



VENICE2022

“9th international symposium on energy from biomass and waste”
Venice, 21-23 Nov 2022

Lignin biorefinery: a way to improve the sustainability of bioenergy production?

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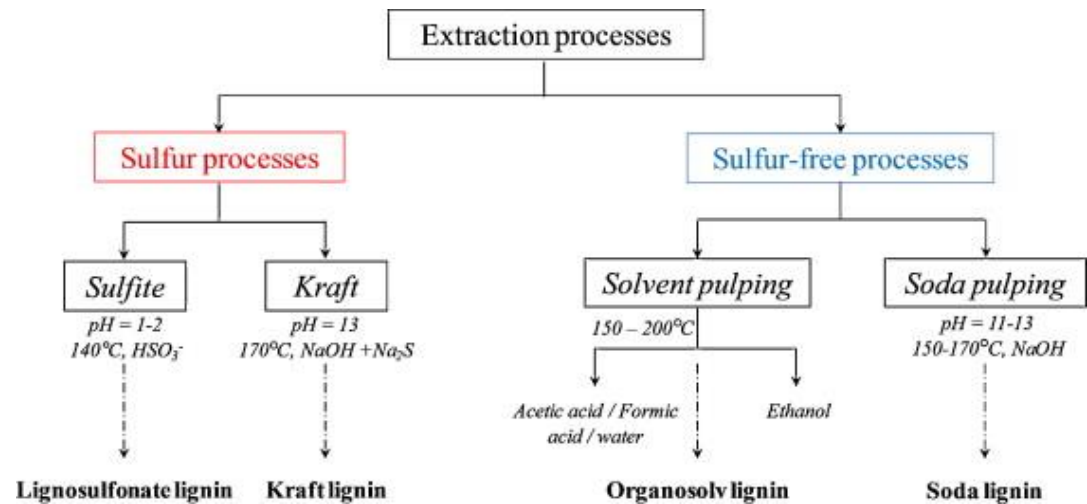
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Outline

- Context
- Lignins as multifunctional biomolecules and source of energy
- Lignin valorisation and 2G bioethanol production
- Conclusions

Context (1)

- Lignocellulose: most abundant terrestrial plant material (*Paul & Dutta, 2018*)
 - Annual global production estimated to $181.5 \cdot 10^9$ t
 - Over 90% of the total plant biomass
- Development of 2G biorefineries
- Lignin in biomass: up to 30% of wood
- Technical lignin global production: 50-100 Mt/yr (*Bajwa et al 2019*)
 - Pulp & paper industry
 - Bioethanol production



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

Context (2)

