Les lignines de deuxième génération

Bernard KUREK

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Fractionnement des Agroressources et Environnement

Reims

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La lignification

Les lignines

Pourquoi 2G??

Et au-delà…

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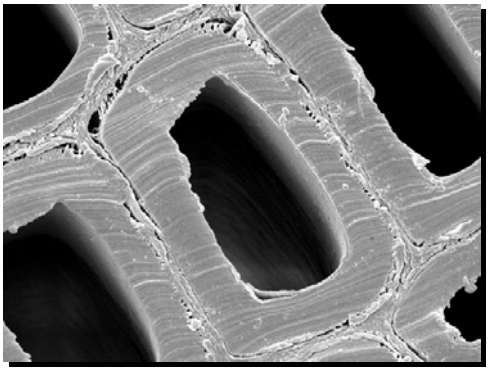
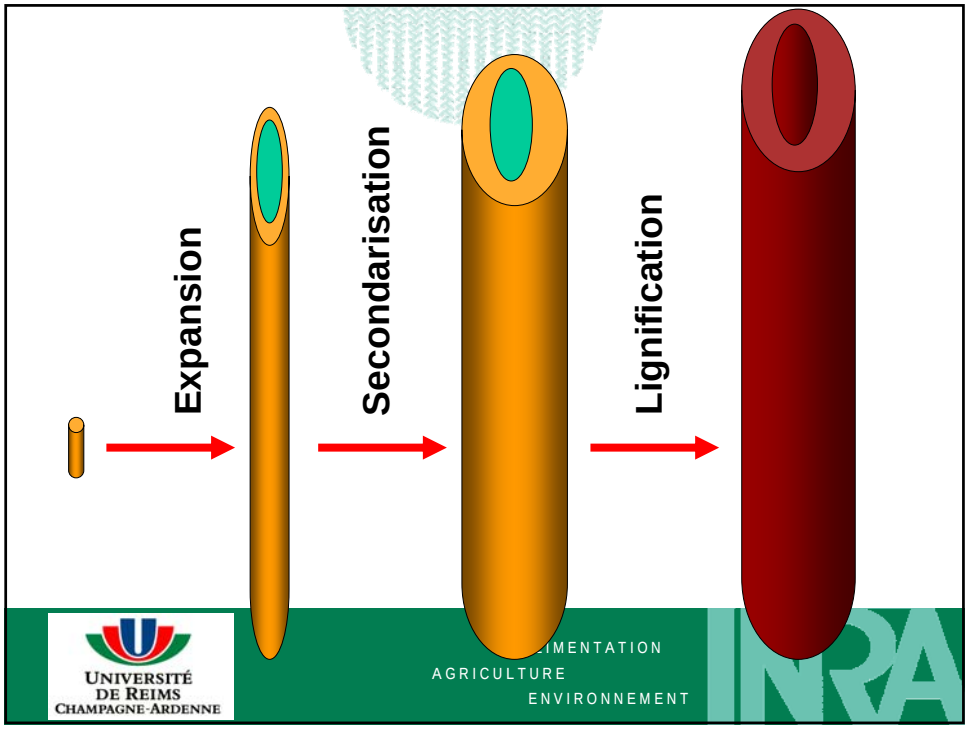
La lignification



L' arbre de jade….

