Combining chemical tools and biological transformation for a cascade valorization of lignin

Prof. Stéphanie Baumberger
stephanie.baumberger@agroparistech.fr

ijpb

INRA SCIENCE & IMPACT

48th international colloquium of GFP - 27 November 2019, Mulhouse

AgroParisTech

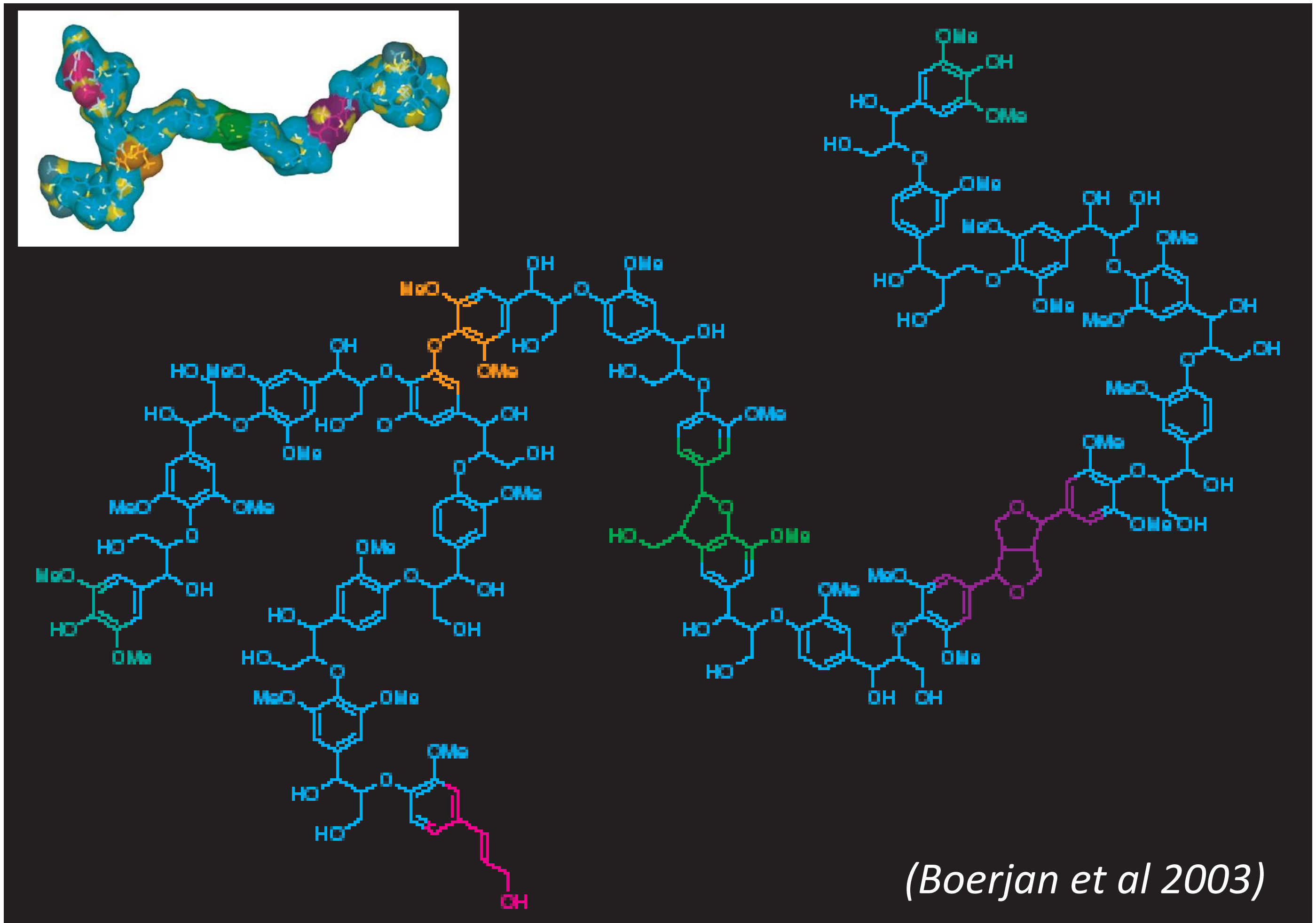
Outline

- Lignins: versatile natural phenolic polymers
- Multifunctionality of industrial lignin-derived products
- Strategy for lignin engineering in Zelcor project

Lignin model

"Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenylpropanoids"

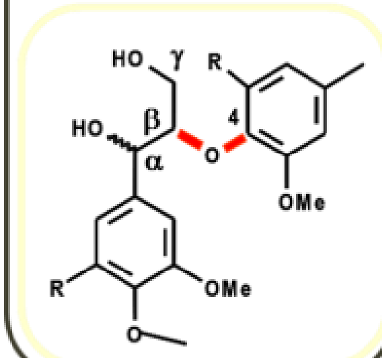
(Ralph et al., 2004)

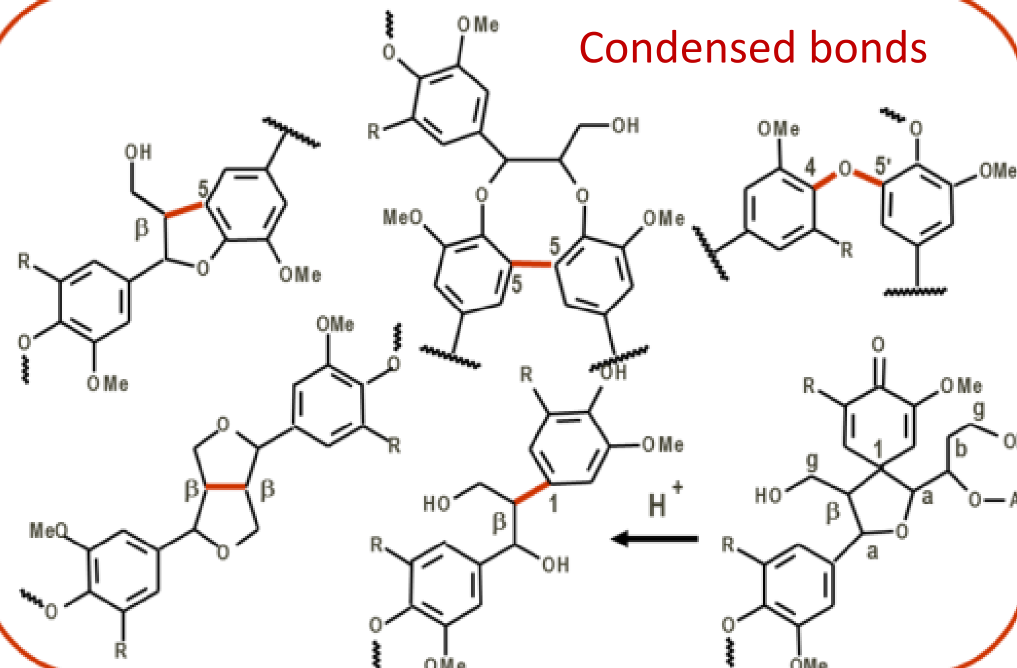


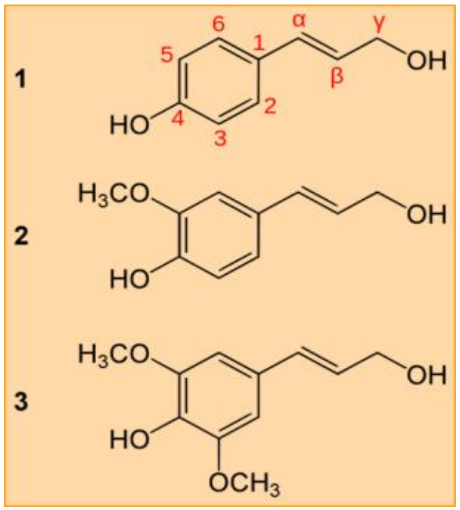
(Boerjan et al 2003)

Main monolignols and their possible bonding

β-O-4 bonds







p-Coumaryl alcohol **H**

Coniferyl alcohol **G**

Sinapyl alcohol **S**

- Proportions function of botanical origin, plant tissue, development stage, environmental factors
- Controled by genetic and physico-chemical phenomenon