- Review of techno-economic, environment, and socio-economic studies

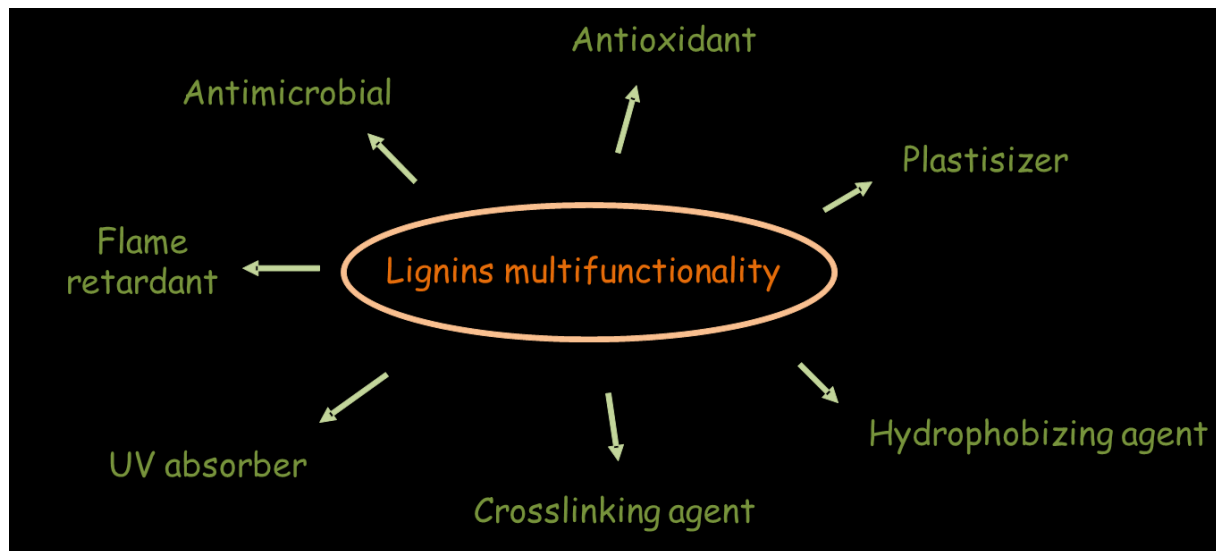
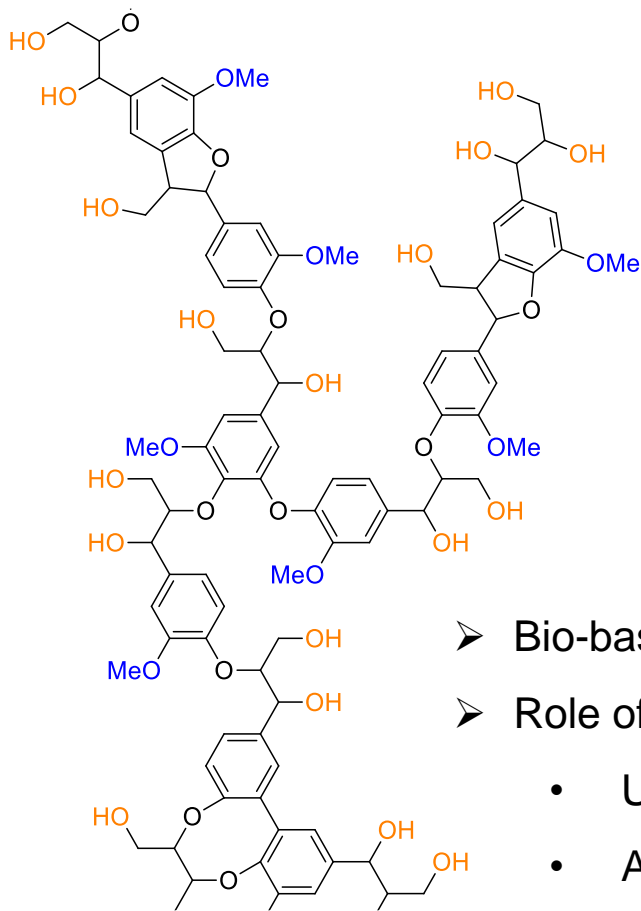
(Wengel et al. 2020)

- Lignin a key to commercial success on pulp production: energy supply + value-added products from the surplus
- Limited markets (heat and power, vanillin, lignosulphonates, niche markets)
- Barriers to large-scale commercialization: availability (quantity and quality), infrastructure cost of innovation
- 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*)

Lignins: a 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
 - Thermo-chemical conversion ⇒ pyrolysis products; syngaz
 - Lignin catalytic depolymerization into specific aromatics ⇒ additives for fuels