INRA – Versailles-Grignon

qui peut se lignifier…


Expansion
Secondarisation
Lignification
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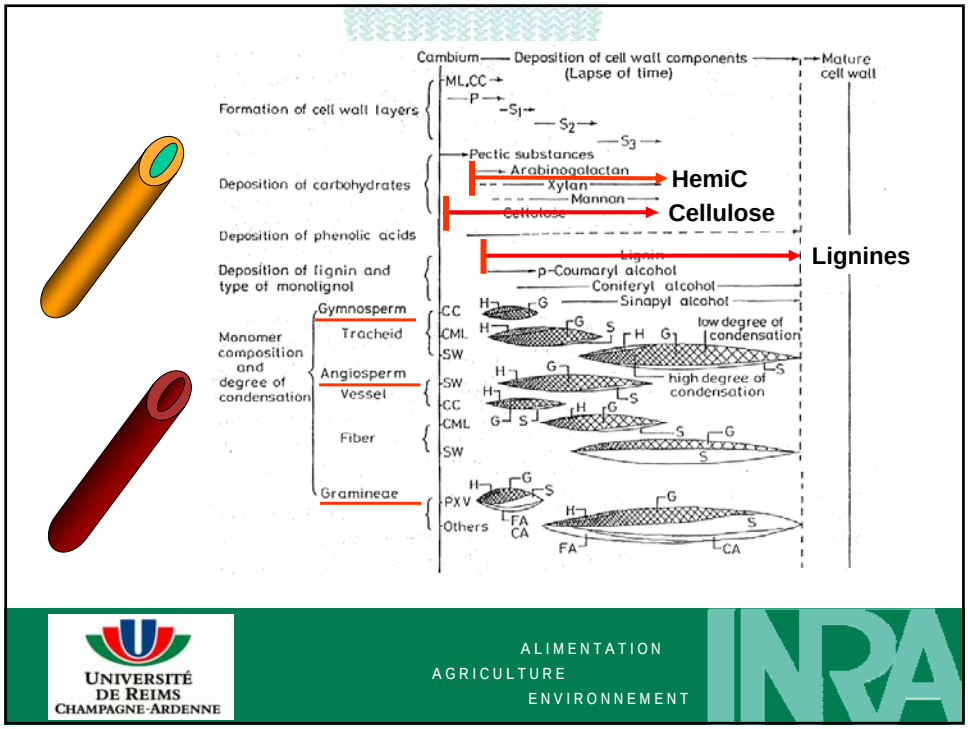
Cambium
Deposition of cell wall components
(Lapse of time)
Mature cell wall
Formation of cell wall layers
ML,CC
P
S1
S2
S3
Deposition of carbohydrates
Pectic substances
Arabinogalactan
Xylan
Mannan
Cellulose
HemiC
Cellulose
Deposition of phenolic acids
Lignin
Lignines
Deposition of lignin and type of monolignol
p-Coumaryl alcohol
Coniferyl alcohol
Sinapyl alcohol
Monomer composition and degree of condensation
Gymnosperm
Tracheid
CC
CML
SW
Angiosperm
Vessel
SW
CC
CML
Fiber
SW
Gramineae
PXV
Others
low degree of condensation
high degree of condensation
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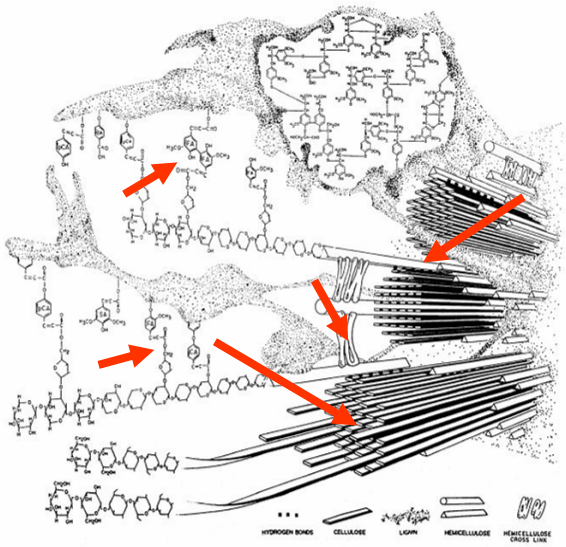
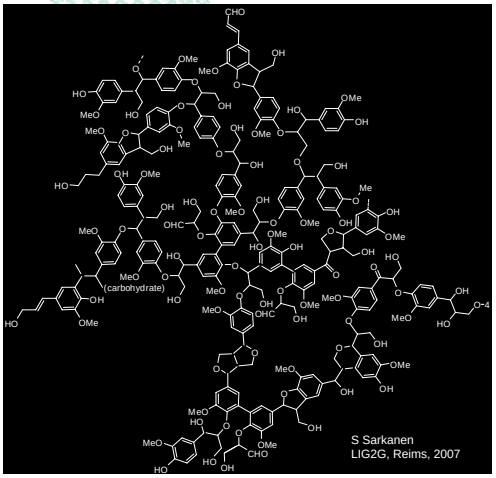


Figure 1. Secondary cell-wall (CW) structure. Components are arranged so that the cellulose microfibrils and hemicellulosic chains are embedded in lignin. Specific linkages and components of non-core lignin are shown for a generalized grass secondary CW. Non-core lignin components include *p*-coumaric (*p*CA), ferulic (FA), *p*-hydroxybenzoic (BA), sinapic (SA), and cinnamic (CA) acids.

