



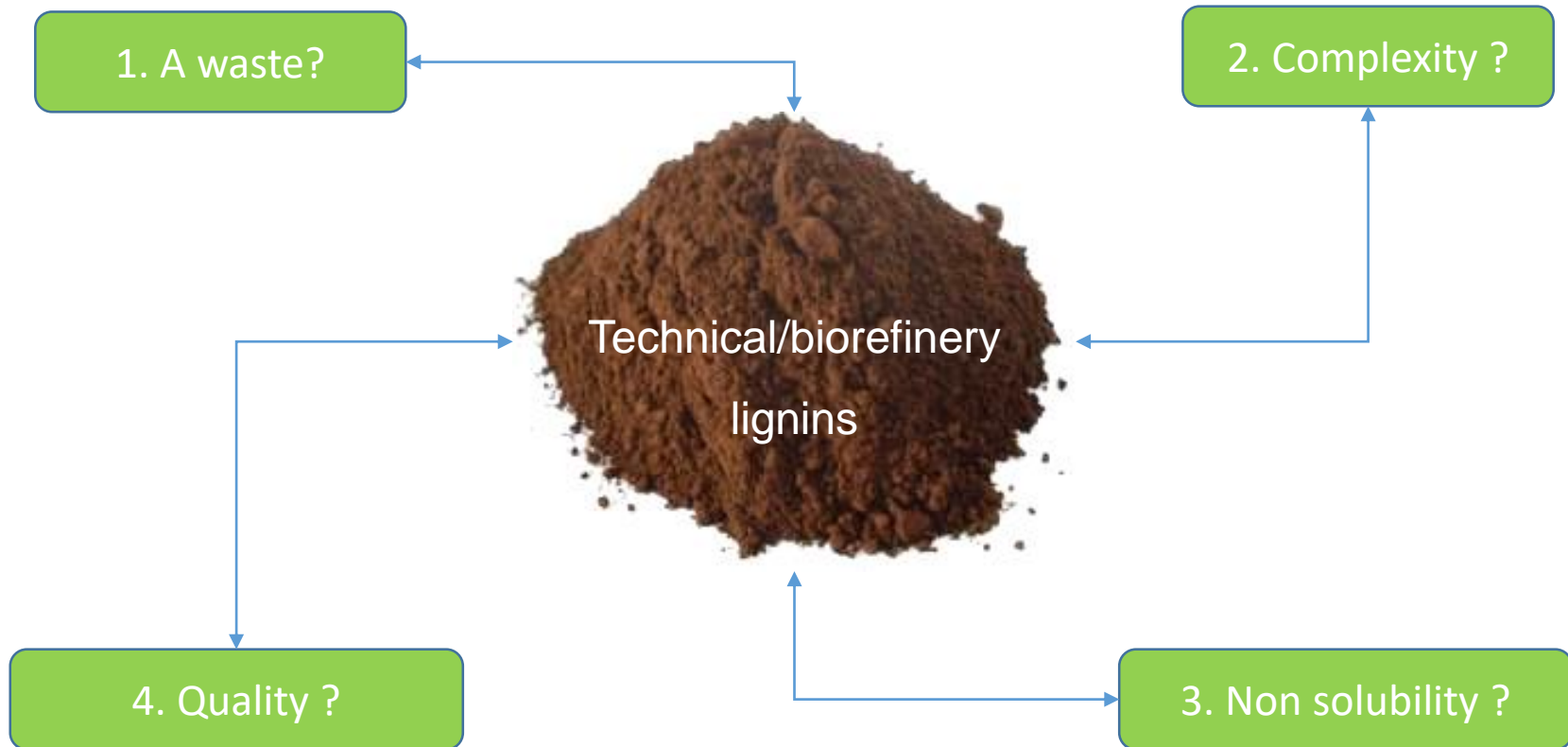
CA17128 LignoCOST Working Groups meeting

Reims, 31st January – 2nd February 2023

Lignin valorization:
considerations based on 30 years of collaborative research

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Outline





1. A waste?

Lignin potential has been recognized for over 35 years

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*With compliments
Feldman*

LIGNIN-POLYMER SYSTEMS AND SOME APPLICATIONS

« Lignin is a renewable, non-toxic, commercially available and low costing resource which has the potential of being utilized as a basic raw material for the chemical industry. In spite of many years of development effort however, **this potential has not been fully realized**. One of the many reasons ...is the fact that the technical processes by which lignin is obtained, ... reduce its reactivity » (*Feldman et al 1986*)



LIGNIN BIOPOLYMERS

Borregaard's lignin-based biopolymers are renewable, wood-based alternatives to fossil-based chemicals and polymers used in a broad range of industries. Our products are tailor-made to obtain the optimal performance in your application.

With over 90 years experience in lignin-based biopolymers, we are continuously developing our unique product offering. Our environmentally friendly products are used as:

- Binding agents
- Dispersing agents
- Crystal growth modifiers
- Emulsion stabilisers and
- Complexing agents.

Stora Enso | [Contact](#) | [Products](#) | [Sustainability](#)

Lignin

LIGNIN – nature's own binder that can replace fossil-based materials

Your One-stop Partner in sustainable lignin solutions

LignoStar Group BV is a specialized international marketing and sales organization for lignin products.

With representation in The Netherlands, Germany, France, the UK and Brazil, we have a special focus on lignosulfonates. For this, LignoStar is an independent agent for most leading producers. Our wide range of over 70 different lignin products offers a unique portfolio and One-stop solutions for international clients.



Already commercial products



A bond for the future

A sustainable society requires new ways of working and collaborating. In addition, we need to find new ways to take advantage of the natural resources that we have at our disposal. That's why we at Södra always strive to make the best possible use of our wood raw material to build a sustainable society. Take lignin, for example. Lignin is the tree's binder but it can be much more too. Our lignin is now ready to create new strong bonds for the future. Together, we can replace more fossil materials and further contribute to the green transition. Ready to join our journey?

PRODUCTS

- Newsprint
- Printing and Writing Paper
- Business Communication Paper
- Wrapping Paper
- Functional Speciality Paper
- Linerboard and Corrugated

Lignin Products

SAN X®, VANILLEX®, PEARLLEX®

Lignin is one of the principal components of wood and has unique properties. We are the only lignin manufacturer in Japan and we produce a wide range of lignin products. Our brands, SAN X®, VANILLEX® and PEARLLEX® are used in many industries.

Functions of lignin products

Lignin products have three functions: dispersing, binding and chelating.

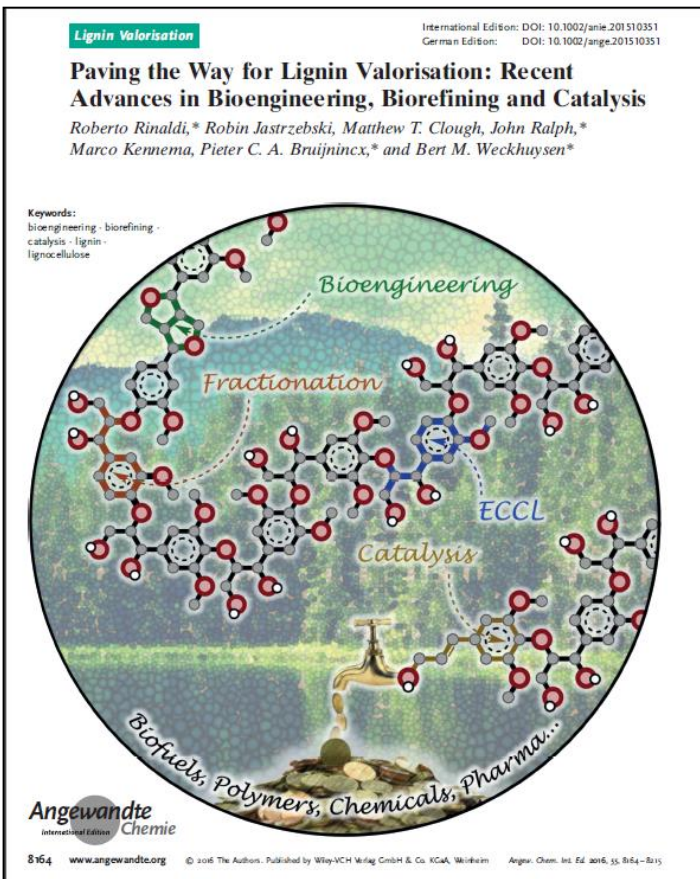
Techno-economic, environment, and socio-economic studies

