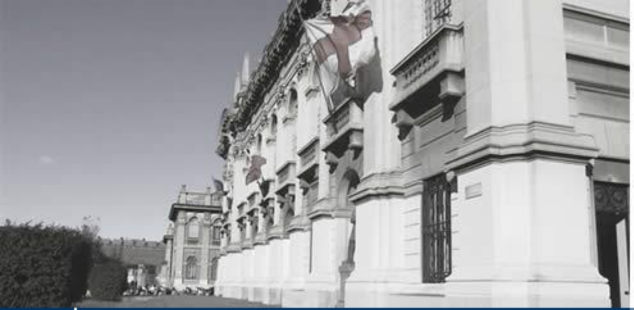


School of Industrial and Information Engineering
Course 096125 (095857)
Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

Biorefinery.

Prof. Attilio Citterio
Dipartimento CMIC “Giulio Natta”
https://iscamapweb.chem.polimi.it/citterio/it/education/course-topics/

Outline.

- Types of biorefineries: seeds and lignocellulose
- Fractionation process of seed and lignocellulose biomass
- Paper industry and cellulose technology
- Valorization of liquid and solid wastes (lignin, fats, etc.) and diversification of cellulose uses.
- Evolution to systems of integrated biorefineries.

Lignocellulosic Resources.

Agricultural residues and industrial co-products

- Straw (cereal, oil crops, sugar crops, fiber crops)
- Grain shells (cereals, oil crops)



Forestry products and residues

- Woody plants (coniferous, broadleaved)
- Sawdust

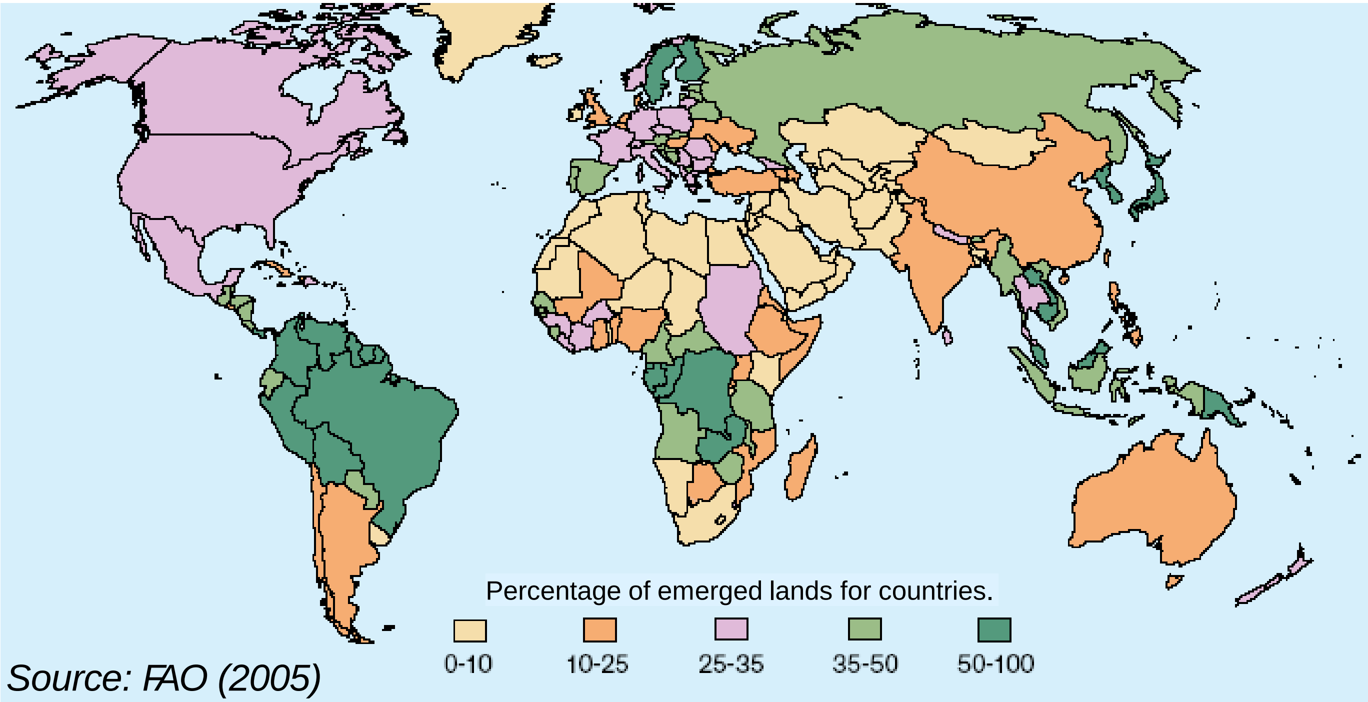


Industrial and municipal waste

- Industrial effluents
- Sewage sludge
- Green waste


Abundance and Availability of Lignocelluloses.

- Availability of forest and agricultural biomass in the world
- Forests = 30% land surface - about 4×10^9 ha
- Deforestation: 3% in 15 years (20 000 ha/day).



Average productivity of agricultural and forestry resources : 10 ton MS/ha·year.

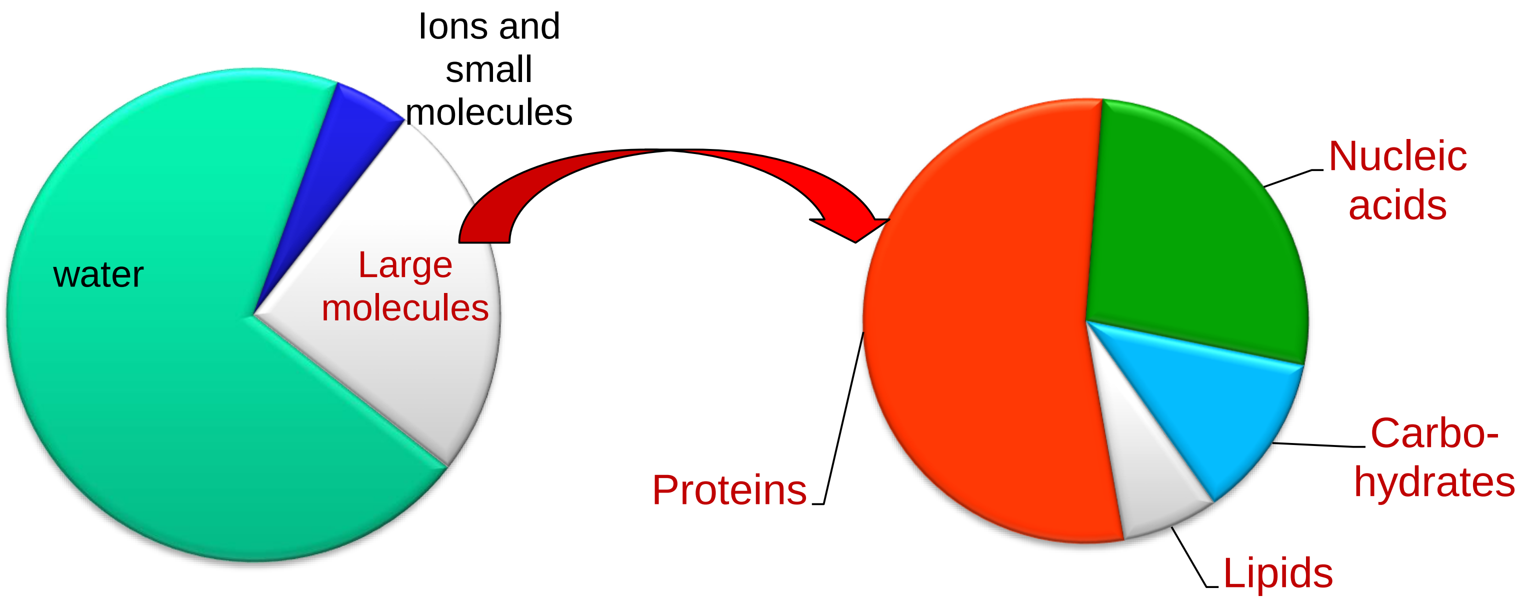
Agricultural non-Food Residues in Italy.

- Cropland ~ 1.5×10^8 ha
- Cereals 2007 : 500 million ha ↔ 4 to 8 t/ha of «Straw»,
- 3 to 6 billion tons
- A part returns to soil (soil quality)
- A part is collected for livestock (litter, feed)

- The remaining ~1 billion ton is available for other uses in 2030…
- **For biofuels or other chemicals?**

DOE (US) 2005

Substances in Living Cells.



The functions of macromolecules are related to their shape and the chemical properties of their monomers. Some of the roles of macromolecules include:

- ❖ Energy storage
- ❖ Structural support
- ❖ Transport
- ❖ Heredity
- ❖ Protection and defence
- ❖ Means for movement, growth, and development
- ❖ Regulation of metabolic activities

Biomass Feeding Constituents.

Starch: 70-75% (wheat)

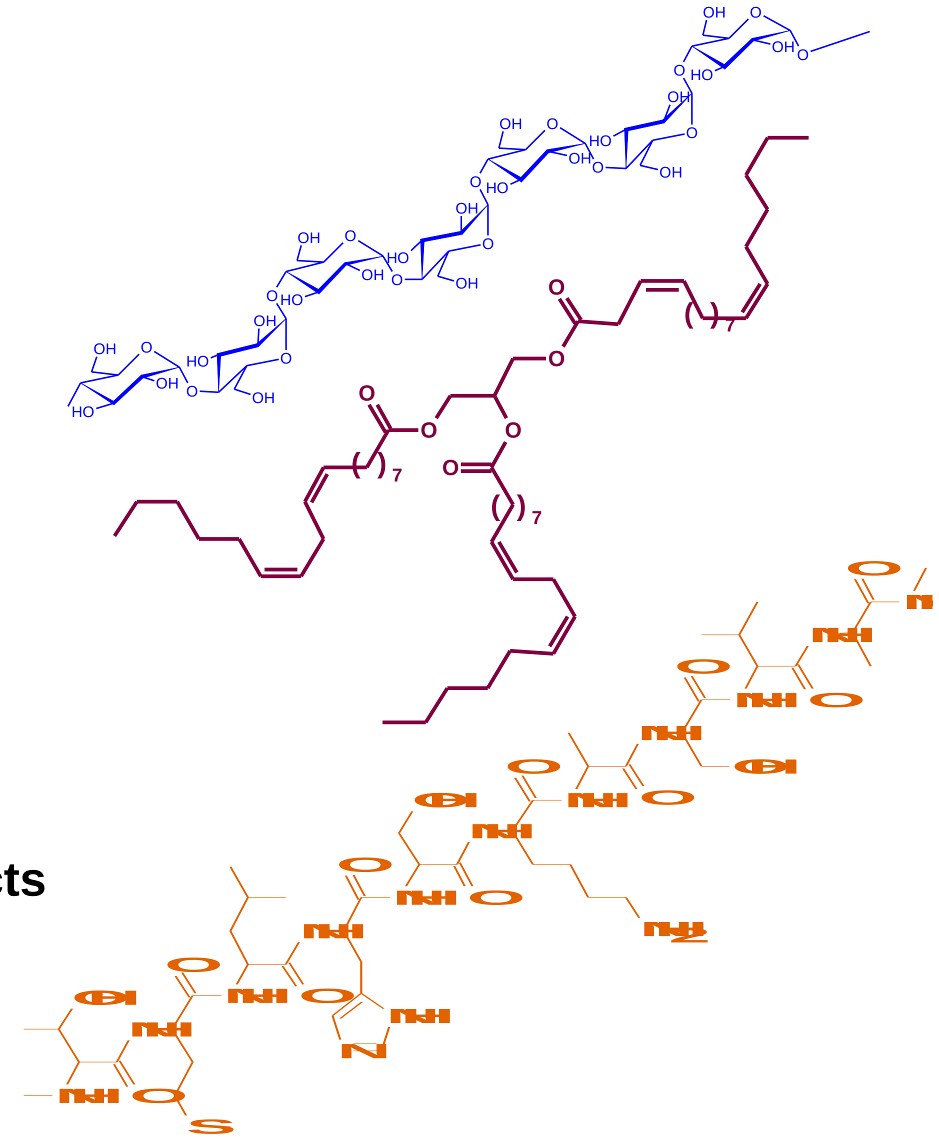
- Rapidly available and hydrolysable
- Basis for actual "*bio-refineries*"

Oils: 4-7% (wheat), 18-20% (soy)

- Rapidly separable from plant
- Basis for *oleochemistry* and for *biodiesel*

Proteins: 20-25% (wheat), 80% (soy)

- Key components of foods
- Applications in chemical products and materials.



Biomass Non Feeding Constituents.

Lignin : 15-25%

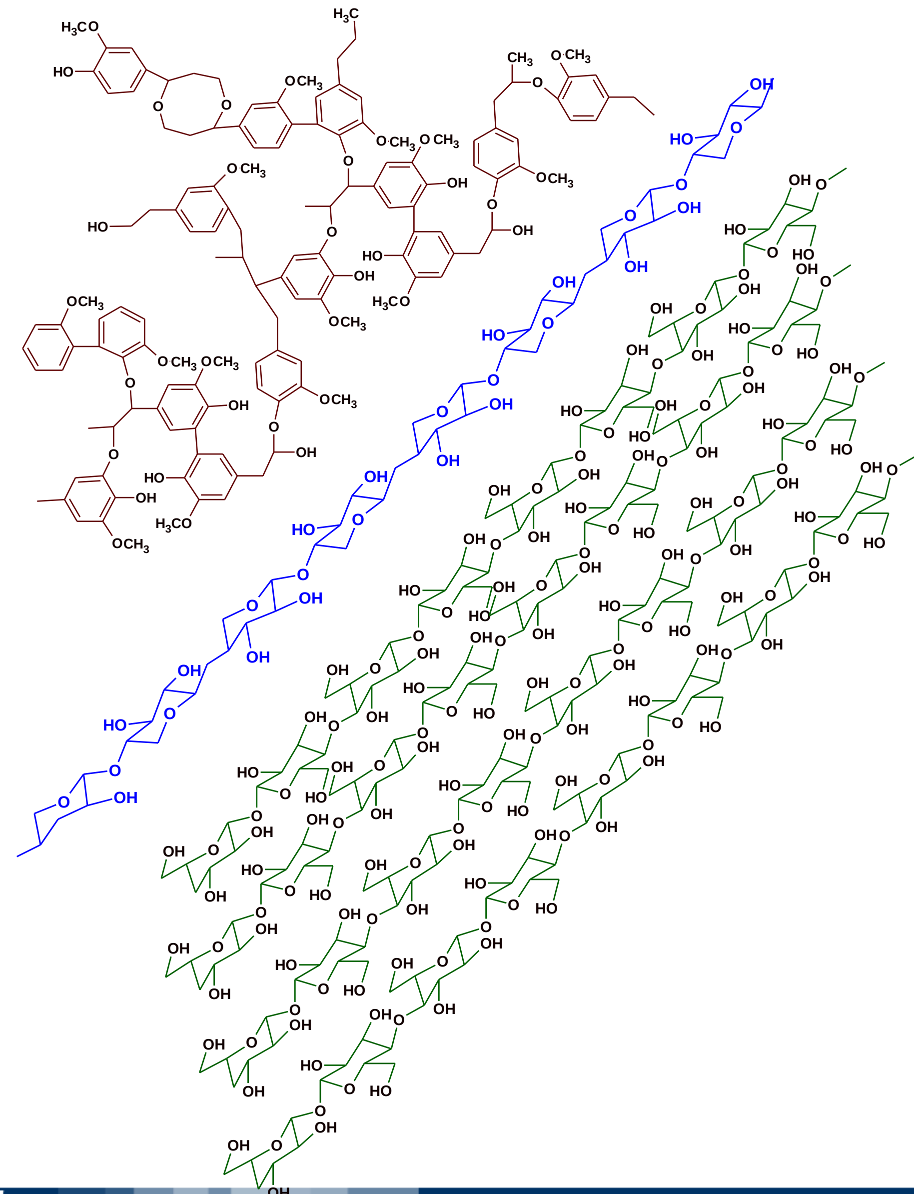
- Complex network of aromatics
- High energy content
- Resists biochemical conversion.

Hemicellulose : 23-32%

- Xylose is the 3[nd] most abundant sugar in biosphere
- A collection of 5- and 6-carbon sugars linked together in long, substituted chains-branched.
- Marginal biochemical feed.

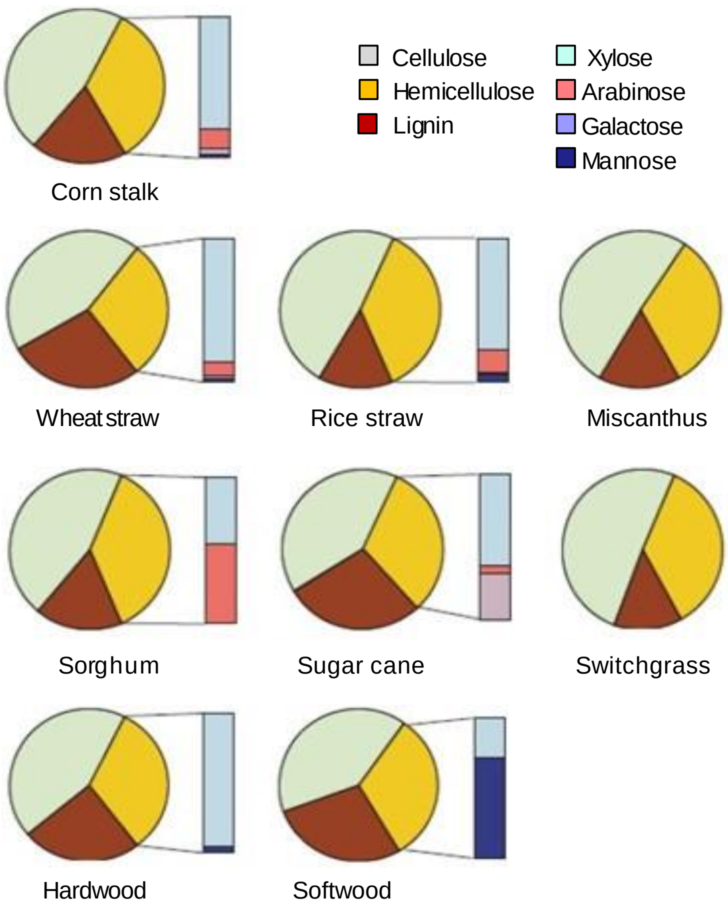
Cellulose : 38-50%

- Most abundant carbon form in biosphere
- Long polymer chains of β-linked glucose, good feedstock.



Composition and Structure of Lignocelluloses.

Cellulose and hemicelluloses are the abundant polysaccharides of lignocellulosic biomass:

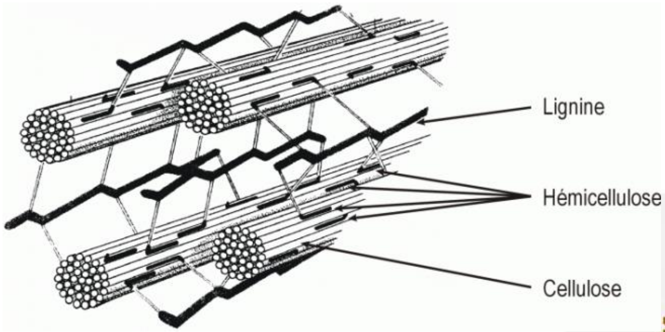


- Cellulose (15-40%)
- Lignines (15-30 %)
- Hémicelluloses (20-40%)

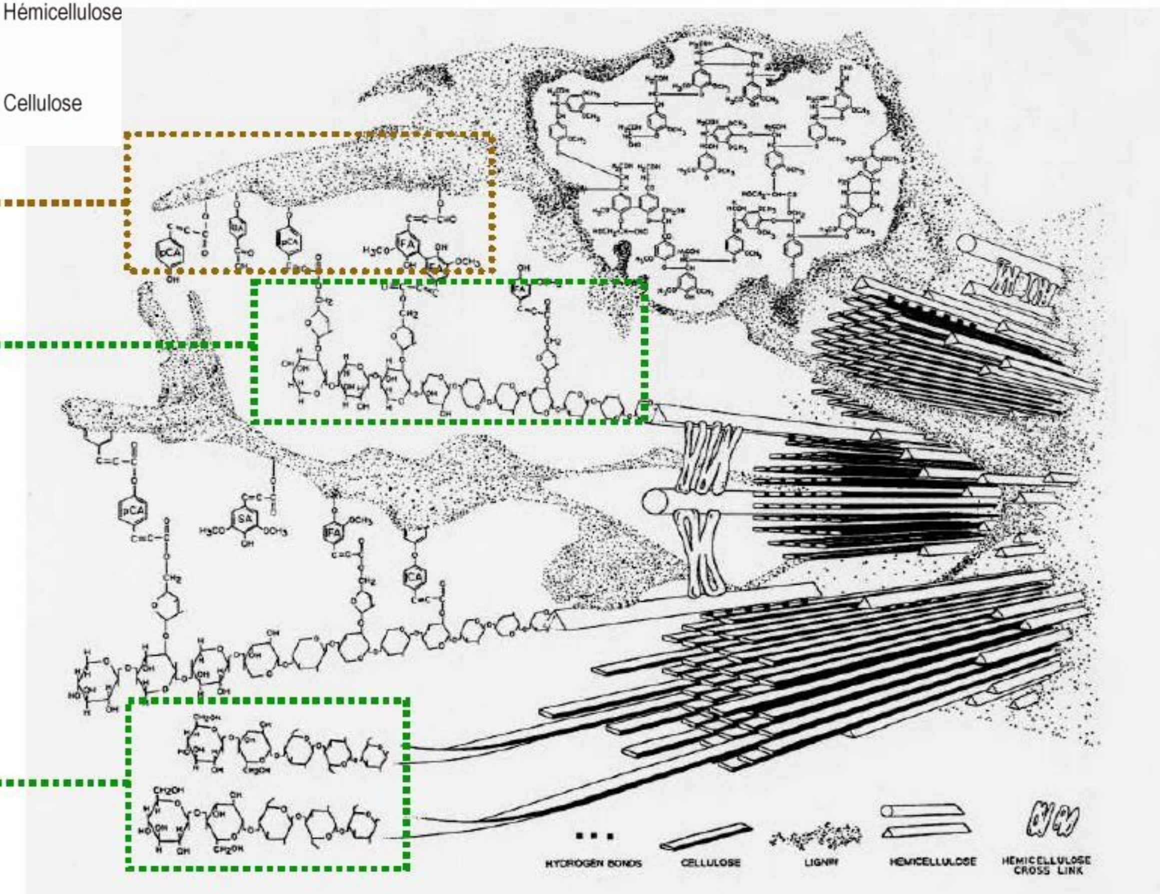
On dry matter

Pauly et Keegstra, 2018

Structure of Lignocellulosic Cellular Wall.



Schematic representation of secondary wall of grasses



Lignines

Polysaccharides

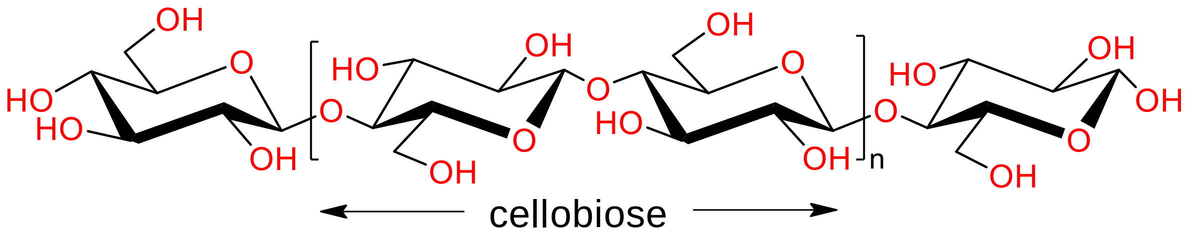
- **Hémicelluloses** (xylanes, mannanes, xyloglucanes, arabinogalactanes)
- **Pectines** (galacturonanes, arabinanes)
- Hétéropolymères C5 +/- C6
- **Cellulose**
- Homopolymère (C6)

Source: Bidlack et al.

Constituents of Biomass – Cellulose.

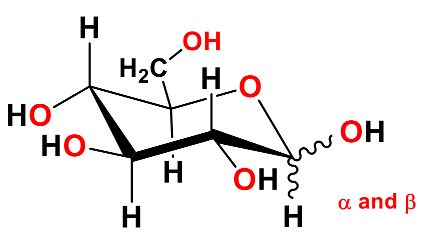
Cellulose: A polymer of glucose units in β-1,4 linkages, is a linear molecule consisting of 1,000 to 10,000 β-D-glucose units with no branching. Neighboring cellulose chains form hydrogen bonds leading to the formation of microfibrils with partially crystalline parts (simplified in the figure). Hydrogen bonding among microfibrils forms microfibers and microfibers react to form cellulose fibers.

Cellulose fibers usually consist of over 500,000 cellulose molecules.

