Application of Lignin & Future Perspectives

LignoCOST lignin conference

May 31 - June 3, 2022 in Wageningen (NL)

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Contents

- Wageningen Food & Biobased Research
- Lignocellulose
  - Pretreatment / fractionation
  - Lignin production
  - Lignin last versus lignin first
- Lignin applications
- Future perspectives

Wageningen Food & Biobased Research

Applied research for sustainable innovations

- In-depth knowledge of the entire agri-food chain
- Market oriented R&D approach
- Multi-disciplinary applied R&D project teams; 250 employees
- Up-scaling: from lab to pilot
- Connection with the University of Wageningen

Sustainable Food Chains

Biobased Products

Healthy & Delicious Foods

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Research programmes

- Postharvest quality
- Food waste prevention & utilisation
- Food innovations for responsible choices
- Smart customised nutrition & health
- Protein for life
- Biobased chemicals & fuels
- Renewable materials
- Biorefinery

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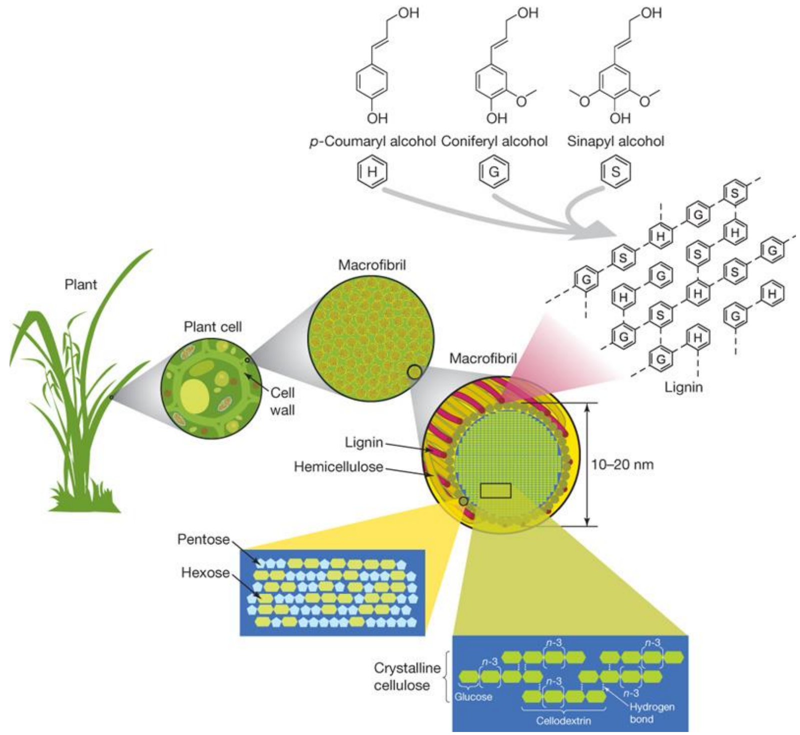
Lignocellulose



Rubin, 2008

Biomass	Lignin content (%)
Wood	20-30
Straw, hemp, flax, miscanthus, bagasse	15-25
Digestate	5-25
Grass	5-15
Coconut husk	30-50
Wood bark	20-30

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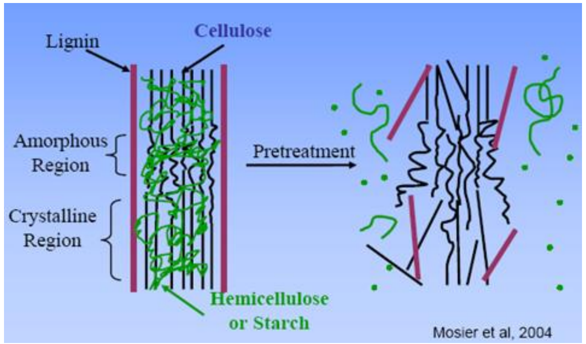
Pretreatment of lignocellulose