Lignins: multifunctional biomolecules

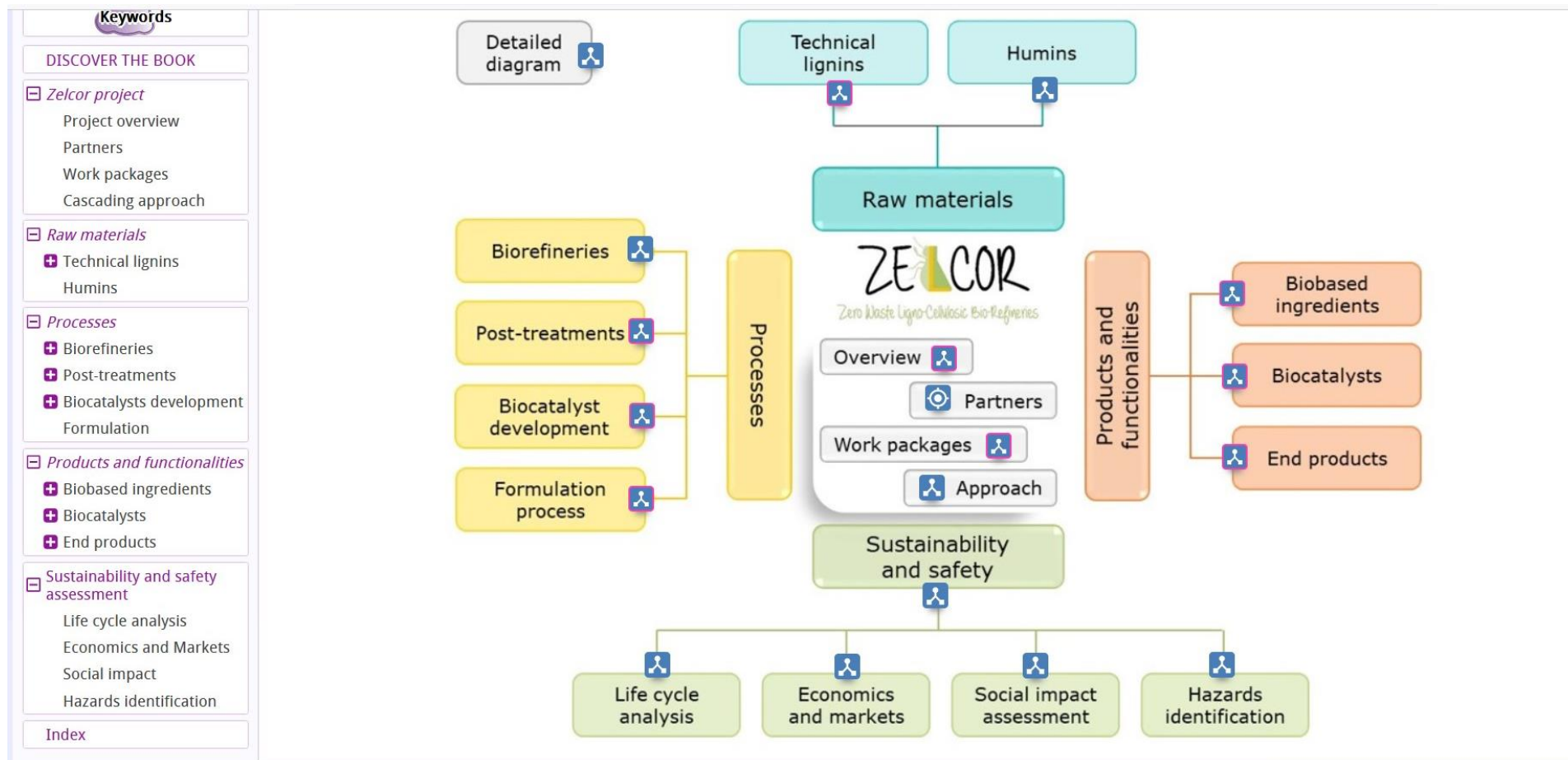


- Bio-based molecules of interest for chemical, plastic, and cosmetic industries
- Role of lower-molar mass phenolic compounds (ethyl acetate/ethanol extracts)
 - Up to 30% of some technical lignins like grass soda lignins
 - Antioxidant, antimicrobial and insect repellent properties
 - Promote recondensations during lignin depolymerisation treatments

(Majira et al., 2019; Vachon et al. 2020)