Les lignines



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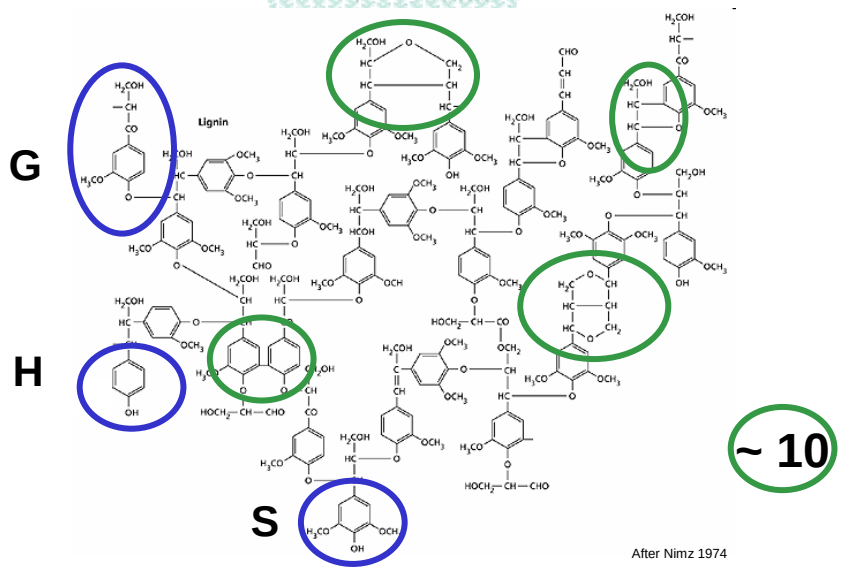

After Nimz 1974

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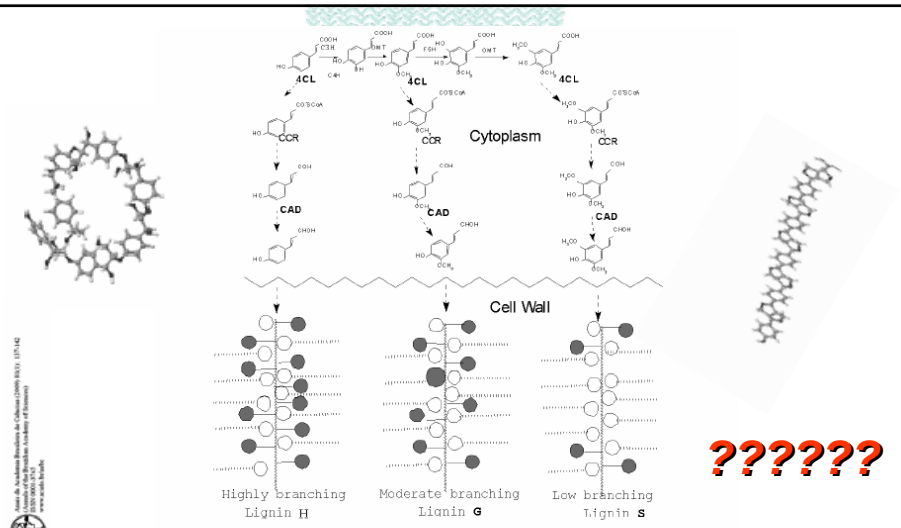

Fig. 1 – Syringyl and Guaiacyl lignins biosynthesis (pre-polymerization). **PAL**-Phenylalanine Amonia-lyase, **C3H**-4-Hydroxycinnamate-3-hydroxylase, **5H**-Ferulate-5-hydroxylase, **OMT**-5-Adenosyl-methyonine:caffeate/5-Hydroxyferulate-O-ethylransferase, **4CL**-Hydroxycinnamoyl:CoA ligase, **CCR**-Hydroxycinnamyl:CoA reductase, **CAD**-Cinnamyl alcohol dehydrogenase, **C4H**-Cinnamate-4-hydroxylase

??????