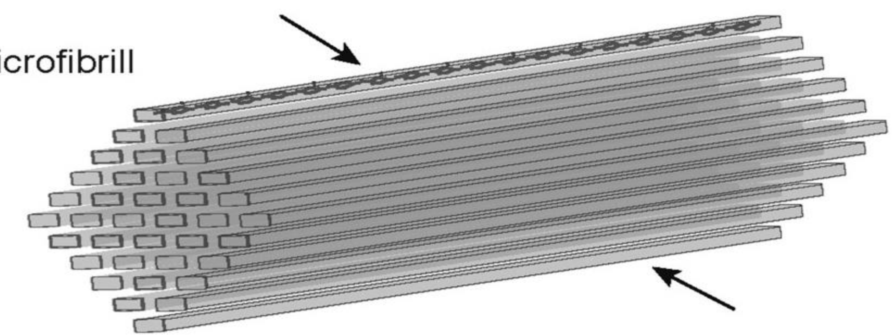


Linear polymer

glucose

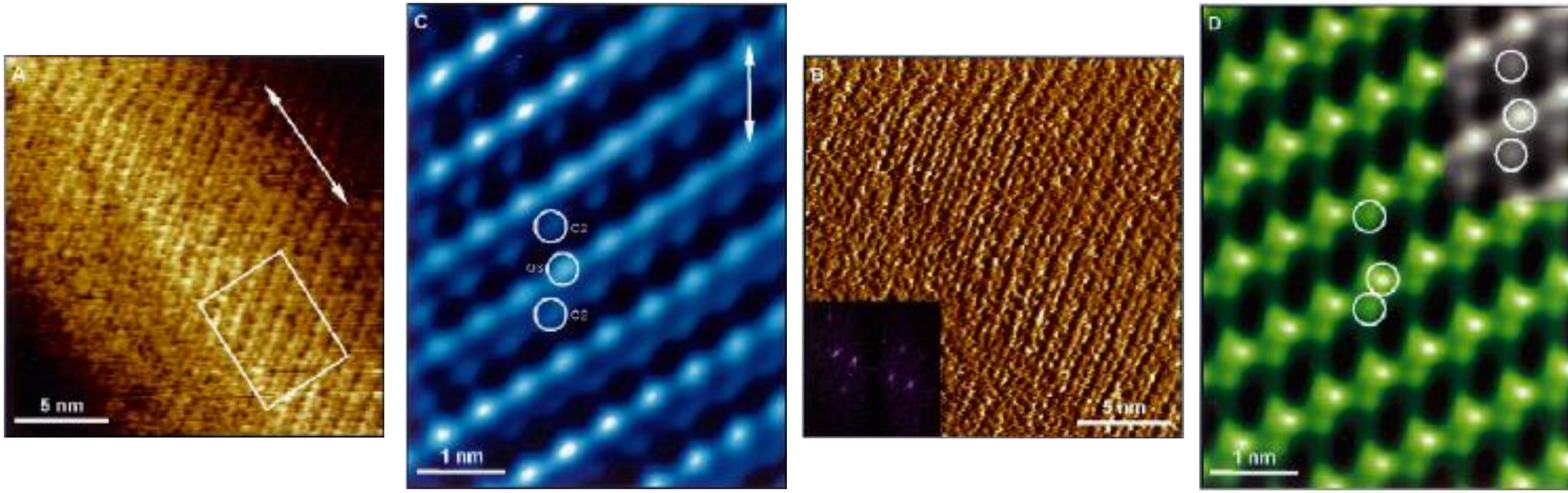


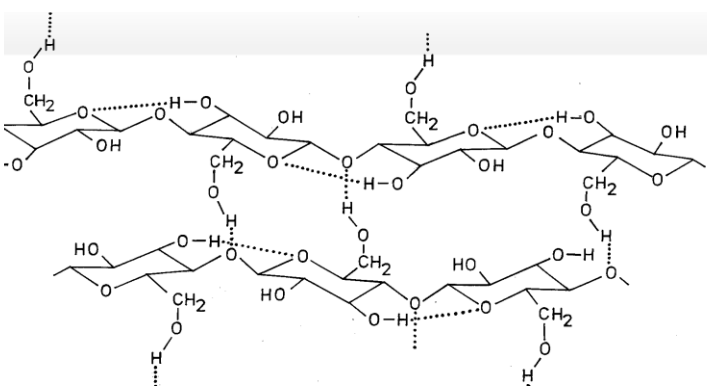
Cellulose microfibrill

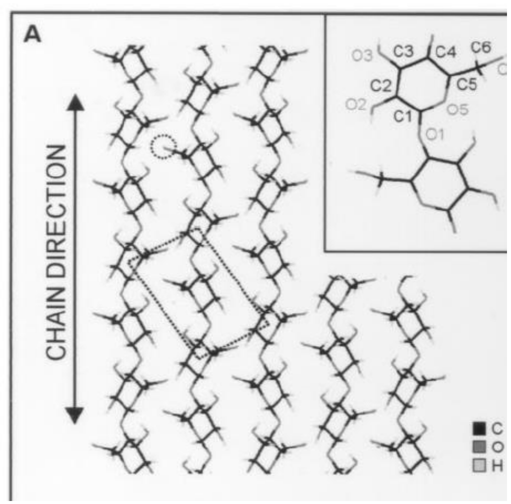


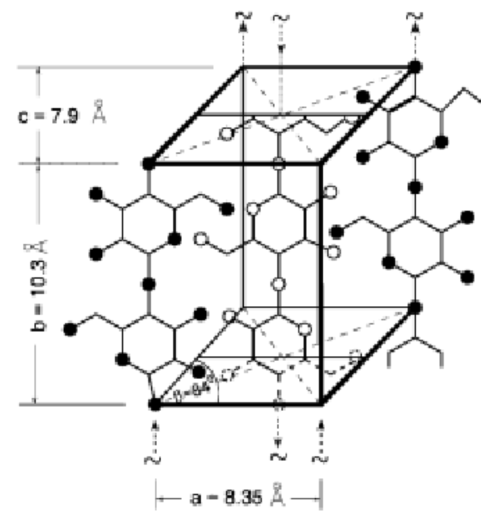
Horn et al. Biotechnology for Biofuels 2012, 5, 45.

High Resolution AFM Images of Surface of a Cellulose Crystal.









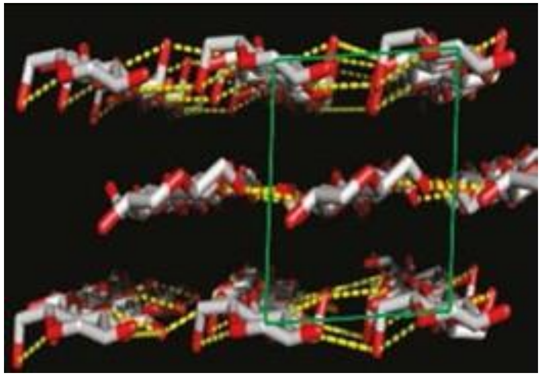
Allomorphs of Cellulose.

Cellulose I = native crystalline structure of cellulose

Two allomorphs formed by parallel chains aligned side-by-side via hydrogen bonding in flat sheets

- (triclinic unit cell)
- (monoclinic unit cell)

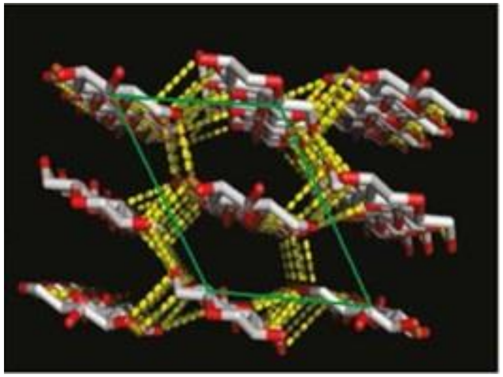
Conversion of cellulose I in cellulose II occurs through technological treatments (ex. ionic liquid pretreatment)



Ionic liquid

→

pretreatment



Cellulose I_{β} **Cellulose II**

Cellulose Crystals.
Monocline System: a ≠ b ≠ c; $\alpha = \gamma = 90°C$

Type	Source	Dimension nm			
		a	*b*	*c*	β, degree
Cellulose I	cotton	0.823	1.030	0.790	83.3
Cellulose II	cotton mercerized viscose fiber	0.802 0.801	1.036 1.036	0.903 0.904	62.8 62.9
Cellulose III		0.774	1.030	0.990	58.0
Cellulose IV		0.812	1.030	0.799	90.0

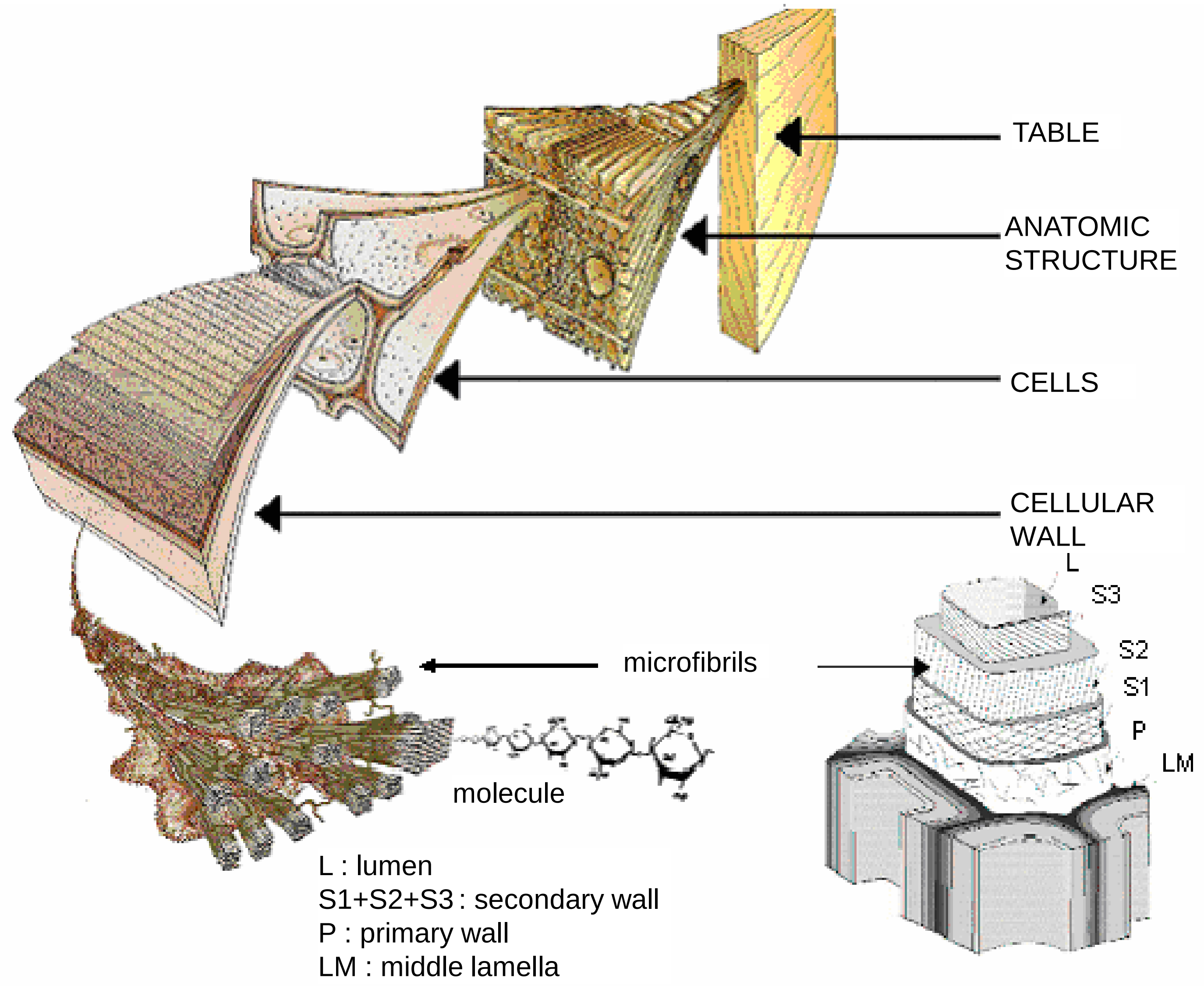
Cellulose I **Native conformation, molecules aligned along the b axis of unit cell**

Cellulose II with **Is formed following a strong swelling, due to for example treatment of NaOH at almost 15% concentration. It is seen in regenerated cellulose or/and mercerized cellulose.**

Cellulose III **Is produced when the native is treated with liquid ammonia (NH_3) or diamines by dry evaporation of swelled substance.**

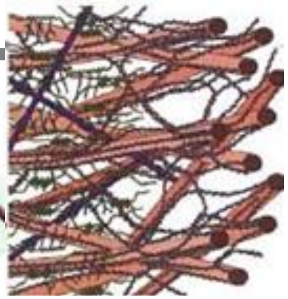
Cellulose IV: **Is generated when cellulose is treated with heat and glycerol or glycols.**

Different Levels of Lignocellulose Organization.

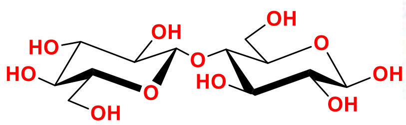


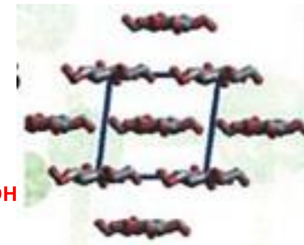
Lignocelluloses: Sources of Fibers at Different Levels.

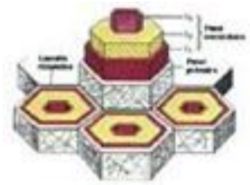
Hemicelluloses polymer of **pentoses** and **hexoses**, with esterification



Carpita & Mc Cann (2000)







Cellulose: polymer of β–glucose

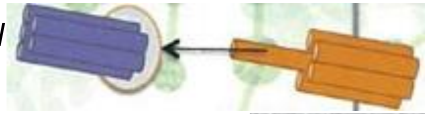
Cellulose crystallite of Φ = 3-5 nm

Vegetal wall 1-10 μm Exo-cellular composite

Tissue (fiber): 20-40 μm Alveolar composite

Organ: Stem Alveolar composite

microfibril



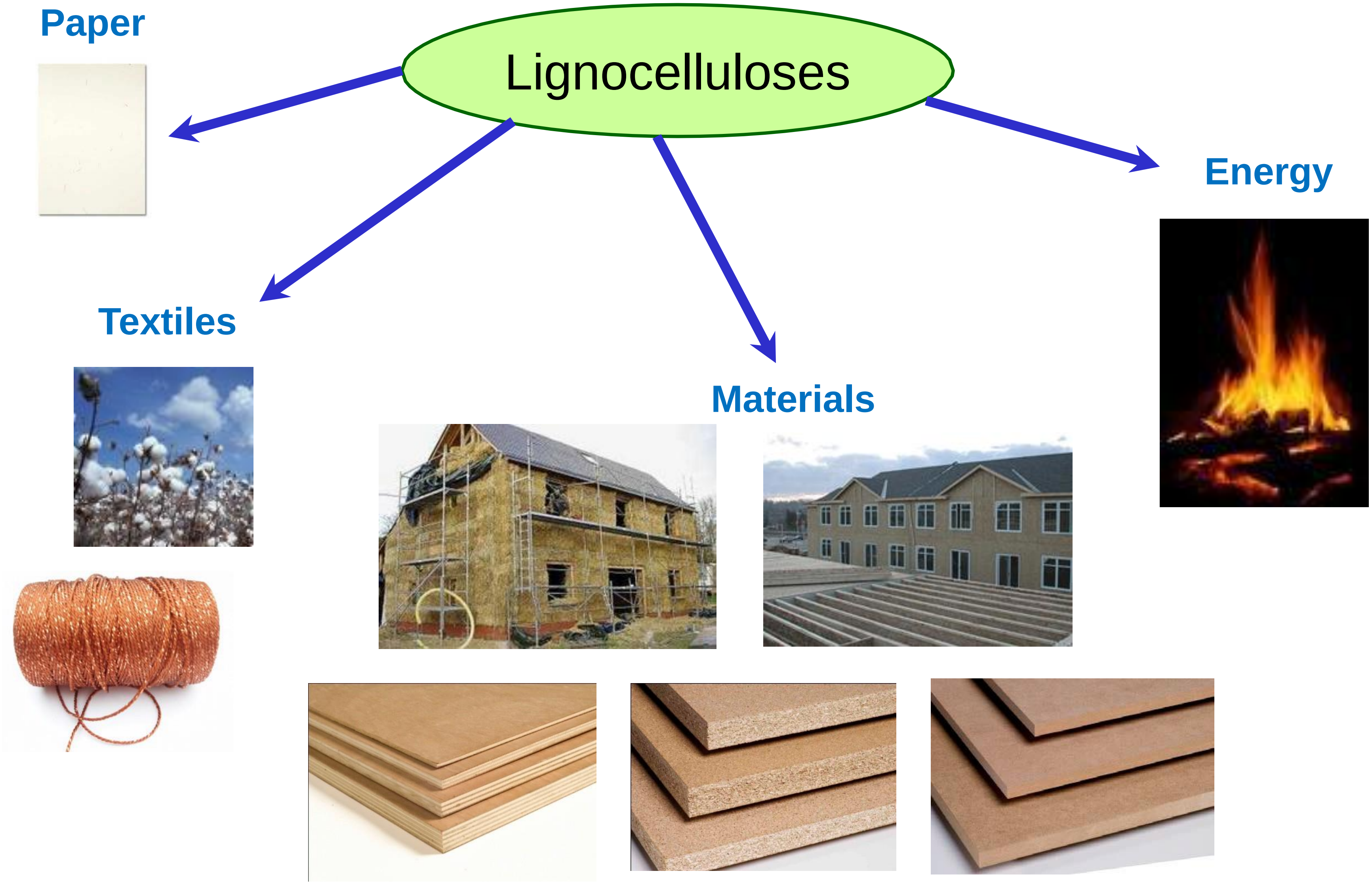
p-coumaric, coniferic, sinapilic alcohol

Extracellular reticulation

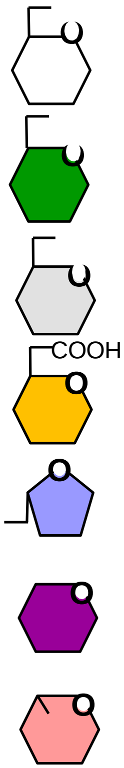
Cotton fiber

hemp *(Helbert)*

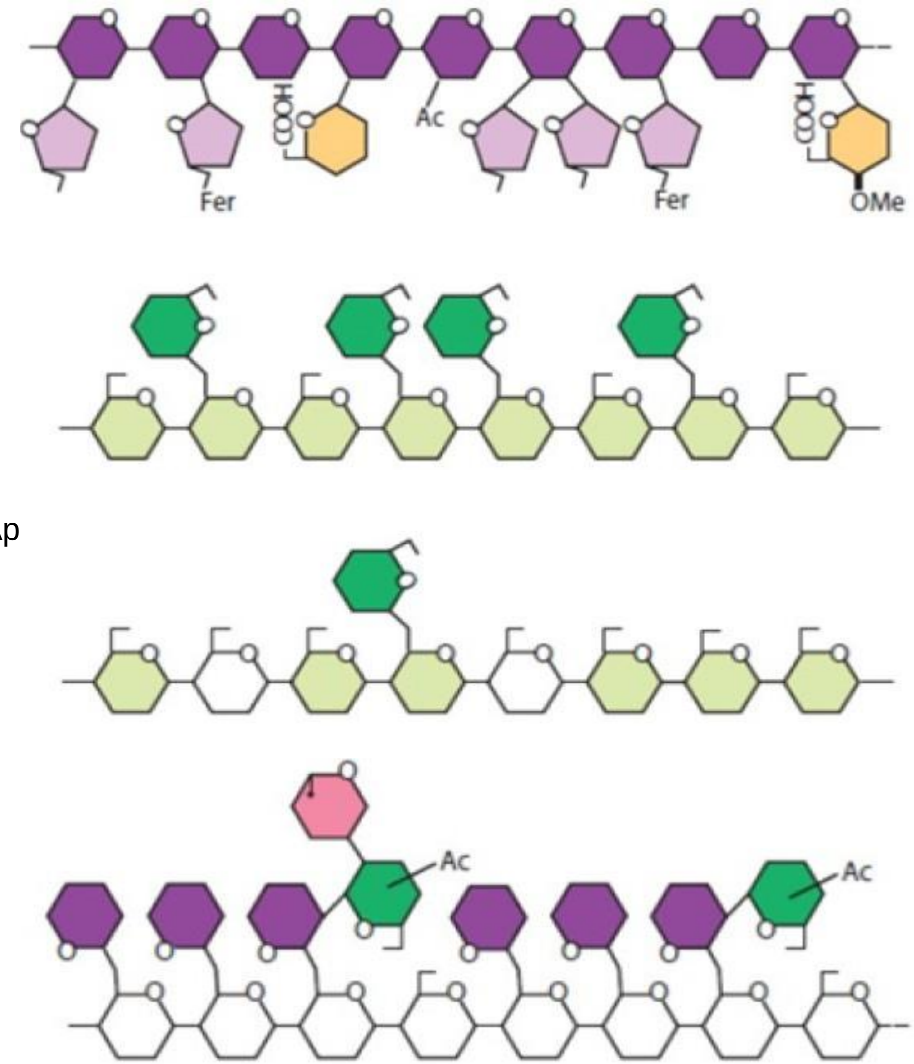
Traditional Uses of Lignocelluloses.



Constituents of Biomass – Hemicelluloses.



- D-Glucose Glcp
- D-Galactose Galp
- D-Mannose Manp
- D-Glucuronic acid GlcAp
- L-Arabinose Araf
- D-Xylose Xylp
- L-Fucose Fucp



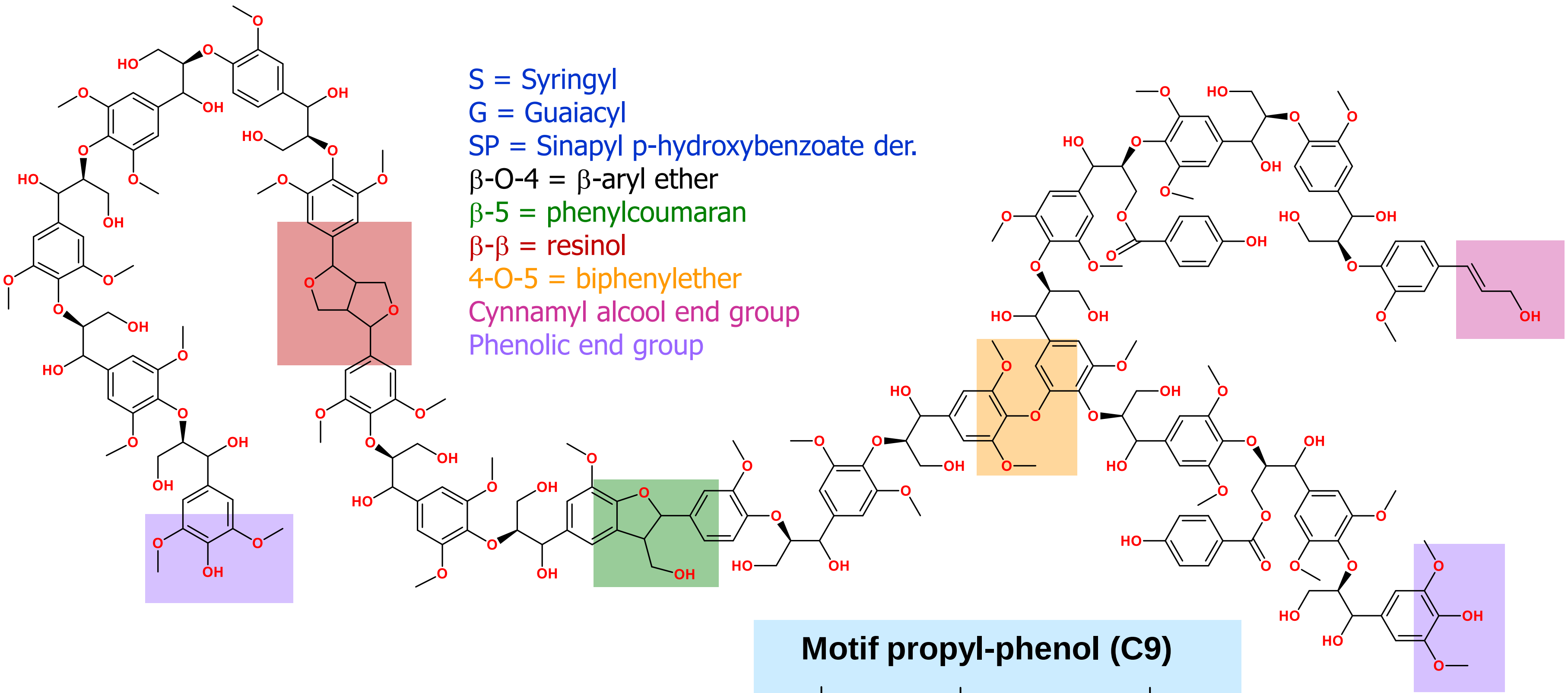
Glucurono arabinoxylanes

Galactomannanes

Galactogluco-mannanes

Xyloglucanes

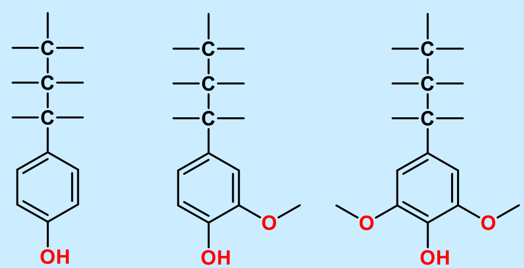
Lignin: amorphous cross-linked polymer with high molecular weight.