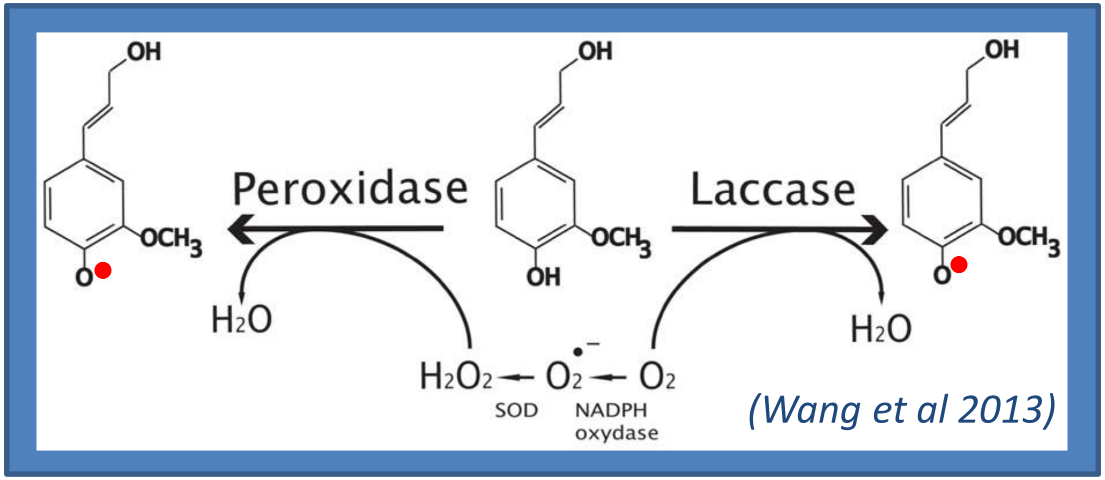
Mechanisms of polymerisation

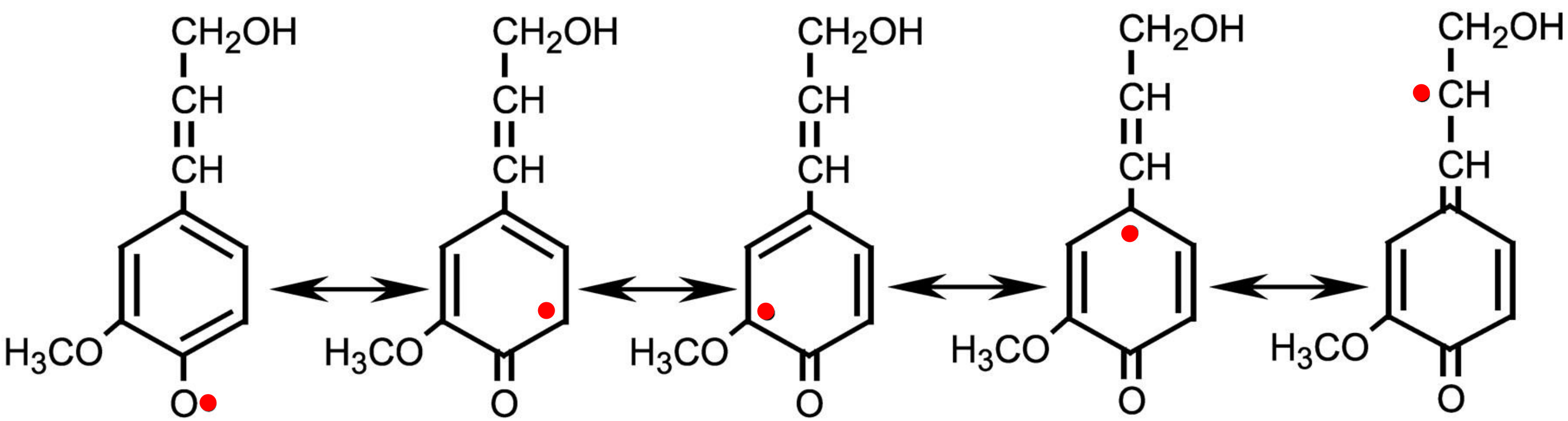
Monolignol

⇩

Enzymatic oxidation (oxido-reductases)

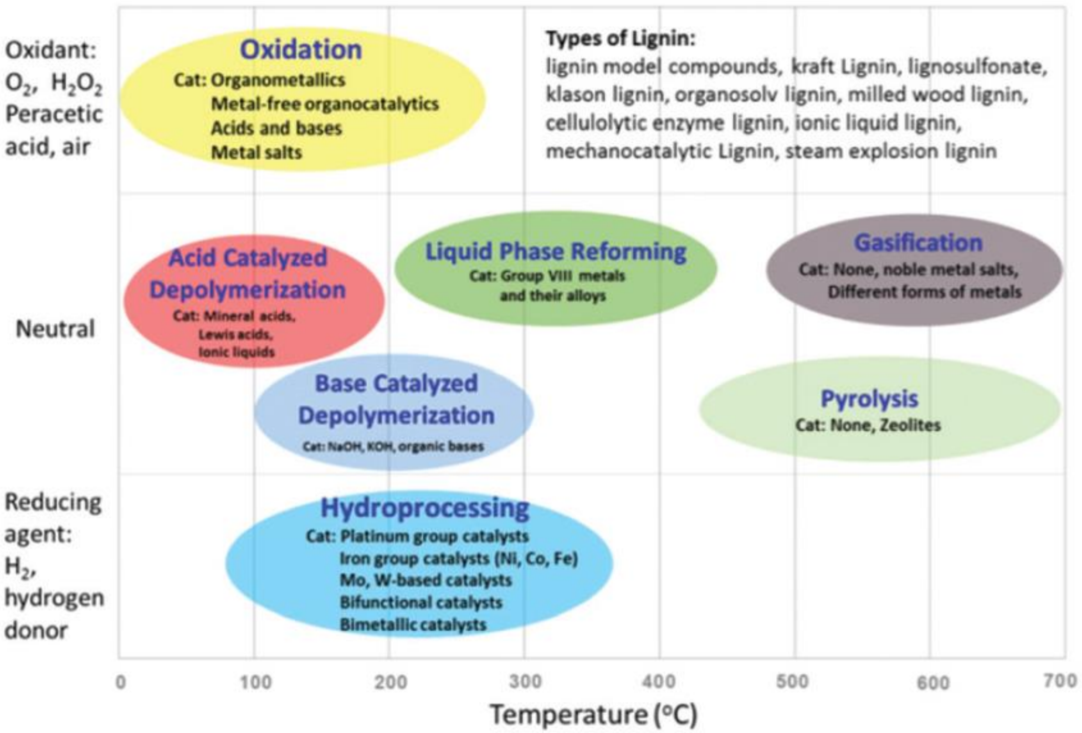
⇩





Lignins: a « recalcitrant » material

- Non soluble polymer in most common organic solvents
- Creation of resistant carbon-carbon bonds during conversion processing
- Drastic treaments required for extensive depolymerization

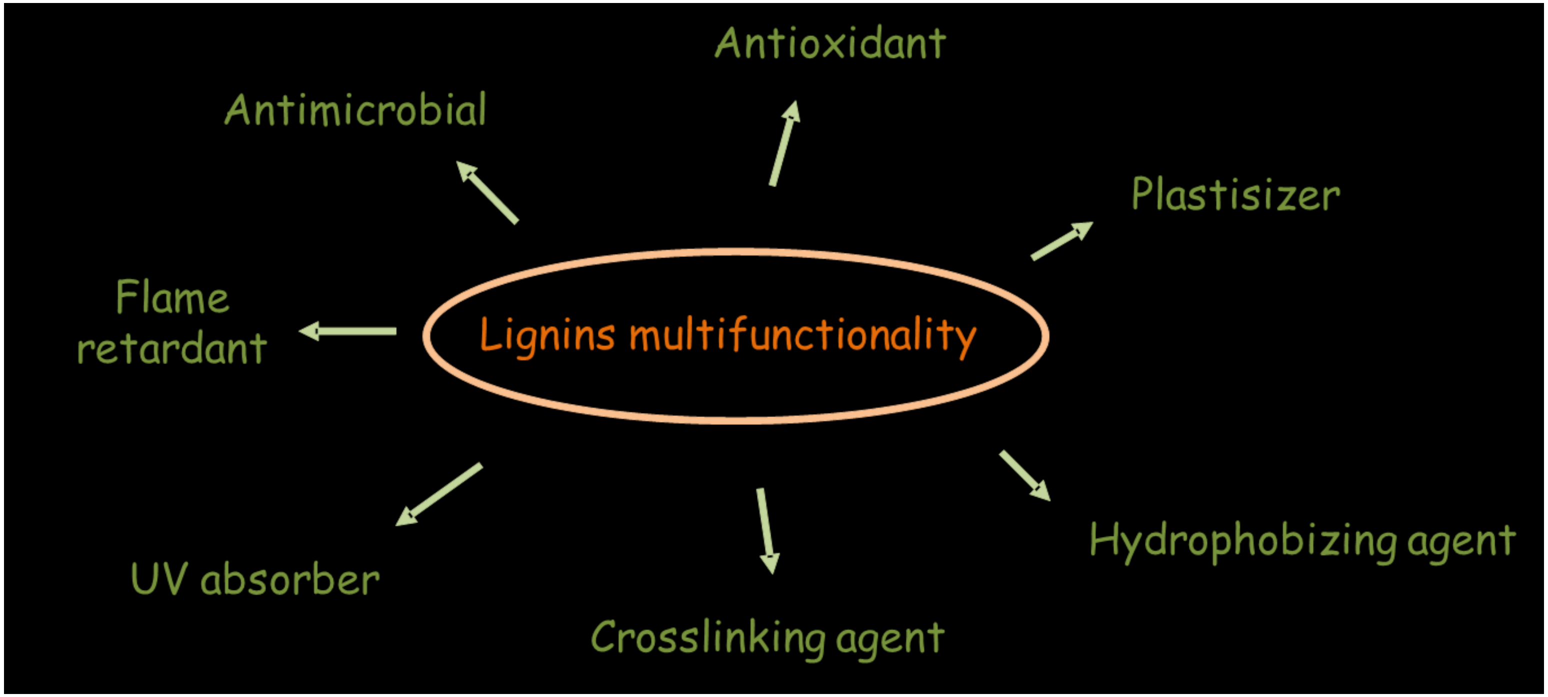


< 200°C ⇨ partial depolymerization

200-400°C ⇨ up to 80% bio crude oil production with maximum 20% phenolic monomer yield / lignin