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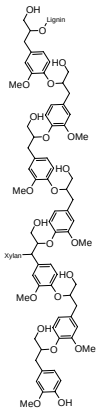
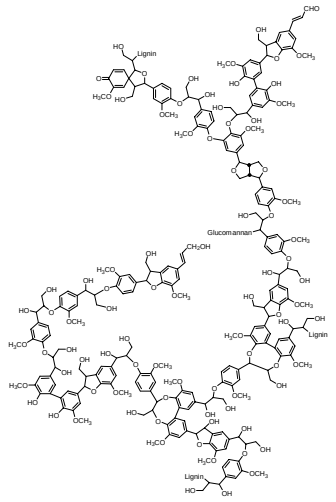
Suggested lignin structures in spruce wood

(G. Gellerstedt, LIG2G, Reims, 2007)



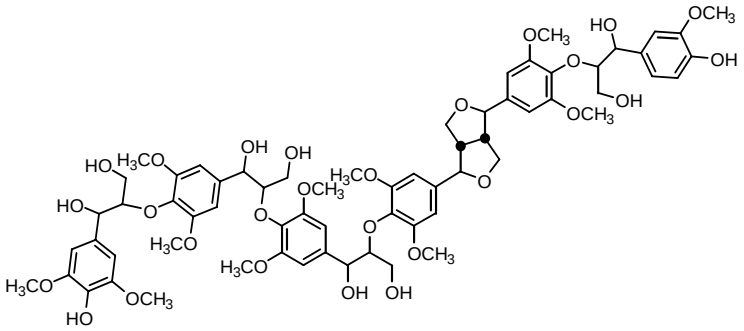
Linear xylan-lignin



Branched glucomannan-lignin

MS-identification of lignin fragment from *E. globulus* lignin

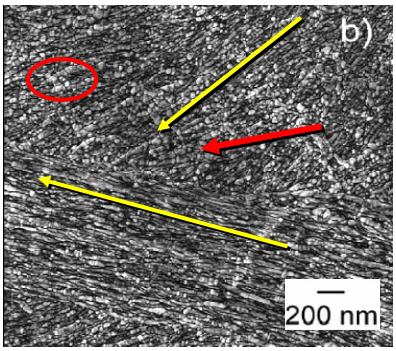
(G. Gellerstedt, LIG2G, Reims, 2007)

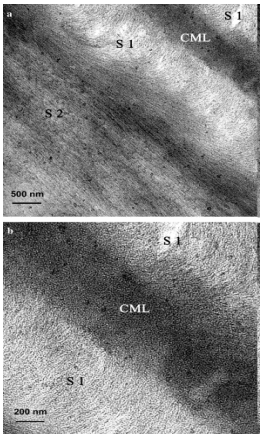


Evtuguin et al, 2003

Distribution des lignines dans les parois

AFM





Jörg Fromm
Journal of Structural Biology
Volume 143, Issue 2, July 2003, Pages 77-84

TEM

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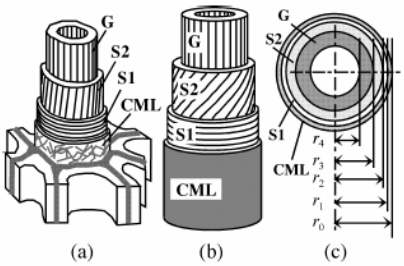
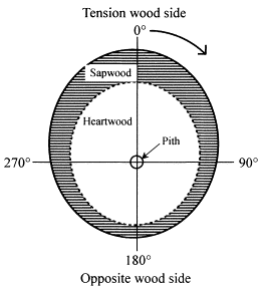
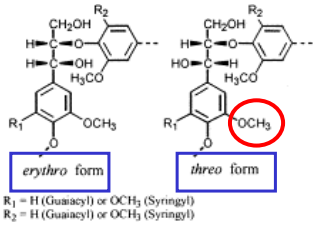