S = Syringyl
G = Guaiacyl
SP = Sinapyl p-hydroxybenzoate der.
β-O-4 = β-aryl ether
β-5 = phenylcoumaran
β-β = resinol
4-O-5 = biphenylether
Cynnamyl alcool end group
Phenolic end group

Motif propyl-phenol (C9)

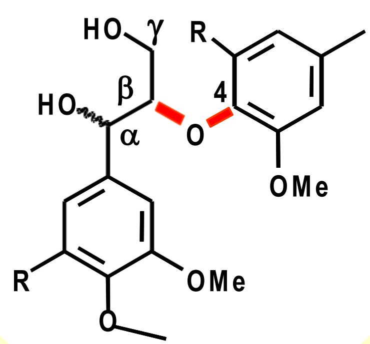
Monomers of lignin



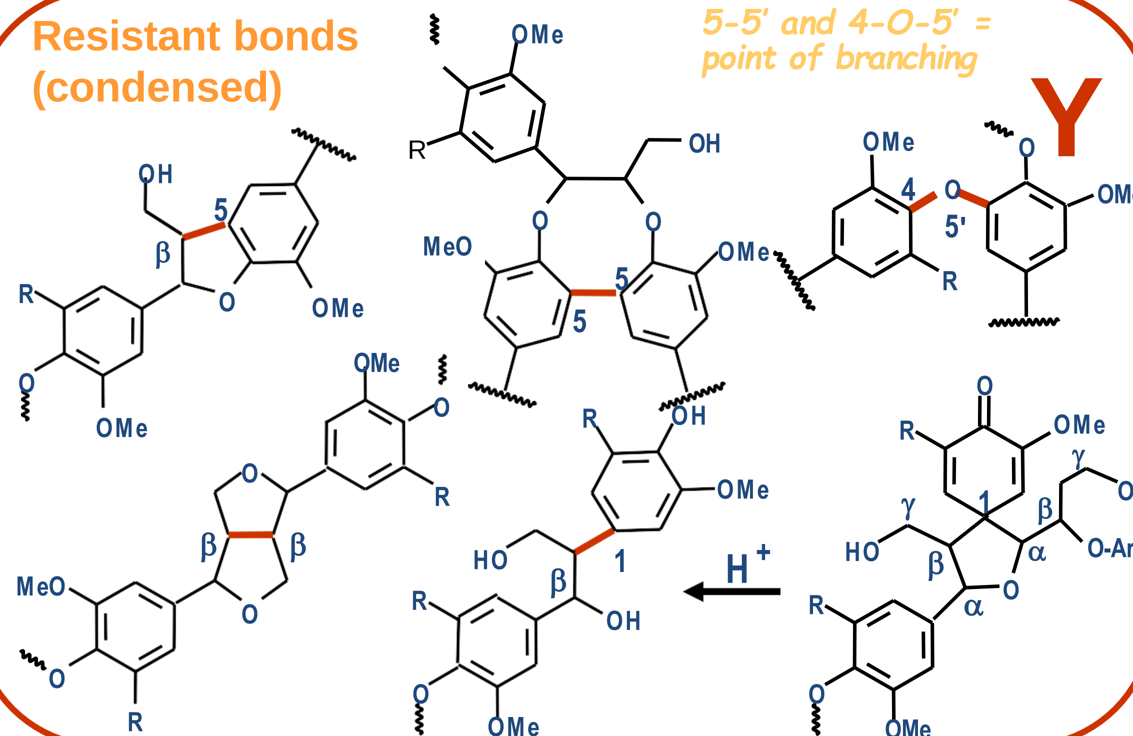
Annual plant | Resinous | Foliage

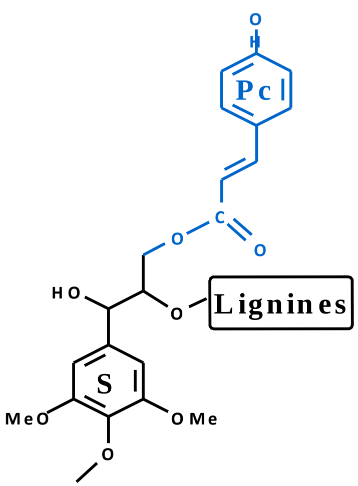
Labile and Resistant Bonds in Lignins

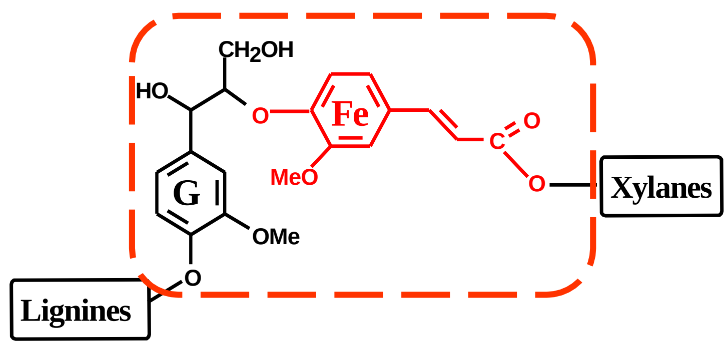
Labile bond
β-O-4 (ou 8-O-4)



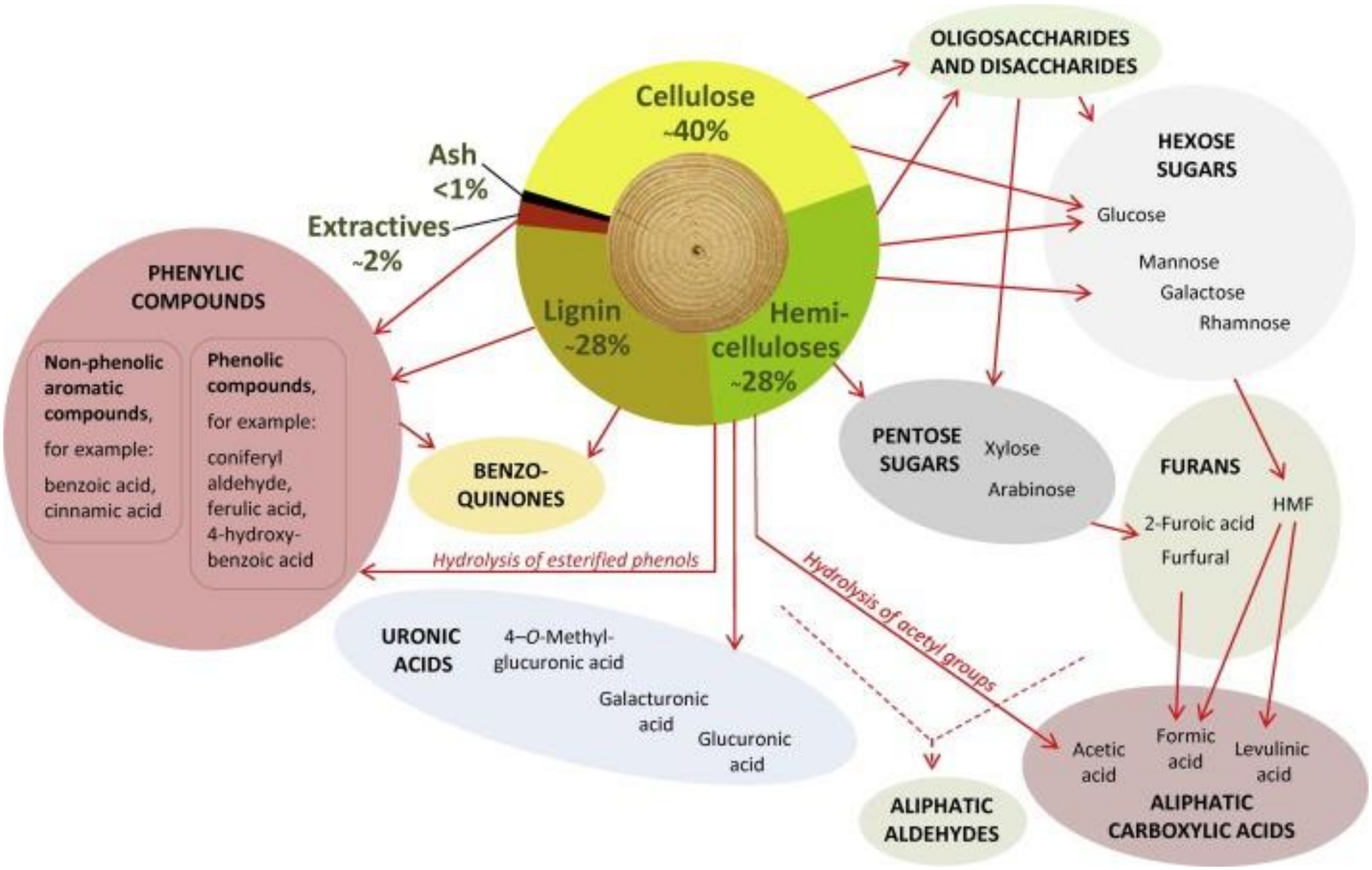
Resistant bonds (condensed)







Lignocellulose Fractionation.

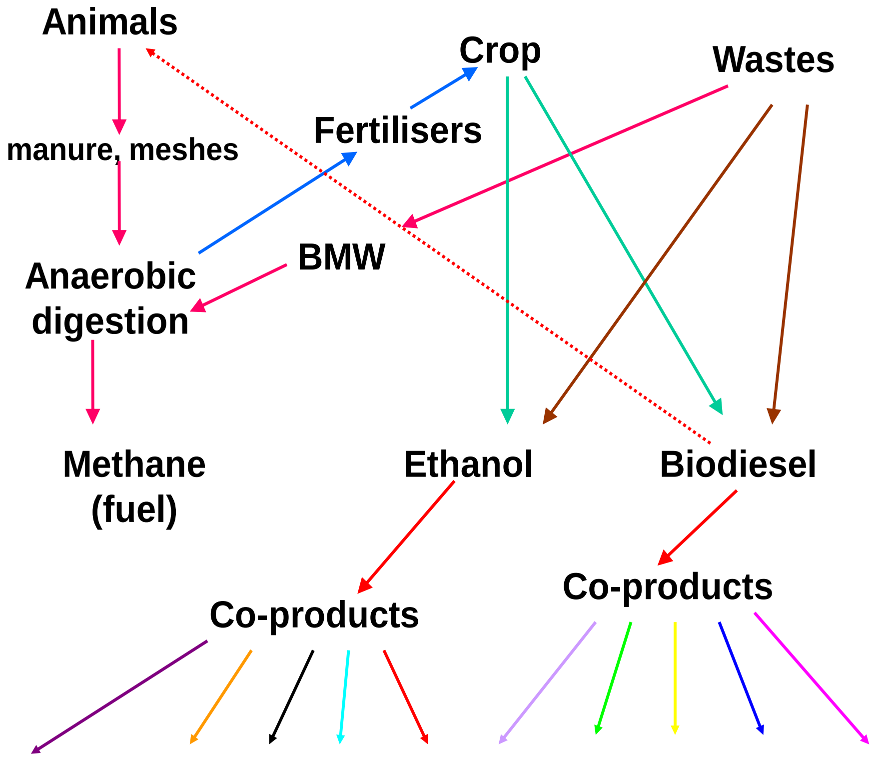


L. J.Jönsson, C. Martín Bioresource Technology 199, 2016,103-112

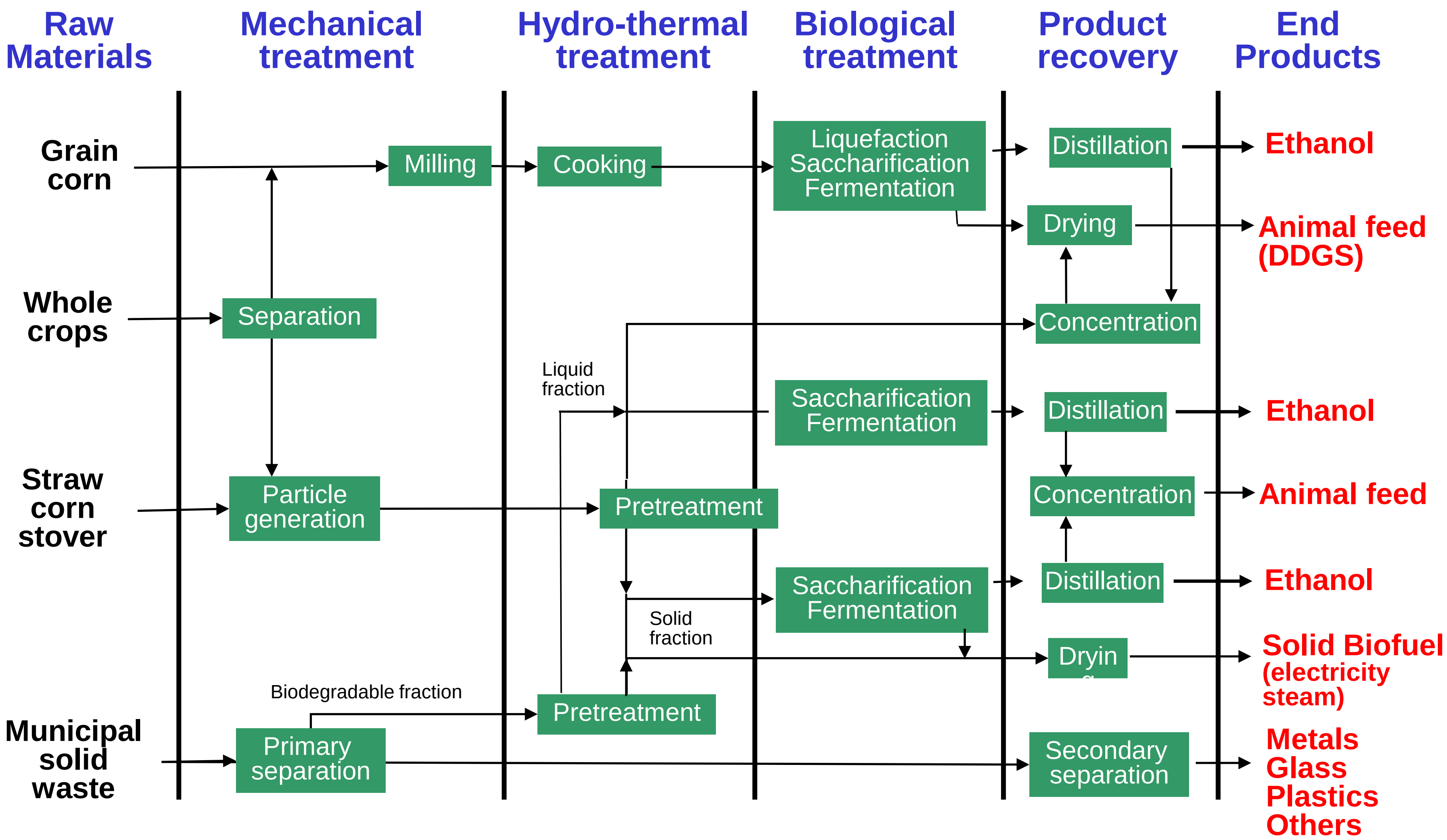
An Integrated Approach (Bio-refinery).

Using feedstock from agriculture, forestry and organic wastes we can obtain:

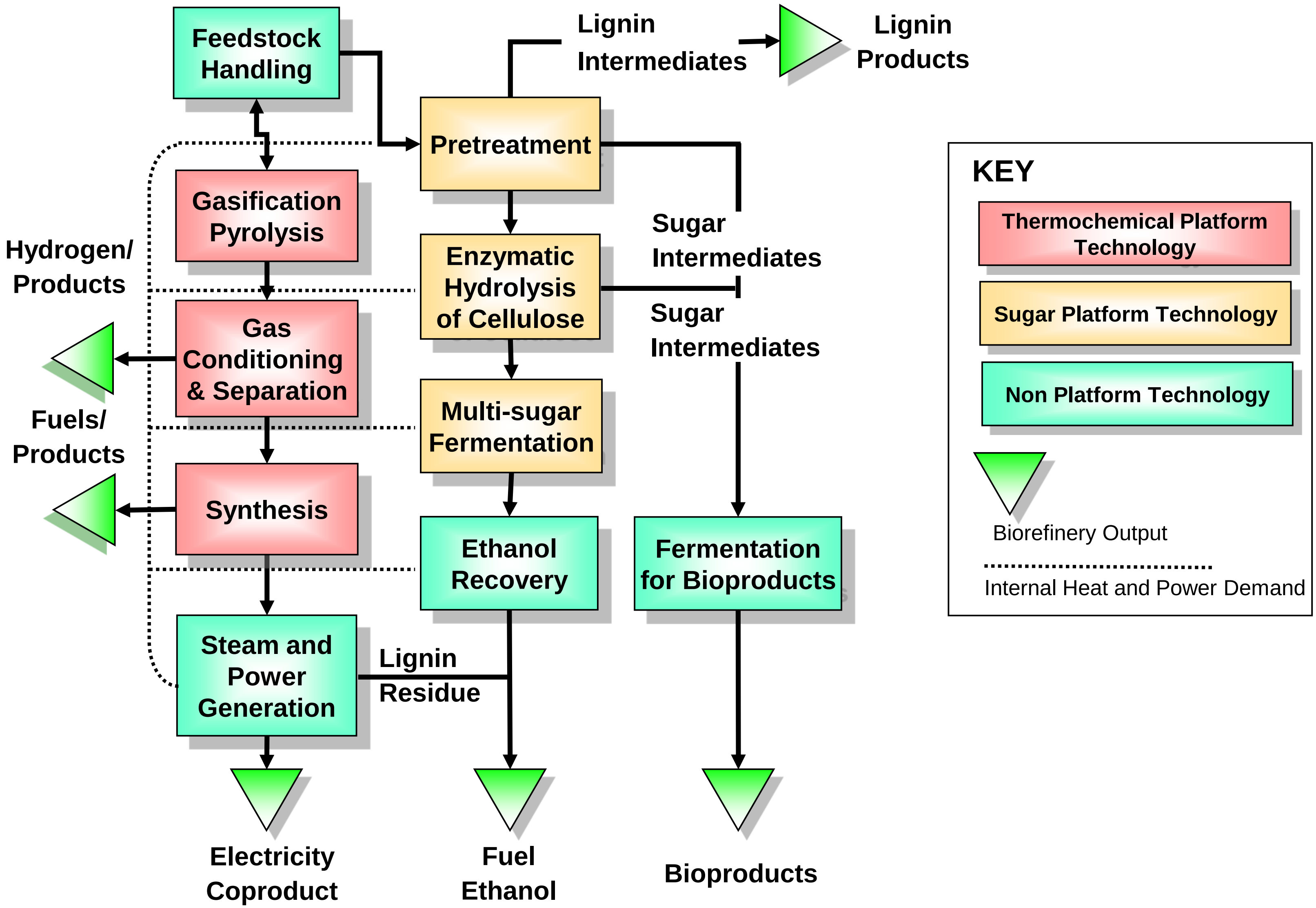
- Fuels, fertilizers and animal feed
- Thousand of potential co-products (furfural, xylitol, carbon dioxide, lactic acid, glycerol, …..)
- Create a Bio-refinery
- An holistic view will be necessary!



Integrated Biomass Utilization System.



Schematic of an Integrated Bio-refinery.



Biorefining Definition.

- From IEA Bioenergy Task 42 on Biorefineries:
  - Sustainable processing of biomass
  - into a spectrum of marketable products and energy

→ Biorefinery: concepts, facilities, plants, processes, clusters of industries

→ Sustainable: maximising economics, social aspects, minimising environmental impacts, fossil fuel replacement, closed cycles.

→ Processing: upstream processing, transformation, fractionation, thermo-chemical and biochemical conversion, catalytic processes, extraction, separation, downstream processing

→ Biomass: wood & agricultural crops, wood, straw, organic residues, forest residues, aquatic biomass

→ Spectrum: multiple energetic and non-energetic outlets

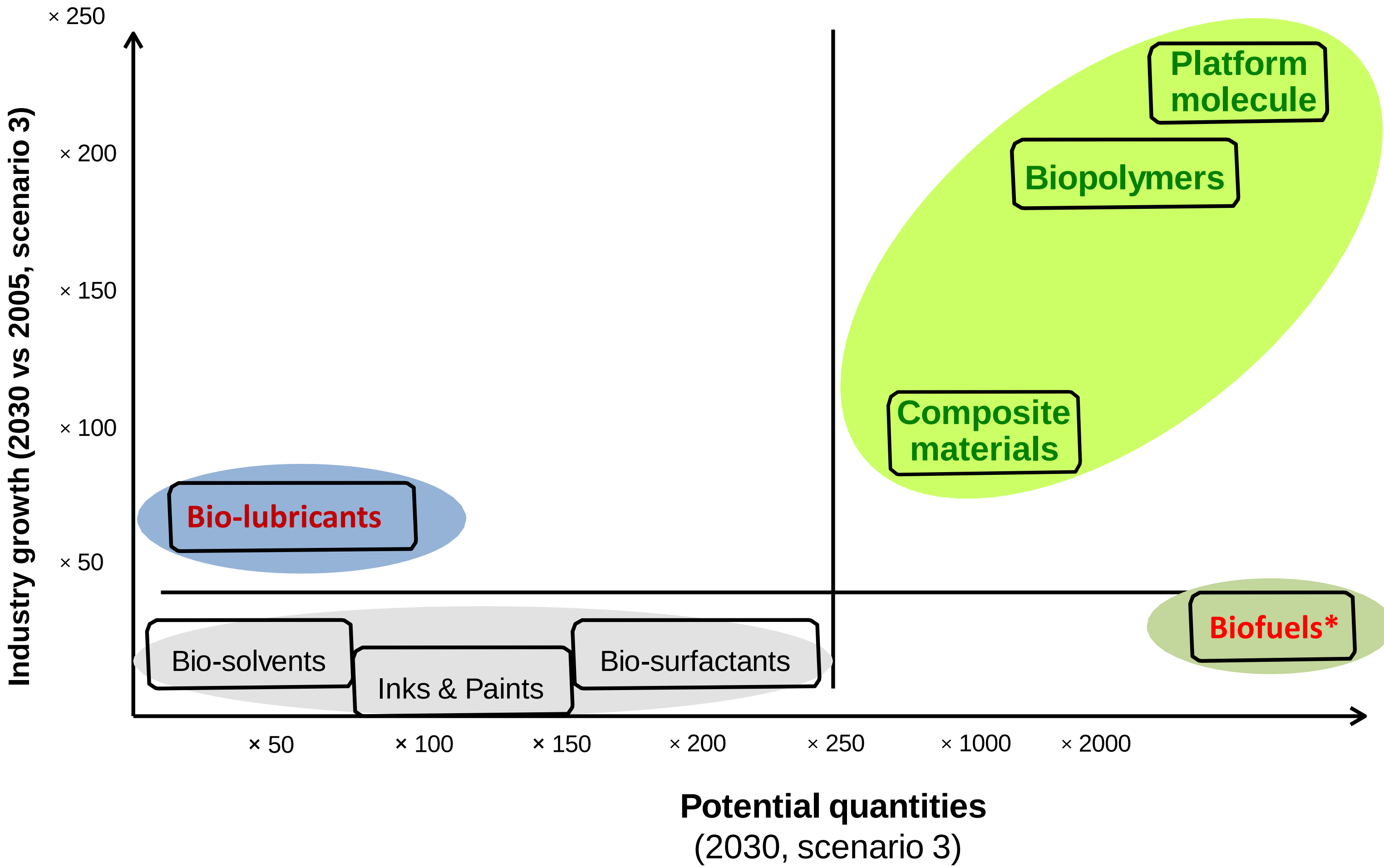
→ Marketable: a current market exists or a future market is expected to become available, taking into consideration both market volumes and prices

→ Products: both intermediates and final products, i.e. food, feed, materials and chemicals

→ Energy: fuels, power and heat

... Bio-sourced Molecules for Chemistry.