> 400°C ⇨ loss of the phenolic monomers structures

… with broad multifunctionality



⇨ Bio-based molecules of interest for chemicals, plastics, and cosmetics industries

… and existing markets

Lignin products from pulp and paper industry

UPM's BioPiva™ lignin is a 100% bio-based, renewable substitute for fossil-based materials.

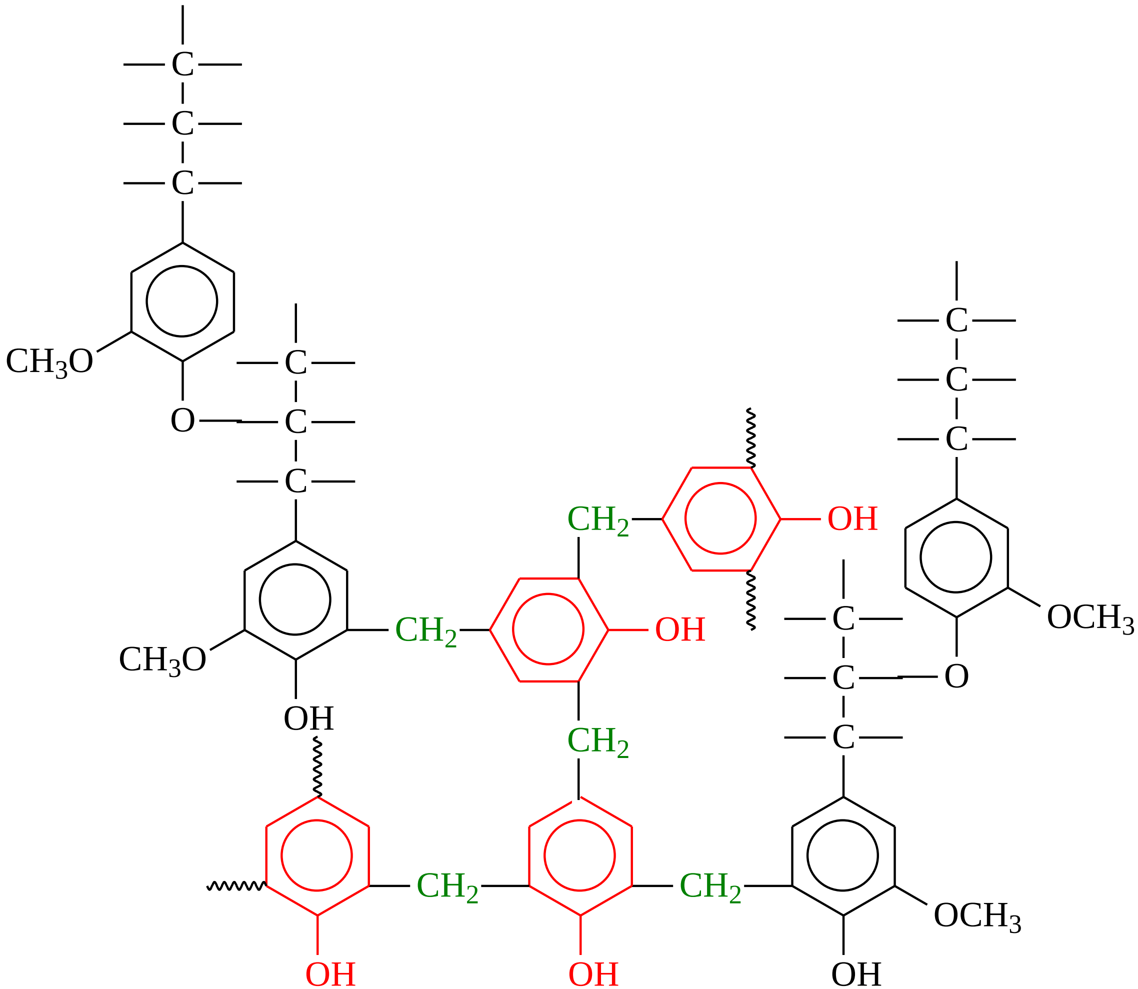
Almost a quarter of the dry mass of each tree is lignin, which is separated in the pulp production process and traditionally used as bioenergy through incineration. New, innovative uses of lignin, however, offer an effective way of reducing environmental impacts of different industries and dependency on fossil materials.

UPM is a pioneer in decades-long research on the utilisation of lignin, in resins, adhesives, bioplastics and polyurethanes, for example.

Since autumn 2017, lignin has been used as part of the WISA BioBond gluing technology in UPM Plywood's production. As of today, lignin can replace approximately two thirds of the phenol typically used in the adhesive – and the target is to further increase this proportion.

http://www.upmbiochemicals.com

Phenol-formaldehyde resins partially based on lignins



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

Lignin in fuel oil

Lignin fuel in lime kilns

Lignin pellets

https://www.borregaard.com/Products-Solutions

Dispersants

Kaolin/Water

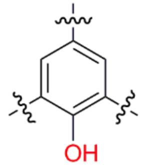
Lignin to carbon fibres

Spun lignin fibres

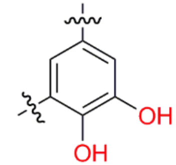
Other applications
- **Binders**
- **Benzene/Phenols**
- **Activated carbon**

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

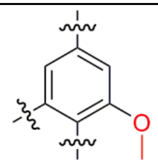
Functional groups of technical lignins



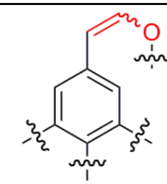
Phenols



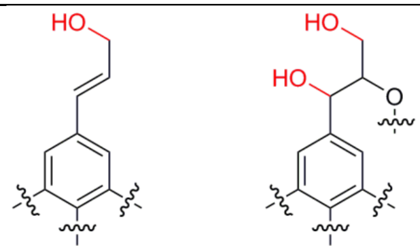
Catechols (soda and Kraft process)



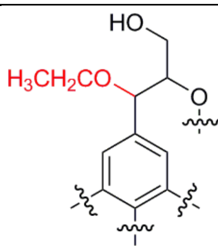
Methoxyls



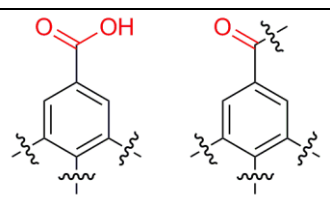
Enol ethers (Kraft process)



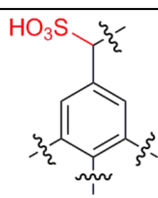
Aliphatic alcohols



Ethyl ethers
(ethanol process in acidic medium)