- Fibres
  - Pulp, Paper, Building materials, textiles
- Dissolving cellulose (e.g. textiles)
- Sugars
  - Make the polysaccharides accessible to catalysts
  - Using low/high pH, high temperatures, oxidative agents, mechanical forces (explosion)
  - Catalysts for polysaccharide hydrolysis: enzymes or acid
  - Micro-organisms can use the monosaccharides in fermentation processes
  - Isolation of lignin (up to kg scale)
  - Mild fractionation technologies

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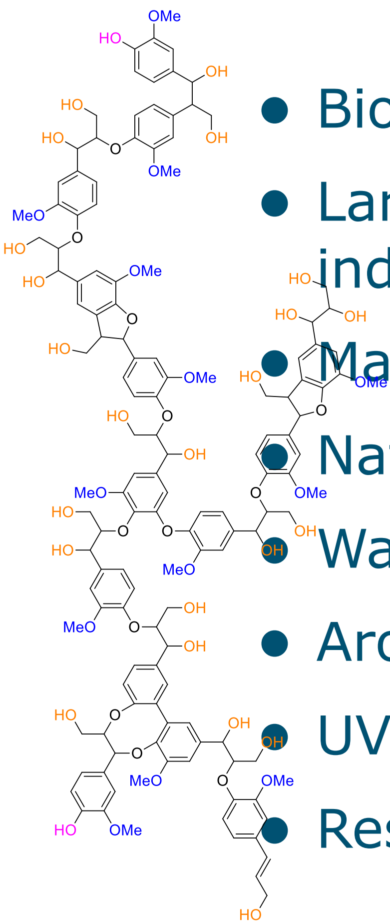
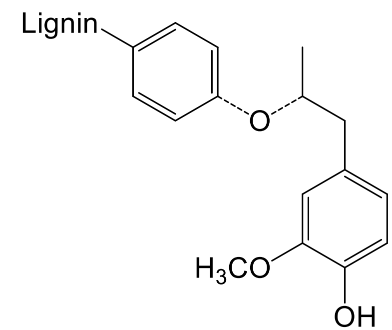
What is lignin and why interesting?

- Lignin = 15-25% of lignocellulosic biomass

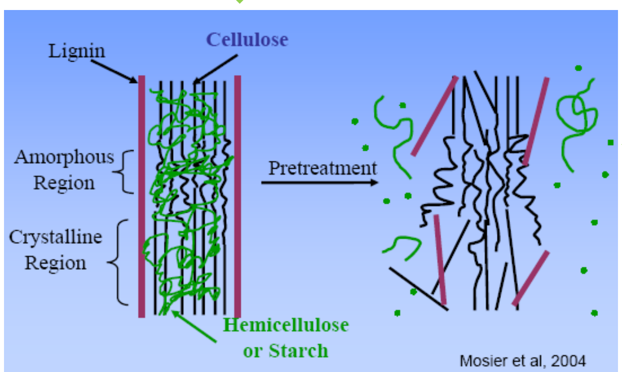


- Biobased
- Large side stream of paper & pulp industry and biofuel industry (>>70 M tonnes/y)
- Mainly used as energy source
- Natural binder
- Water resistent
- Aromatic ringstructure
- UV stabiliser
- Resembles products derived from fossil resources

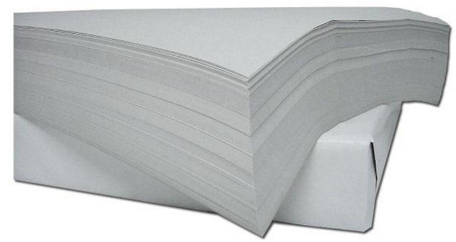


Production of lignin

Pulping / fractionation



Cellulose



Paper, textiles or biofuel (bioethanol)

Lignin

Materials, fuels and chemicals

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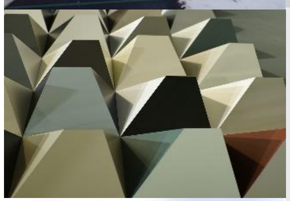
Lignin last → lignin first

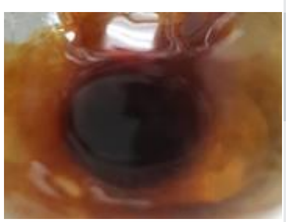
- Traditional processes focus on cellulose or sugars AND lignin last