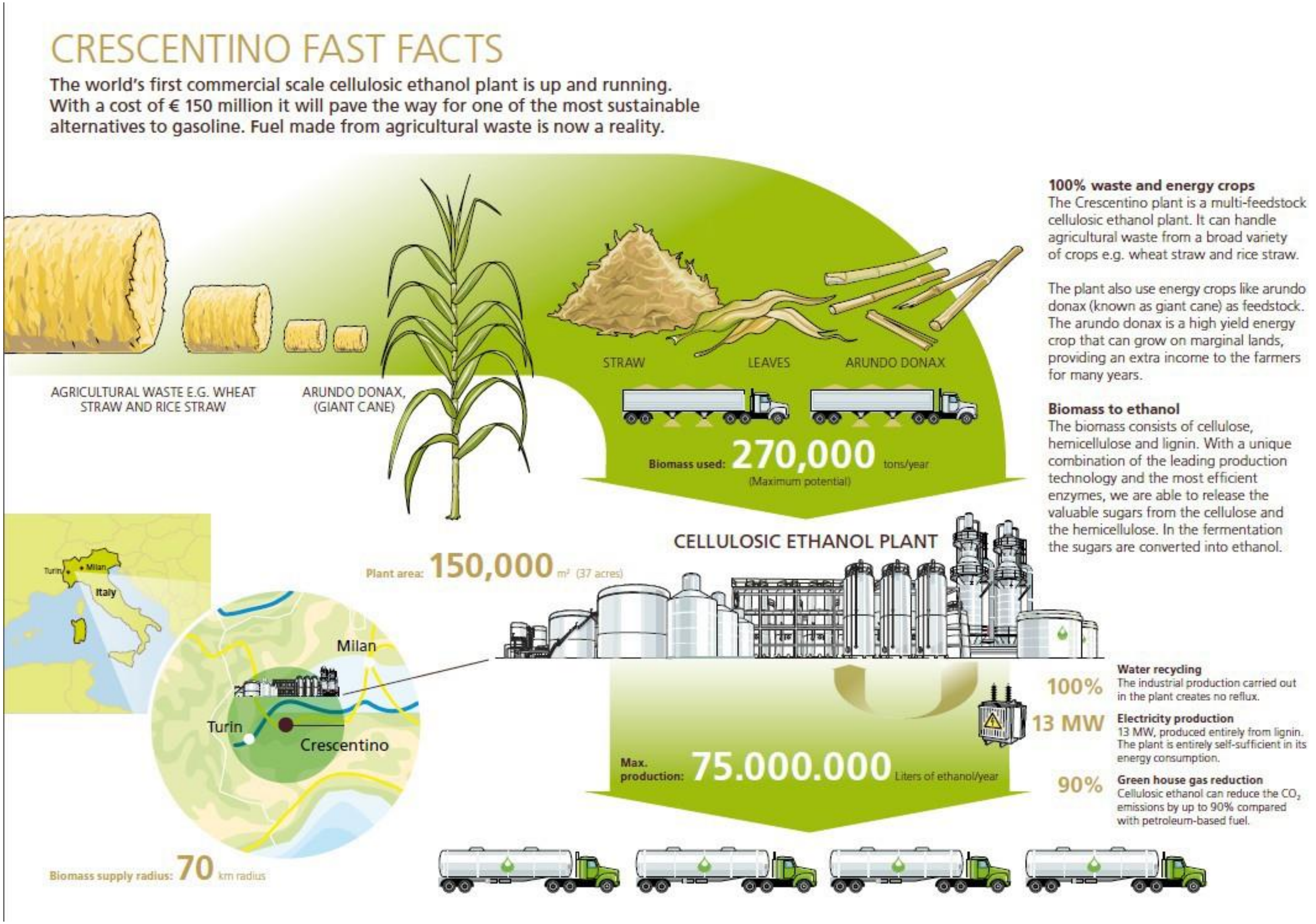
➢ Industry growth vs. potential quantities matrix:



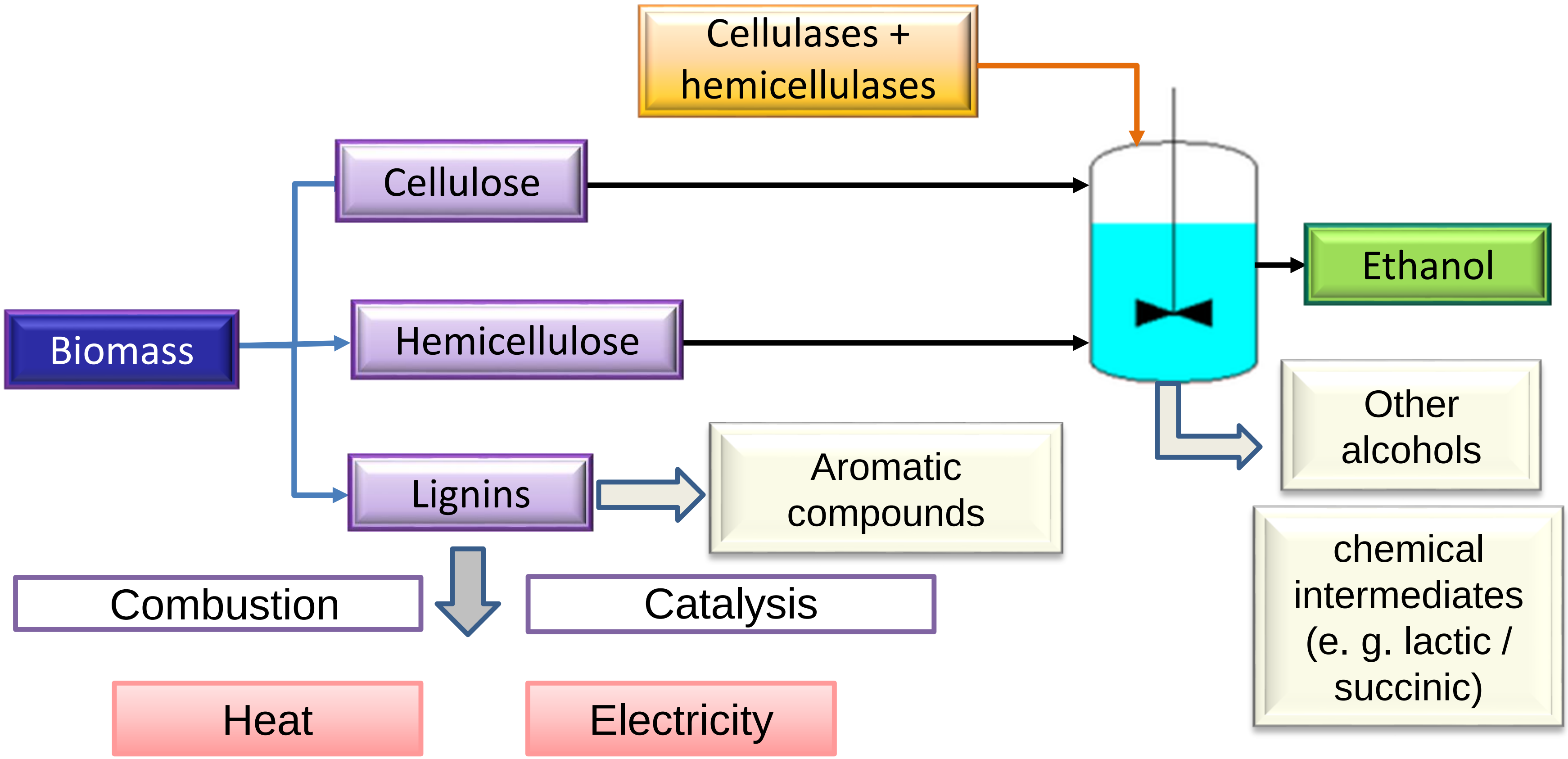
Alcimed

* data expressed in Ktep

Development of Lignocellulosic Bio-refineries.



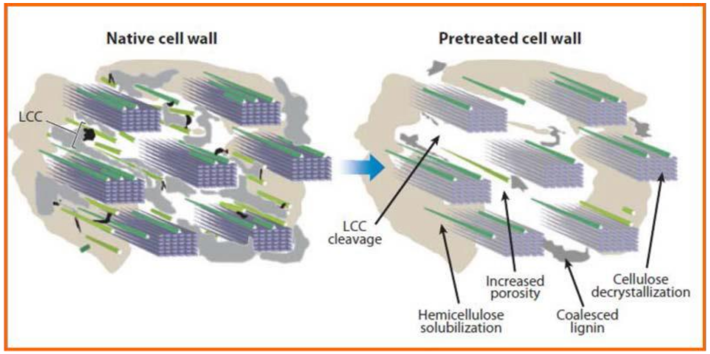
Essential Step of the Process: Fractionation.



Different Types of Possible Preprocessing.

Pretreatments

Physical	Mechanical	Chips
	Steam / CO_2 explosion	
	Ammonia Fiber Expansion (AFEX)	
Chemical	Organosolv	
	Ionic liquid	Cellulose, hemicellulose, lignin
	Acid	
	Alkali	
	Liquid hot water	
Thermochemical	Ozonolysis	Heavy oil
	Liquefaction	Bio-oil
	Pyrolysis	FT oil
	Gasification	Biogas
Biological	Anaerobic digestion	
	Fermentation	Chips
	Enzyme	




Raw unpretreated triticale straw

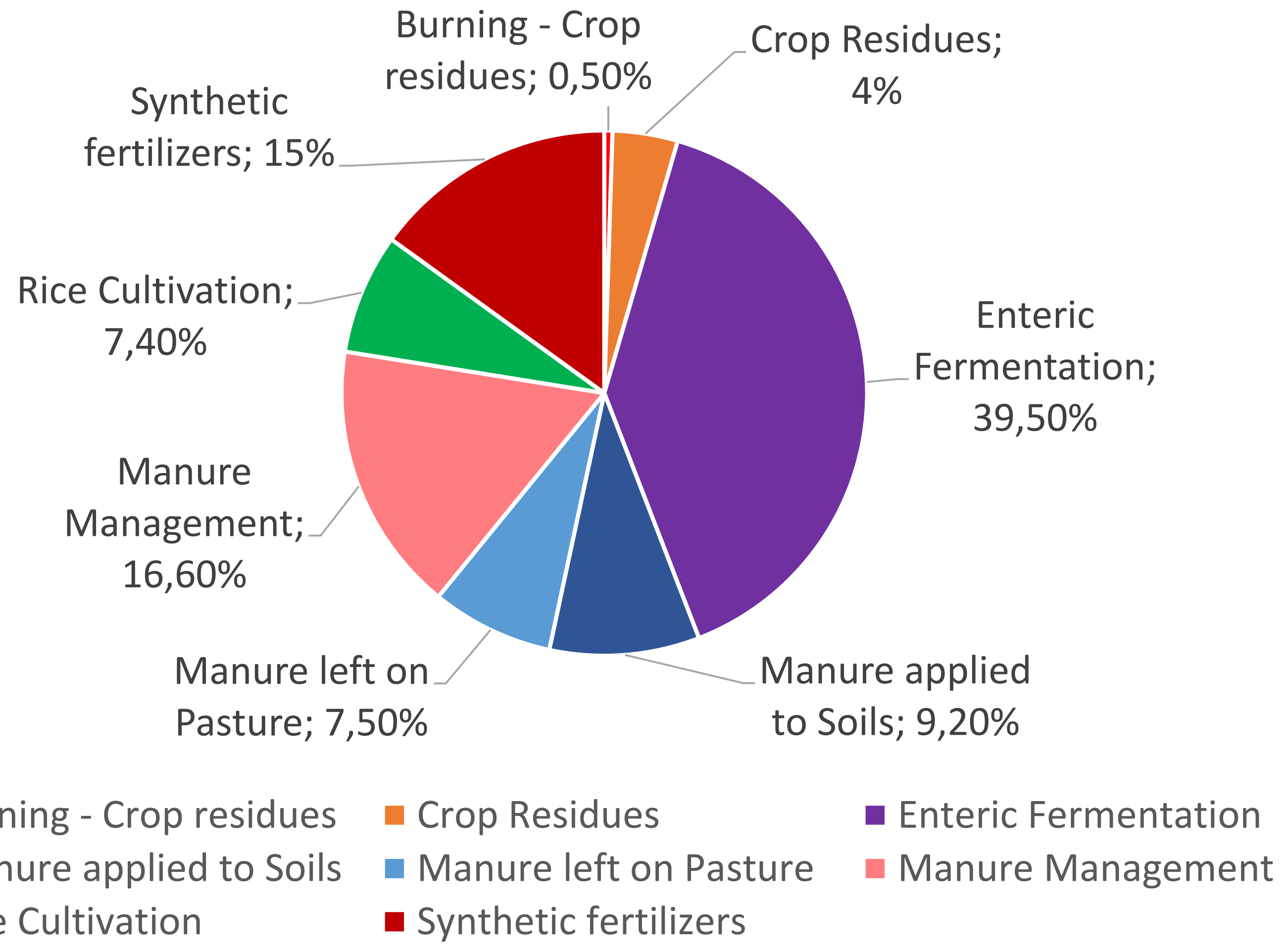

Steam Exploded triticale straw

Effect of steam explosion on the aspect of straw (http://lignofuel.wordpress.com)

Kumar et al. Industrial & Engineering Chemistry Research ***2009*** *48 3713-3729.*

Agriculture Emissions by Sector (CO_2 equivalent).

ITALY - Avearge 1990-2017



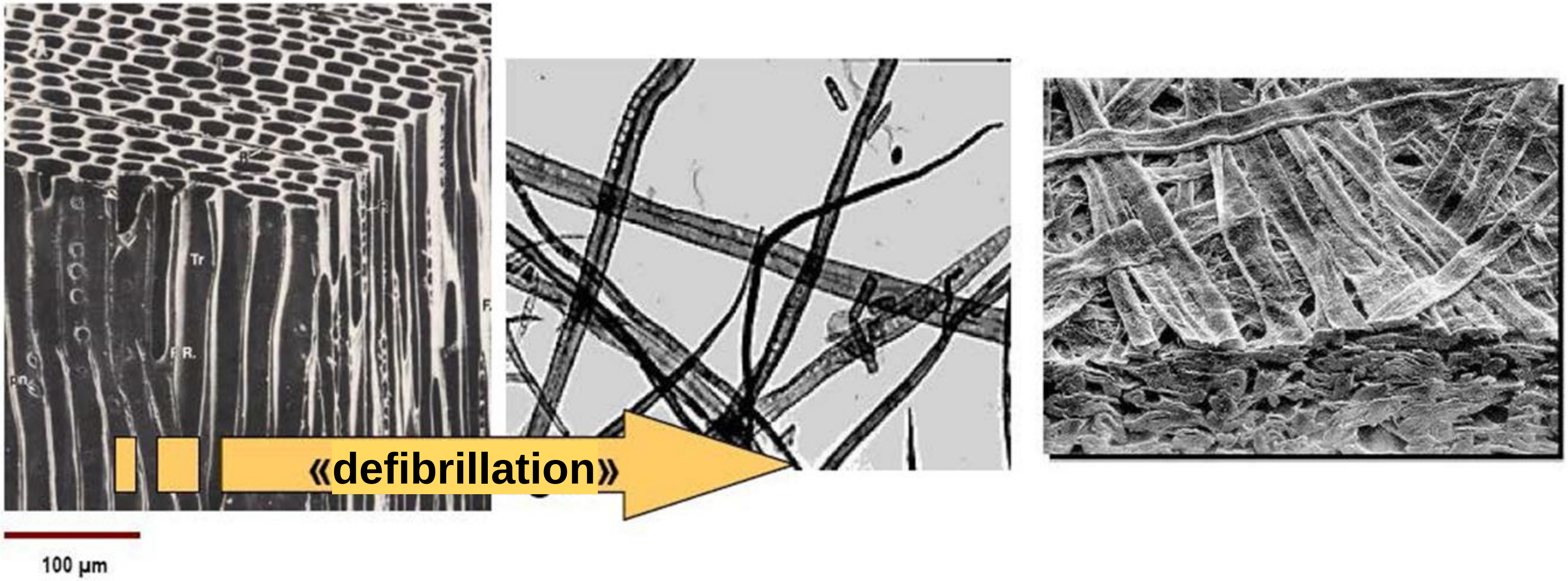
The Paper Process by Fractionation of Lignocellulose Biomass - Principle of manufacturing.

- III° century AC : invention of paper in Chine (from bamboo, linen and hemp)
- XV° century : invention of printing ⇨ trituration of cloths
- 1719 : The physic A. Ferchault de Réaumur suggested to emulate the insects for manufacture paper from wood:

«America wasp makes, to build their nest, some very thin paper fibers by extraction from common wood in their environment. They teach us how we can manufacture the paper from plant fibers, without using clots or tissues»

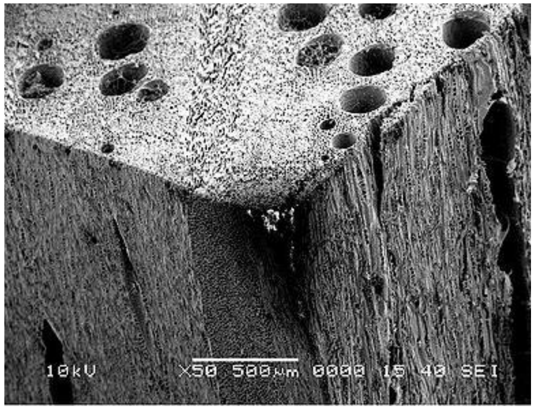
- 1844 : F.G. Keller invented the mechanical pulp of wood ⇨ start of the German paper industry.
- 1885 : Development of chemical pulp process.

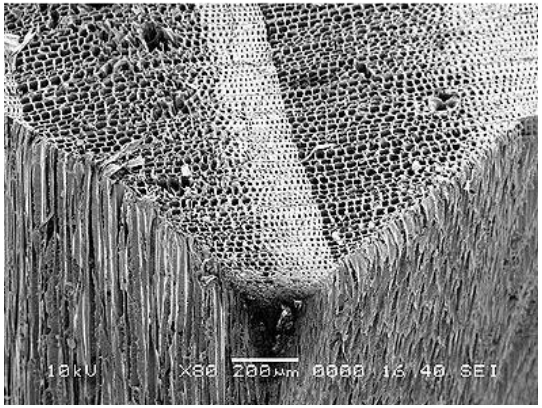
Manufacturing Principle of Paper Pulp.



Hardwood (oak)

Conducing cells = vessels





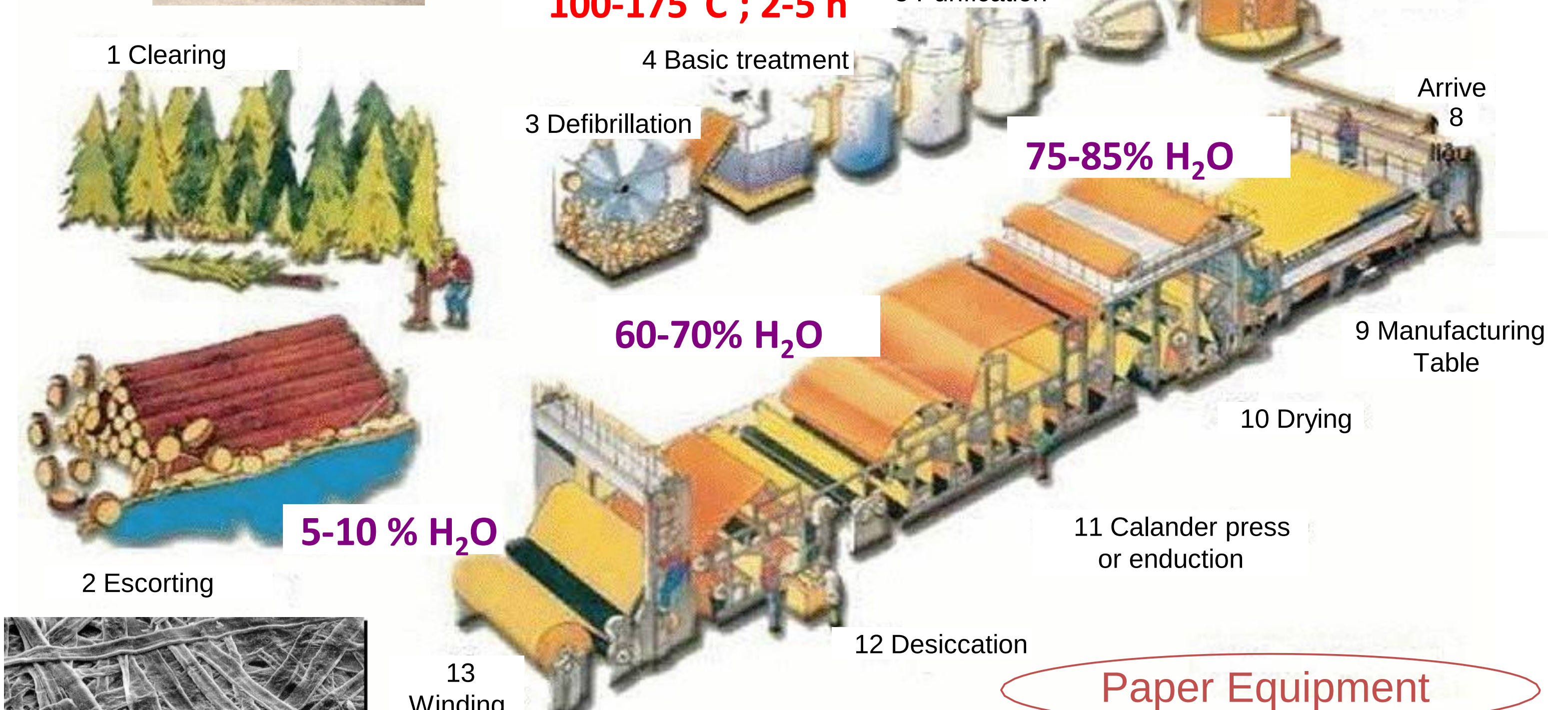
Softwood (pin)

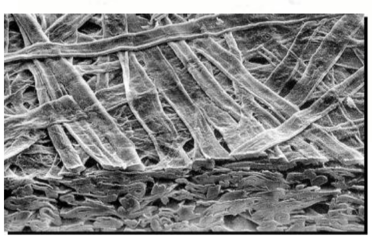
Conducting cells = tracheids

Characteristics of Fibers from Their Origin.

Fiber Source	Length (mm)	Diameter (microns)	L/D Ratio
Wood			
Softwood Pine	3.0	40	75
Hardwood Aspen	1.2	26	46
Non-Wood			
Bamboo	3.0	15	200
Rye Grass Straw	1.5	13	110
Kenaf (Bast)	2.6	20	130
Kenaf (Core)	0.6	30	33
Bagasse	1.5	20	75

Paper Manufacturing Technology.





Different Processes to Obtain Pulp.

Two routes to pulp

Defibrillation by shear
(millstone, discs)

cerig.efpg.inpg.fr

Mechanical pulp

- Journal paper
- Sanitary use paper

Delignification
(cooking in the presence of chemical reagents)

www.novibond.com

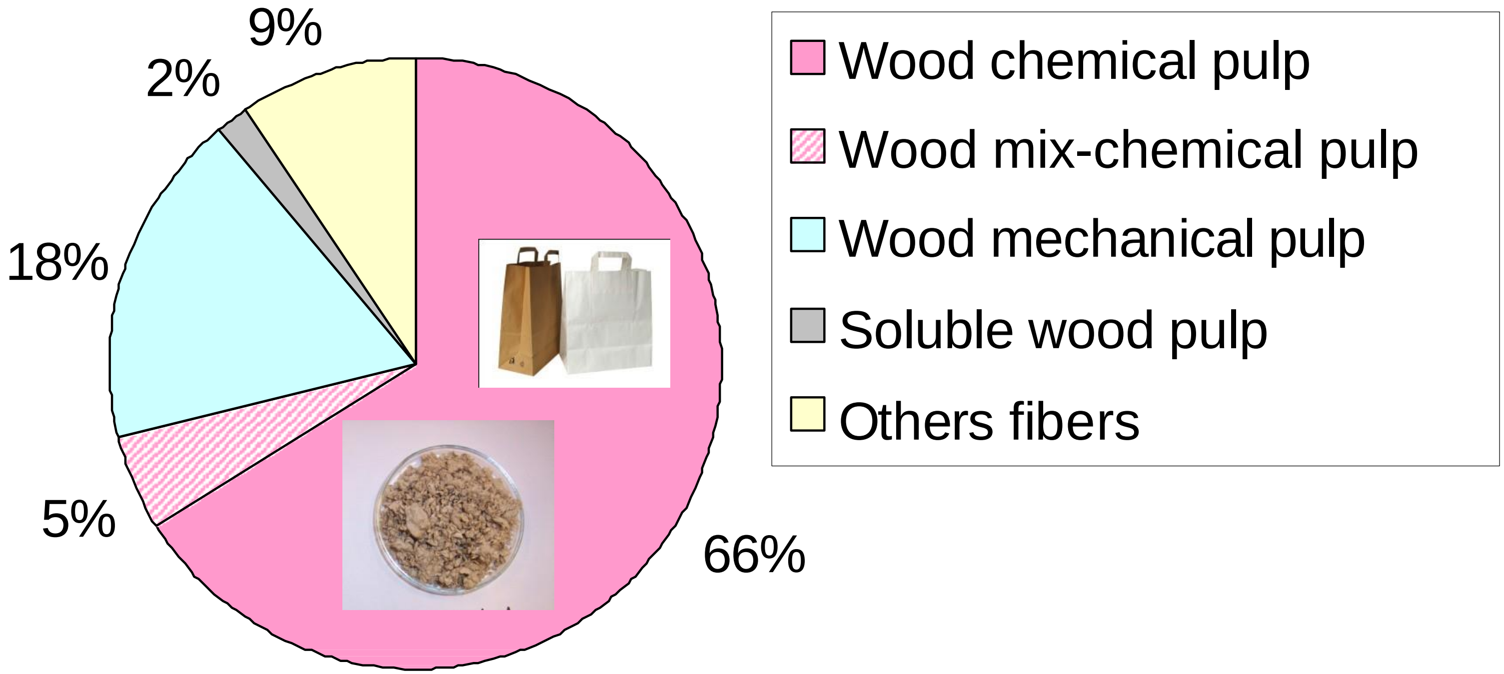
Chemical pulp

- Packaging / cardboard
- Impression paper
- Writing paper
- Special papers

World Production of Different Types of Pulp.

World Production of paper pulp : 190 Mt .

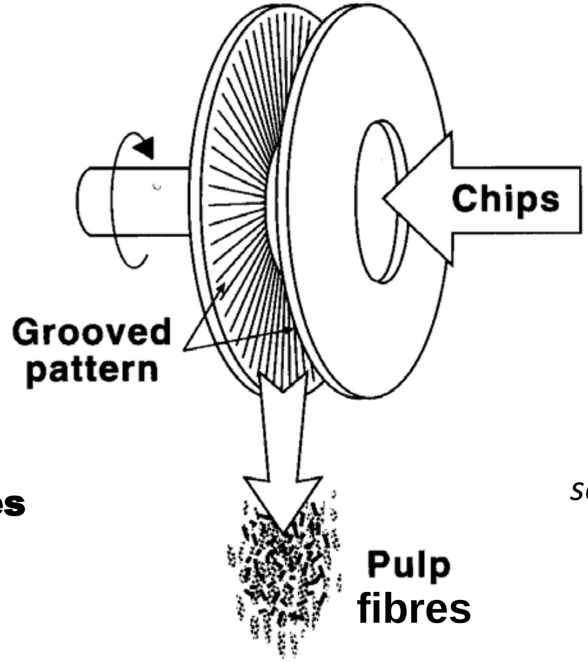
Mainly wood chemical pulp.



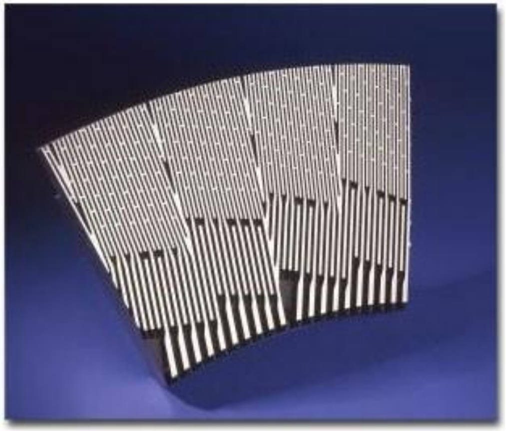
Source FAO 2007

Mechanical Process.

- Mechanical pulp of millstones (defibrillate by mill)
- Mechanical pulp of chips (defibrillate by disk)
- Thermo-mechanical pulp TMP (drying > 100°C then defibrillate under pressure)
- Chemo-thermo-mechanical pulp CTMP (hydroxide and sodium sulfite > 100°C then defibrillate under pressure)



disks rainurés



secteur d'un disque de raffinage

(Sundholm, J. (1999)

Chemical Process.

www.novibond.com

Paper Mills

Two main chemical processes

Use of sulfured reactive chemicals

Dissolution of about 50% of wood

Sulfate Process (Kraft)

Black liquor

- Great versatility
- Pate difficile to blanching
- Packaging and printing paper

Sulfite (bisulfite) process

Brown or red liquor

- Non adapt for softwood (pine)
- Pate facile to blanching
- More adapt for special papers (ex. handkerchiefs) and cellulose derivatives (cellophane, cellulose acetate, …)

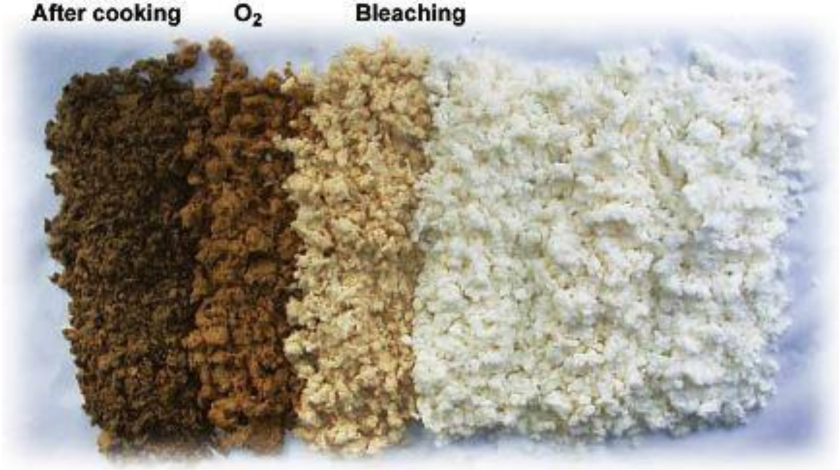
Sulfate wood pulp (= Kraft process) : 90 % of chemical pulp produced and consumed in Europe.