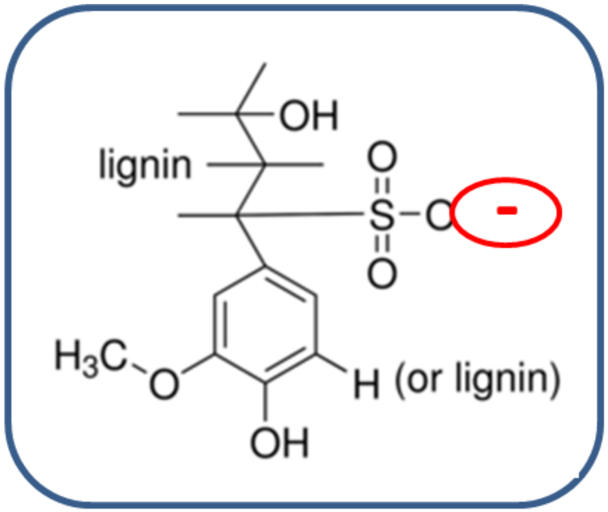


Carboxyls and carbonyls



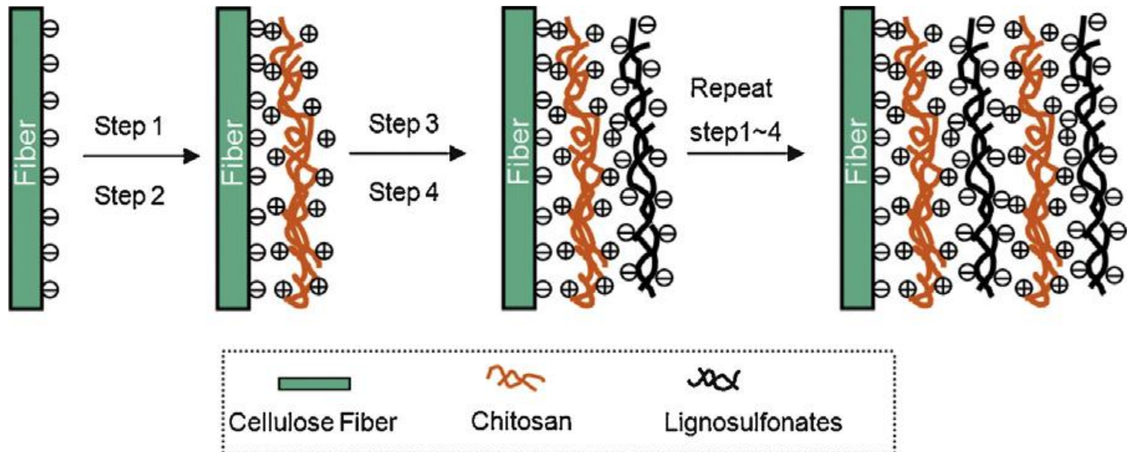
Sulfonates (bisulfite process)

Lignosulfonates specificities

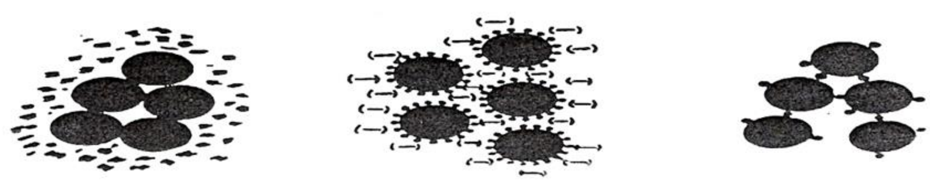


Water soluble polyelectrolytes

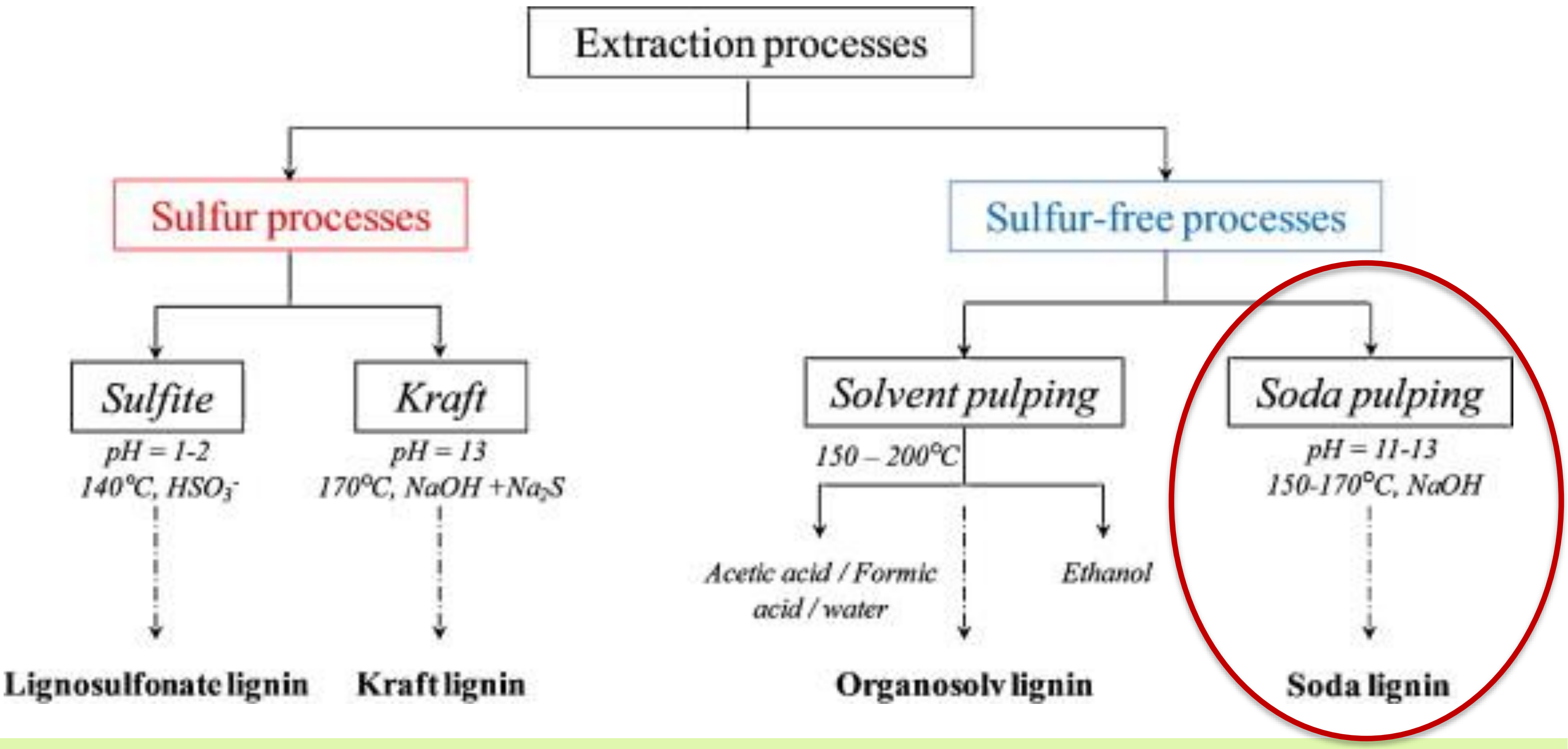
Self-assemblying and stabilisation of dispersions



(Li and Peng, 2015)



Possibility to select lignins to meet user requirements

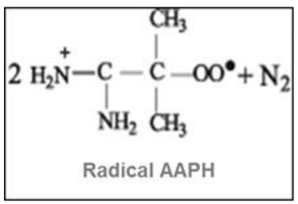


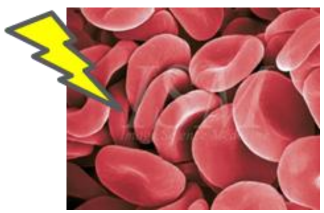
	Lignosulfonate lignin	Kraft lignin	Organosolv lignin	Soda lignin
M_n (g mol^{-1})	15,000–50,000	1000–3000	500–5000	800–3000
M_w / M_n	6–8	2.5–3.5	1.5–2.5	2.5–3.5
T_g (°C)	130	140–150	90–110	140

(Laurichesse and Averous, 2014)

Lignin antioxidant properties

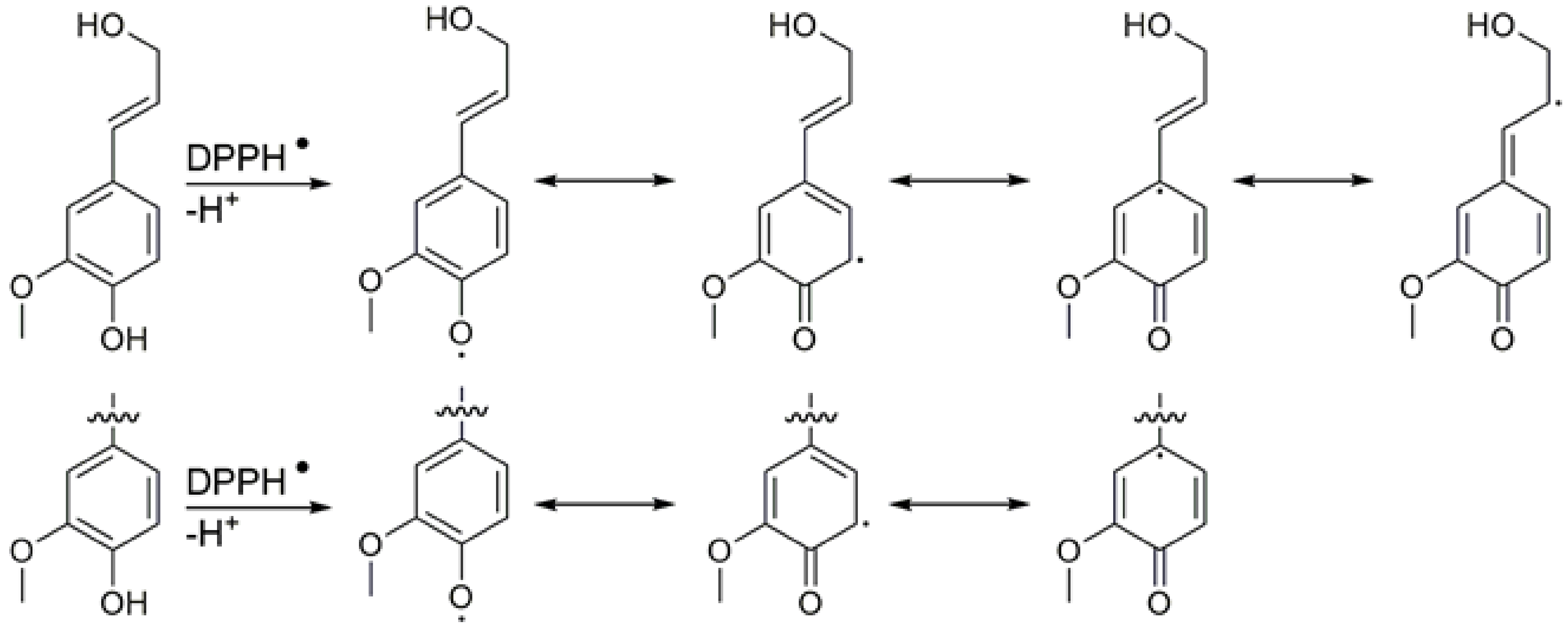
Human cell protection against oxidative stress
(Vinardell et al. 2008)