- Review (*Wengel et al. 2020*)
 - Lignin a key to commercial success on pulp production: energy supply + value-added products from the surplus
 - Possibility to reduce the carbon footprint of 2G bioethanol production by using the lignin rich residues in materials: e.g. -82 g CO₂e/MJ of ethanol (composite filler; *Pourhashem & Bajwa, 2018*)
 - Barriers to large-scale commercialization: availability (quantity and quality), infrastructure cost of innovation
 - Limited markets (heat and power, vanillin, liginosulphonates, niche markets)

Various tools developed to diversify the uses

- Bioengineering
- Fractionation
- Catalysis

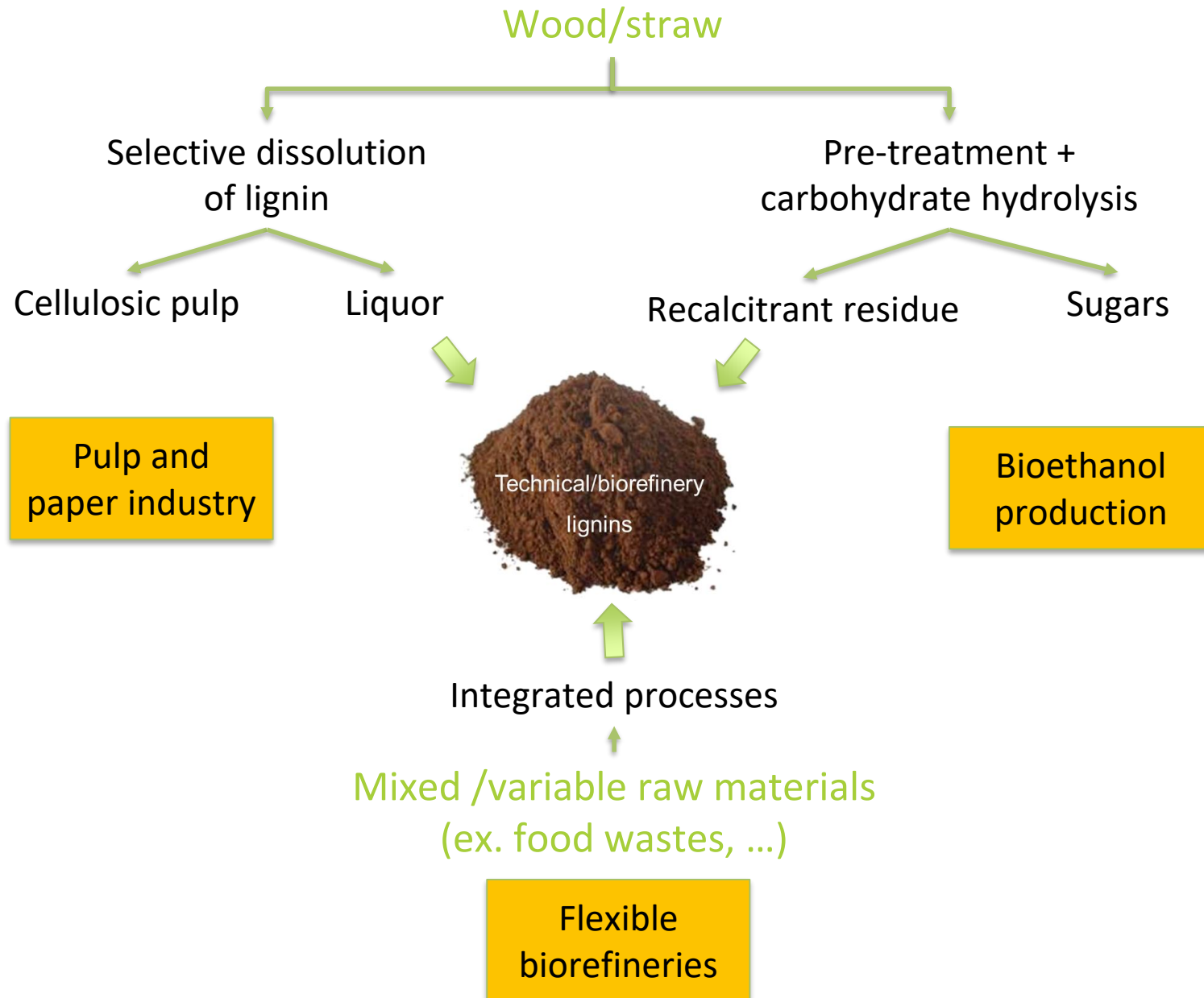
Taking into account yields and quality



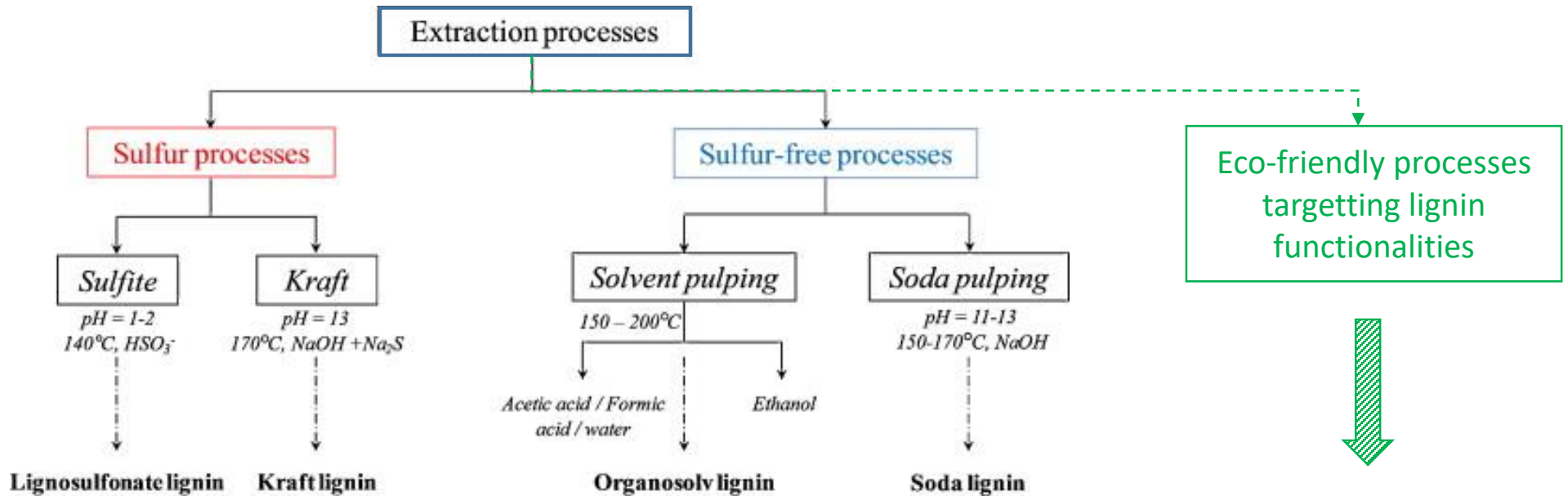
« With the emergence of evermore **selective and tailored lignin valorisation processes** and the growing **ability to alter lignin structure in the growing plant**, lignin-derived chemicals and materials may be expected to find increasing widespread applications, opening up new avenues for the polymer, chemical and fuel industries »

« Start-to-finish analysis of the progress achieved in lignin valorisation » (Rinaldi et al, 2016)

Diversification of the sources and types of lignins



New generation of processes



*Technical lignins from pulp & paper industry
(Laurichesse and Averous, 2014)*

- Need for
- New catalysts
 - New characterization methods
 - Green chemistry assessment

“However, to achieve the valorization of lignin in the fabrication of personal care products, it is necessary to overcome several challenges related to their **molecular complexity** and unattractive color.” (Espinoza-Acosta et al 2022)