Bleaching Process.

Blanching of dark pulp.

Objective : degrade the residual lignin and convert the chromophore groups

⇨ paper more blank and less susceptible to yellowing



Use of gaseous chlorine replaced by two technologies:

- ECF (Elementary Chlorine Free) = blanching of products with chlorine dioxide and hydrogen peroxide.
- TCF (Totally Chlorine Free) = blanching with ozone and hydrogen peroxide.

⇨ decrease of organo-chloro side compounds in effluents.

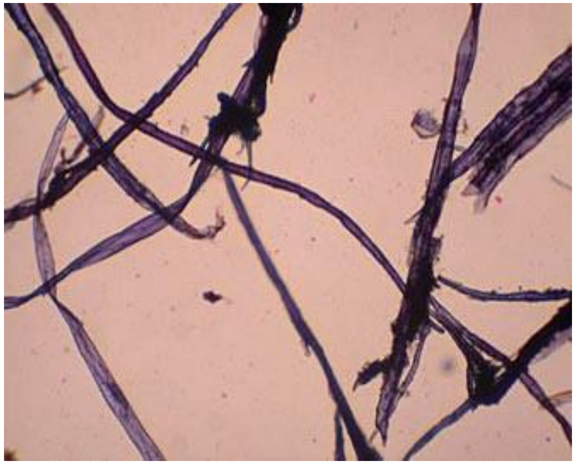
⇨ use of optical brighteners.

(Source : intra-science.com)

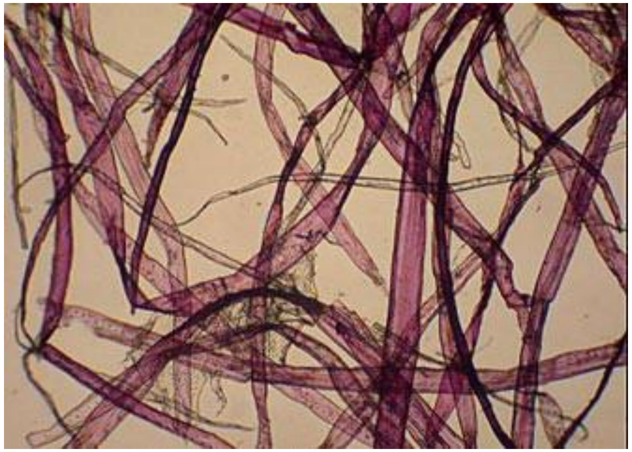
Mechanical Route vs. Chemical Route.

Mechanical pulping

- ***Energy consumption:*** 1000 KW/ton of pulp
- ***Yield (from wood material):*** 95%
- ***Fiber length:*** Fragments of different dimension
- ***Paper strength :*** Low
- ***Production in Europe:*** 32%
- ***Production Cost:*** *Lower*



CTMP pulp from resinous

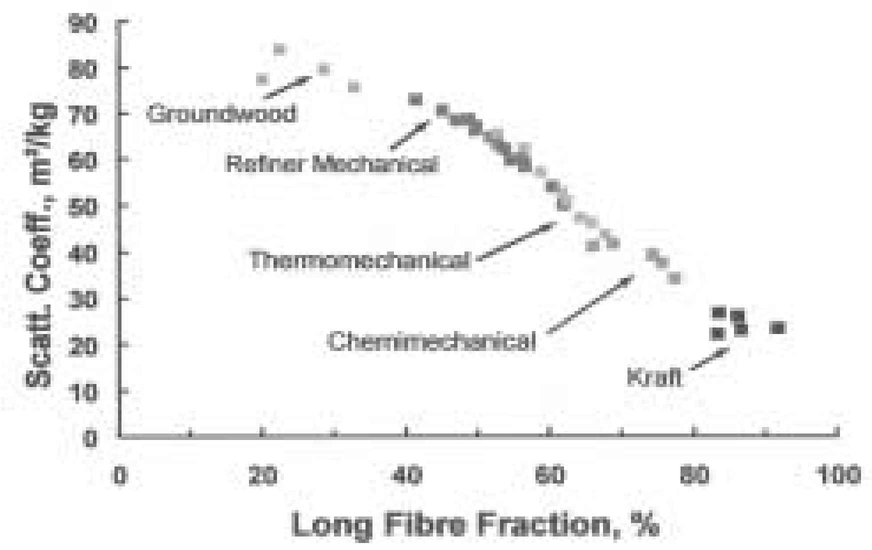


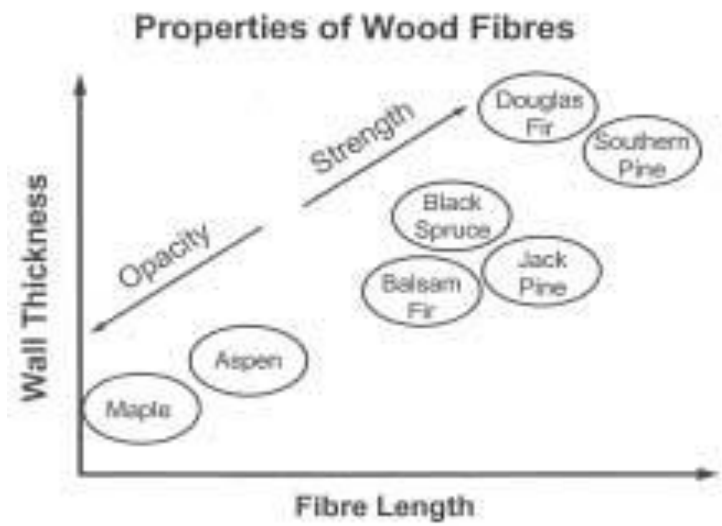
Mix of chemical pulp of hardwood and softwood

Chemical pulping

- ***Energy consumption :*** self-contained
- ***Yield (from wood material):*** 45%
- ***Fiber length :*** Mainly long fibers
- ***Paper strength :*** High
- ***Production in Europe:*** 66%
- ***Production Cost:*** Higher than mechanical

Influence of Fibers Length on Paper Properties (Opacity, Density and Mechanical Strength).



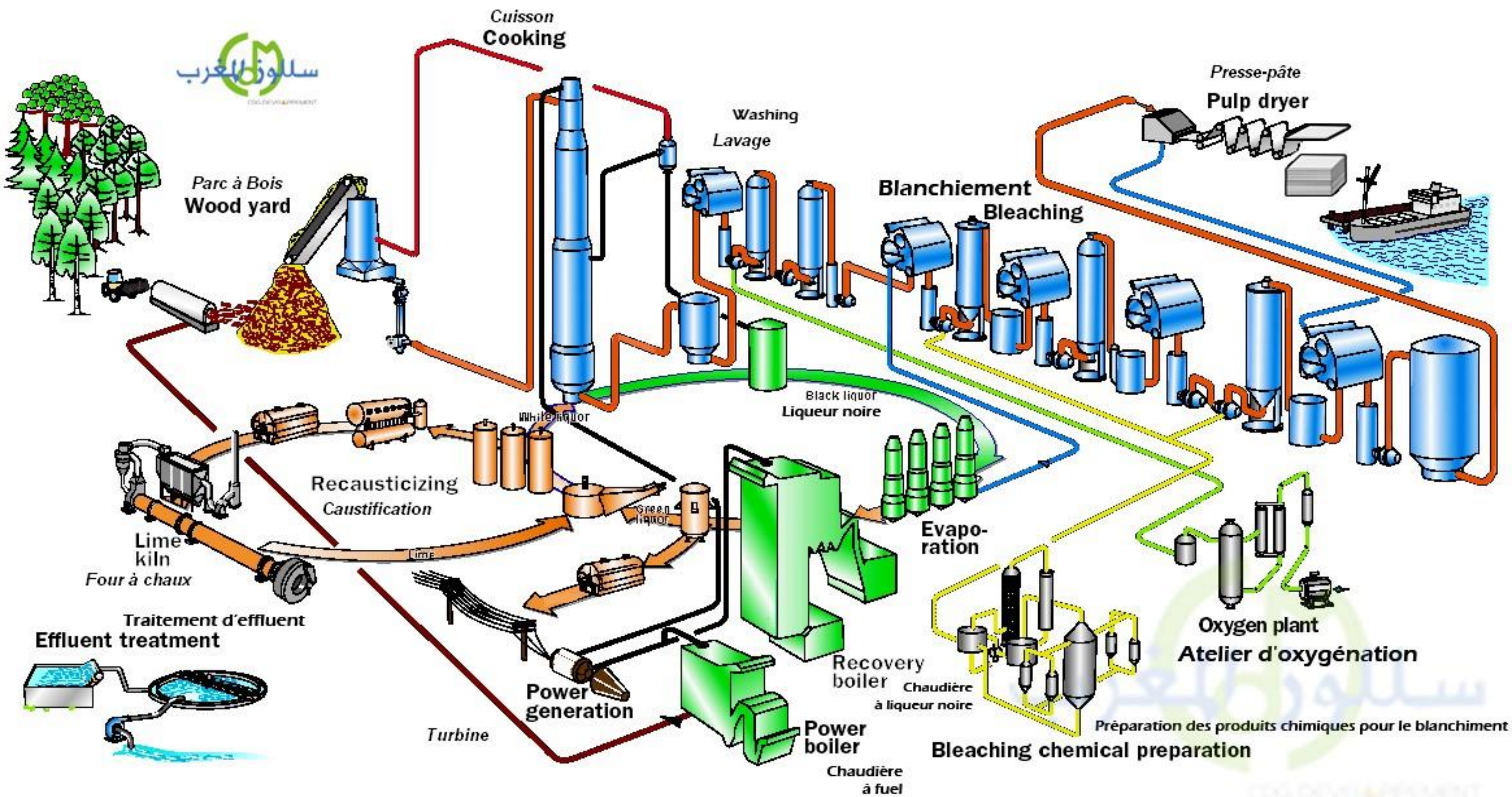


The proportion of long fibers depend on:

- The botanical origin
- The type of process
- The intensity of refining (mechanical process)
- The temperature and chemical treatment.

Mc Donald et al. (2004)

Chemical Pulping Process.



BALANCE:
Thermal Autonomy : 92%
Electrical Autonomy : 37%
Recycling of liquid solution : 95 %

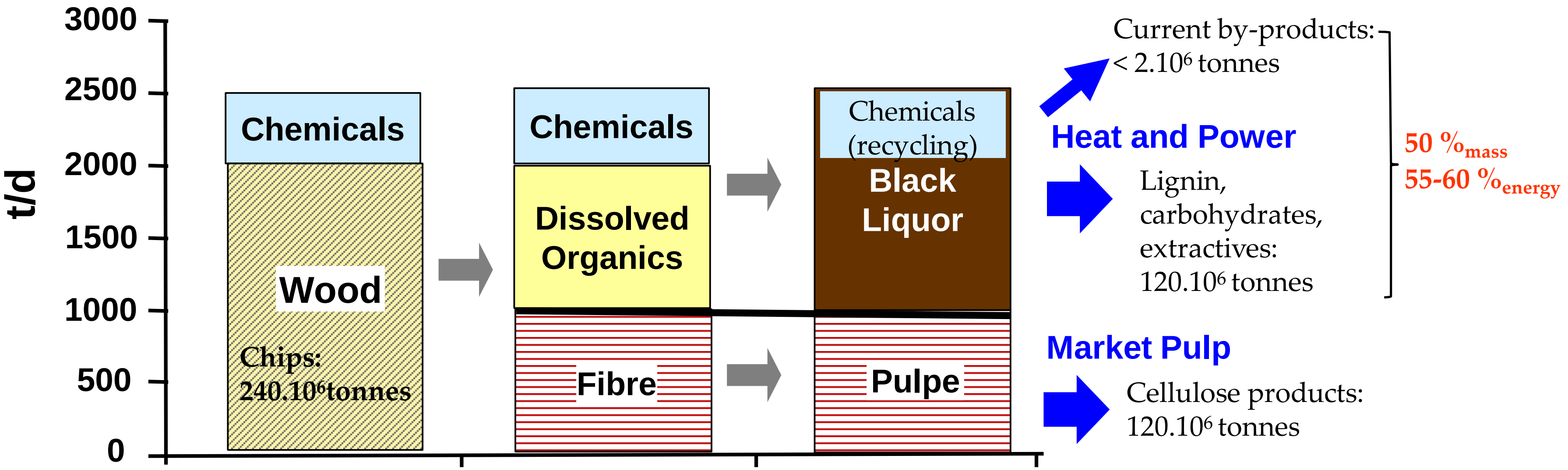
INNVENTIA, "Biorefinery within the Pulp & Paper sector", 2009.

Pulp and Paper Typical Balance.

A 1000 t/d Kraft Pulp Mill

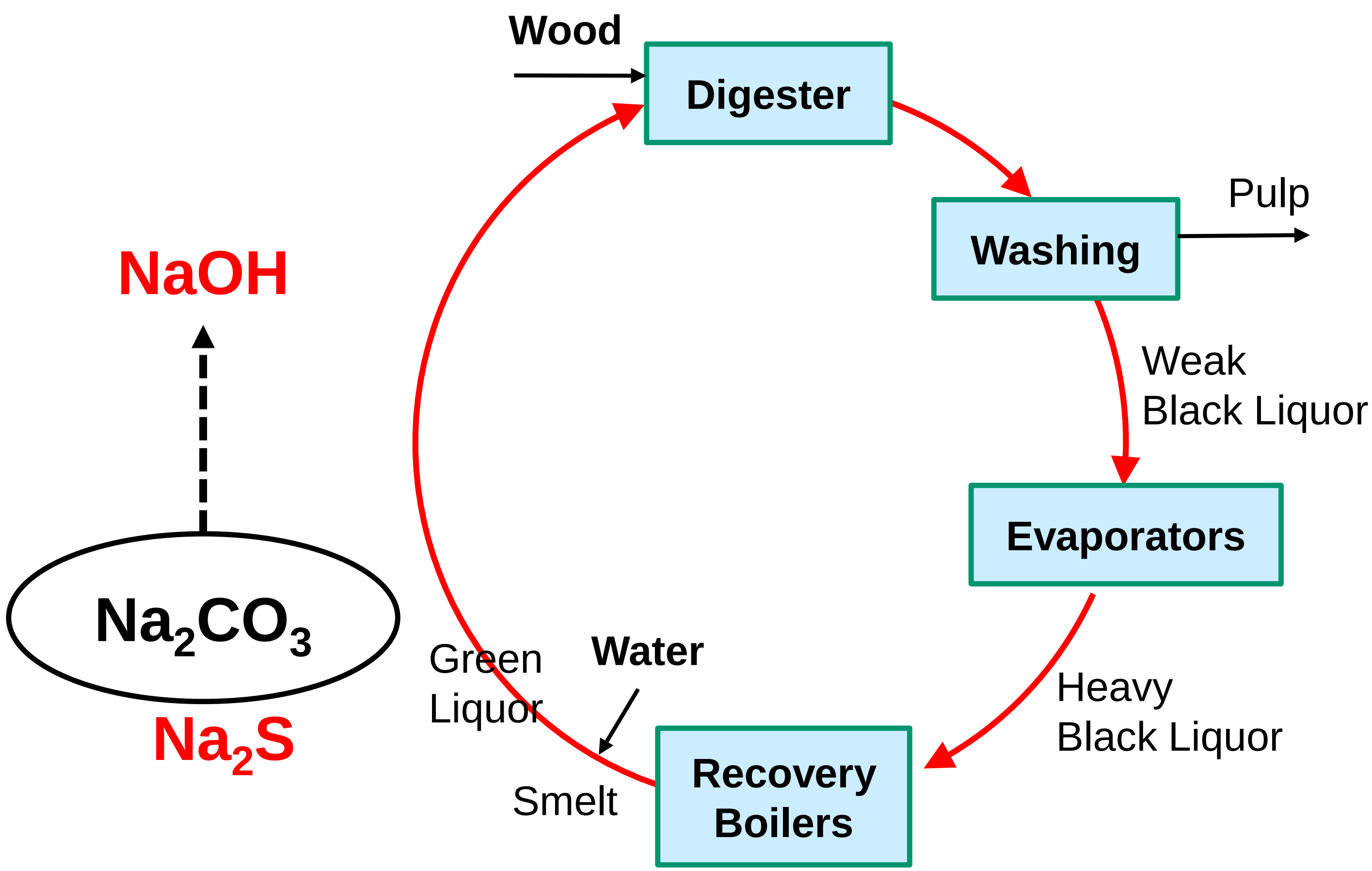
Produces 1500 t/d BL d.s.

~ 5000 t steam/day ------- ~ 650 MW/day (estimated)



A modern pulp mill: 4300 t/d ⇨ 21500 t steam/day and ~ 2800 MW/day

Kraft Recovery Process.



FIBRIA, “Biorefinery and the Pulp & Paper Industry”, 2010.

Environmental Impact Progressively Reduced.

Energy consumption for ton of product

Year	1982	1990	1995	2000	2005
TOE	100	86.5	85.7	85.5	84.0

(Tonne of Oil Equivalent , base index 100, year 1982)

Waste of oxidizable materials

Year	1980	1985	1990	1995	2000	2005
Waste	100	70.9	68.0	45.6	38.8	35.0

(Kg/ton of paper-paperboard produced, base index 100, year 1980)

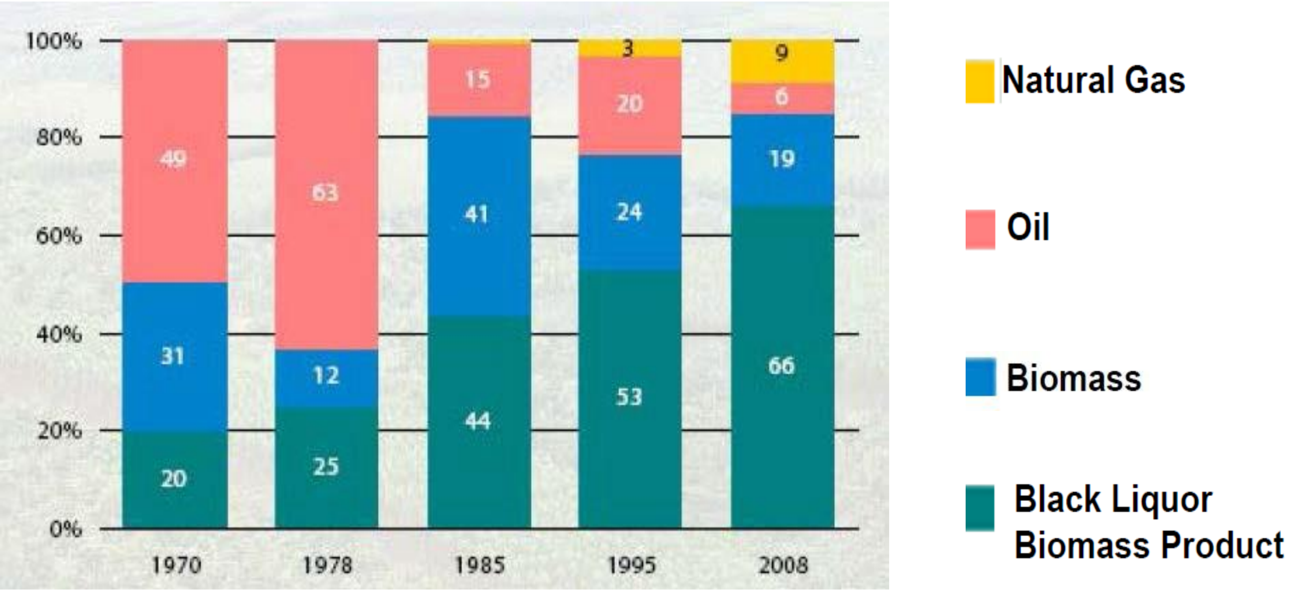
Water consumption

Year	1980	1985	1990	1995	2000	2005
Water	100	80.4	51.9	43.3	39.2	33.5

(m^3/ton of paper-paperboard produced, base index 100, year 1980)

Growing Part of Energy Produced from Cooking Liquor and from Biomass.

- Pulp, paper and printing industry:
  - 4th largest industrial consumer of energy
  - Generates about 50% of its own energy needs
    - → from biomass residues
    - → extensive use of combined heat and power
- Nowadays black liquor main use: 98% of Kraft lignin burnt.
- Evolution of the Brazilian Pulp and Paper Energy Matrix (1970 – 2008)



IEA // BRACELPA

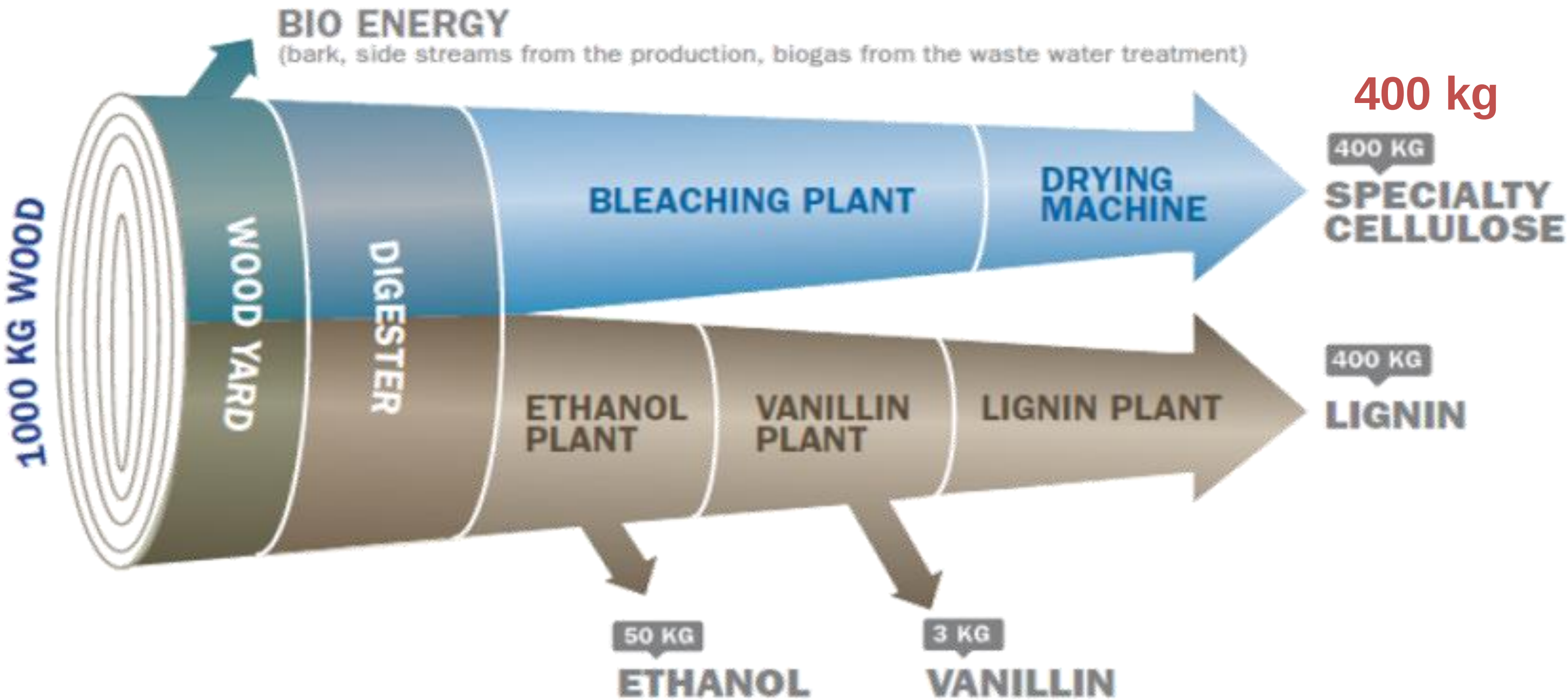
The Case of a Paper Industry Converted to Bio-refinery.

Borregaard bio-refinery, Norway (paper production from 20th century)
History: production of bisulfite pulp from fir wood.

Specialty cellulose	Lignin	Vanillin	Bioethanol
Construction materials	Concrete additive	Food	Car care
Cosmetics	Animal food	Perfumes	Paint/varnish
Food	Dyestuff	Pharmaceuticals	Pharmaceuticals
Tablets	Batteries		Bio-fuel
Textiles	Briquetting		
Filters	Mining		
Paint/varnish	Soil conditioning		

A Complete Valorization of Biomass.