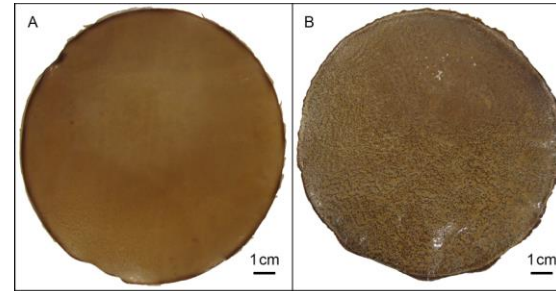
Product	EC_{50} (µg/ml)
Soda lignin	44,9 ± 6.7
Lignosulfonates	133,6 ± 9.0
Kraft lignin	85,9 ± 4.6
Steam explosion	74,6 ± 1.0
(−)-Epicatechin	42,3 ± 3.0

Radical scavenging mechanism

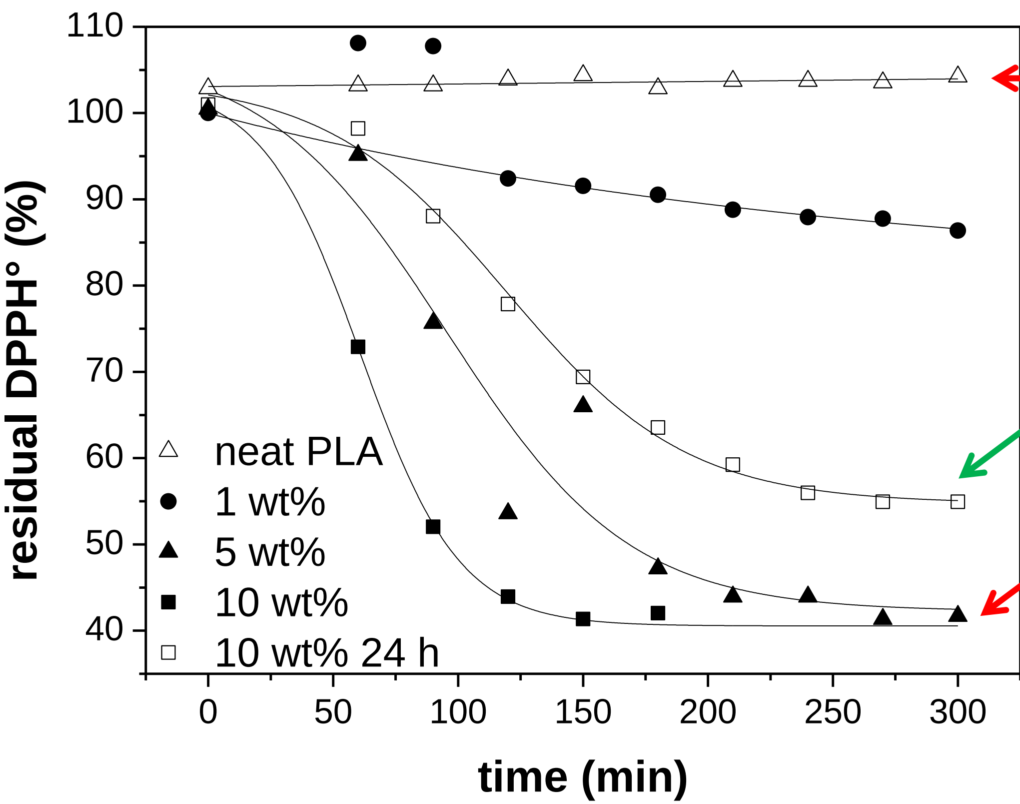


Formation of a phenoxy radical by transfer of one electron to the DPPH• radical and stabilisation of the phenoxy radical through resonance effect

Use of lignin as antioxidant in multifunctional films



Film polylactic acid (PLA) – lignins



Film 0% lignin
No extraction

Film 10 % lignin
Extraction by ethanol (24 h)

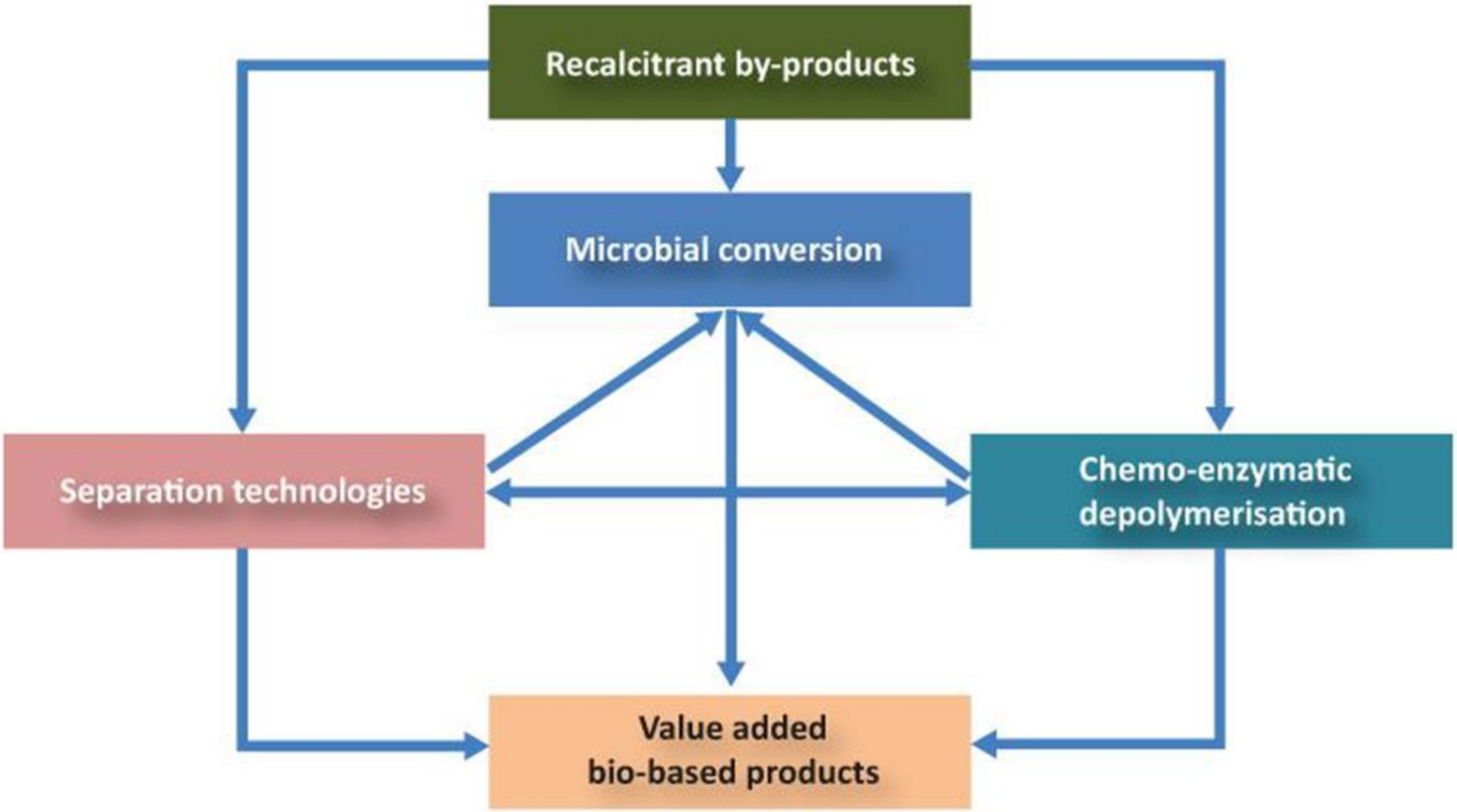
Film 10 % lignin
No extraction

(Domenek et al 2013)