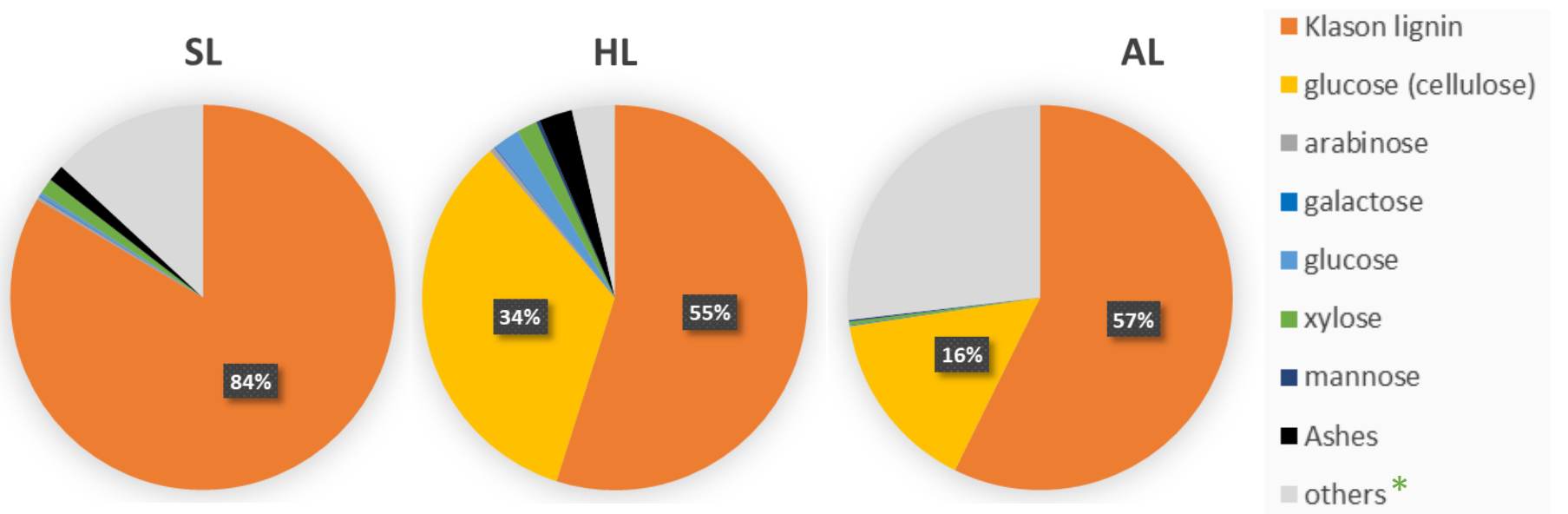
2. Complexity?

“However, because of **lignin’s complexity**, its efficient utilization, either as a polymer or from its derivable small-molecule products, is currently problematic” (Li et al 2018)

“ Lignin (15–30 wt%) is a **complex aromatic heteropolymer** derived from three cinnamyl alcohol monomers, ...” (Huang et al 2020)

Mixture of compounds of different chemical nature

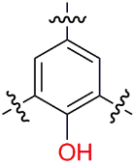
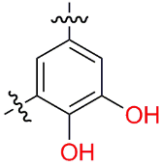
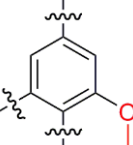
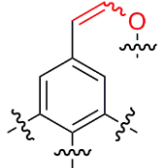
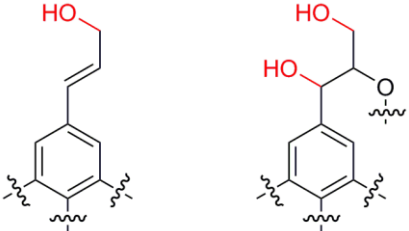
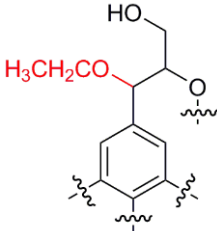
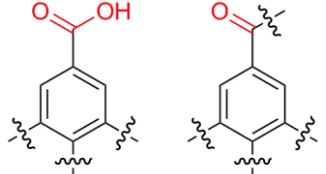
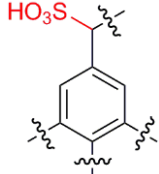
- Composition of 3 types of biorefinery lignins (Zelcor project)
 - SL=grass soda lignin (Protobind 1000, Green value LLC)
 - HL=wheat straw hydrolysis lignin from bioethanol production
 - AL= softwood acidic lignin (Dawn technology)



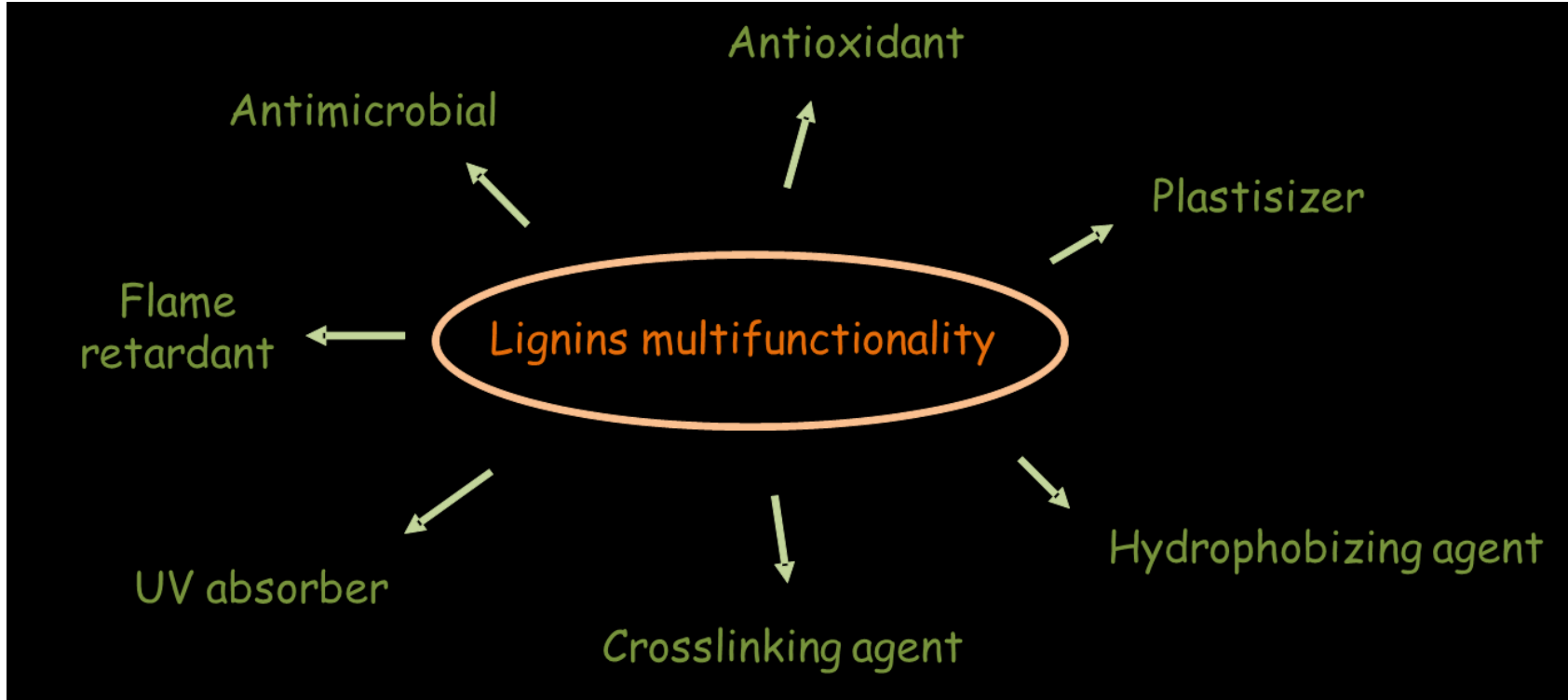
* acid soluble lignin, uronic acids, extractives, proteins