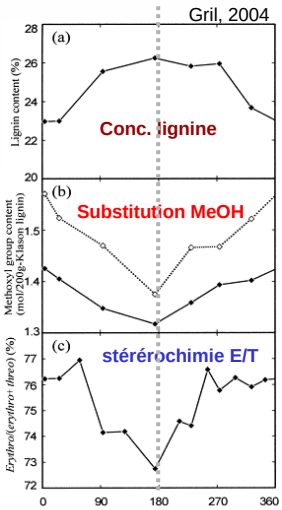
Fig.1. Multilayered structure of the gelatinous fiber. (a); Microscopic structure, (b); A mechanical model, (c); Crosscut surface of the mechanical model. Each consists of compound middle lamella (CML), outermost layer of the secondary wall (S1), its middle layer (S2), and gelatinous layer (G).



Akiyama, 2003



Gril, 2004



Position angulaire périphérique

- Variation saisonnière: largeur
- Variation temporelle: hauteur

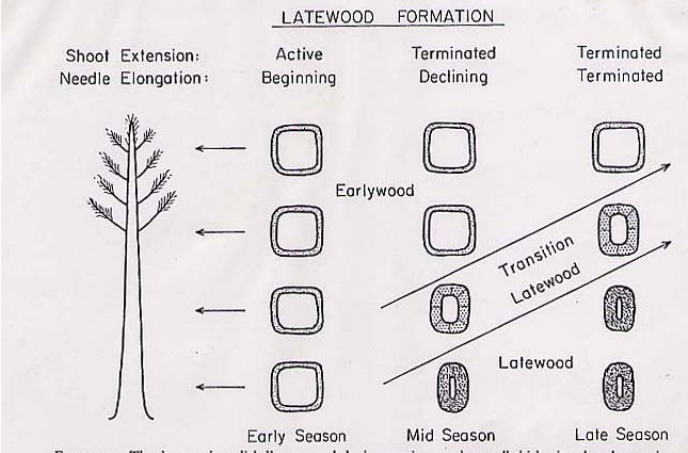
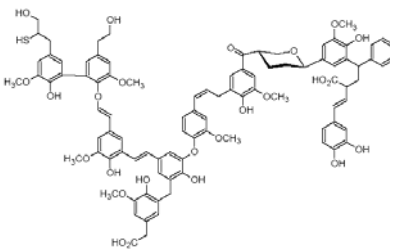


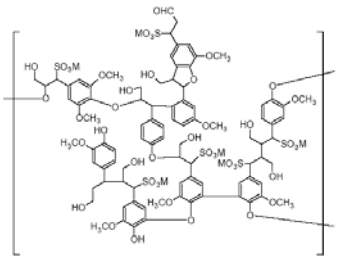
FIGURE 23. The decrease in radial diameter and the increase in secondary wall thickening that characterize latewood usually begin near the stem base and progress upward as the season advances.

http://members.jcom.home.ne.jp/chutatsu/ikurin.html

POURQUOI 2G??



Kraft



Lignosulfonates

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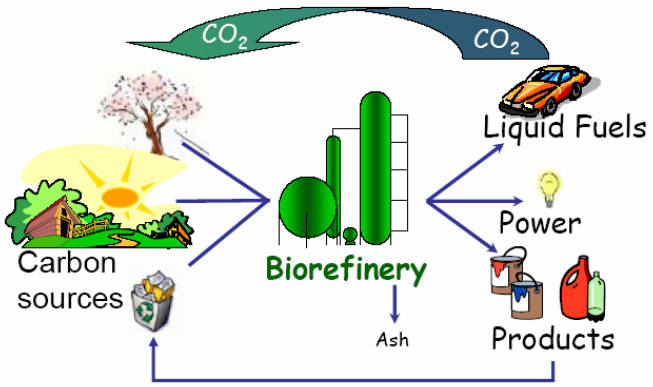