- Novel processes focus on lignin first and co-produce cellulose or sugars and high quality lignin
- Both options offers opportunities for added value and bulk applications

- Lignin from traditional processes → bulk or larger markets?
  - Kraft, soda, hydrolysis
- Lignin from lignin first processes → added value & niche applications?
  - Solvent based
  - Lignin oil or lignin structures with native features

Examples of lignin applications



Application	Scale of operation	TRL	Main challenges
Bio-asphalt	Demonstration (>25 roads in NL) (50% substitution)	6-7	Costs reduction, industrial handling
Thermoset resins (PF type)	Several commercial (50% substitution) Demo/pilot	9 5-6	Reactivity
Polyurethanes	Pilot (30% substitution)	5-6	Viscosity, reactivity
Coatings (can, paper, packaging)	R&D	2-4	Functionality, performance
Marine / jet fuels	Pilot	5-6	Sulphur-free, NOx-free, viscosity
Aromatic chemicals	R&D/pilot	2-4	Selectivity, coke formation

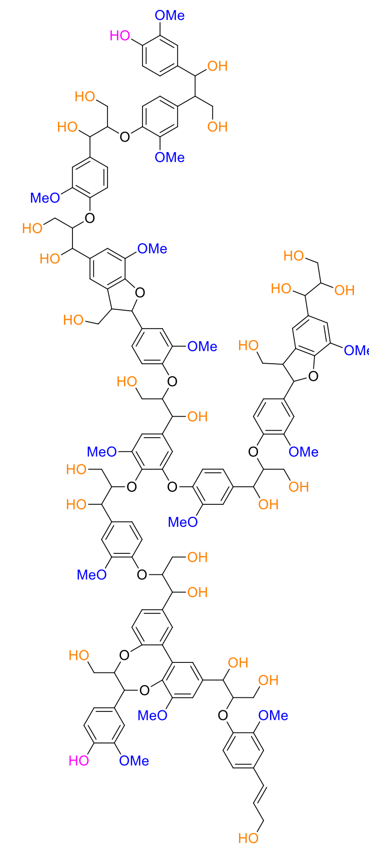
Drivers for lignin as bitumen substitute

- Lignin is a natural binder, UV stabiliser, anti-microbial properties
- Significant GHG savings & long term storage of biogenic carbon
- Solution for scarcity of bitumen in near future
- A way to guarantee the binder quality
- Substitution of fossil resource
- Adding extra functionality to asphalt
- Longer lifetime results in less maintenance (business case!)

- Asphalt/bitumen market is large (90M tonnes each year based on bitumen)

Lignin as bitumen substitute

- Lignine is natural binder
- Brown / black powder
- Relatively hydrophobic
- High carbon content (2/3 C; 1/3 O)
- Thermoplastic biopolymer (Ts ≈ 100-150°C)
- UV-stabiliser
- Substitute larger fractions in bitumen



Road from lab to demonstration

- Literature and patents showed lignin and bitumen can be mixed
- Selection of lignin with suitable properties
- Need for dry lignin powder
- Link lignin properties to asphalt binder properties
- Lignin-bitumen binder processable at lower temperature (vegetable oil)
- Labscale tests

- Pilot tests (1 m^2)