⇒ Advantage for bioconversions

Diversity of functional groups

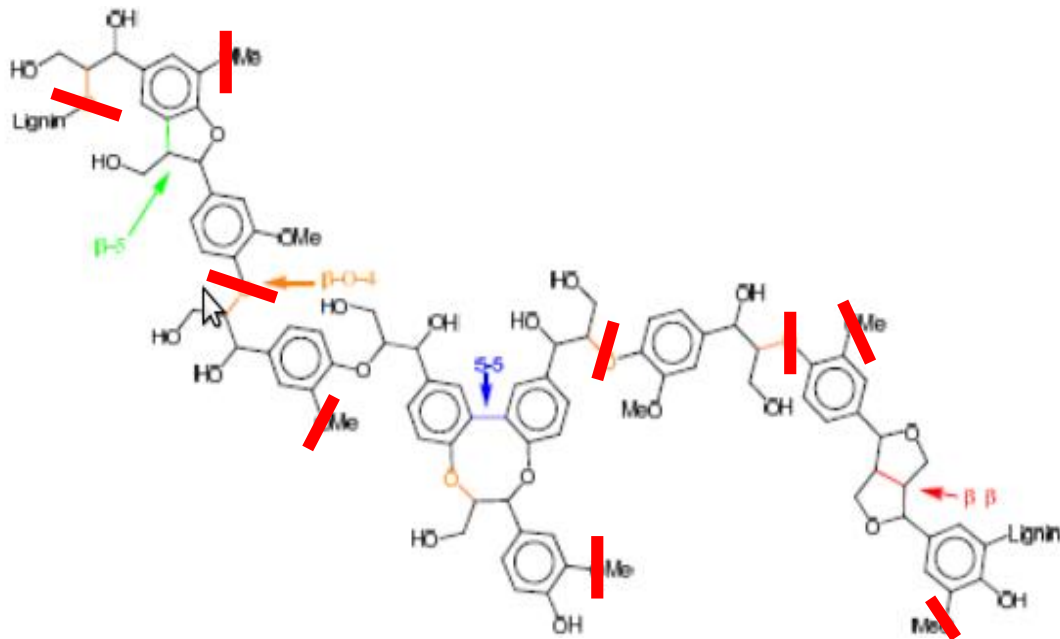
 <p>Phenols</p>	 <p>Catechols (soda and Kraft process)</p>
 <p>Methoxyls</p>	 <p>Enol ethers (Kraft process)</p>
 <p>Aliphatic alcohols</p>	 <p>Ethyl ethers (ethanol process in acidic medium)</p>
 <p>Carboxyls and carbonyls</p>	 <p>Sulfonates (bisulfite process)</p>

Advantage: multifunctionality and tunability



Distribution of C-C and β -O-4 linkages

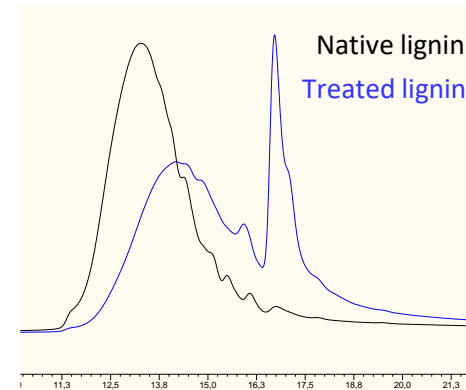
⇒ Possibility to release soluble compounds through selective ether cleavage



Structure of softwood lignins



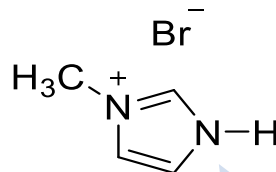
Soluble compounds with increased phenol content



HPSEC profile of a maize dioxan lignin before and after depolymerisation (treatment ionic liquid + MW)

Example of the development of a depolymerisation process

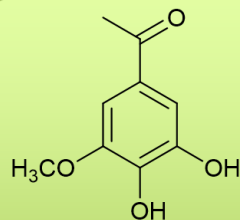
- Optimization of the treatment with [HMIM]Br
 - Efficiency of ether bond cleavage
 - Antioxidant properties of the products
 - Reduction of the reagent consumption
 - Recycling of the reagent
 - Assessment of risk and toxicity



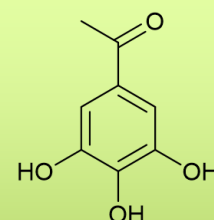
Transfer to industrial lignins (soda, Kraft)

Optimisation and scaling-up to 15 g

Validation on lignin models at 100 mg scale (previous collaboration with UVSQ)

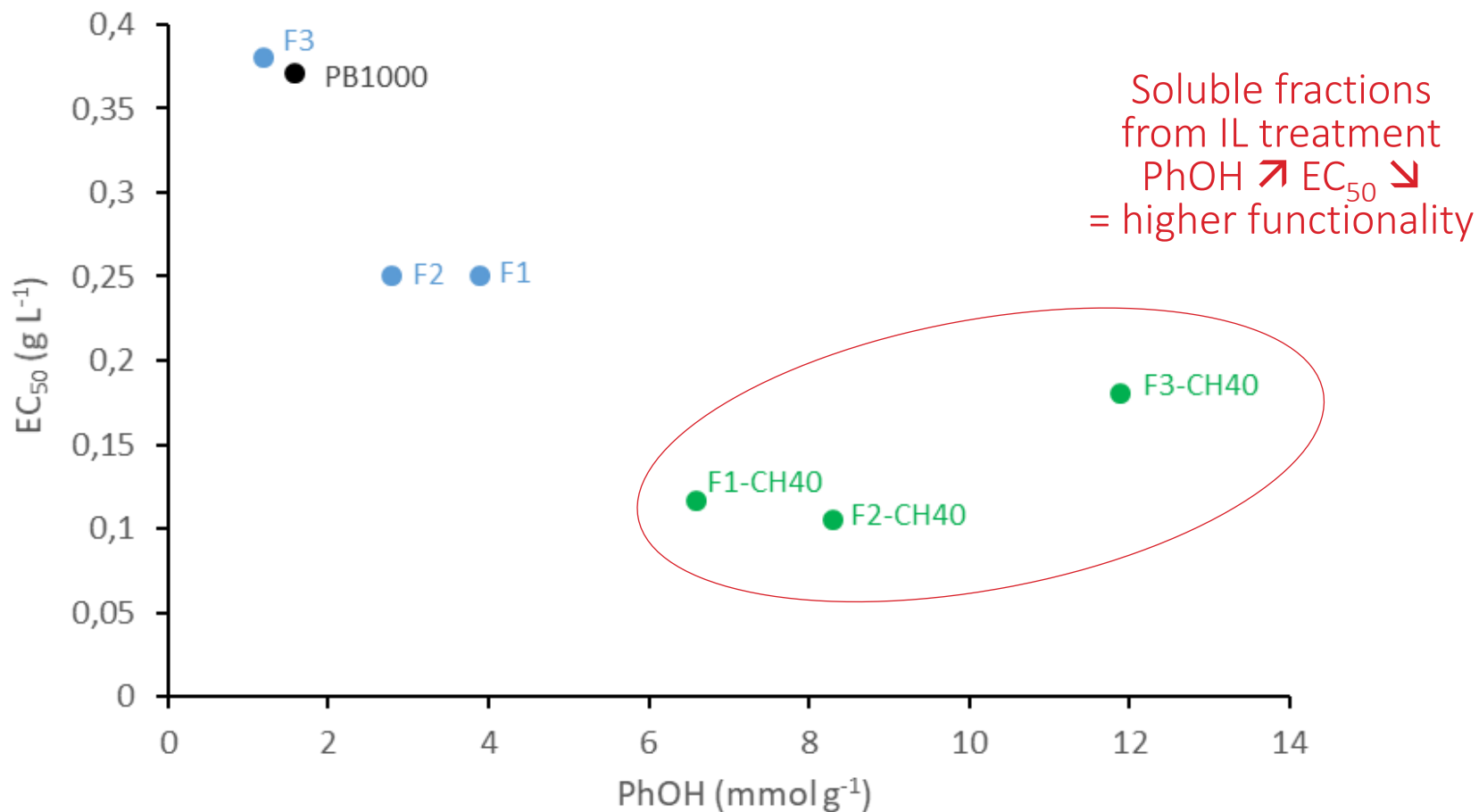


1-(3,4-dihydroxy-5-methoxyphenyl)-ethan-1-one



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

Powerfull antioxidants (> BHT)

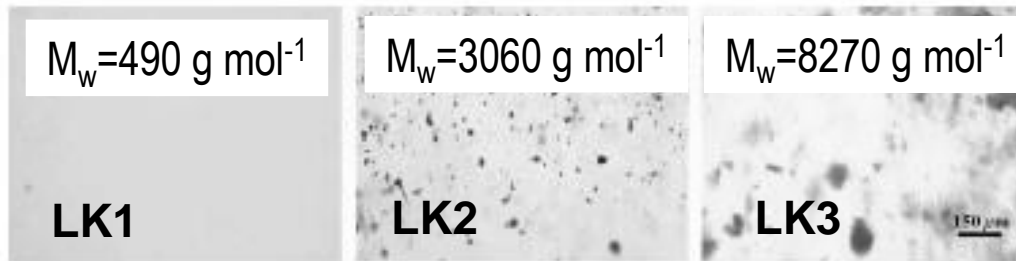


Relationship between radical scavenging properties (EC_{50} , DPPH test) and phenol content (^{31}P NMR) of lignin fractions (*Majira et al 2020*)

