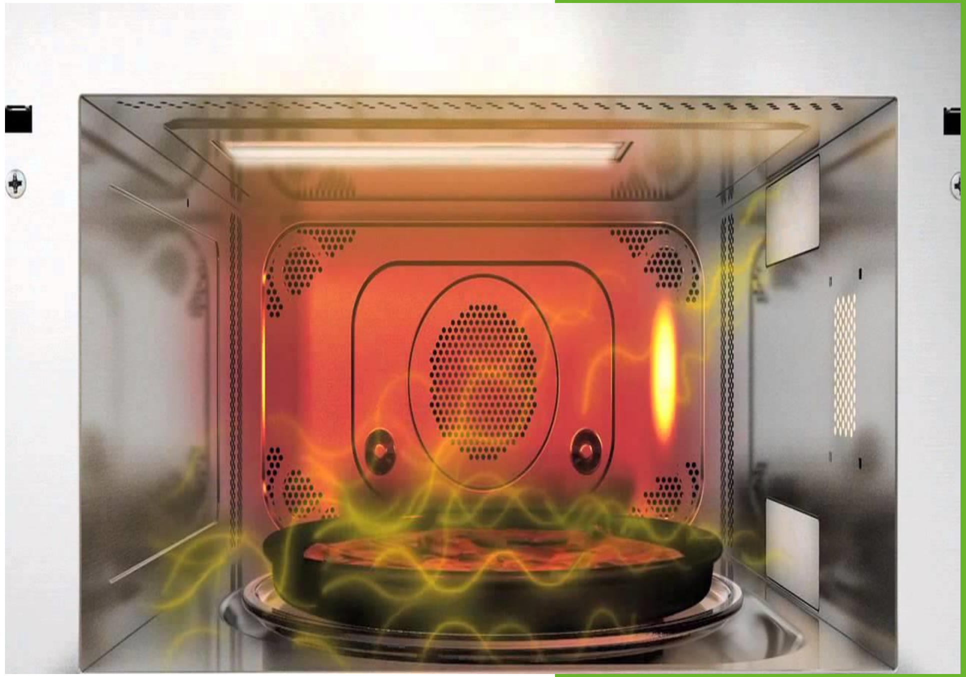
Modification by microwave radiation





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How to choose the right modification?

- Type and place of use
- Mechanical and physical stresses
- External or internal use
- Appearance and surface roughness

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Chemical processing of wood

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Bioethanol production

- The current use of fossil fuels has resulted in a critical environmental situation
- Their combustion produces carbon dioxide, methane and significant amounts of nitrogen oxides
- The use of ethanol as a fuel in internal combustion engines reduces exhaust emissions and thus reduces air pollution

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Bioethanol production

- Biofuels, which are produced from different types of biomass, can be solid, liquid or gaseous. Depending on the type of biomass used, they can be divided into four generations:

- **The first generation** is biofuels made directly from food crops
- **Second generation** biofuels are biofuels that are produced from non-food crops such as wood, organic waste and food waste

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Bioethanol production

- Biofuels, which are produced from different types of biomass, can be solid, liquid or gaseous. Depending on the type of biomass used, they can be divided into four generations:

- **The 3rd generation** is represented by biofuels made from algae and other aquatic plants
- **The fourth generation** of biofuels focuses on the production and use of genetically modified organisms (GMOs) or the use of advanced biochemical processes and procedures

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Technological operations of bioethanol production

- The production of bioethanol is based on the following technological operations:

1. Feedstock storage
2. Cleaning and treatment of biomass
3. Biomass pretreatment
4. Enzymatic hydrolysis of cellulose and viscosity reduction

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Technological operations of bioethanol production

- The production of bioethanol is based on the following technological operations:

5. Detoxification of inhibitors
6. Fermentation
7. The purification, distillation and dehydration of ethanol
8. By-product treatment

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