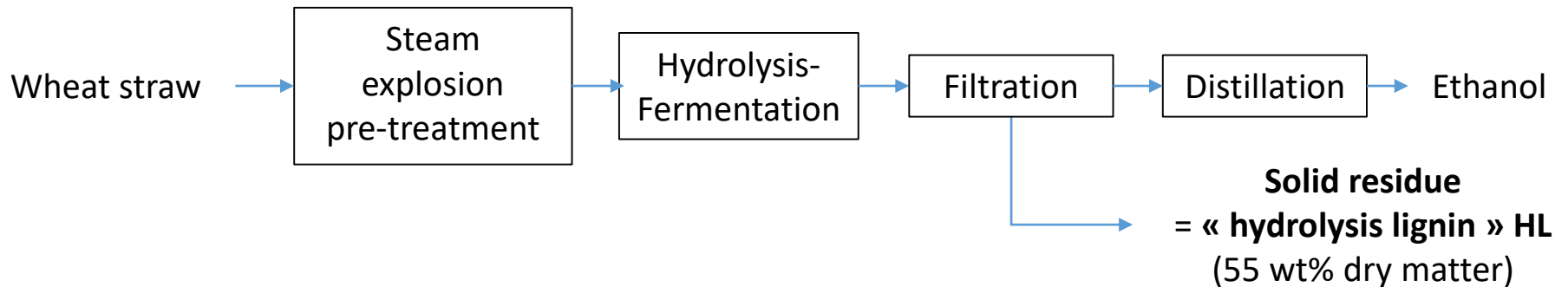
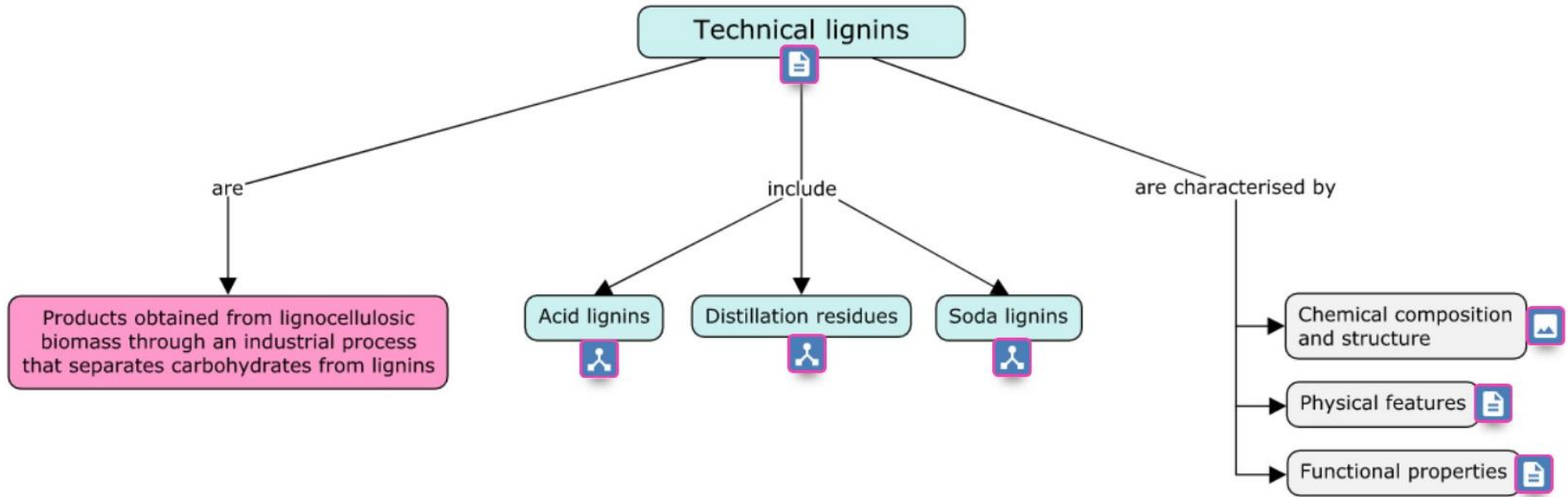
Zelcor project (H2020 BBI JU, 2016-2021)