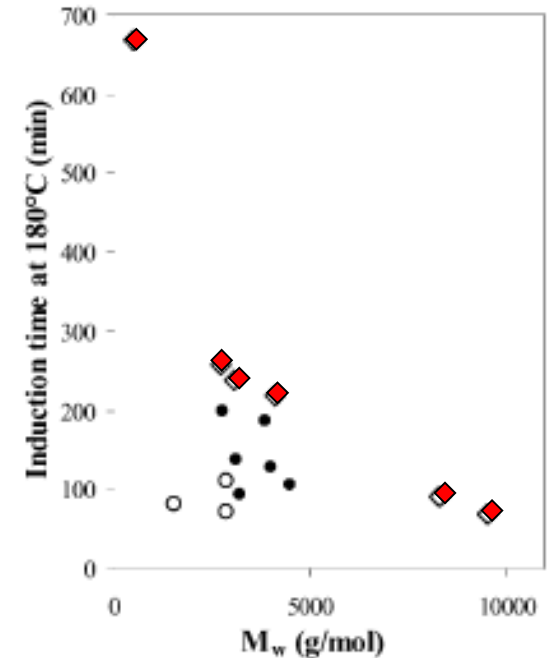
Molecular heterogeneity related to molar mass distribution

⇒ Advantage for uses as additives in thermoplastics:

- ⇒ LMW compounds: miscible with the matrix, confer antioxidant, antimicrobial and insect repellent properties (*ex. soda lignin extract; Vachon et al., 2020*)
- ⇒ HMW compounds: role of filler, mechanical reinforcement



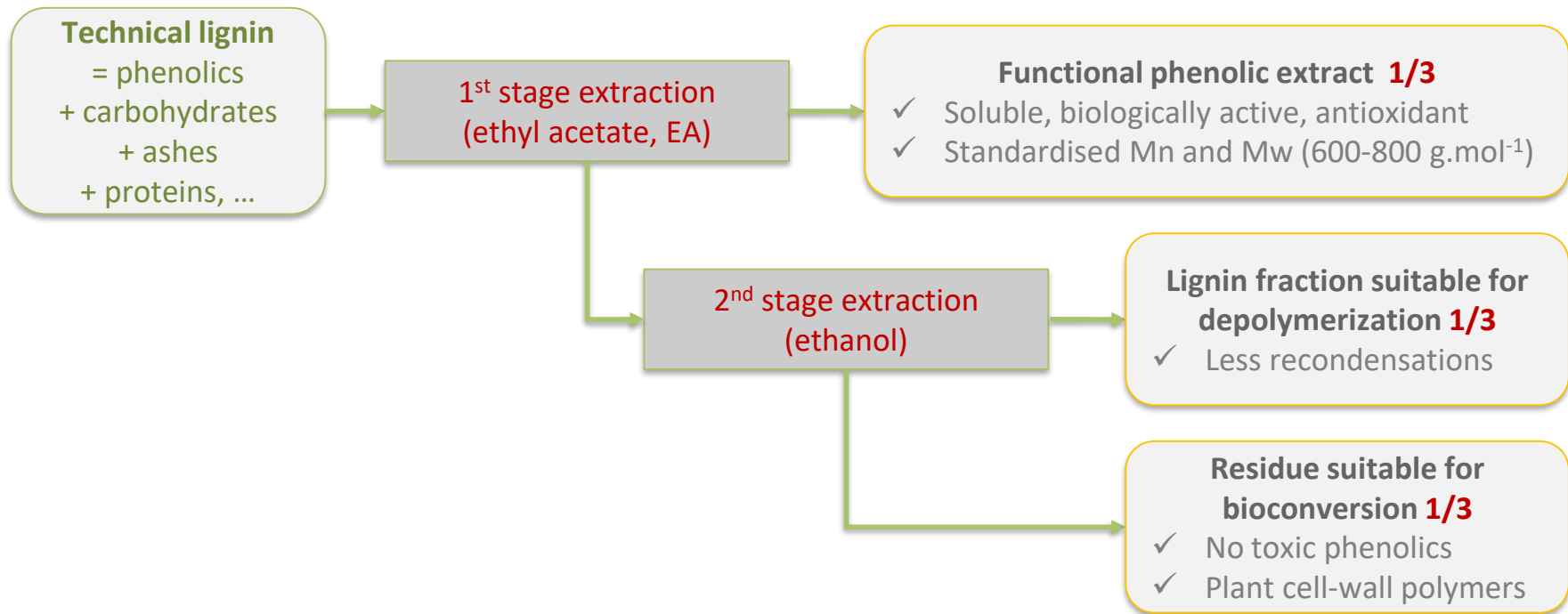
Micrographs of PP matrix containing distinct fractions of Kraft lignins (*Pouteau et al., 2004*)



Oxidation induction time of the material as a function of KL fractions M_w (*Pouteau et al., 2003*)

⇒ Possibility to settle a cascading process

- Combined solvent extraction - depolymerization - bioconversion





3. Solubility?

Some lignins are already soluble

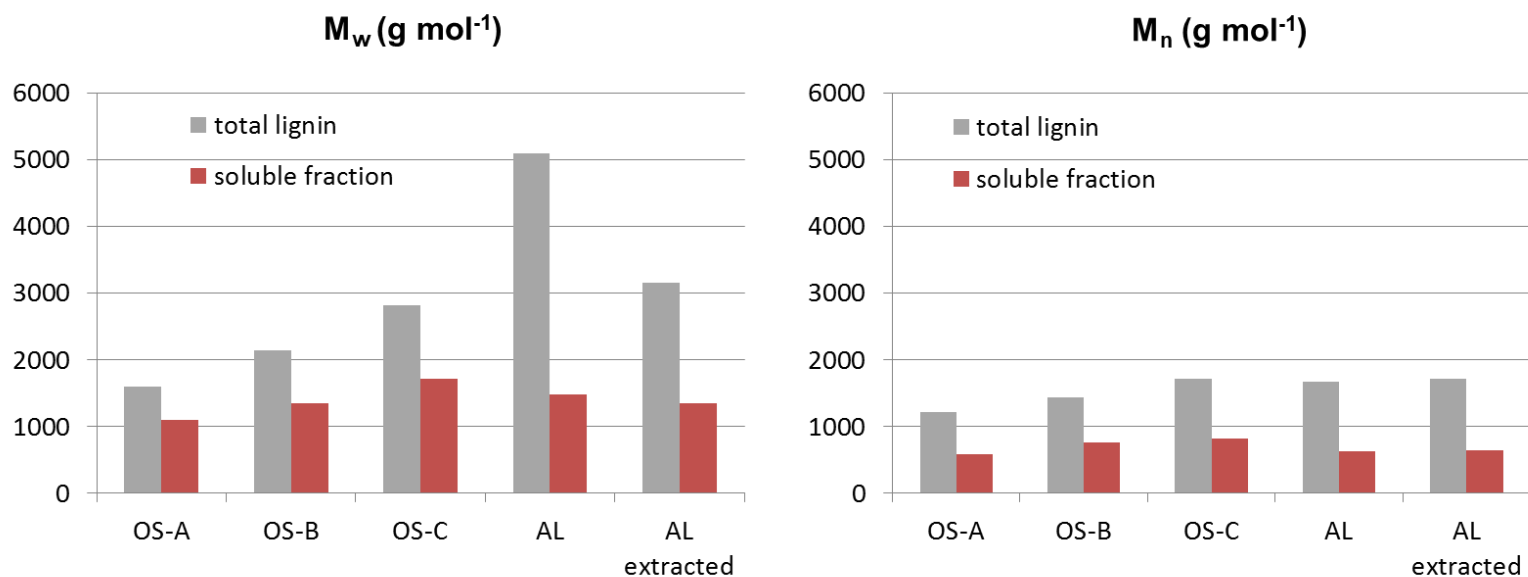
- Lignosulfonates: 100% soluble in water
 - ⇒ Application in various colloidal systems (waste water treatments, drilling mud, binder in composites)
 - ⇒ Substrate for aqueous-medium chemistry
 - ex. substitution of a phenol-formaldehyde resins by lignosulfonate-carbonyl compound systems (*Allais et al, 2019 – Patent Fr3032197*)
- Organosolv, soda and Kraft lignins : 80-100% soluble in organic solvents (aqueous ethanol, acetone and dioxan, DMF, THF ...) and dispersible in water as colloidal particles



Soda lignin powder, organic solution, and aqueous colloidal dispersions (*Rivière, 2020*)