Zelcor project

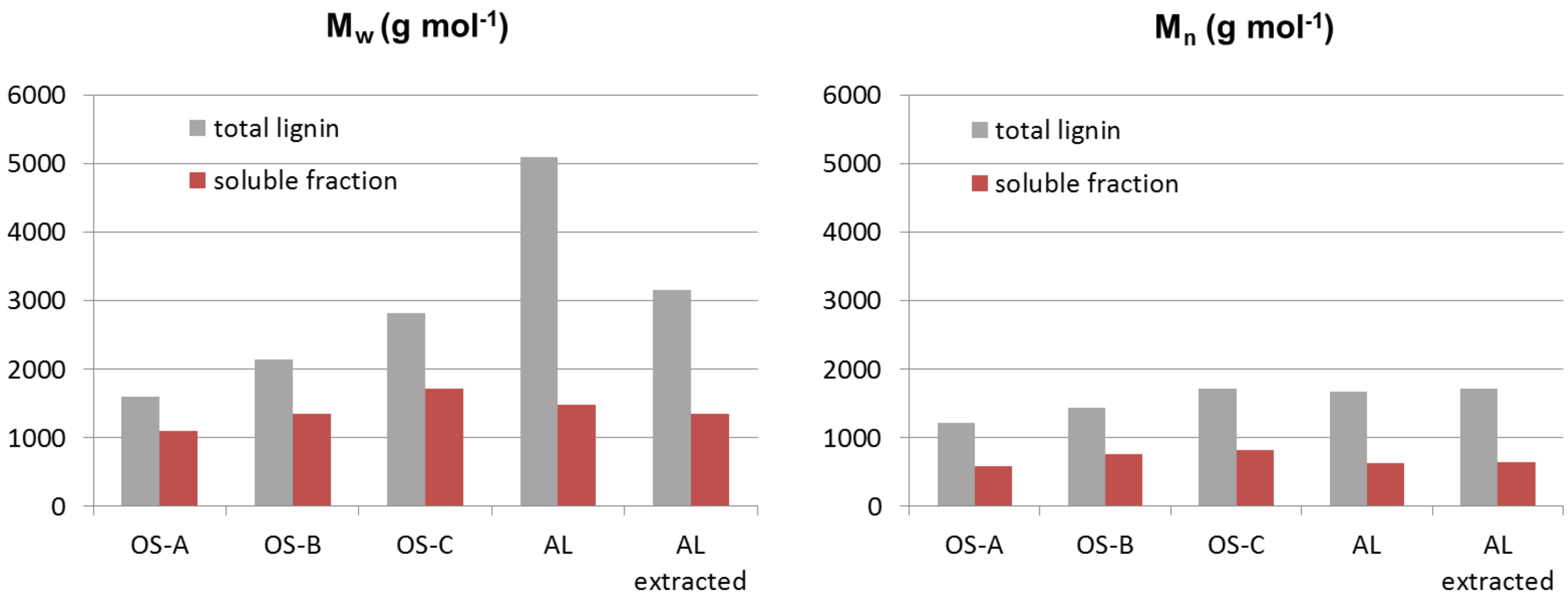
This project has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation program under grant agreement No 720303

Concept



Bio-based Industries Consortium
Horizon 2020 European Union Funding for Research & Innovation
This project has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation program under grant agreement No 720303

Solvent selective extraction of lignin oligmers



Average molar masses of grass lignins and their ethanol soluble fractions (OS=organosolv lignin; AL=alkali lignins)

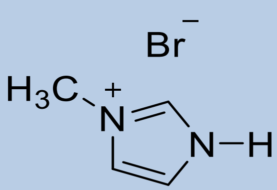
Lignin depolymerisation using ionic liquids (IL)