Zero Waste Ligno-Cellulosic Biorefineries by Integrated Lignin Valorisation



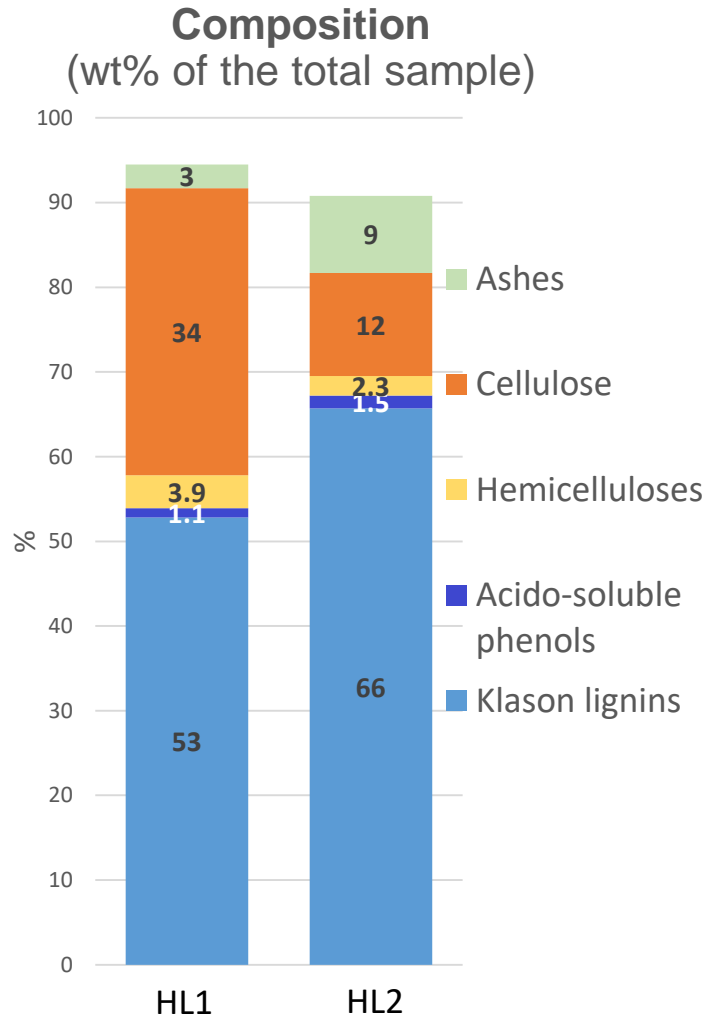
Padovani, J., Pion, F., C. Fernandez, S. Baumberger, B. Kurek **2021**. *The Zelcor book: an electronic knowledge book for the cascading use of biorefinery recalcitrant side streams into high added-value biobased products and fine chemicals*
<https://plastic-apps.transform.inrae.fr/zelcor>.

➤ Focus on 3 types of recalcitrant raw materials

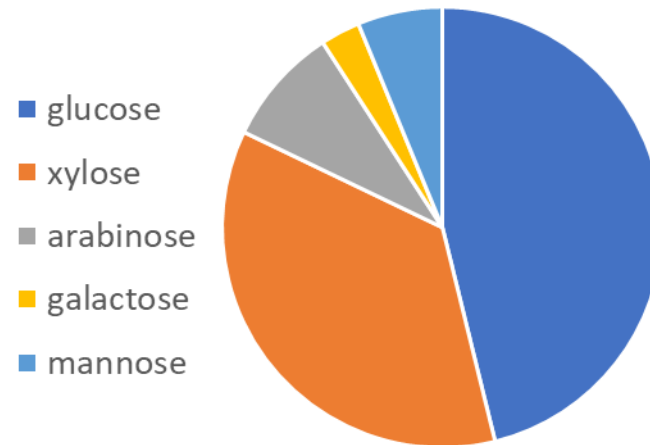


Characteristics of the hydrolysis lignins (HL)

HL1: pilot plant; HL2: demo plant



Hemicelluloses composition (HL1) (relative wt%)



Proteins: 6.5 wt% (HL1)

Characteristics of the hydrolysis lignins (HL)

HL1: pilot plant; HL2: demo plant

Functional groups (HL1) - ^{31}P NMR (mmol.g $^{-1}$)

Total OH	5.7
Carboxylic OH	0.2
Aliphatic OH	4.5
Phenolic OH	1.0
Non-condensed G + H units	0.5

Constitutive units - thioacidolysis ($\mu\text{mol.g}^{-1}$ and mol %)

Total H+G+S (/Klason lignin)	244
%H	2.5
%G	46.8
%S	50.7

Composition of the extractives (solvent: ethyl acetate; mg.g $^{-1}$)