- Demo tests (10 m^2)
- Demonstration roads

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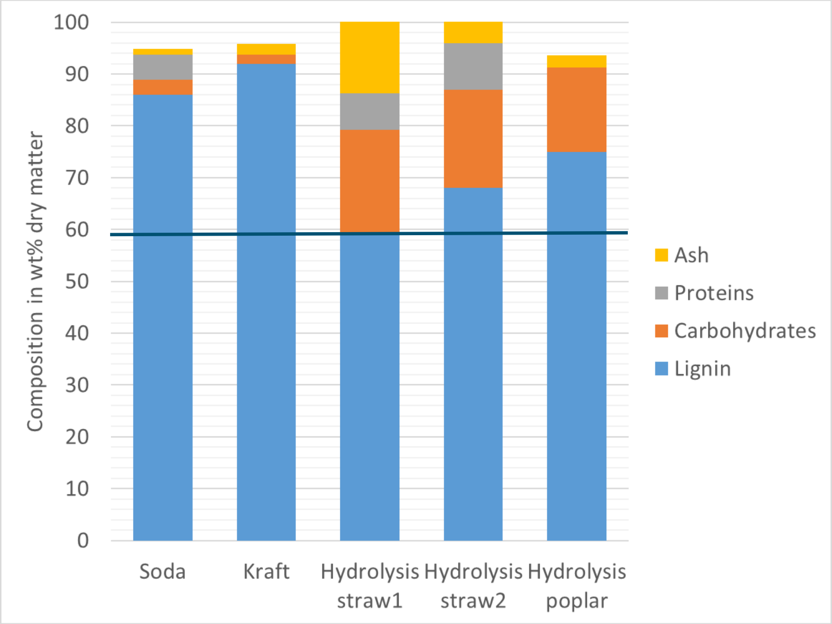
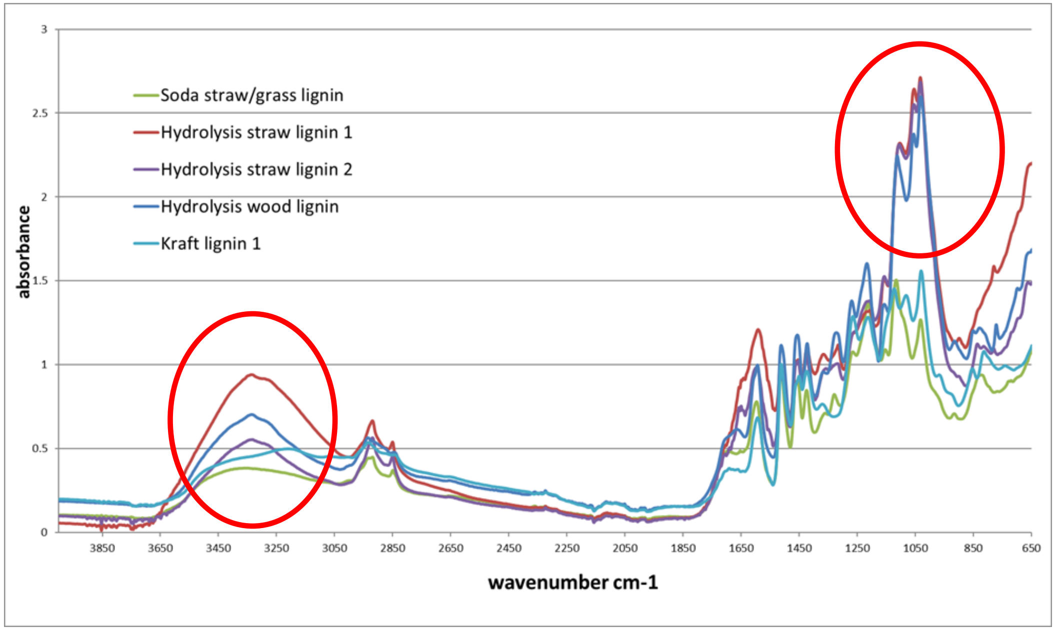
Selection of suitable lignin

- Large number of technical lignins tested
  - Pulp & paper industry
  - Biorefinery industry (cellulosic ethanol, biochemicals)





Fast screening tool FT-IR

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Landa P., Gosselink R.J.A., Lignin-based bio-asphalt, WO2019/092278