Figure 1 - Biorefinery Concept

Pacific Northwest National Laboratory

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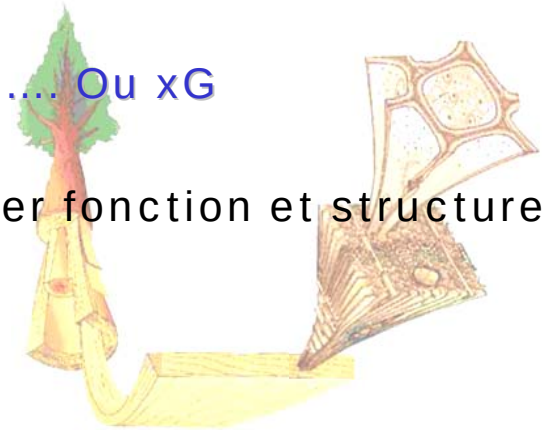
1G, 2G .... Ou xG

Accorder fonction et structure!!



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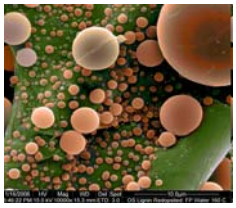
LIG2G ou LIGxG

- In situ *vs* lignine technique
- Fractionnement
- Isolement
- Purification



NREL

- Propriétés du polymère
- Propriétés d'usages

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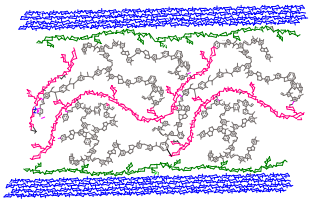
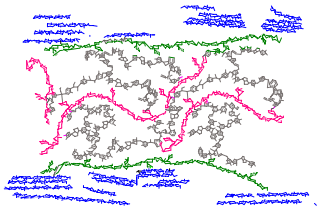
Dissolution of wood/pulp fibres by the use of enzyme

(G. Gellerstedt, LIG2G, Reims, 2007)



Endoglucanase
(Novozyme 476)



Action of urea

- Breaks down the crystallinity of the cellulose by forming hydrogen bonds between the microfibrils
- Dissolves any material containing > ~50% lignin
- Removes enzyme contamination from the fibres

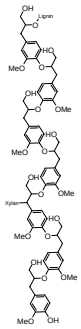
Action of alkaline borate solution

- Dissolves all remaining components

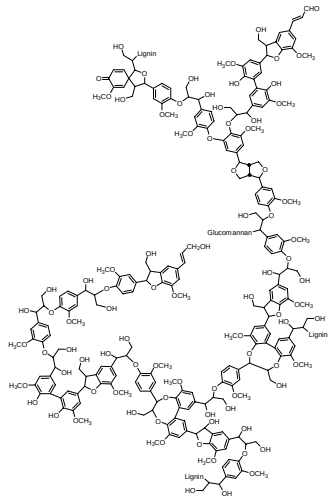
KTH ROYAL INSTITUTE OF TECHNOLOGY

Suggested lignin structures in spruce wood

(G. Gellerstedt, LIG2G, Reims, 2007)