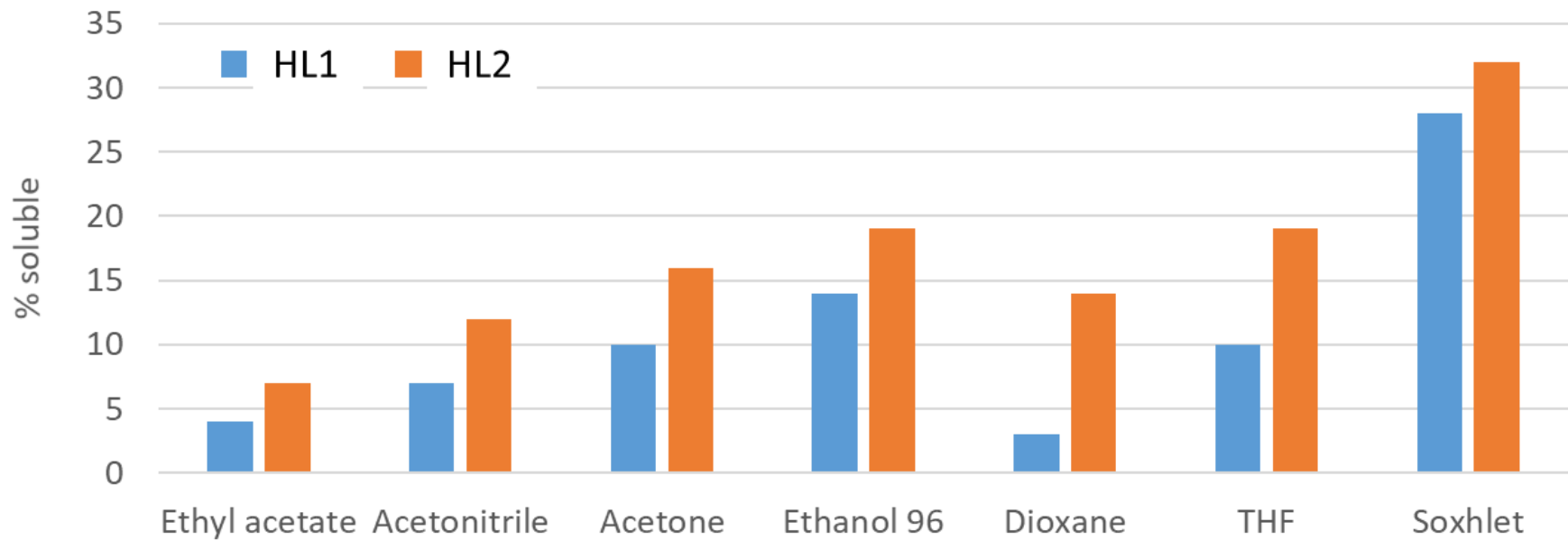
Total extractives	2.83
ferulic acid	0.76
<i>p</i> -coumaric acid	0.76
vanillin	0.32
syringaldehyde	0.10
vanillic acid	0.18
syringic acid	0.14

Characteristics of the hydrolysis lignins (HL)