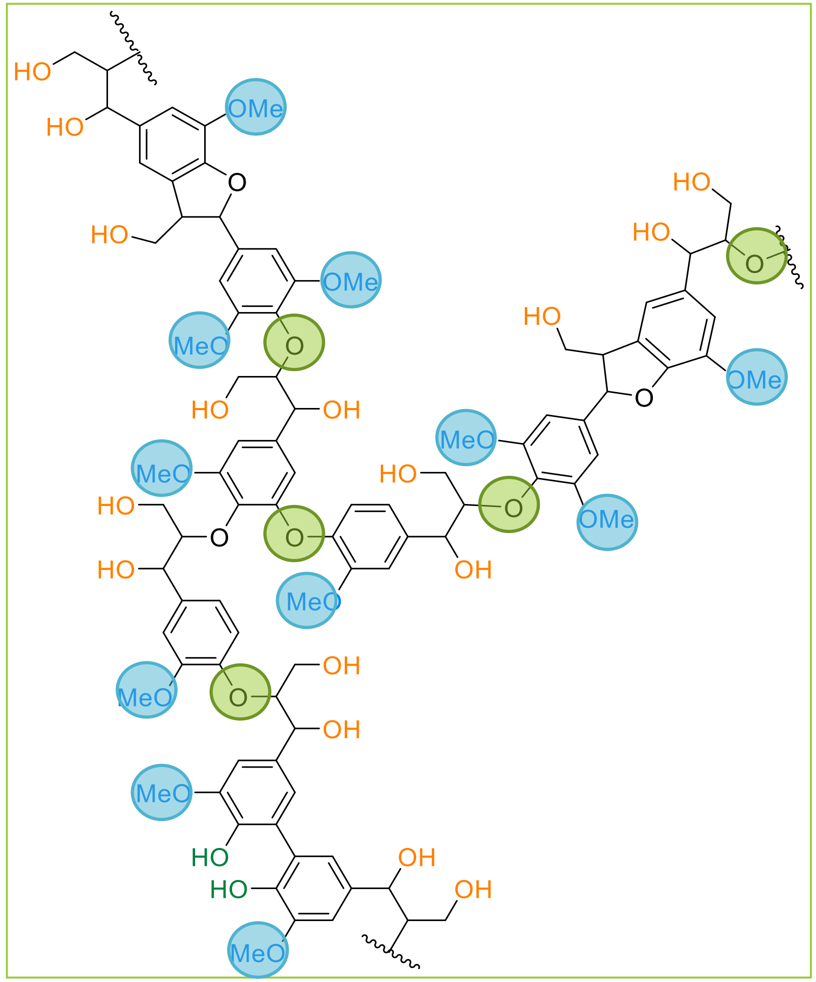
Target of IL treatment: ether bonds

- Methoxyl groups
- β-O-4 bonds

Release of lignin fragments and monomers with higher content of phenolic groups

Imidazolium based ionic liquid

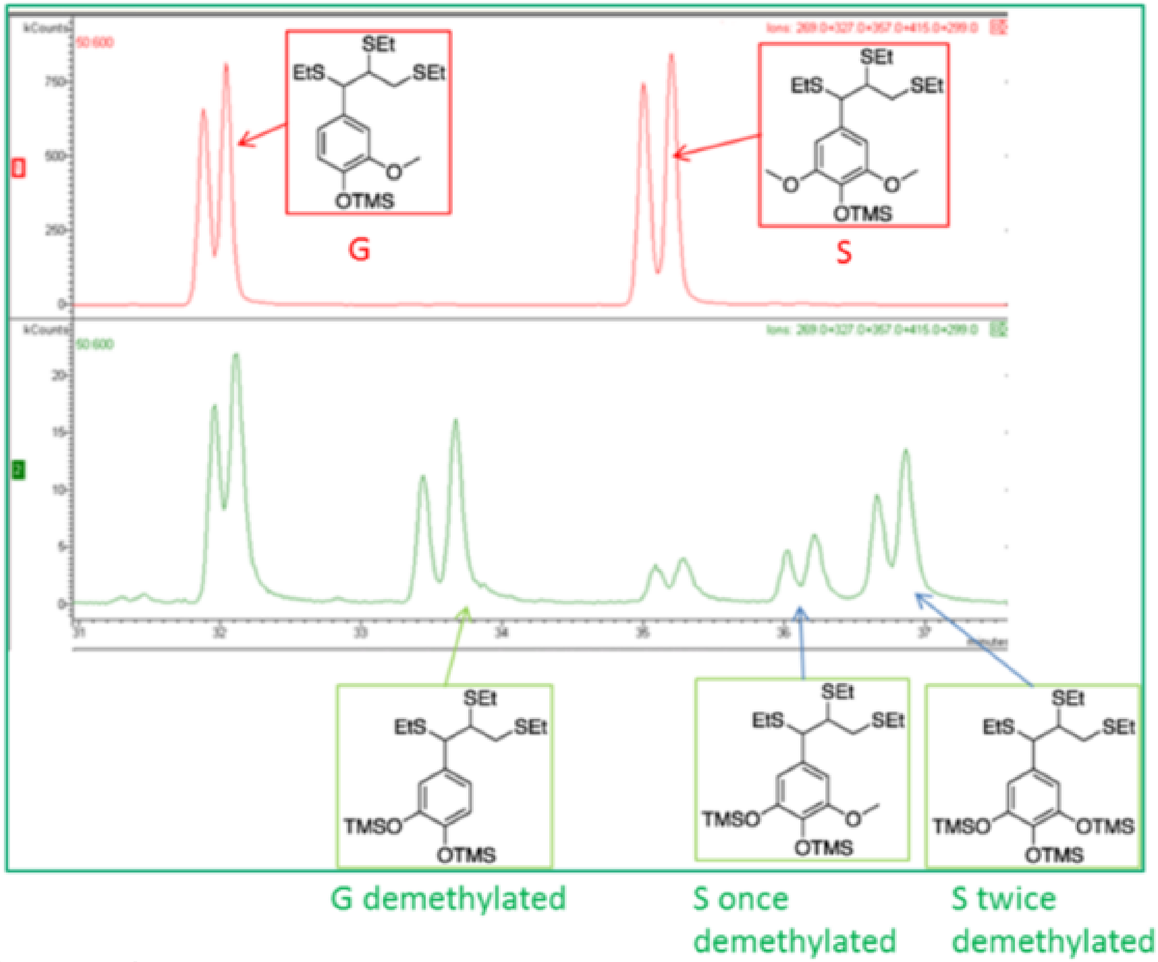




Evidence of demethylation

Thioacidolysis – GC MS

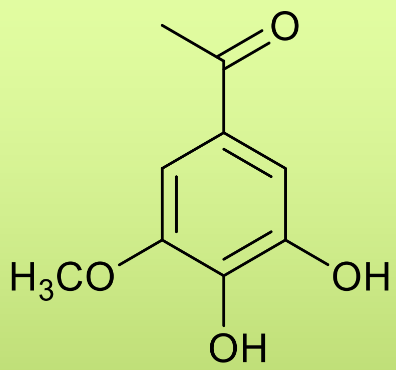
↔ lignin units involved in the polymer through β-O-4 bonds



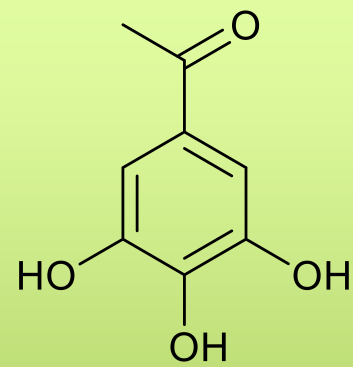
(Thierry et al., 2018)

Evidence of demethylation

Direct GC-MS analysis of the free monomer fraction



1-(3,4-dihydroxy-5-methoxyphenyl)-ethan-1-one

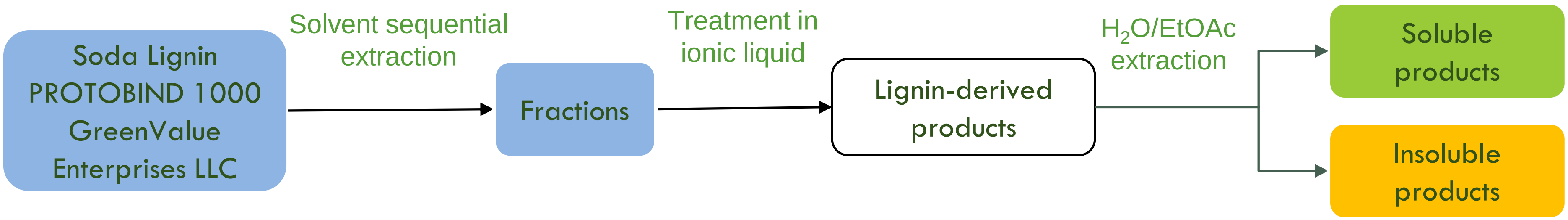


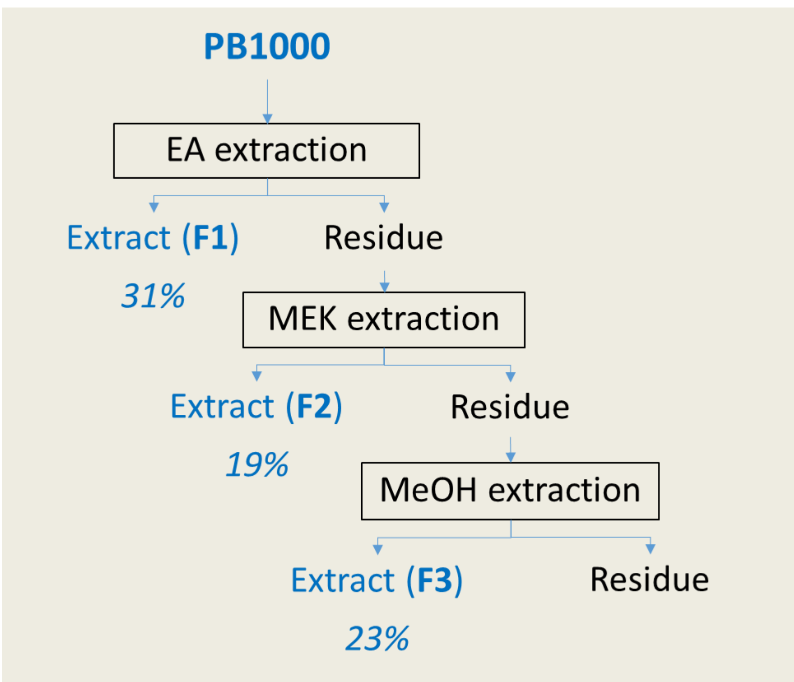
1-(3,4,5-trihydroxyphenyl)-ethan-1-one

(Majira et al., 2019)

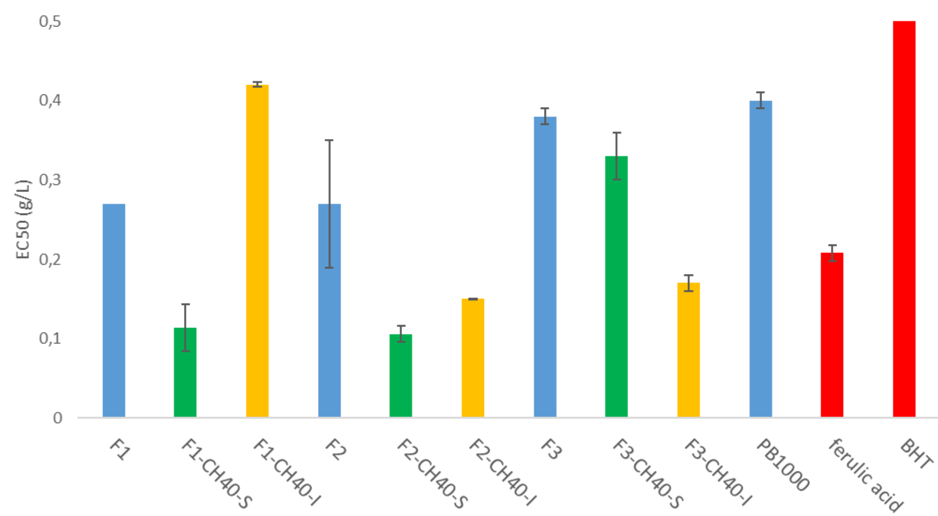
Depolymerisation products = powerfull antioxidants (> BHT)