50 kg
(combustion of bark, effluents, biogas from STEP waters)



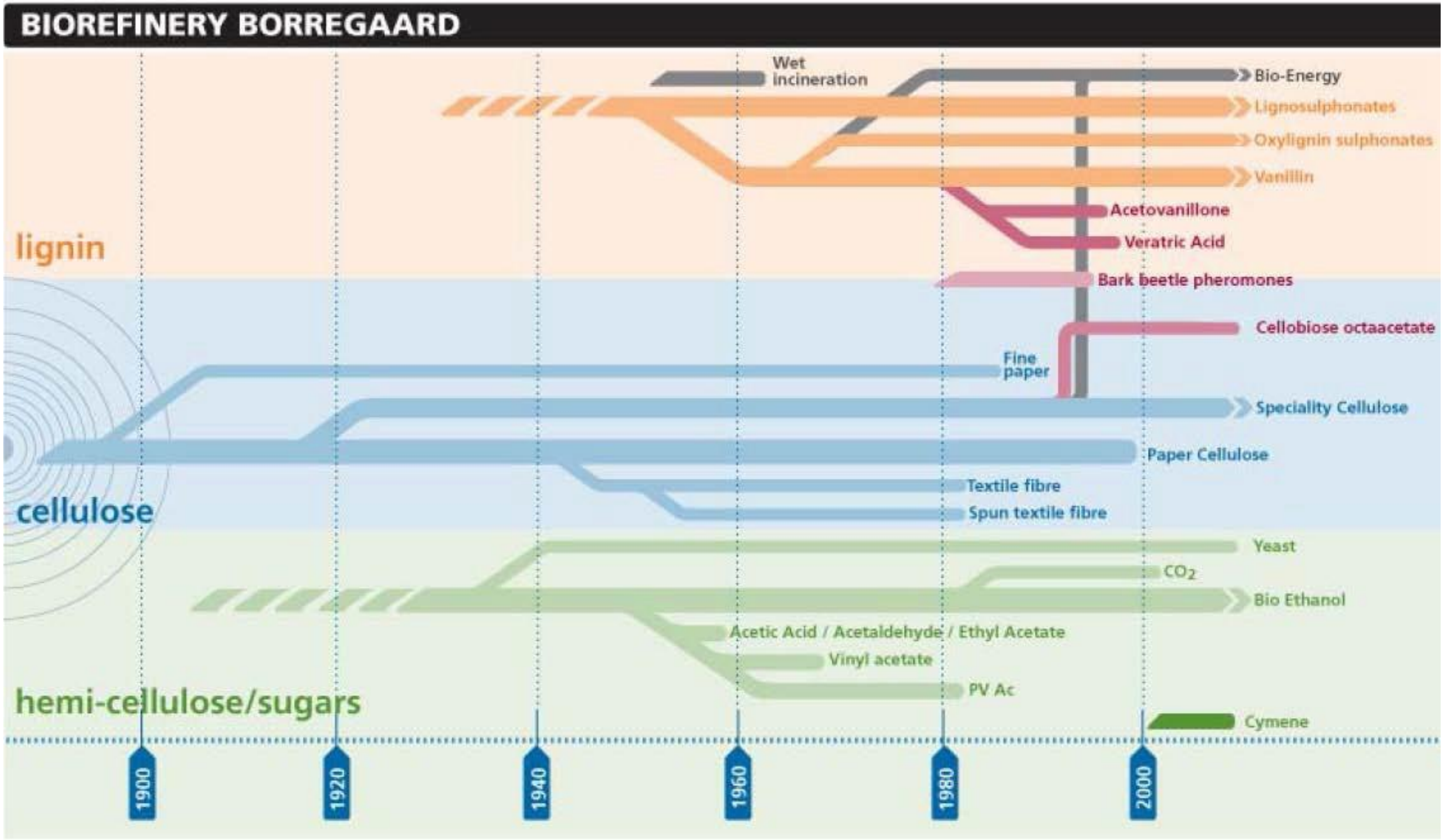
400 kg

50 kg **3 kg**

> 90 % of biomass is converted into commercial value products.

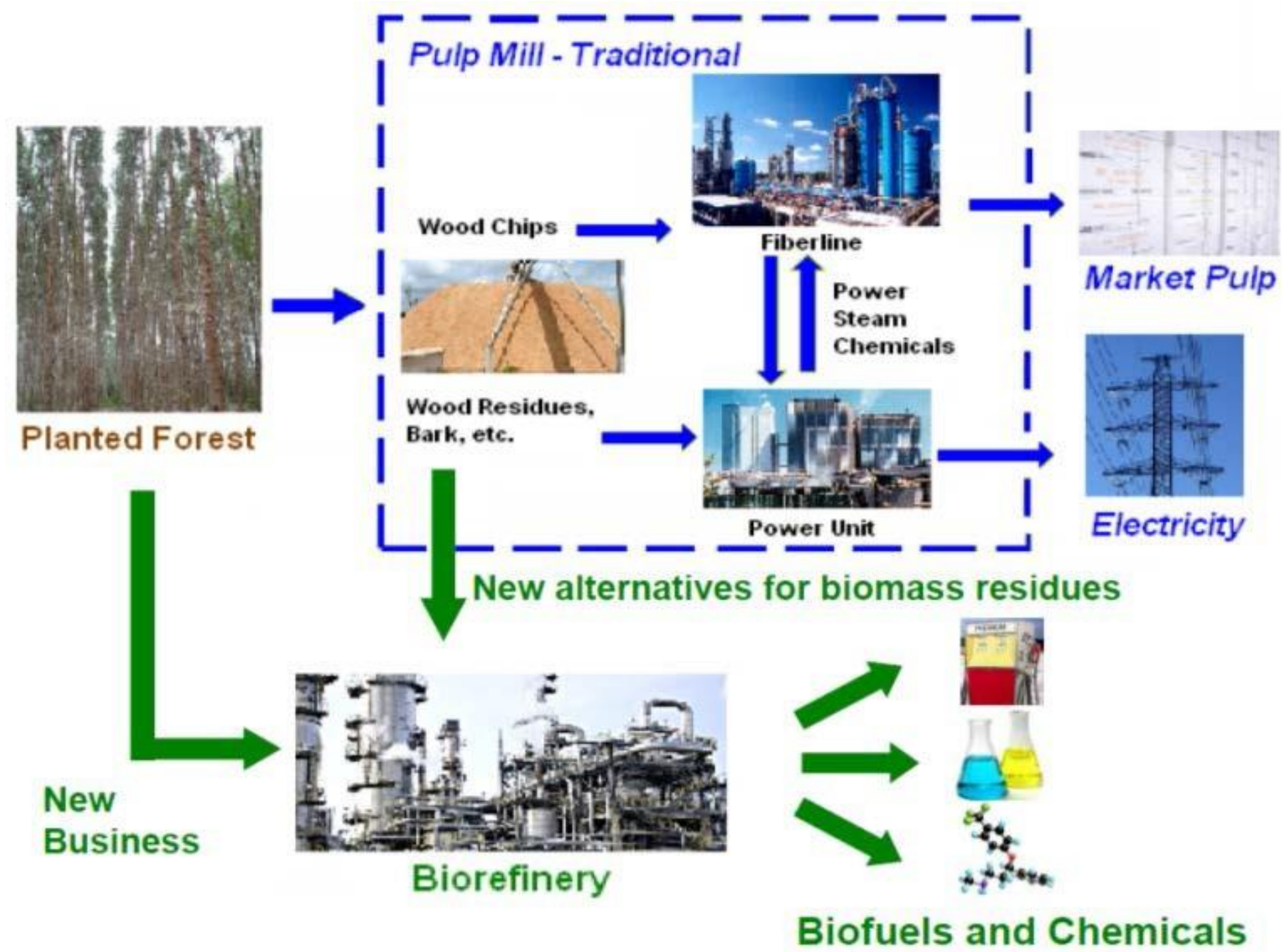
www.borregaard.com

… Result of a Progressive Diversification.



FIBRIA, “Biorefinery and the Pulp & Paper Industry”, 2010.

Alternatives to Traditional Pulp Mill.



Complementarity of Routes.

Towards a valorization of all constituents of wood … Complementarity of thermochemical, chemical and biological routes for the production of energy, chemical intermediates and materials.

Thermo-chemical Vs Physico- / Bio-chemical

Energy ← → **Chemicals/Materials**

- ***DME***
- ***Ethanol***
- ***FT-diesel***
- ***Heat***
- ***Electricity***
- ***Solid fuel***

from: **Lignin**, **Cellulose**, **Bark**, **Forestry residues**

Lignin
- ***Phenols***
- ***Carbon fibers***
- ***Binders***
- ***Dispersants***
- ***Activated carbon***

Hemi-cellulose
- ***Fibre additives***
- ***Barriers***
- ***Hydrogels***
- ***Composites***

Cellulose
- ***Fibres***
- ***Derivatives***
- ***Nanocellulose***

Extractives
- ***Specalities***

Wood as Chemical Resource.

- 1500s: Wood tar
- 1672-1800s: Potash (K_2CO_3)

→ Thermal treatments

- 1910s: Turpentine (essential oils)
- 1913: Tall Oil

→ Physical treatments (separation, distillation)

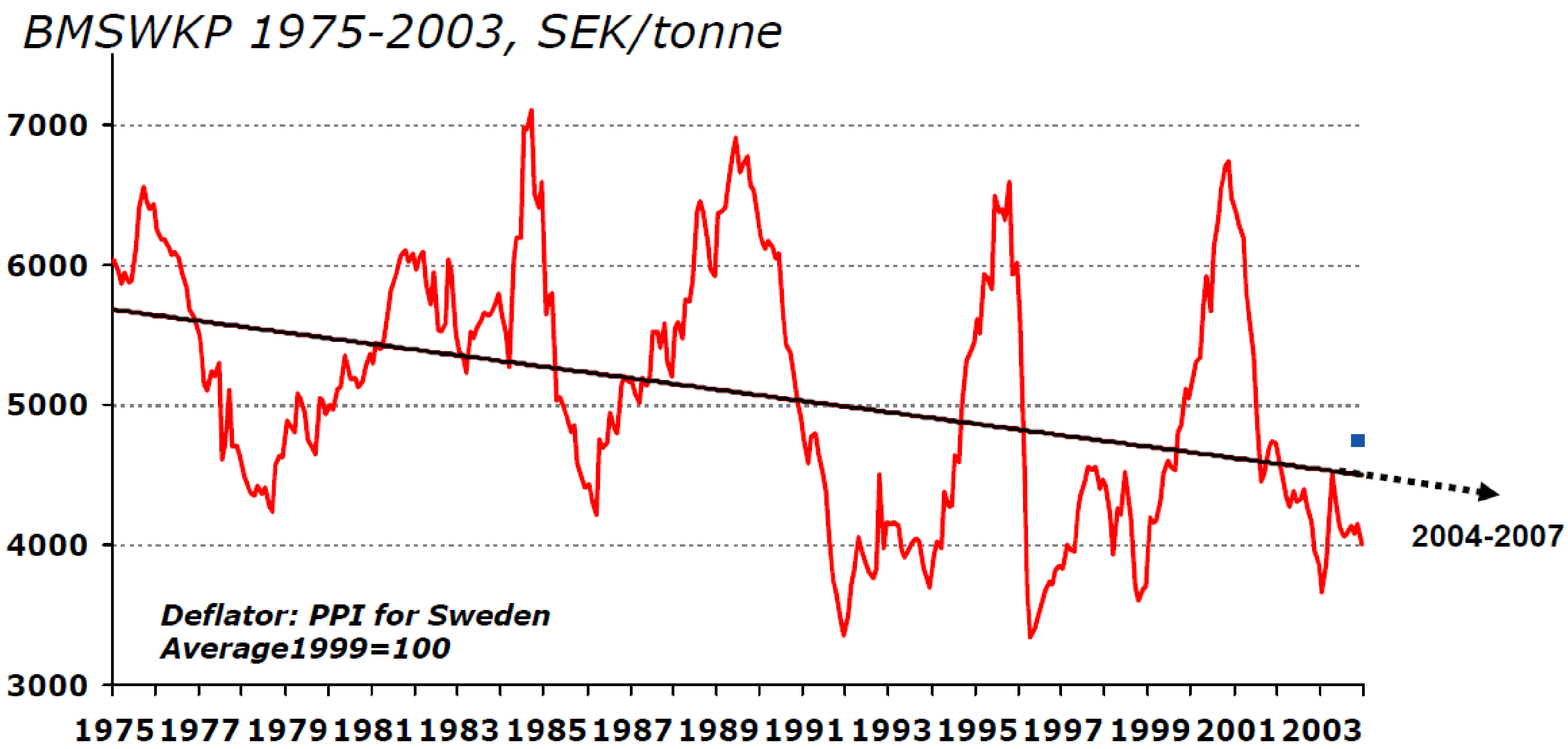
1844: mechanical pulp
1880s: chemical pulp

- 1921: sulfite, ethanol
- 1944: CarboxyMethylCellulose
- 1940s: Lignosulfonates

→ Chemical treatments

- 1952: Vanillin → Thermo-chemical treatments
- 1965: Sulfite lignin
- 1968: Furfural, acetic acid
- 1974: Xylitol
- 1974-1991: Protein → Biological treatments
- 1980: Sitosterol, sitostanol
- 1998: Lignans
- Etc... (methanol, levulinic acid)

An economical need: Decrease of price of paper pulp.



The Swedish Energy Agency, "Swedish Pulp Mill Biorefineries: A vision of future possibilities", ER 2008:26.

Decline of Paper Industry in North America and in Europe.

- Pulp and paper industry is in decline in North America (and Europe)
  - Total production of paper and board:
    → decades of steady growth until 2000-2001
    → Since then, dropped about 10%:
      - more than 20 mills shut down permanently in 2009,
      - after more than 25 closed their doors in 2008.
  - Modern capacity is coming most notably in East Asia and S. America,
    → thanks to:
      - lower costs, improving infrastructure, and increased local demand.

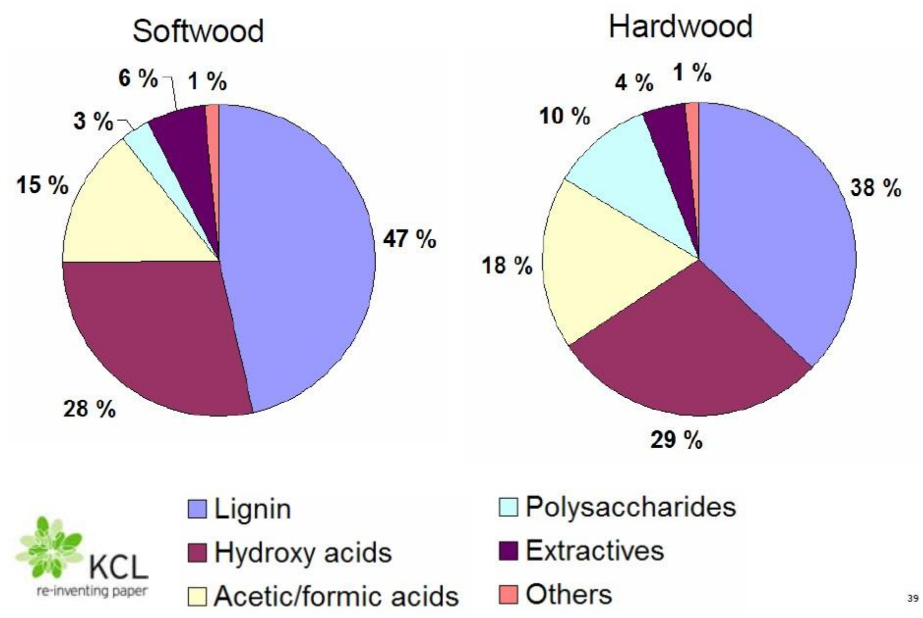
- But … after 2016 the growth of pulp price was triggered by the increase of paper consumptions (for hygienic use in developing countries, e.g. Chine)

http://www.lemonde.fr/economie/article/2017/04/22/la-pate-a-papier-leve_5115574_3234.html

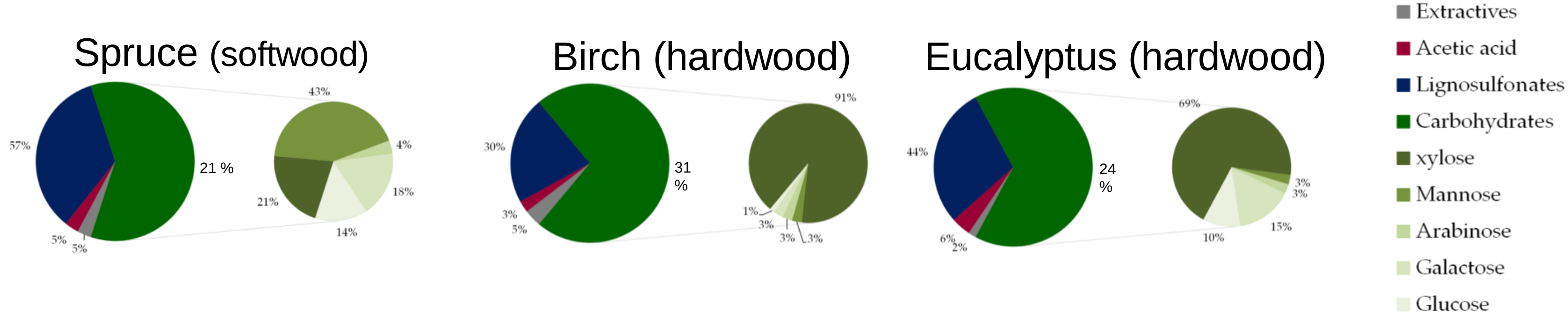
K. Patrick & G. Ostle, "Outlook: North America 2010", *Paper 360°* (2010): 8-11.

Valorization of Cooking Liquors.

- Black liquor



- Sulfite liquor



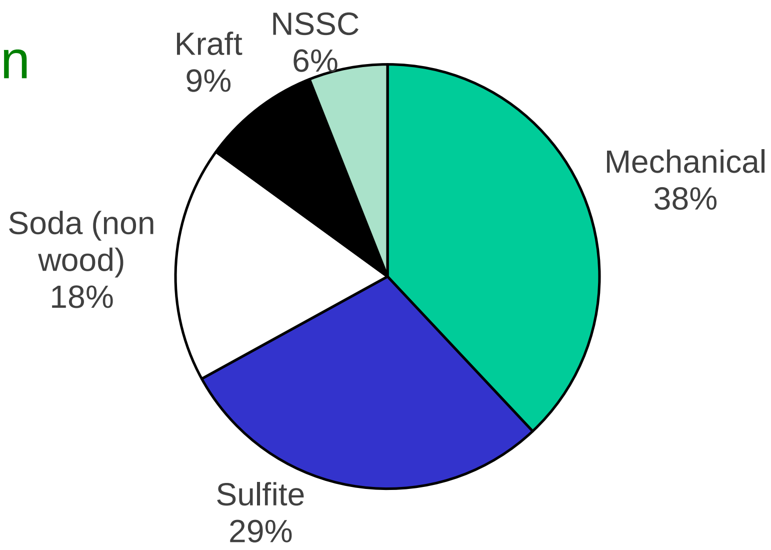
Fernandes et al. “Second Generation Bioethanol from Lignocellulosics”, In: Bioethanol, InTech, 2012, ISBN: 978-953-51-0008-9-58.

Energy Valorization: Direct Combustion or Biogas Production.

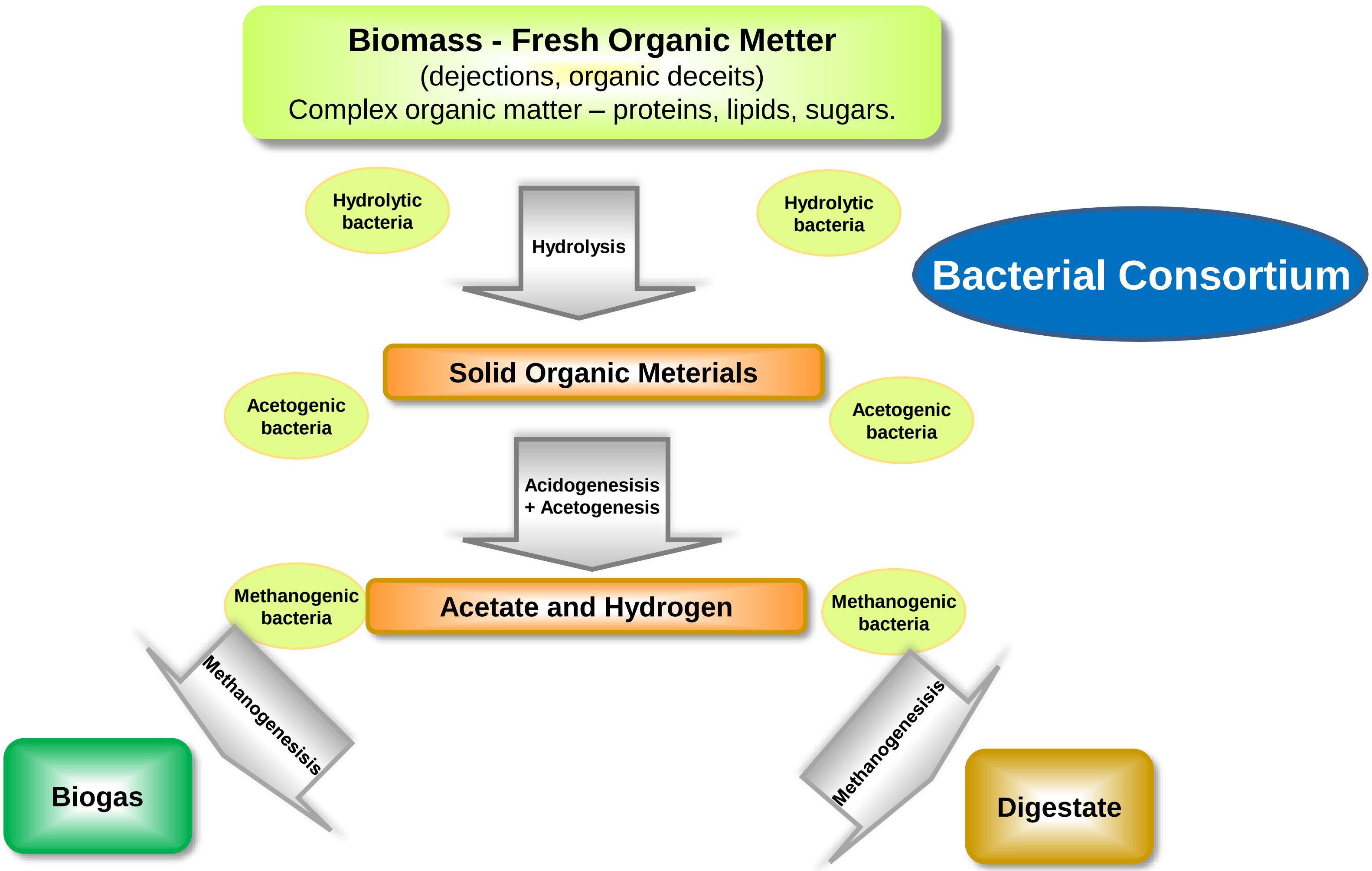
- Heat and electricity:
  - Net calorific value of cooking liquor: 220 kg fuel oil / tonnes_{pulp}

	Heating value (MJ/kg)
Cellulose	17.6
Hemicellulose	16.5
Lignin	23.7

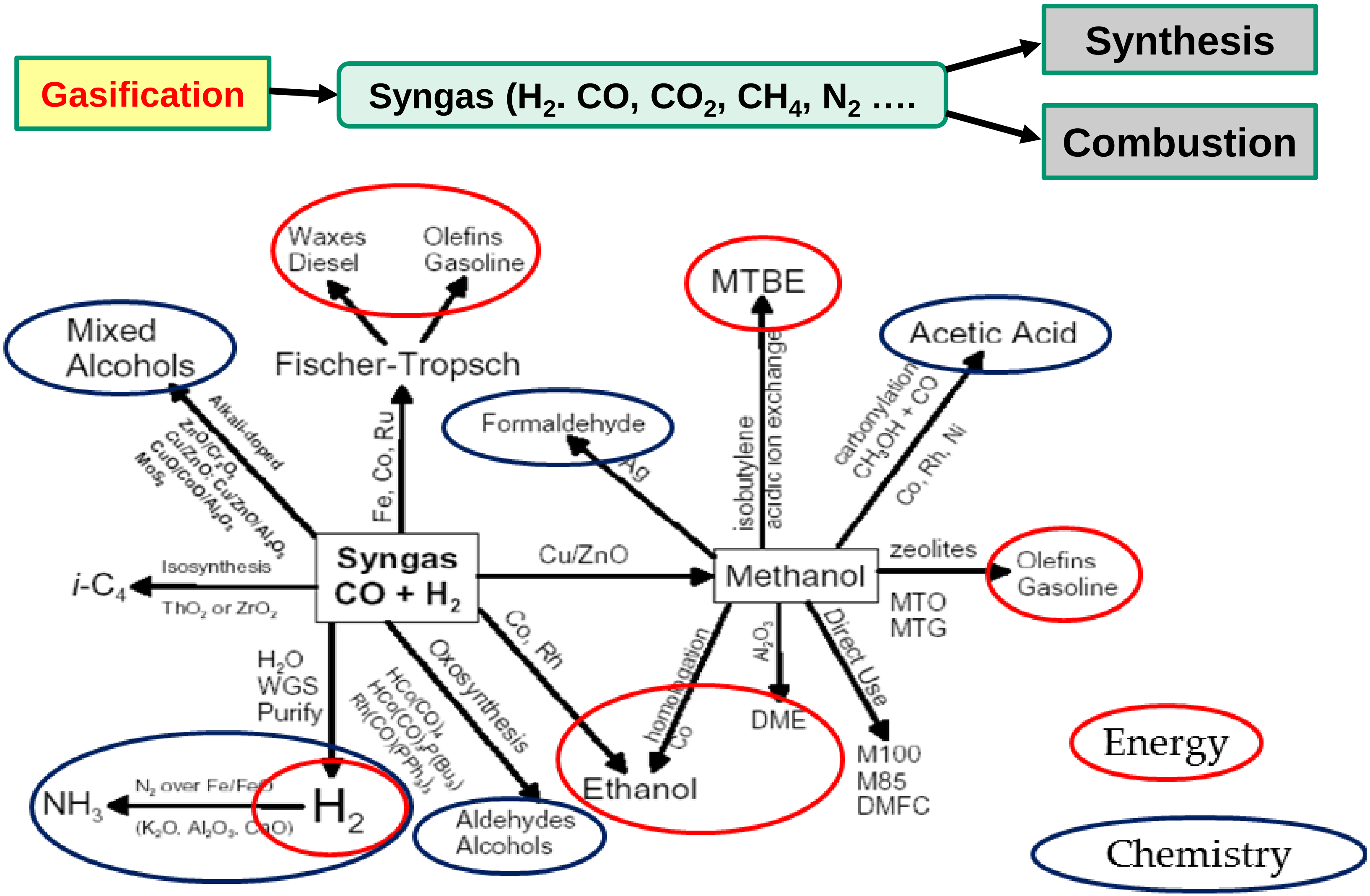
- Biogas anaerobic methane production
  - In 2006:
    - → 203 biogas plants at pulp mills
      - 67% paper mills
      - 33% pulp mills



The Bio route to Biogas and Digestate.



http://www.biogaz-energie-renouvelable.info/methanisation_schema.html



TAPPI, "Status of the biorefinery development in Scandinavia", 2006 / Sousa, "Biorefinery development pathways", 2010.