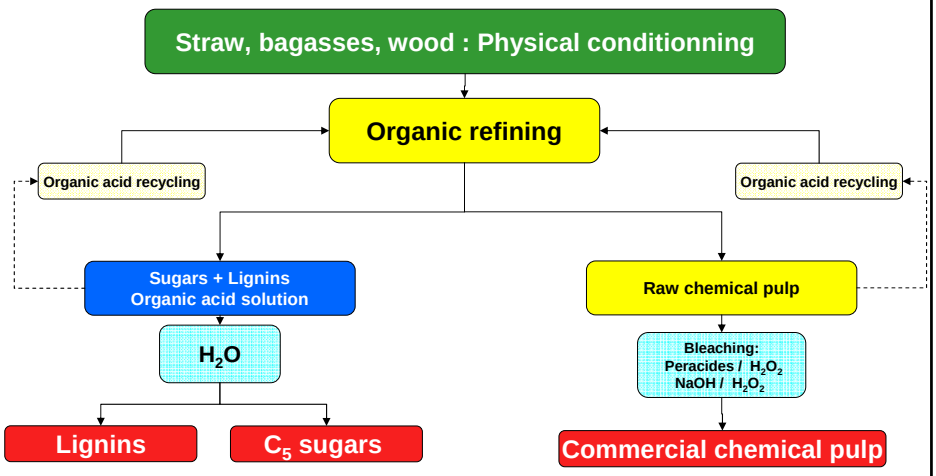


Linear xylan-lignin

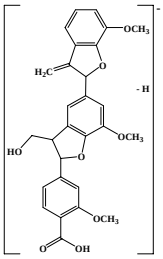


Branched glucomannan-lignin

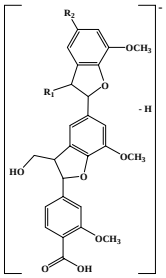
THE CIMV PROCESS



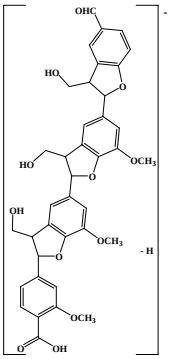
(M. Delmas, LIG2G, Reims, 2007)



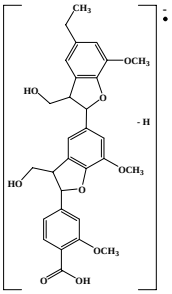
$[C_{28}H_{25}O_8]^-$
54



55 $[C_{28}H_{27}O_8]^-$: R_1=CH_3 ; R_2=H
13 $[C_{28}H_{27}O_9]^-$: R_1=CH_2OH ; R_2=H
15 $[C_{29}H_{29}O_9]^-$: R_1=CH_2OH ; R_2=CH_3
17 $[C_{30}H_{29}O_{10}]^-$: R_1=CH_2OH ; R_2=$COCH_3$
57 $[C_{30}H_{31}O_{11}]^-$: R_1=CH_2OH ; R_2=CHOH-CH_2OH



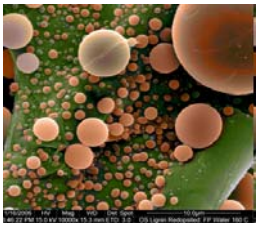
$[C_{38}H_{35}O_{12}]^-$
24



$[C_{30}H_{32}O_9]^{\cdot-}$
56

Propriétés des lignines

… en quoi l'avancé des connaissances est importante pour les applications



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THE INTERNATIONAL LIGNIN INSTITUTE

MULTI-POLARITY PRODUCTS		MATERIALS	AGRICULTURE	HIGH-PURITY VALUE APP.
dispersion	**others**			
ceramics oil well drilling clay bricks & tiles cements concrete gypsum board dyestuffs electrolytes paper sizing	complexing agents flocculating heavy metal binders ion exchanging water softening protein coagulants destabilization of oil emulsions corrosion protection anti-scaling metal cleaners grinding aids	phenolic resins polyurethanes epoxies particle boards resin boards rubber reinforcing bloc copolymers polyesters composites polyolefins biodegradables carbon sieves activated carbons carbon fibres heat resistance antioxidants anti-inflamation paper bounding	soil rehabilitation slow release fertilisers artificial humus fertiliser encapsulation composting aid manure treatment humus improvement soil stabilisation insecticides granulation pelletising chelates	antibacterial effects HIV inhibition digestion regulation antioxidants plant immunology growth stimulators oxygen scavengers hydrogels
emulsion				**MISCELLANEOUS**
wax asphalt bitumen vitamins micronutrients				energy production diesel fuel foam stabilizers binders tanning agent hydrophobization absorbents

http://www.ili-lignin.com/index.php

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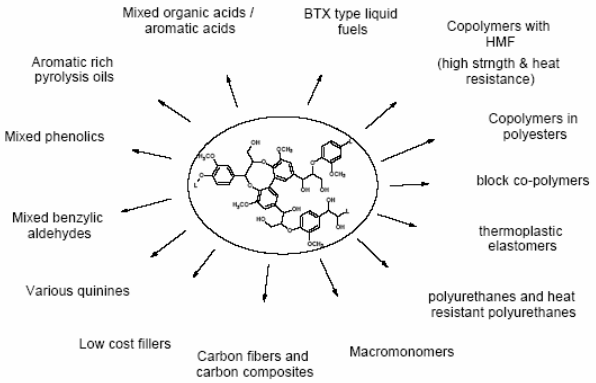