Advantage of partial solubility

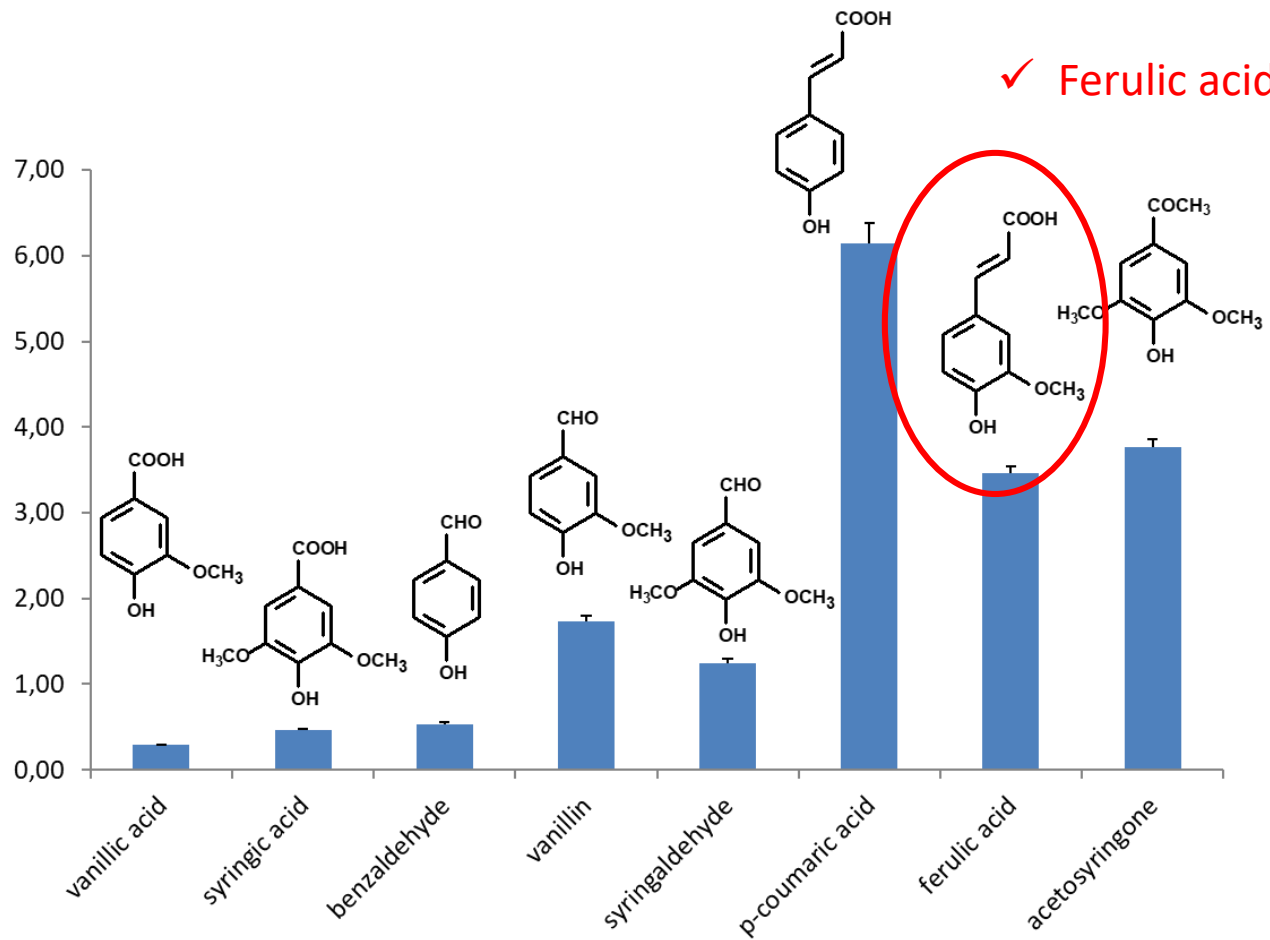
- Possibility to fractionate and obtain standardized fractions and/or to enrich in compounds of interest



Average molar masses of lignin samples and their ethanol extracts

(Aguíe et al., 2015)

Composition of the phenolic monomer fraction of a soda lignin extract (mg.g⁻¹)

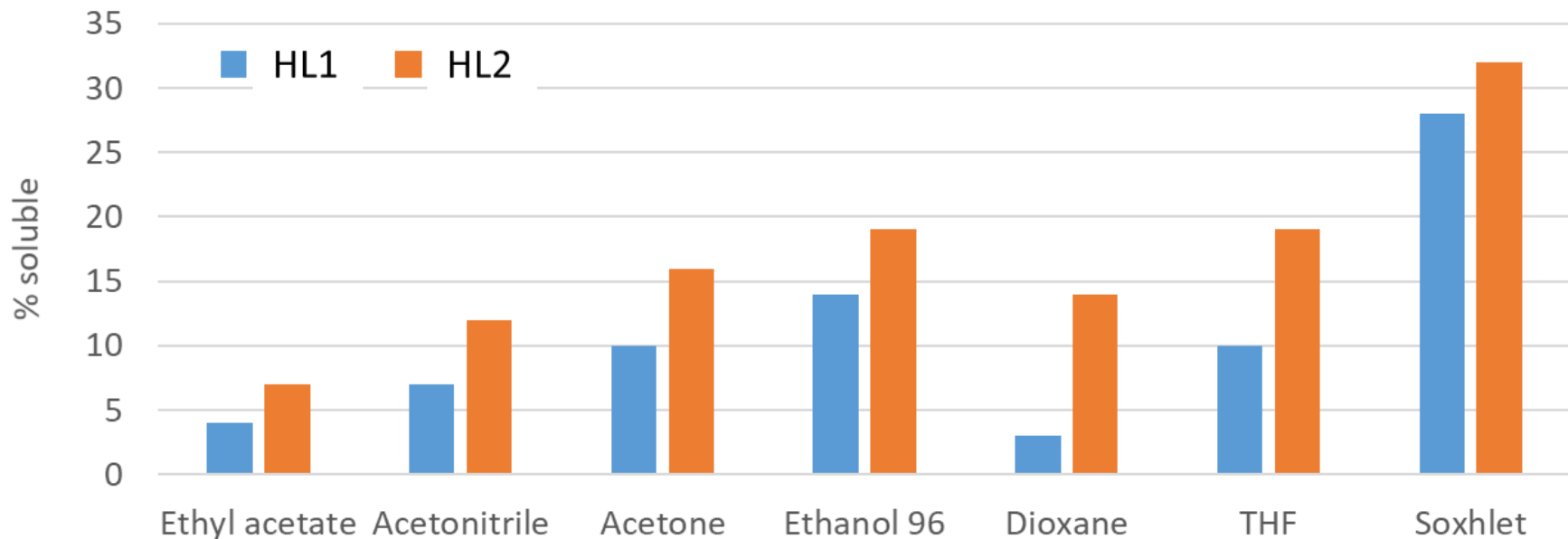


✓ Ferulic acid: 19% of the fraction

(50/50 CH₂Cl₂/ethyl acetate extraction; GC-MS)

Low solubility of hydrolysis lignins

Solubility of two hydrolysis lignins (HL) HL1: pilot plant; HL2: demo plant
 Organic solvents or water+ethanol soxhlet extraction (wt%)



⇒ Need for specific valorization strategies

Bioethanol production residue – Valorization routes

Direct use

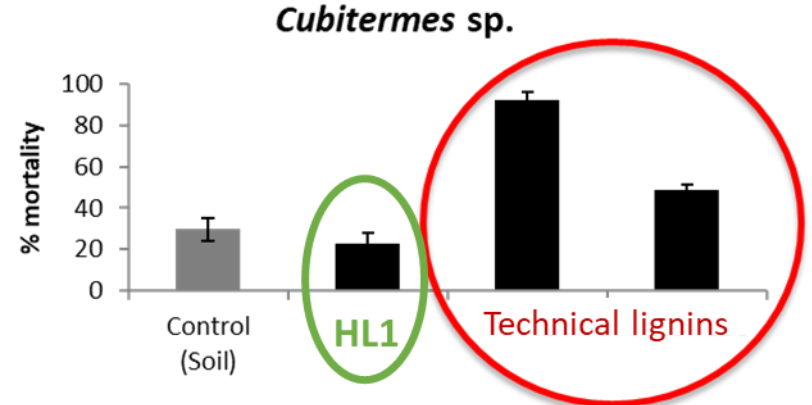
Filler in polyolefin-based films
Incorporation by extrusion
2-5 wt% in HDPE