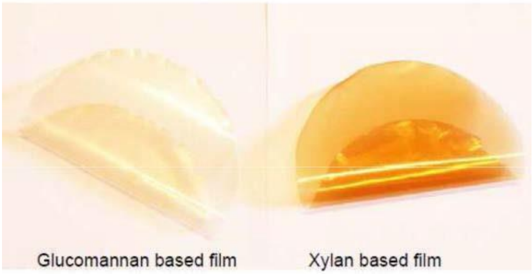
The Physical- / Bio-Chemical Route: Valorization of Hemicelluloses and Sugars into C5.

- Production of ethanol (fuel energy): through C5 fermentation
  - → Extract from wood chips prior to pulping
  - → Or extract from sulfite liquor

- Production of chemicals:
  - → Xylan and glucomannan (hydrogels, films, foams)
  - → Acetic acid, succinic acid (fermentation)
  - → Xylitol, furfural
  - → Butanol, organic acids, fatty acids and alcohols (emulsifiers)
  - → Monomers for polymerization

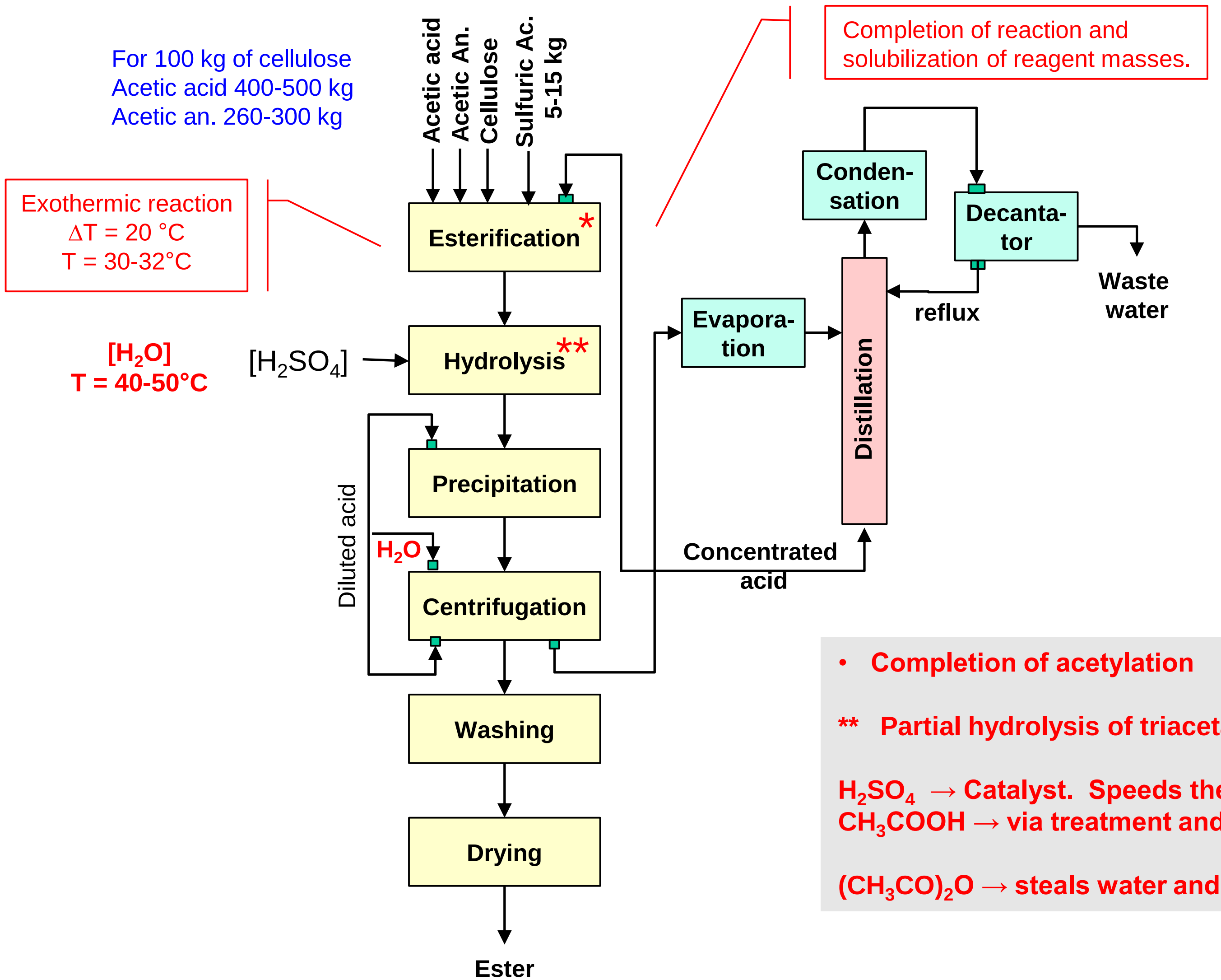
- Production of materials

Hemicellulose - Nano-fibril cellulose composite films



Glucomannan foams

Valorization by Functionalization: Cellulose Acetate (Triacetate → Diacetate).



- * Completion of acetylation → Triacetate

** Partial hydrolysis of triacetate to diacetate

H_2SO_4 → Catalyst. Speeds the esterification kinetic.
CH_3COOH → via treatment and solubility

$(CH_3CO)_2O$ → steals water and activates acetylation

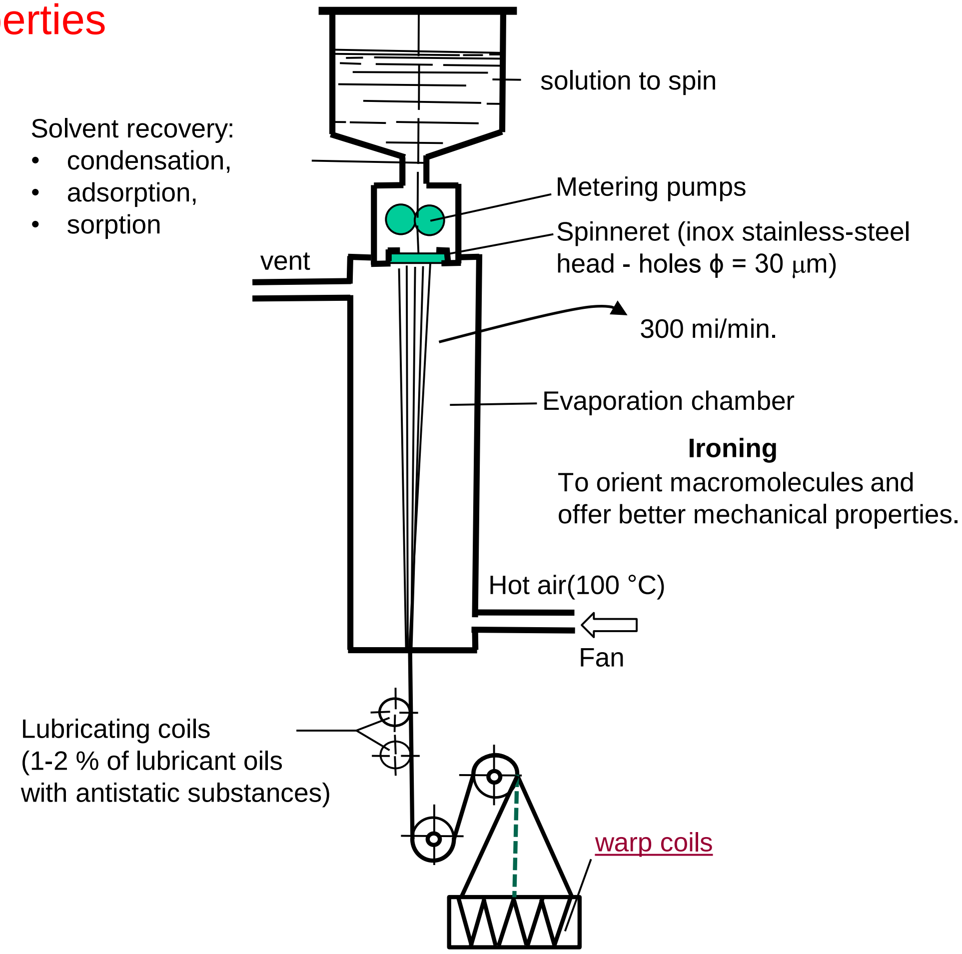
Cellulose Acetate: Final Spinning.

$$[C_6H_7O_2(OH)_3]_n + 3n\ CH_3CO_2H \rightleftarrows [C_6H_7O_2(OOCCH_3)_3]_n + 3n\ H_2O$$

- Can be solubilized in CH_2Cl_2
- Hydrophobic properties

$$[C_6H_7O_2(OH)_3]_n + 0.7n\ H_2O \rightleftarrows [C_6H_7O_2(OOCCH_3)_{2.3}]_n + 0.7n\ CH_3CO_2H$$

Is dissolved in 35% acetone.
Present intermediate characteristics between hydrophilic (OH) and hydrophobic.
Good recovery of humidity.



Rayon Viscose - Chemistry of Preparation.

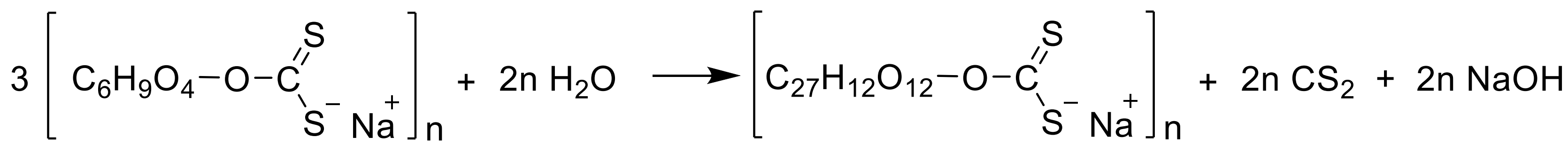
Cellulose under the action of concentrated alkali and carbon disulfide is converted into cellulose xantogenate through following reactions:

$$[C_6H_9O_4\text{-}OH]_n + n\ NaOH \rightarrow [C_6H_9O_4\text{-}ONa]_n + n\ H_2O$$

$$[C_6H_9O_4\text{-}ONa]_n + n\ CS_2 \rightarrow [C_6H_9O_4\text{-}O\text{-}C(S)SNa]_n$$

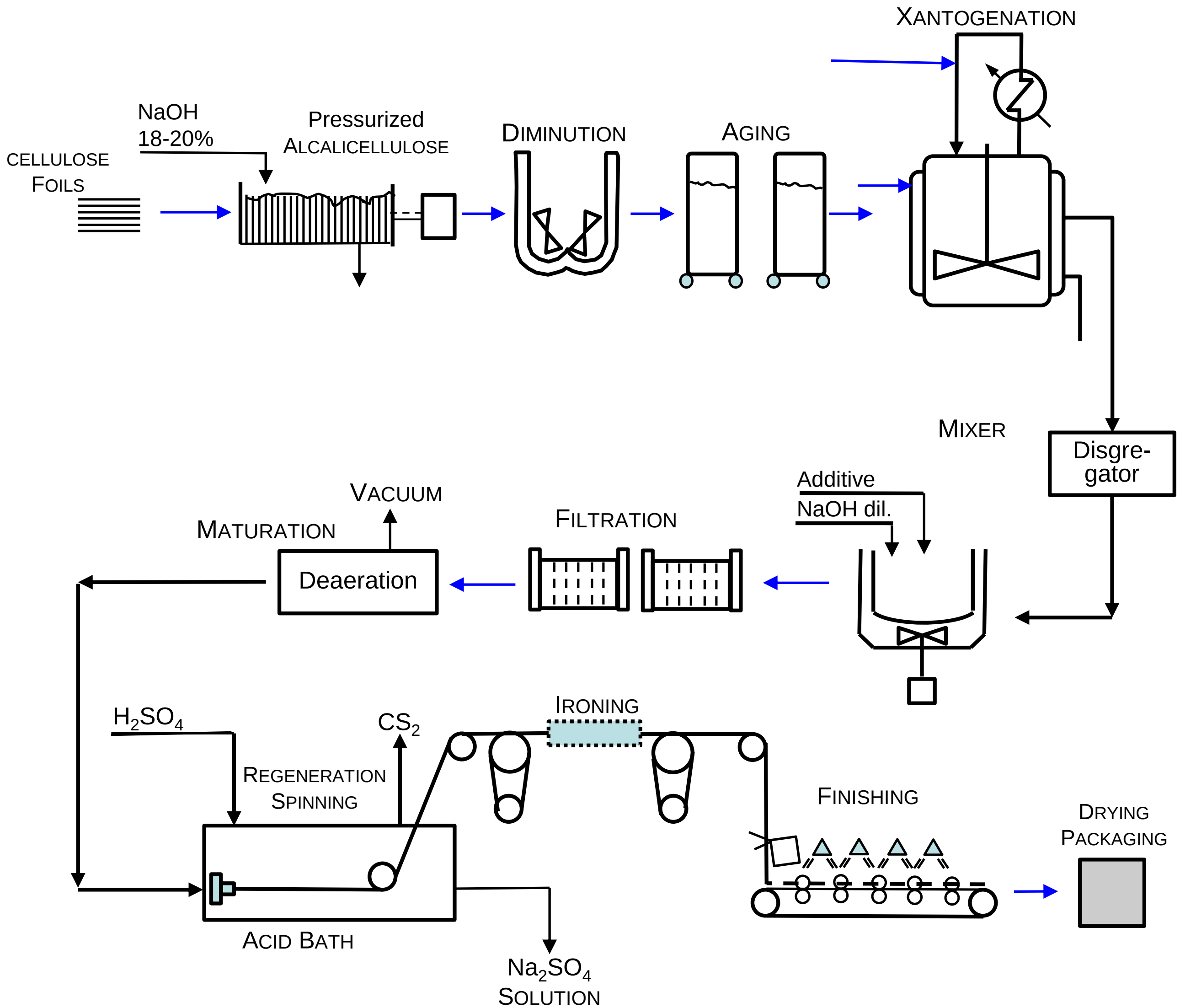
Cellulose Xantogenate or dithiocarbonate

The xantogenate dissolved in NaOH diluted solution is lest to store (maturation) controlling viscosity and simultaneous partial desulfuration:



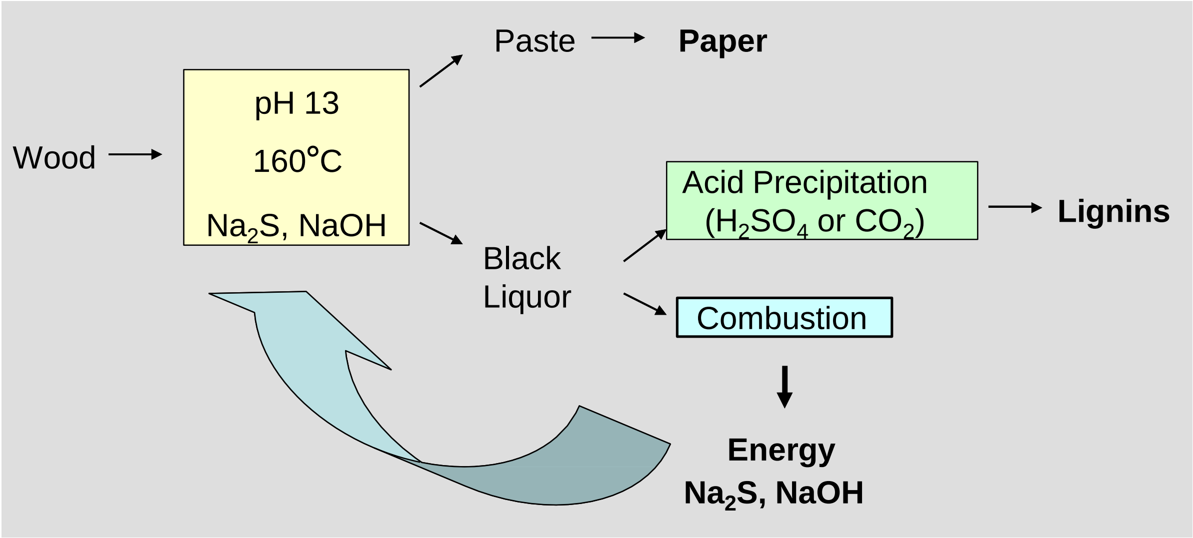
Up to obtain a stable colloidal solution named «viscose».

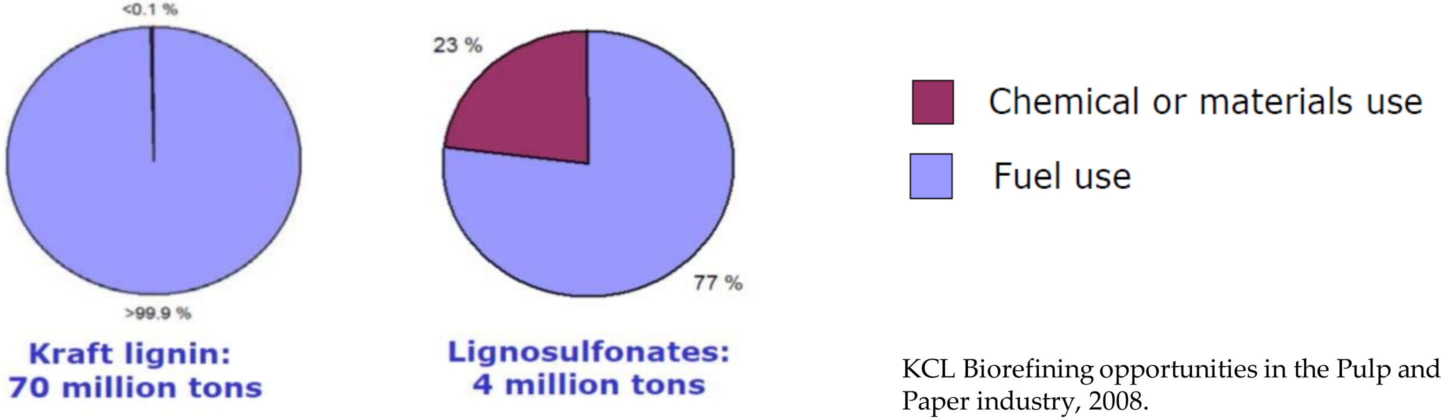
Viscose Rayon Production Plant .



Lignin Valorization.

Recovery of lignin from liquors - ex. Kraft process:

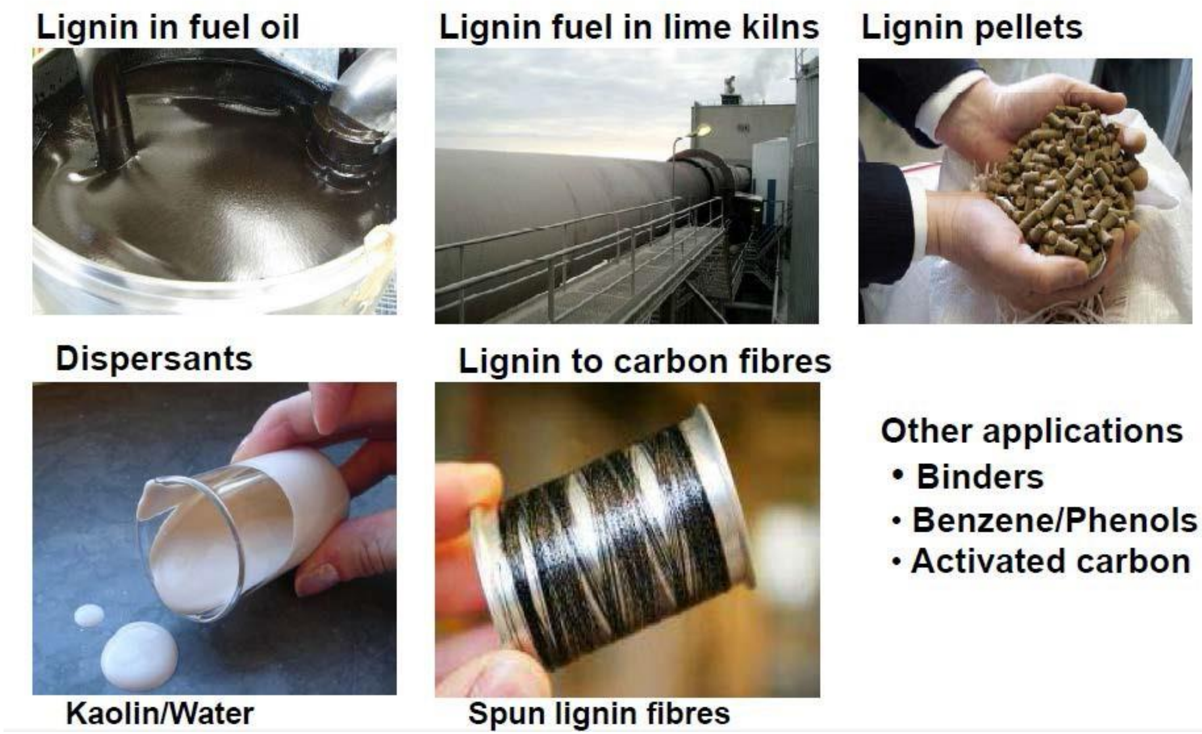




KCL Biorefining opportunities in the Pulp and Paper industry, 2008.

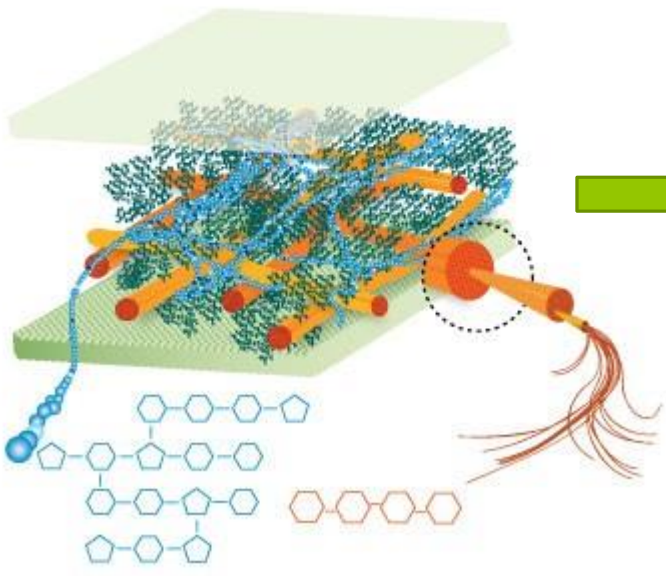
Lignin Valorization (2).

- Low added value applications:
  - Energy, additive in cement (retardant) and asphaltic, binder in feed, …
- High added value applications:
  - Vanillin, phenolic building blocks, resins (composites and wood panels), additives for thermoplastics and polyurethanes, surfactants, anti-oxidative



INNVENTIA, "Biorefinery within the Pulp & Paper sector", 2009.

Reactions Susceptible to Occur During the Cooking Process to Paper.



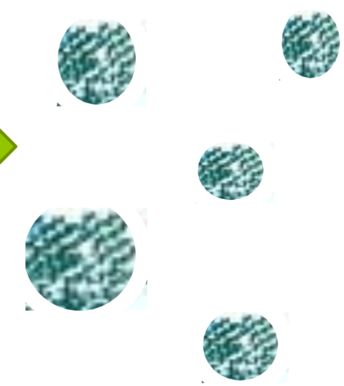
Depolymerization

Oxidation

Re-condensation

Grafting

➪ Solubilization



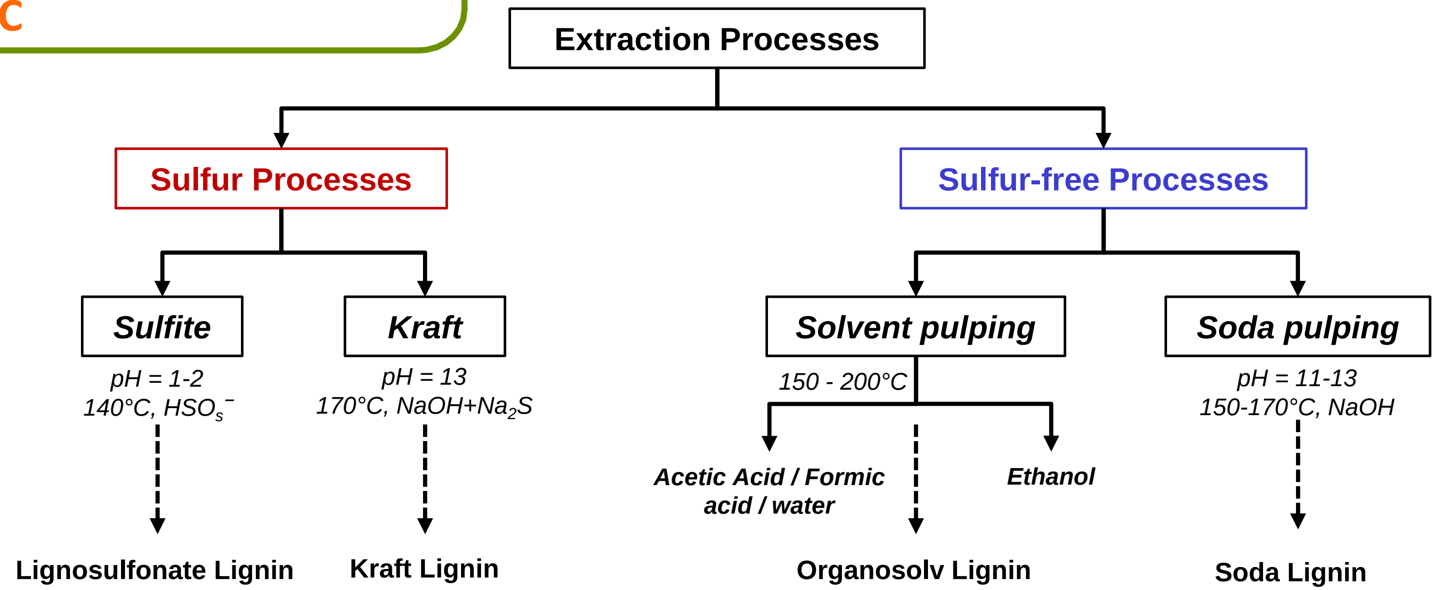
Industrial Lignins

http://2008.igem.org/wiki/images

➪ **Co-product constituted of native lignin fragments modified and of contaminants originated from vegetable walls.**

Influence of Delignification Process on Lignin Properties.