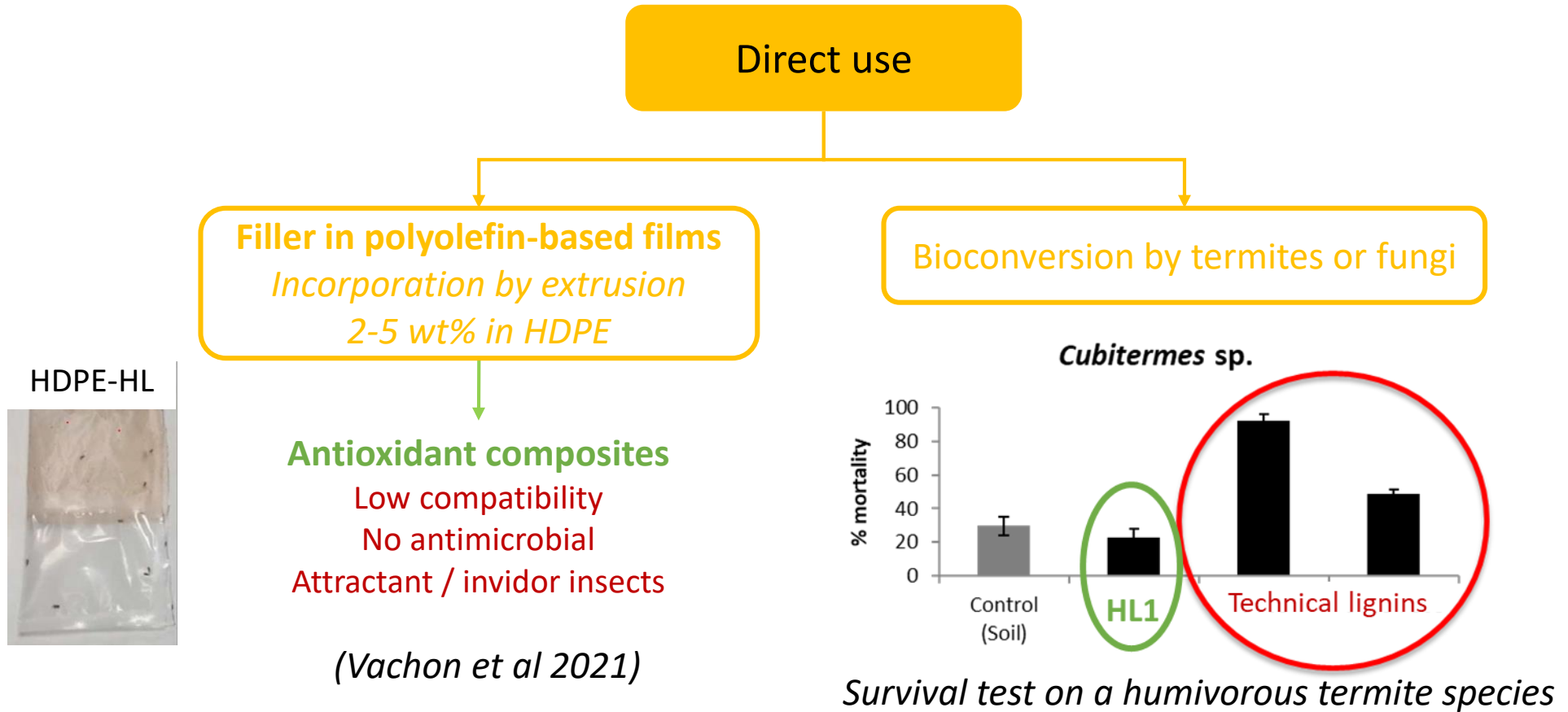
HL1: pilot plant; HL2: demo plant

Solubility

Organic solvents or water+ethanol soxhlet extraction
(wt%)



Bioethanol production residue – Valorization routes



➡ Limited interest for packaging but good substrate for biomass production

Conclusions

- Benefits of fractionating lignocellulosic bioethanol production residues
 - Standardization of the raw material (more homogeneous fractions)
 - Isolation of soluble phenolic antioxidant molecules
 - Diversity of possible products with higher added-value
- Integration into emerging commercial 2G biorefineries to be performed with sustainability assessment of the whole biorefinery system
- Evolution towards biorefineries taking into account the quality of the lignin-rich streams = “lignin-first biorefineries”

Acknowledgements

Institut Jean-Pierre Bourgin UMR 1318 INRAE-AgroParisTech (FR)

- Laurent Cézard, Frédéric Legée, Catherine Lapière: *structural analysis of lignins*
- Florian Pion: *lignin fraction supply and characterization*
- Amel Majira: *phenolic acid purification*

UMR FARE INRAE-URCA (FR)

- Véronique Aguié-Béghin, Bernard Kurek: *study of lignin functional properties*

Aalto University (FI)

- Guillaume Rivière (PhD student), Muhammad Farooq, & Monika Osterberg: *production of lignin colloidal particles and study of nanocomposites*

Sabic Europe BV (NL)

- Jérôme Vachon & Derar Assad-Alkhateb: *study of HDPE-lignin composites*

WFBR (NL)

- Richard Gosselink & Jacco van Haveren: *lignin characterization*

iEES Paris – Université Paris-Est Créteil (FR)

- My Dung Jusselme, Alain Robert, Philippe Mora, Michel Diouf & Edouard Miambi: *bioconversion by termites*



This work has received funding from the Bio Based Industries Joint Undertaking under the EU's Horizon 2020 research and innovation programme under grant agreement N° 720303