Figure A.10 – New Product Opportunities from Lignins

DOE, USA, 2007

[1] JE Holladay [2] JJ Bozell
[1] JF White [3] D Johnson

[1] Pacific Northwest National Laboratory
[2] University of Tennessee
[3] National Renewable Energy Laboratory

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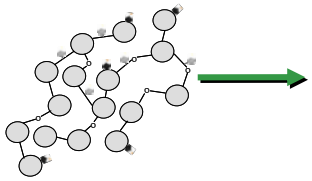
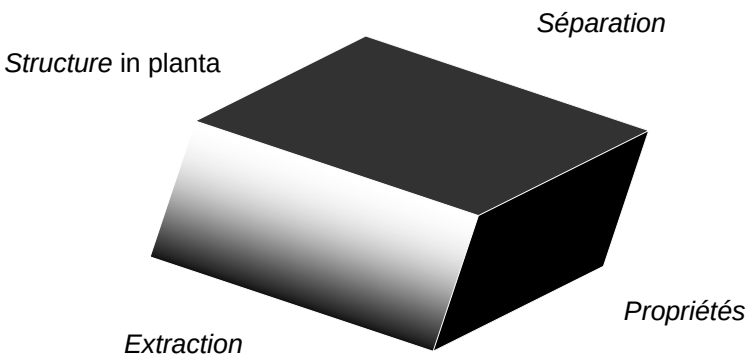


Vers les polymères et matériaux ???

P. Dole, LIG2G, Reims, 2007

Intrinsic mobility	Rigid aromatic tridimensionnal structure	High Tg : In situ lignin : 200°C Extracted lignin : 120 to 180°C depending on Mw
Geometry	Low molecular weight and (Non) linear structure	No entanglements Bad cohesion
Interactions	Semi polar aromatic structure	Solubility parameter around 11/12 $(cal/cm^3)^{1/2}$
		Association properties
		→ Lignin is plasticized by water Tg = 80°C in water saturation conditions
Functionnality	Phenols	Radical reactivity
	Alcools	Condensation reactions
Depolymerization	Two families of bonds	Easy partial hydrolysis, very difficult total depolymerization

En conclusion… LIGxG



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TOPICS

Fundamentals of lignocellulosic enzymes and transformation mechanisms
- Strategies for the discovery of new cell-wall degrading enzymes and/or activities
- Structure and catalytic mechanisms of cell-wall degrading enzymes
- Mechanisms of enzymatic deconstruction of cell-wall polymers
- Pretreatments and biodegradation mechanisms of lignocellulosics

Fundamental for plant building and design
- Fitting biomass diversity with industrial transformations
- Functional genomics of plant cell-wall formation for biotransformation
- Building of tailored cell-wall polymers and fibers in planta for materials
- Tailoring the cell-wall structure for enzyme and microbial biotechnology

Microbial genomics and biotechnology
- Genomics of microorganisms involved in lignocellulose biotransformation
- Metabolic engineering
- Exploring biodiversity and microbial ecology

Industrial applications
- Energy from lignocellulosic
- Fibrous materials from lignocellulosics
- Materials from cell-wall polymers
- Tailored cell-wall polymers

Environmental and Societal issues
- Biogeochemical aspects of non-food biomass production and transformation
- Impact of non-food biomass production on soil fertility
- Waste recycling of non-food biomass processes
- The green and white plant bioeconomy
- Building R&D pipeline for ligno - biotechnologies
- Sustainable innovation for plant biotechnology and plant biotransformation

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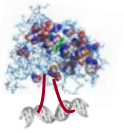
http://www.lille.inra.fr

http://www.inra.fr

Lignobiotech ONE :



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