Selection of suitable lignin

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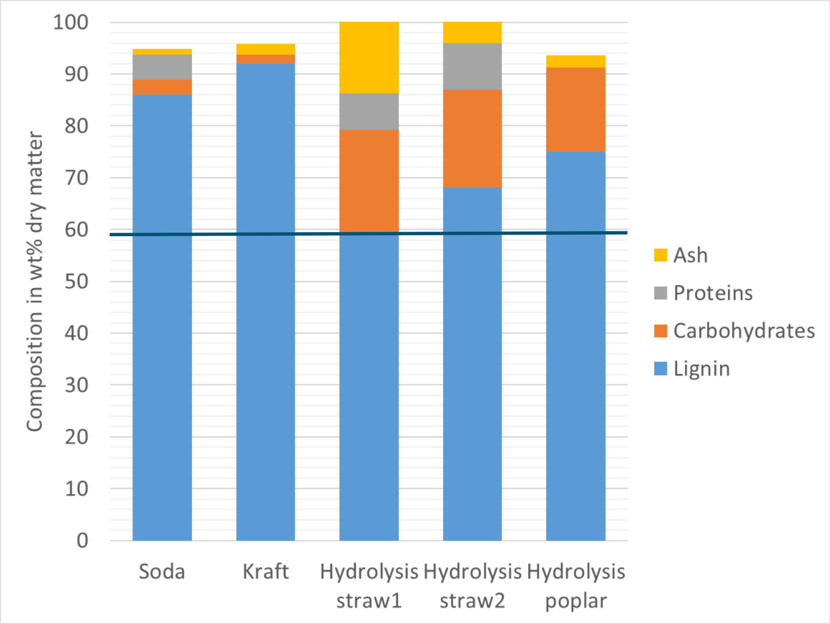

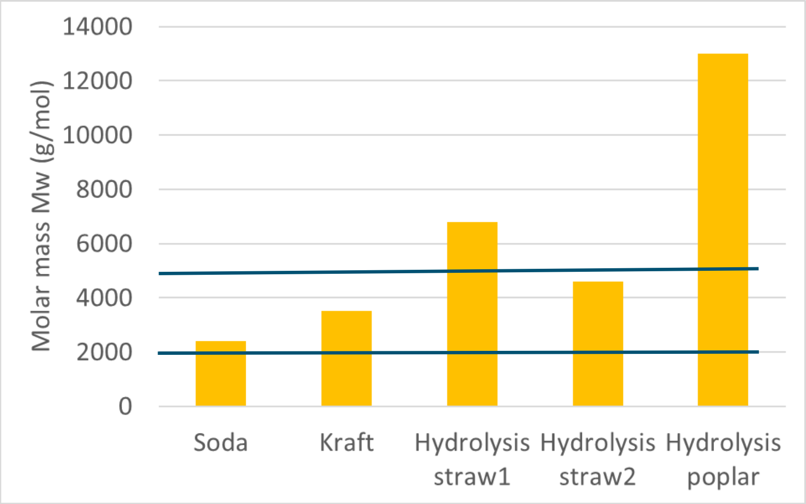

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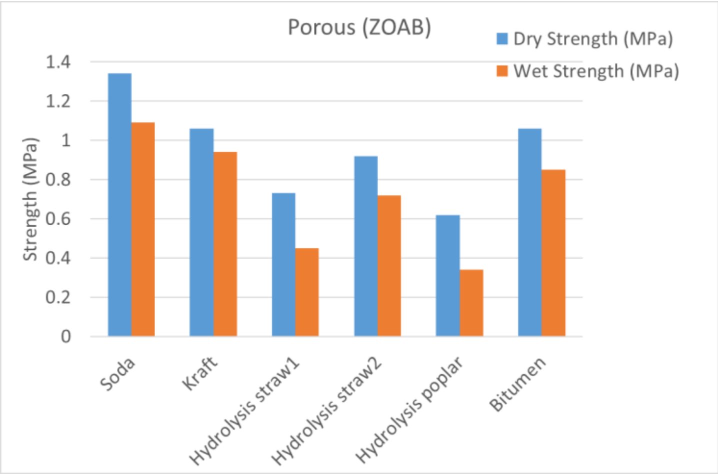
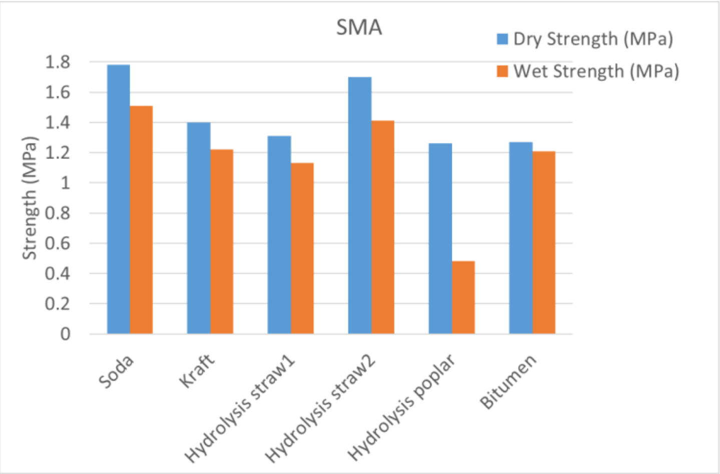
Landa P., Gosselink R.J.A., Lignin-based bio-asphalt, WO2019/092278