IL treatment of soda lignin fractions



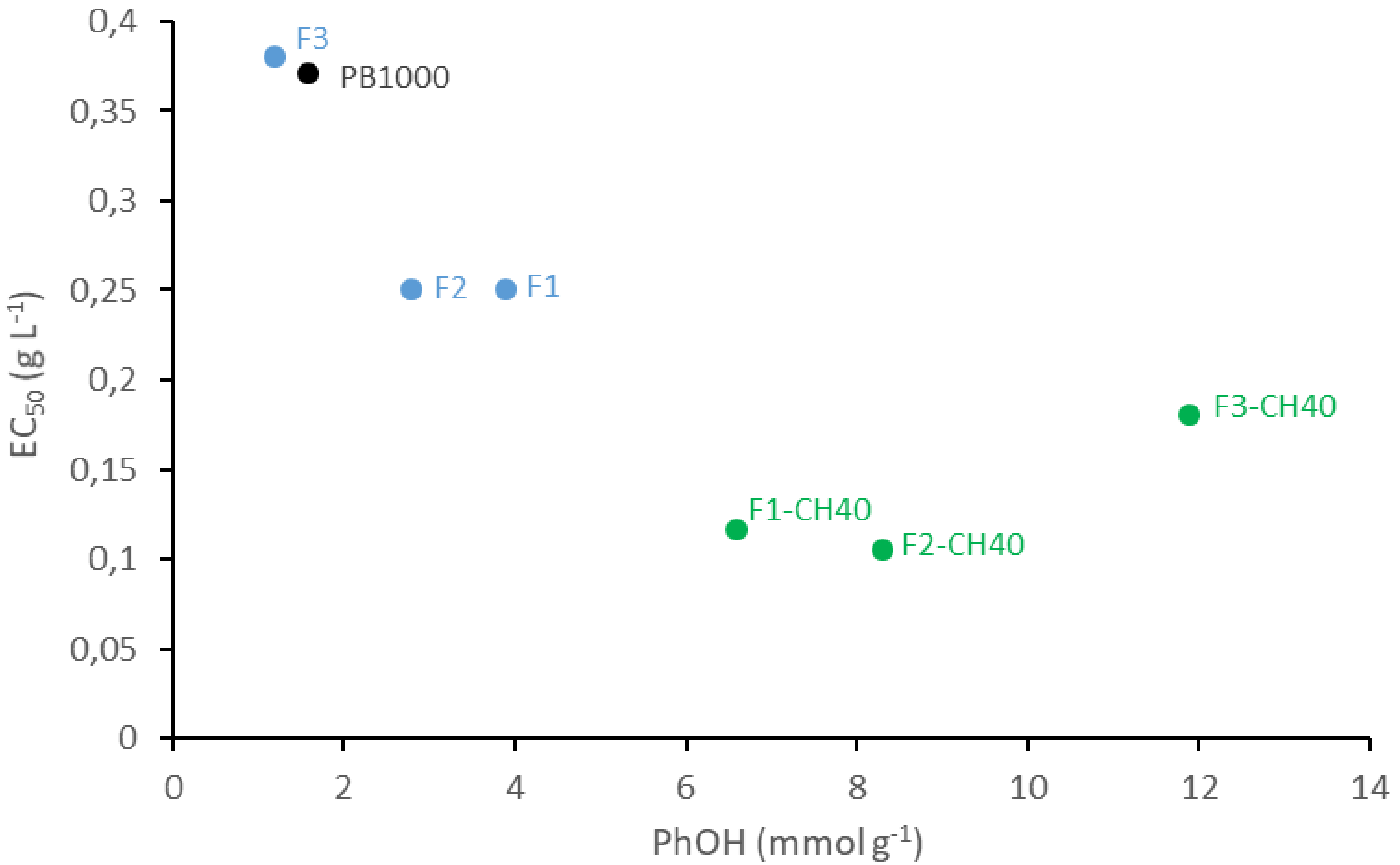


Fractionation scheme



Antioxidant properties of the products

Recovery of final oligomer extracts with improved functionalities



Interest of combining fractionation with depolymerisation

COVER PICTURE

A. Majira, B. Godon, L. Foulon, J. C. van der Putten, L. Cézard, M. Thierry, F. Pion, A. Bado-Nilles, P. Pandard, T. Jayabalan, V. Aguié-Béghin, P.-H. Ducrot, C. Lapierre, G. Marlair, R. J. A. Gosselink, S. Baumberger,* B. Cottyn*

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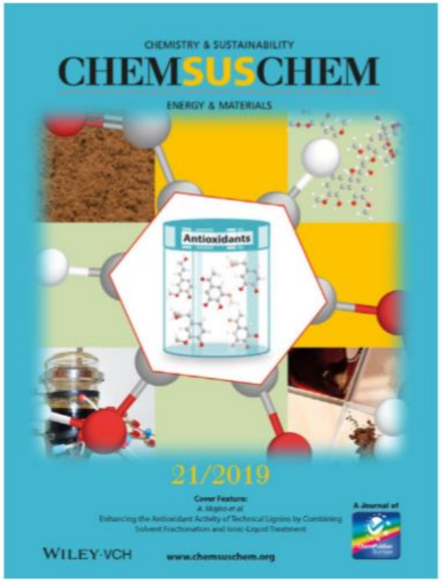
Enhancing the Antioxidant Activity of Technical Lignins by Combining Solvent Fractionation and Ionic-Liquid Treatment



The Cover Feature shows a cascade biorefinery process for the upgrading of technical lignins and sustainable production of phenolic oligomers of interest as substitutes for commercial antioxidants. A grass soda technical lignin undergoes a process combining solvent fractionation and treatment with an ionic liquid, and a comprehensive investigation of the structural modifications is performed. More information can be found in the Full Paper by A. Majira et al.

Interest of combining fractionation with depolymerisation

Lignin
= phenolics
+ carbohydrates +
ash
+ proteins, …

→ **Extraction (solvent 1)** → **Phenolic extract 1**
- ✓ Functional (*soluble, biologically active, antioxidant*)
- ✓ Standardised Mn and Mw*

31%
AOP x 1.5
PhOH x 1.5

Residue → **Extraction (solvent 2) + depolymerisation** →

Phenolic extract 2
- ✓ Functional (*soluble, biologically active, antioxidant*)
- ✓ Standardised Mn and Mw*

3%
AOP x 3.6
PhOH x 3.1

By-product 2
- ✓ Antioxidant

14%
AOP x 2.7

Residue → **Extraction (solvent 3) + depolymerisation** →

Phenolic extract 3
- ✓ Functional (*soluble, biologically active, antioxidant*)
- ✓ Standardised Mn and Mw*

1.5%
AOP x 1.2
PhOH x 4.5

By-product 3
- ✓ Antioxidant

15%
AOP x 2.4

Lignin fraction suitable for bioconversion
- ✓ Detoxified
- ✓ Rich in carbohydrates

*600-800 $gmol^{-1}$

Current developments

ZELCOR
Zero Waste Ligno-Cellulosic Bio-Refineries

- Efforts to reduce the environmental impact of the process
  $\rightarrow$ reduction of solvent consumption, IL recycling

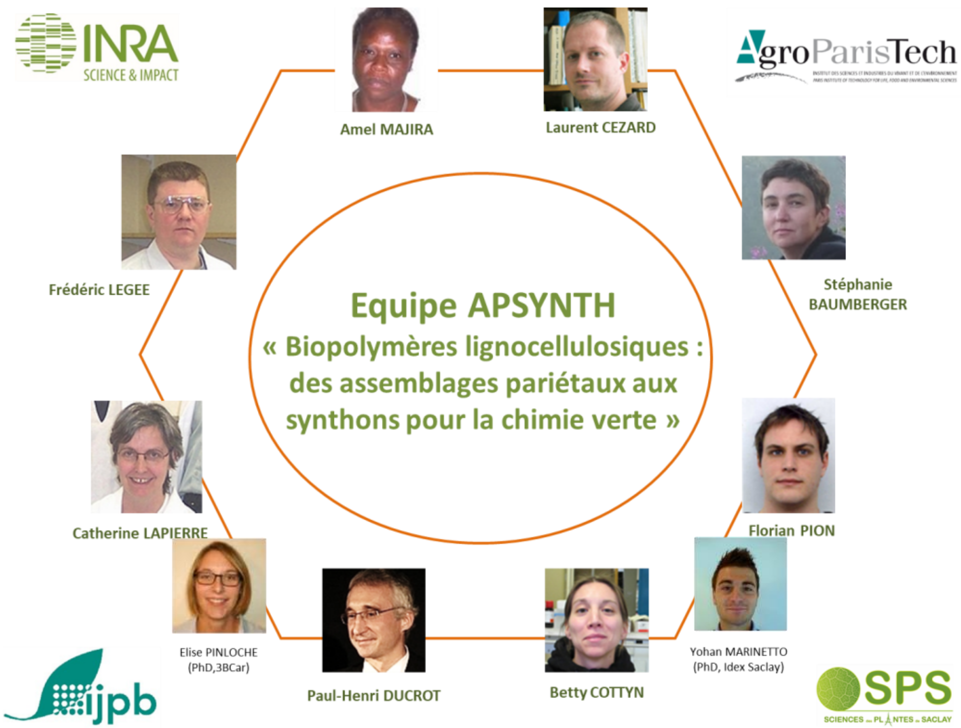
- Design of bioreactors for the conversion of the residues

- Formulation and assessment of products (skin care cream, plastics, colloidal lignin particles, …)

- Large-scale production of enzymes for lignin functionalisation

Acknowledgements

- Zelcor project consortium
- Université de Versailles St-Quentin-en-Yvelines
- Institut de Chimie Moléculaire et des Matériaux d'Orsay
- UMR1318 IJPB Apsynth team and « Observatoire du végétal »



Thank for your attention