M_w : 1000-100000 g.mol^{-1}
M_n : 500-10000 g.mol^{-1}
Polymolecularity index : 2-30
T_g : 90-160 °C



	Lignosulfonate Lignin	Kraft Lignin	Organosolv Lignin	Soda Lignin
M_n (g mol^{-1})	15,000–50,000	1000–3000	500–5000	800–3000
M_w / M_n	6–8	2.5–3.5	1.5–2.5	2.5–3.5
T_g (°C)	130	140–150	90–110	140

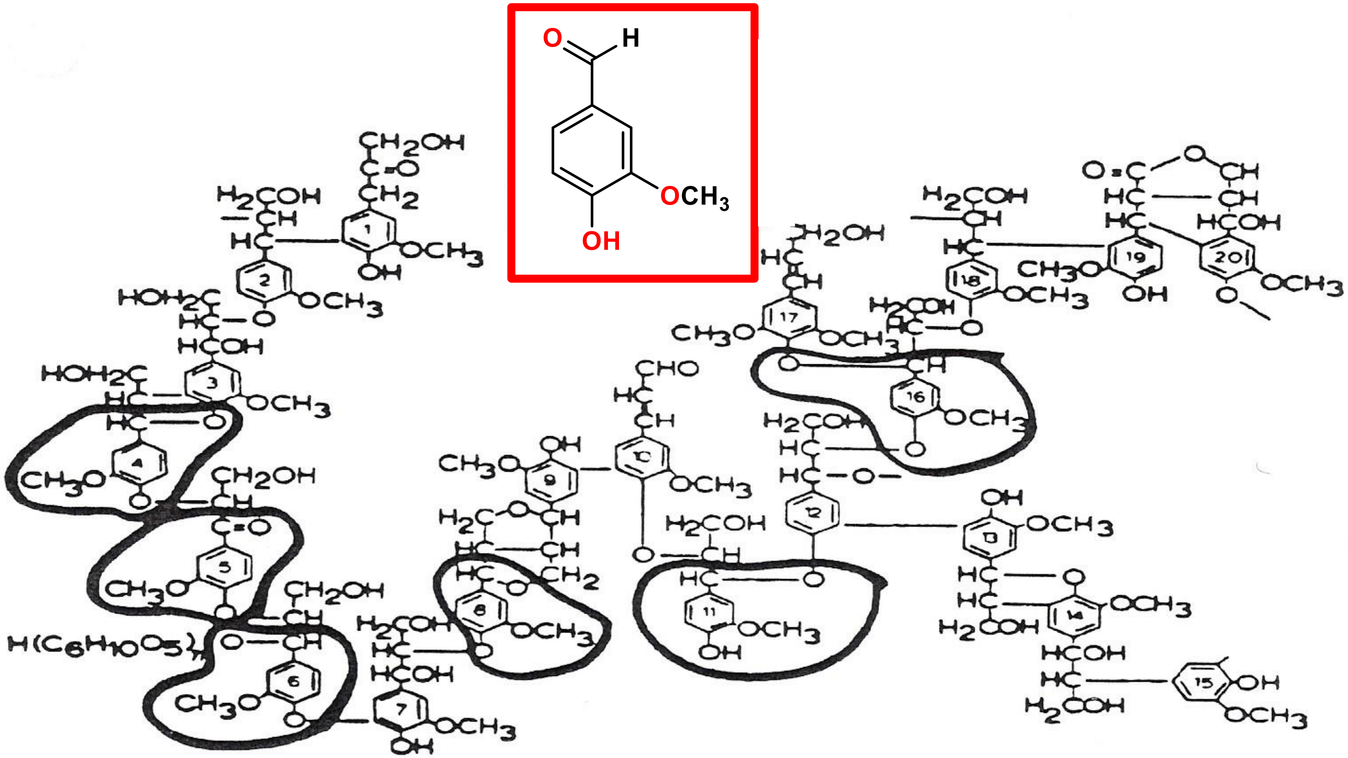
(Laurichesse et Averous, 2014)

Vanillin Production from Conifer Lignins.

Sulfite Liquor (conifers) → Alkaline hydrolysis + Oxidation → **Vanillin** + « oxylignins »

1 ton of wood → 4 kg of vanillin

SO_3 ↘ ; OCH_3 ↘
OH, C=O ↗



Other industrial productions at low level : DMS, DMSO, guaïacol.

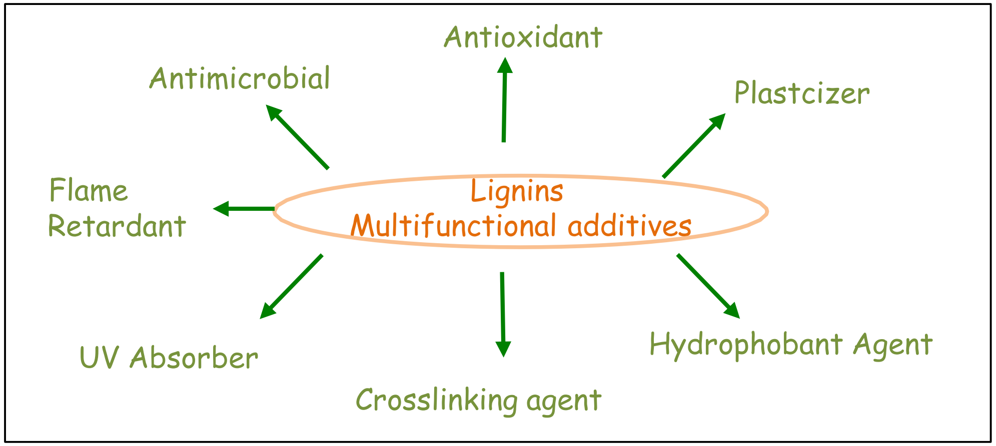
(Abdennadeher et al., 1989; Rodriguez et al., 2002)

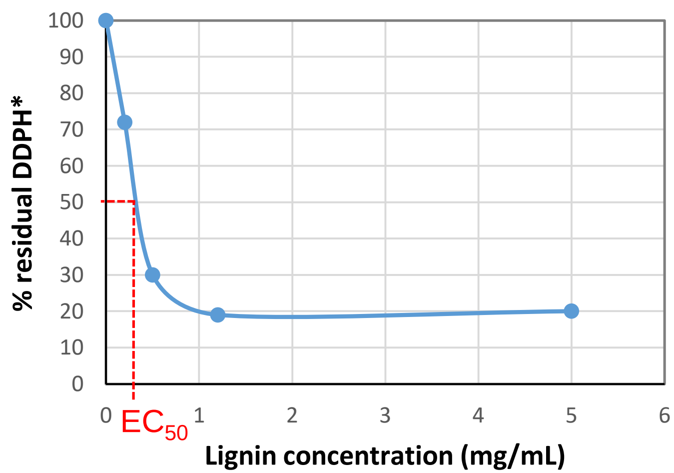
A Multifunctional Source of Added Value.

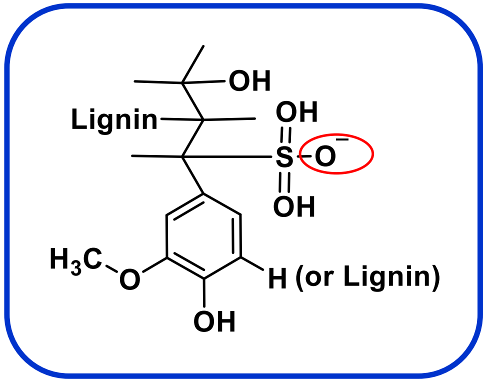
Antioxidant Properties

Product	IC50 (μg/ml)
alkaline Lignins	44,9 ± 6.7
Lignosulfonates	133,6 ± 9.0
Kraft Lignins	85,9 ± 4.6
Explosion Lignins	74,6 ± 1.0
(−)-Epicatechin	42,27 ± 3.0

(Vinardell et al, 2008)



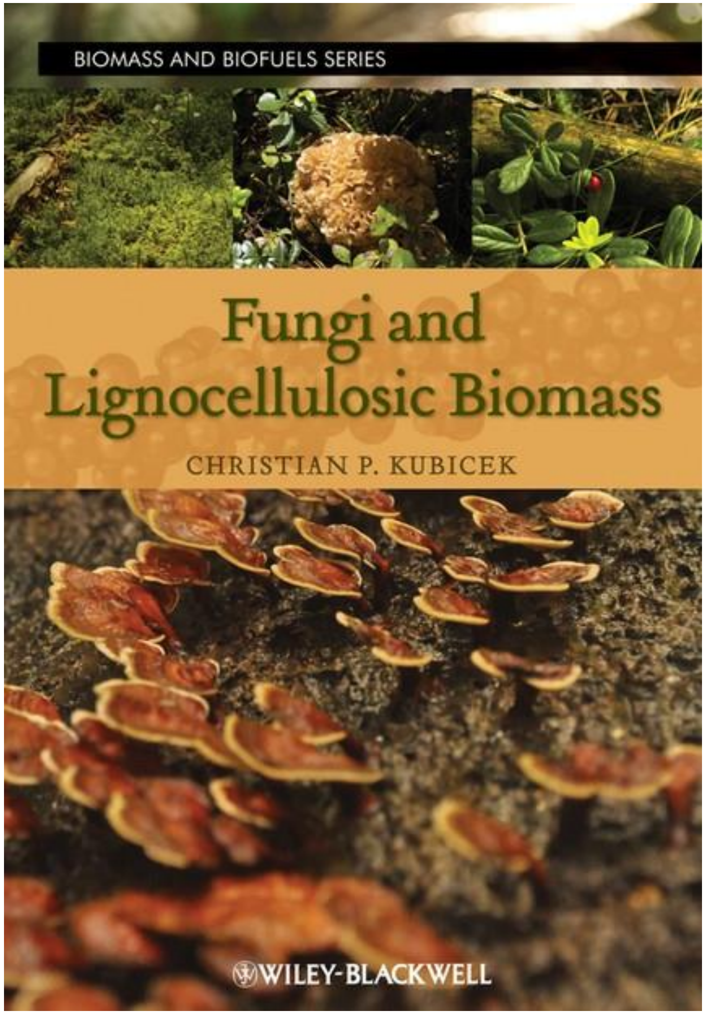


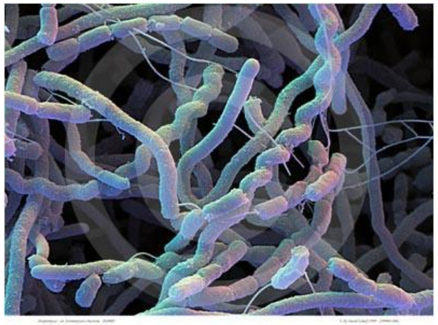


Polyelectrolytes

Dispersion auto-assembling and stabilization

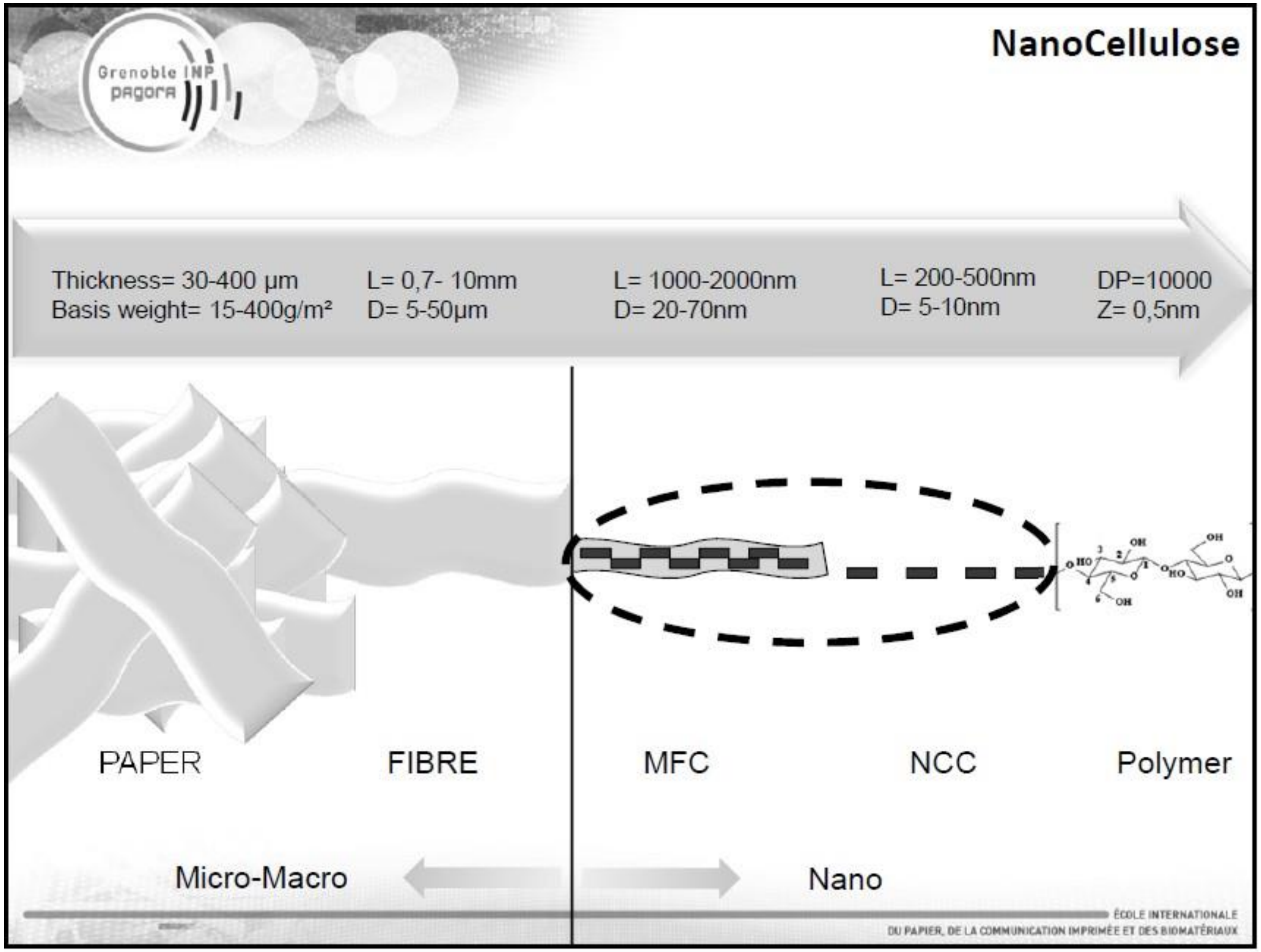
Exploitation of Biocatalysts Present in Living Organisms.





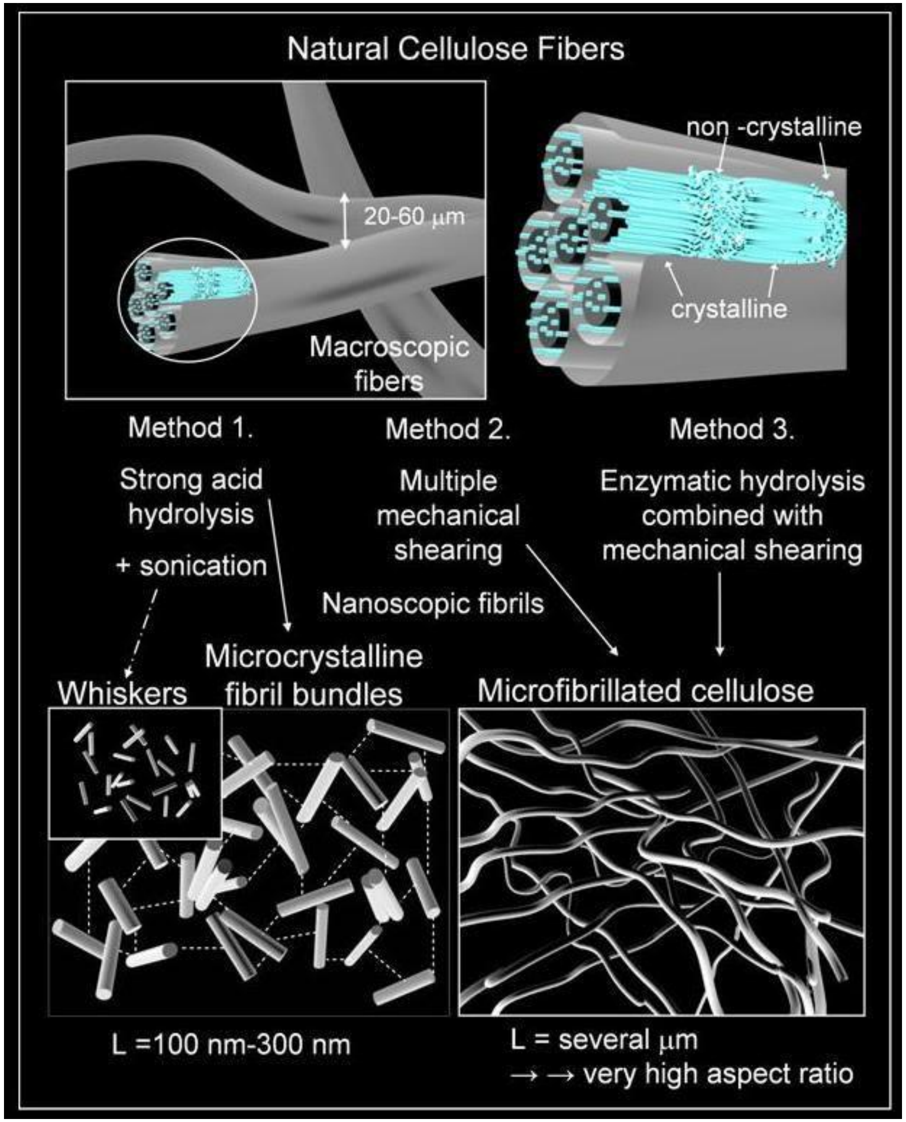
Cellulose Fibers Recovered at Different Scales.

(MFC = microfibrillar cellulose; NCC = cellulose nanocrystals)



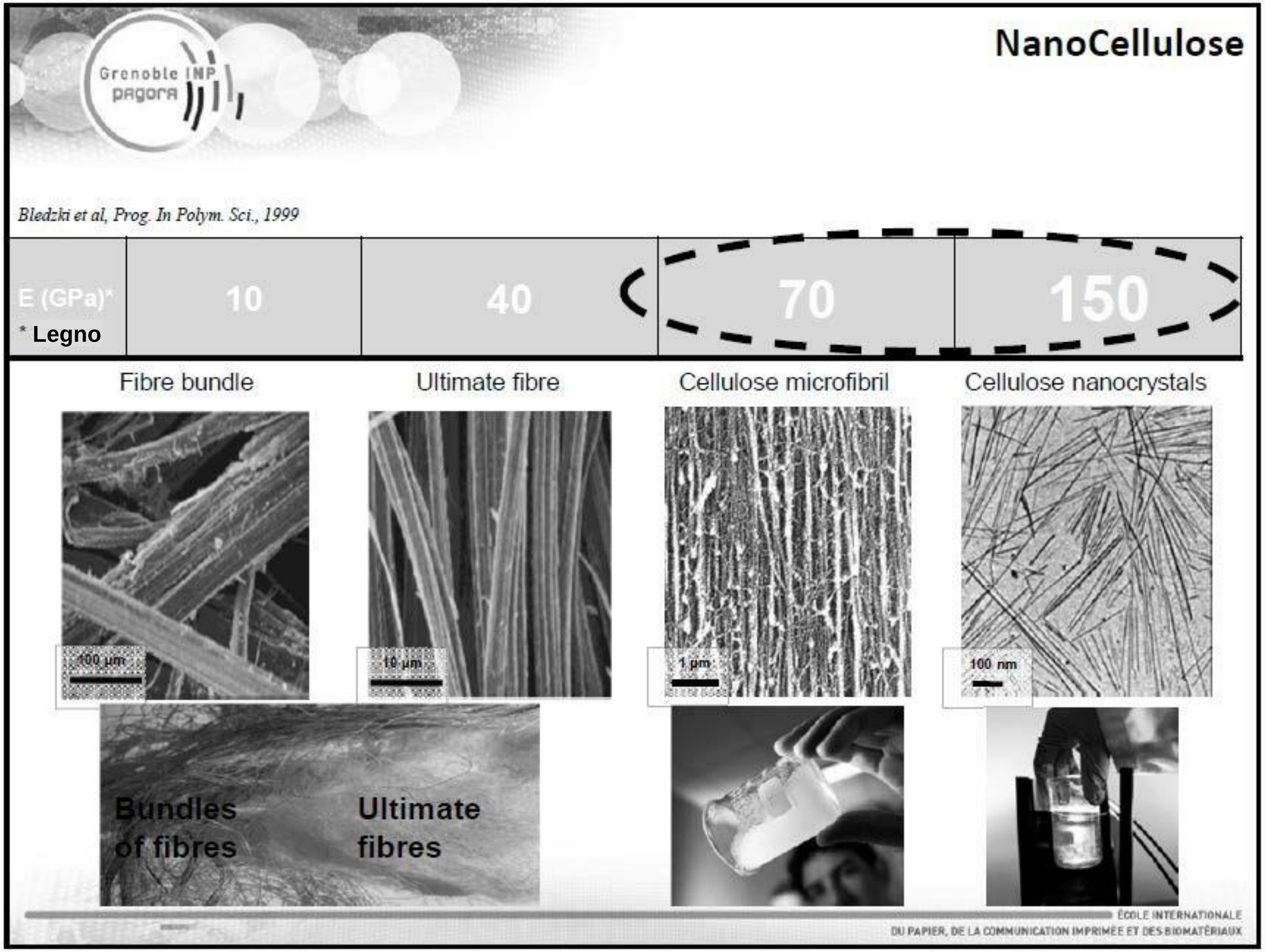
(Lavoine et al., 2012)

Method to Get Nanocellulose.



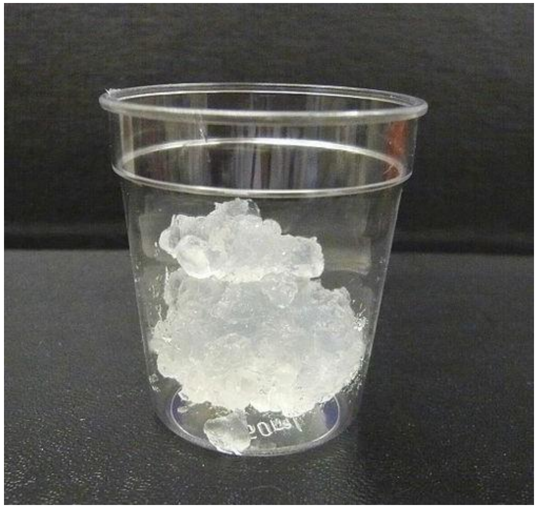
- **Mechanical fibrillation of cellulose fibers → cellulose microfibrils**
  high pressure homogenization; 300-500 bars; up to 30000kWh/t
- **Chemical treatment by strong acid**
  → cellulose nanocristals
  Concentrated sulfuric acid (~60% w/w; 130 min)

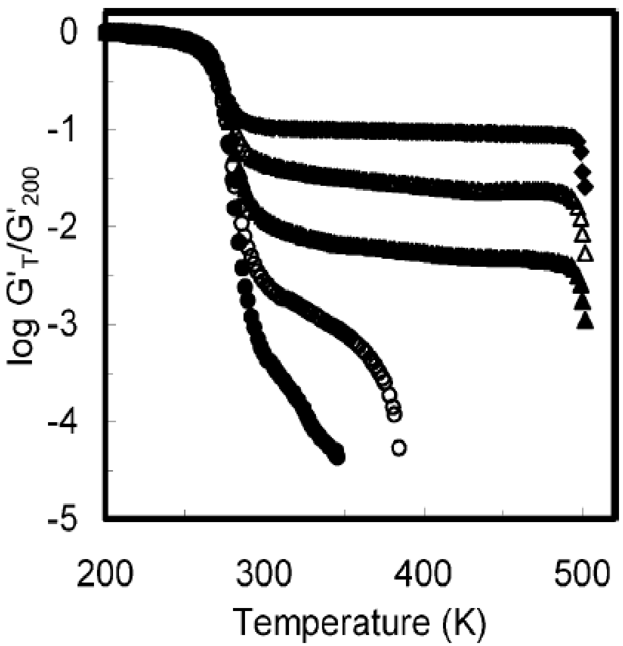
Nanocellulose.



Characteristics of Nanocellulose.

- high aspect ratio (length to width ratio)
- high Young Modulus
- thixotropic gel formation
- barrier properties of the nanocomposites
- transparency of the films after drying





Reinforcing effect of the cellulose nanocrystals

Figure 5. Logarithm of the normalized storage shear modulus (log G'_T/G'_{200}, where G'_{200} corresponds to the experimental value measured at 200 K) vs temperature at 1 Hz for tunicin whiskers reinforced poly(S-*co*-BuA) nanocomposite films obtained by water evaporation and filled with 0 (●), 1 (○), 3 (▲), 6 (△), and 14 wt % (◆) of cellulose whiskers.

Samir et al. 2005