Bioconversion by termites or fungi



Antioxidant composites
 Low compatibility
 No antimicrobial
 Attractant / invador insects

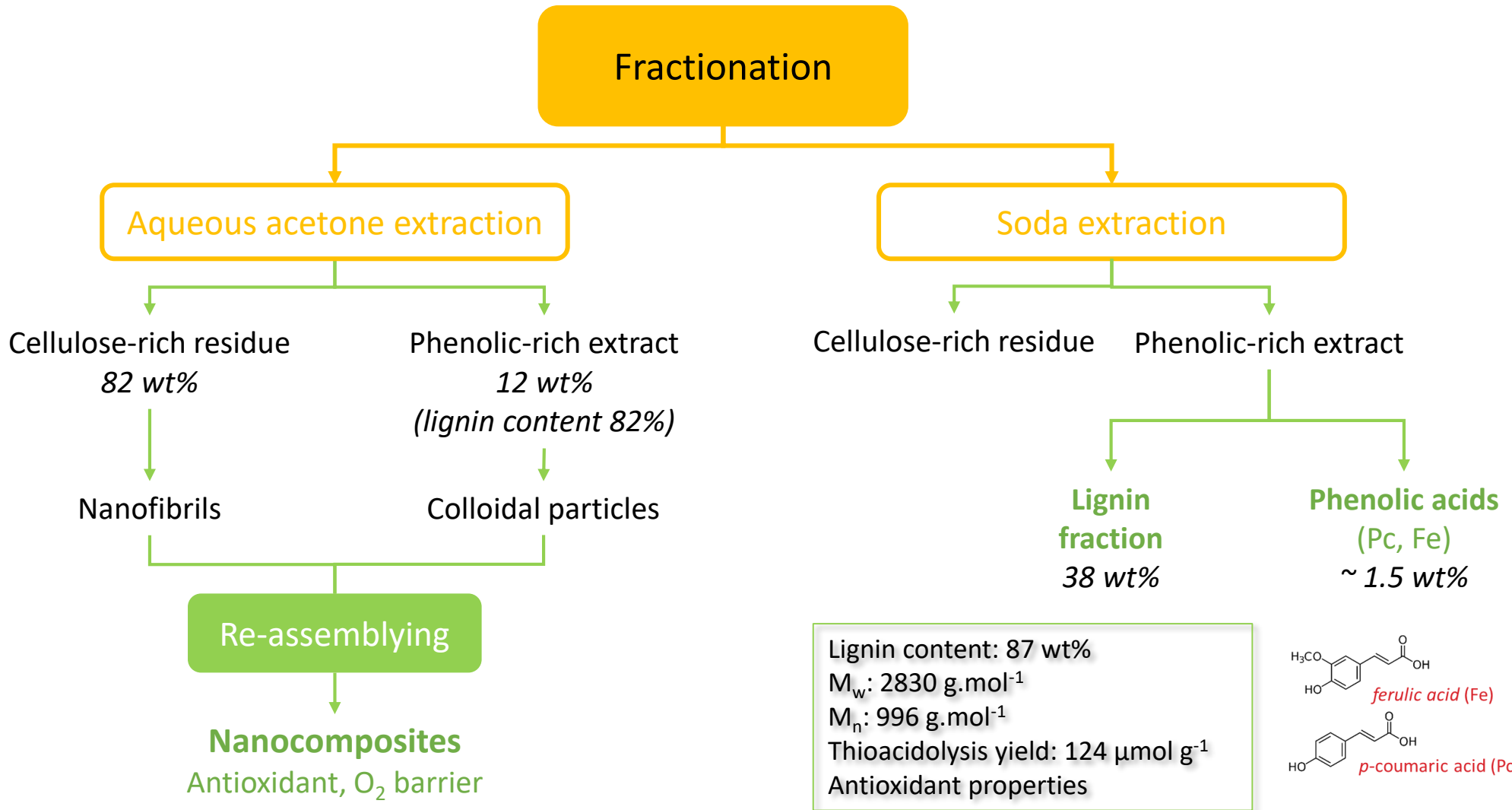
(Vachon et al 2021)



Survival test on a humivorous termite species

➡ Limited interest for packaging but good substrate for biomass production

Bioethanol production residue – Valorization routes



(Rivière et al 2021)



4. Quality?

What is a lignin of « good quality » ?

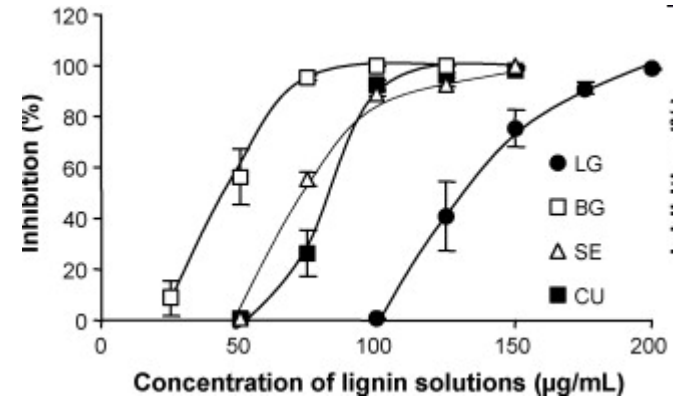
- Lignin with expected functional properties ?

- Ex. antioxidant properties

High proportion of hindered phenol groups ⇔ radical stabilisation by resonance

⇒ grass soda lignins

Product	IC50 (µg/ml)
Bagasse soda	44,9 ± 6.7
Lignosulfonate	133,6 ± 9.0
Curan 100	85,9 ± 4.6
Steam explosion	74,6 ± 1.0
(-)-Epicatechin	42,27 ± 3.0



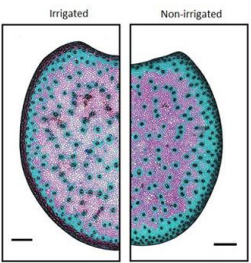
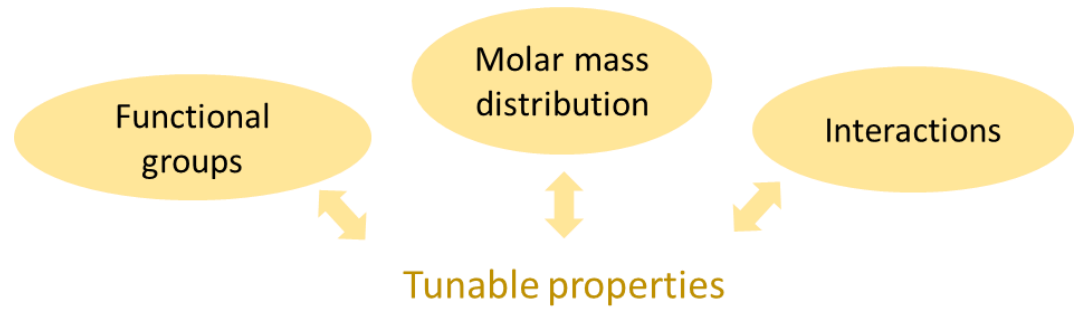
Inhibitory effect of different lignin solutions on the hemolysis induced by AAPH (LG, lignosulfonate; BG, bagasse; SE, steam explosion; CU, curan 100). Results are expressed as mean ± S.E. of at least three independent experiments.

Antioxidant activity of lignins assessed through the inhibitory effect on human erythrocytes hemolysis (*Vinardell et al. 2008*)

What is a lignin of « good quality » ?