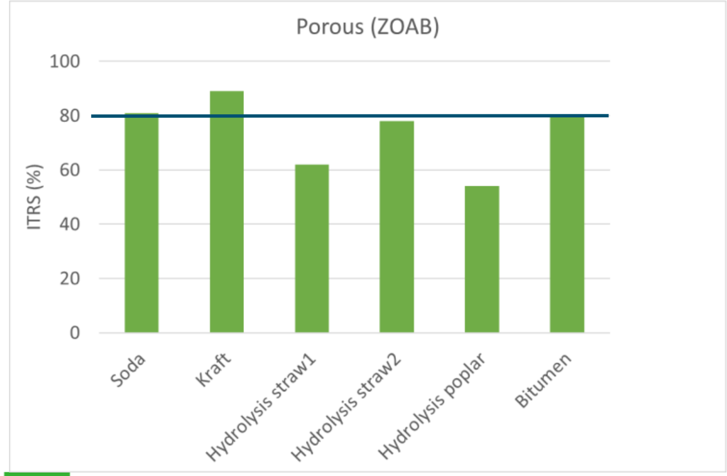
Labscale bio-asphalt tests

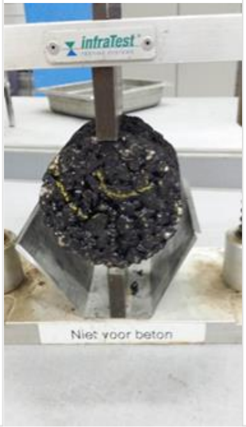
- Porous asphalt (ZOAB)

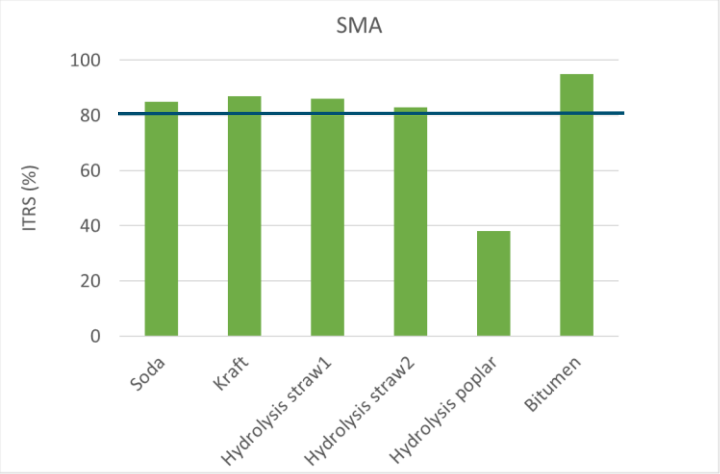
Stone mastic asphalt (SMA)











Landa P., Gosselink R.J.A.,Lignin-based bio-asphalt, WO2019/092278

Labscale bio-asphalt tests

- Some lignin-rich streams fails as asphalt binder

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Labscale bio-asphalt tests

- Stiffness and resistance to fatigue (4-points bending test)

	Hydrolysis lignin	Kraft lignin	Minimum requirement	Maximum requirement
Stiffness (MPa)	4441	6530	3600	11000
Fatigue resistance (Vermoeiing ε6)	107	124	>100	>130
Track formation Fc Max	<0,6	<0,2	0,2	4,0
Durability %	85	85	> 80	
Density (Kg/m^3)	2299	2355		

AC Surf. NEN-EN 12697-24/26

Demonstration Bio-asphalt in Zeeland

- 50% substitution of bitumen by soda lignin
- Manufacturing at lower temperature (130-140 °C, lower CO_2)
- Mixing lignin – bitumen – asphalt ingredients @ asphalt mill
- July 2015 1st lignin bio-asphalt road

- After 6 years lignin asphalt behaves very good!