- Lignin with high purity ?
 - Low carbohydrate content / Low sulfur content / No toxic compounds ?
 - ⇒ organosolv lignins (e.g. ethanol/water): well suited for **cosmetic applications**
 - Hair fixer based on 5-10% wt. organosolv lignin or derivatives (*Lang et al 1992; Patent*)
 - Anti UV cream formulated with 0.5-5% wt. organosolv hazelnut lignin (*Gordobil et al 2020*)
 - ⇒ Organosolv and Kraft lignins adapted to **carbon fiber synthesis** (*Dakla et al 2002*)
- Lignin with high depolymerisation potential?
 - High proportion of units only linked through β -O-4 bonds
 - Low recondensation propension
 - ⇒ new isolation processes preserving or targeting lignin nativ polymer structure
 - = « *lignin-first approach* »

Future research: from plant to functional biomolecules



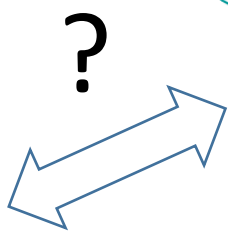
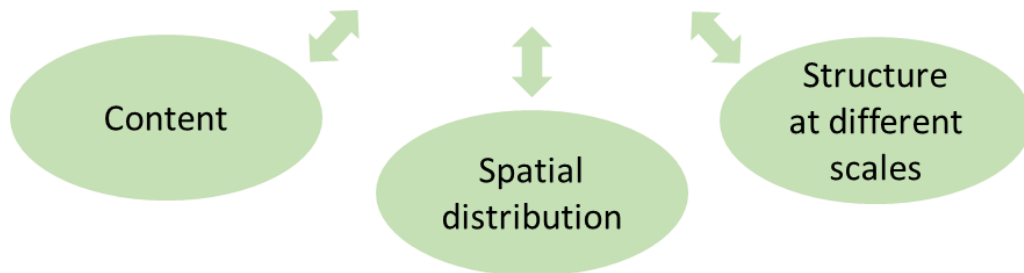
Environmental changes & genetic control

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Various strategy of lignin organisation

Variability in cell-walls

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Challenges

- Development of methods to analyse lignin at different structuration levels and in different media (ex. analysis of oligomers; analysis in ionic liquids or deep eutectic solvents; analysis of non-soluble fractions ...)
- Need for high-throughput selective deconstruction methods allowing analysis of lignin functionalities
- Settlement of new value chains exploiting lignin structure \leftrightarrow limiting factor: up-scaling of fractionation/extraction processes
- Combination with the production of bioenergy production to ensure the sustainability of the biorefineries

Lignins remains a valuable source of bioenergy

- Direct combustion of black liquors (> 98%) ⇒ heat and power
- Biogaz and bioethanol production by fermentation of spent sulfite liquors
- Other potential routes for bioenergy
 - Lignin catalytic depolymerization into specific aromatics ⇒ additives for fuels
 - Thermo-chemical conversion
 - ⇒ Syngaz
 - ⇒ Pyrolysis products + combined heat and power

Lignin biochar



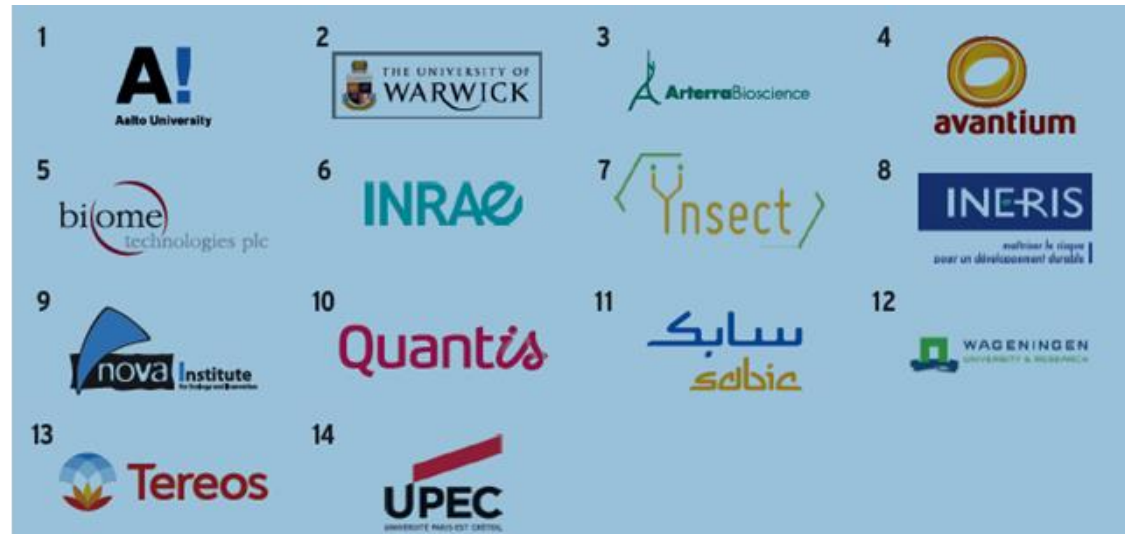
Lignin bio-oil



(de Wild et al, 2013)

Acknowledgements (1)

- Zelcor project consortium 

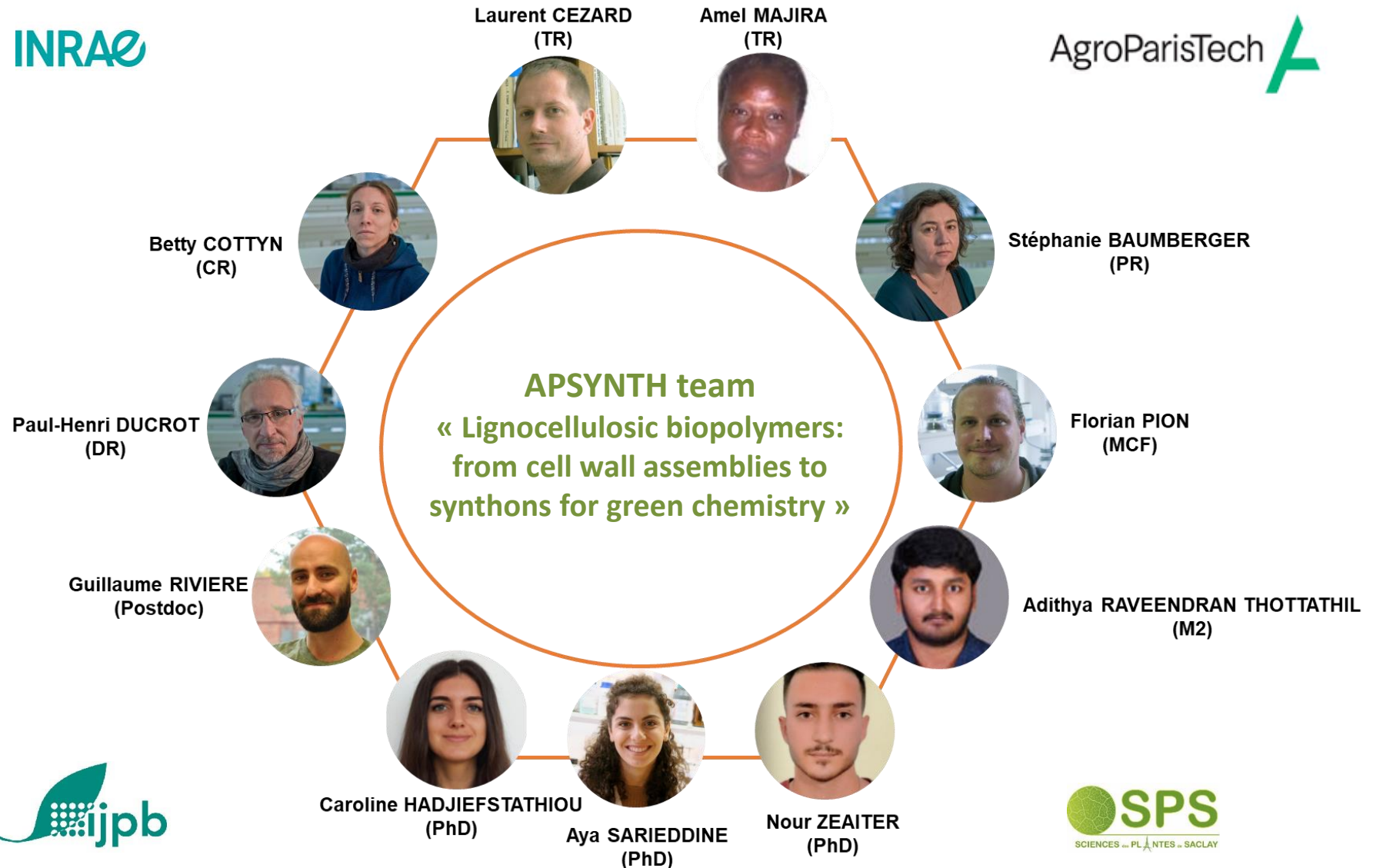


This project has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation program under grant agreement No 720303

- « Plant observatory » OV platform at IJPB

Acknowledgements

A new research scientist position open
<https://jobs.inrae.fr/concours/concours-charges-recherche-classe-normale-profil-h-f/cr-2023-transform-3>



Thanks for your attention