Lignin based cycling path Wageningen

- 3 Lignin selected
    - Soda
    - Kraft
    - Hydrolysis lignin
- Binder = 50% lignin / 50% bitumen
- Asphalt production in mill at 140°C
- 1 km cycling path at Wageningen campus
    - 10 tonnes of lignin
    - Production at 140°C
    - 7 trucks equals 220 tonnes bio-asphalt
    - Top layers in separate sections

Pavement
June 2017

provincie Gelderland

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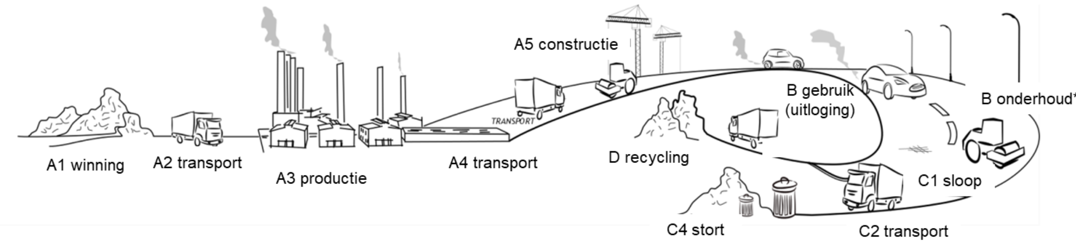
Lignin based asphalt binder

- 35-70% less CO_2 emission (Moretti et al. 2022)
- Extra functionality (lower noise, lower rolling resistance) FIRST RESULTS
- Two technologies
  - Mixing @ asphalt mill (WFBR/AKC): >25 demonstration roads in NL
  - Blending lignin/bitumen binder (TNO/WFBR)
- Certification, LCA, MKI
  - Procurement / tender



- Our final goal: development of a bitumen-free asphalt binder
  - Lignin modification, other Biobased components

P. Landa, Gosselink, R.J.A., Lignin-based bio-asphalt, WO2019/092278
D. van Vliet, Slaghek, T. et al., Bitumen composition, WO2015/137813

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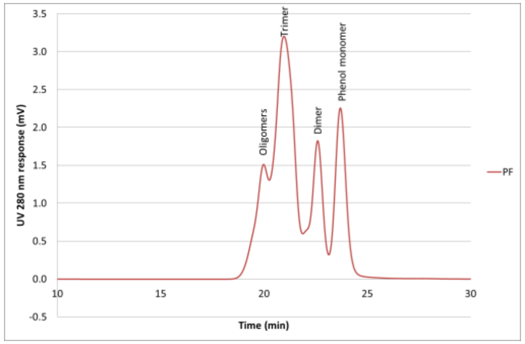
Thermoset resins

- Lignin is a natural glue
  - Binders are used in panel & boards
  - >1 M tonnes phenol formaldehyde (PF) resins globally
- Why lignin?
  - Substitution of expensive phenol part
  - Reduction in emission of formaldehyde
  - Lignin structure resembles PF structure
  - Softwood lignin favourable crosslinking (free ring position)
- Commercial 30% LPF in 2006; commercial 50% LPF in 2019 (Trespa)
- Challenge: reactivity, now further studied



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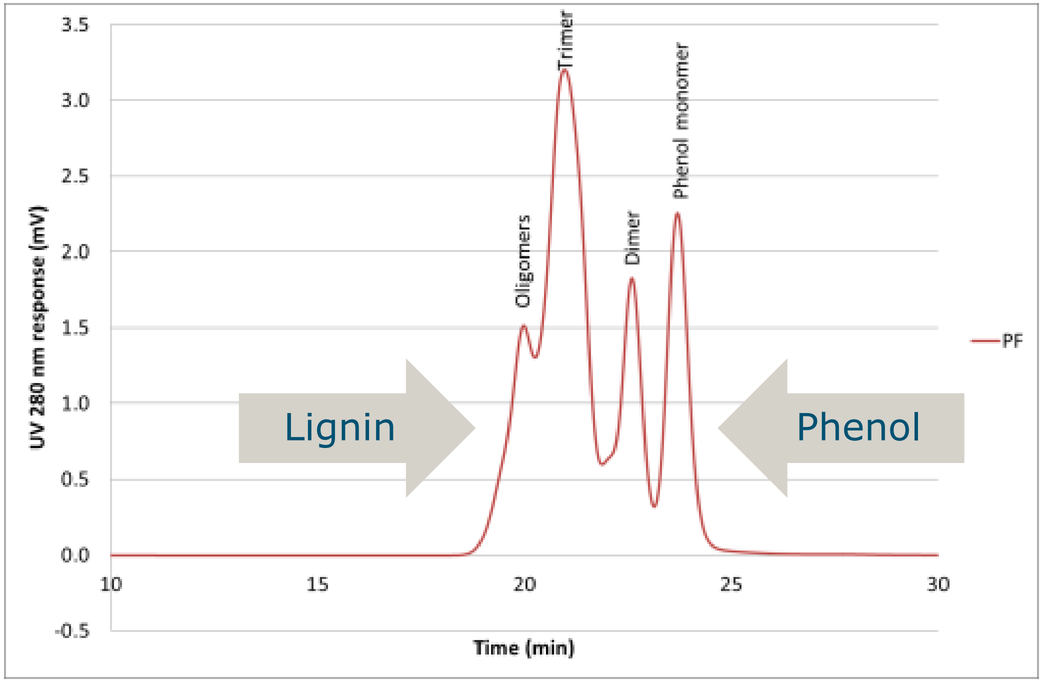
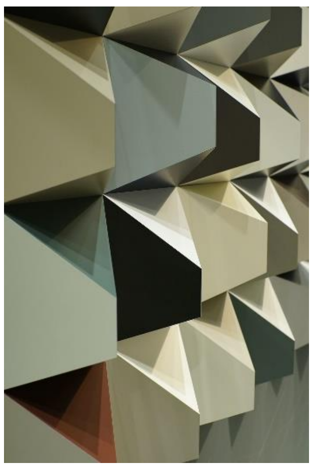
Thermoset resins

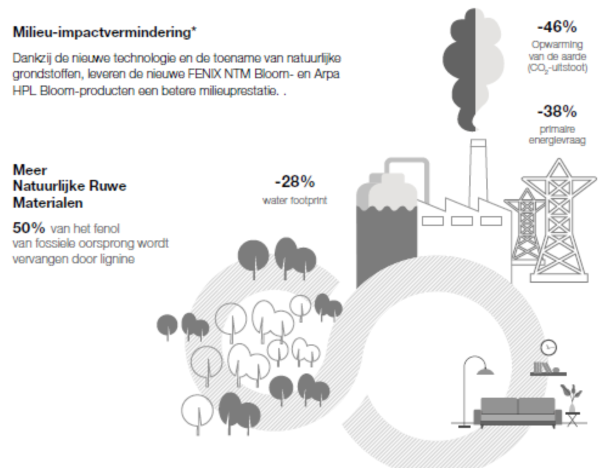
- Alkaline SEC used to follow the resin synthesis

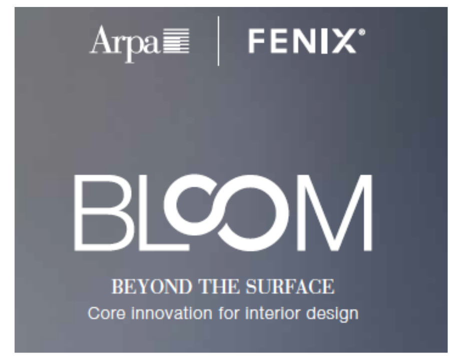


Thermoset resins

- 8 years collaboration with Nemho/Trespa/Arpa (NL/IT)
  - Resulted in a commercial interior HPL glued with a resin in which 50% phenol is substituted by lignin
  - Fenix Bloom product with 46% CO_2 emission reduction





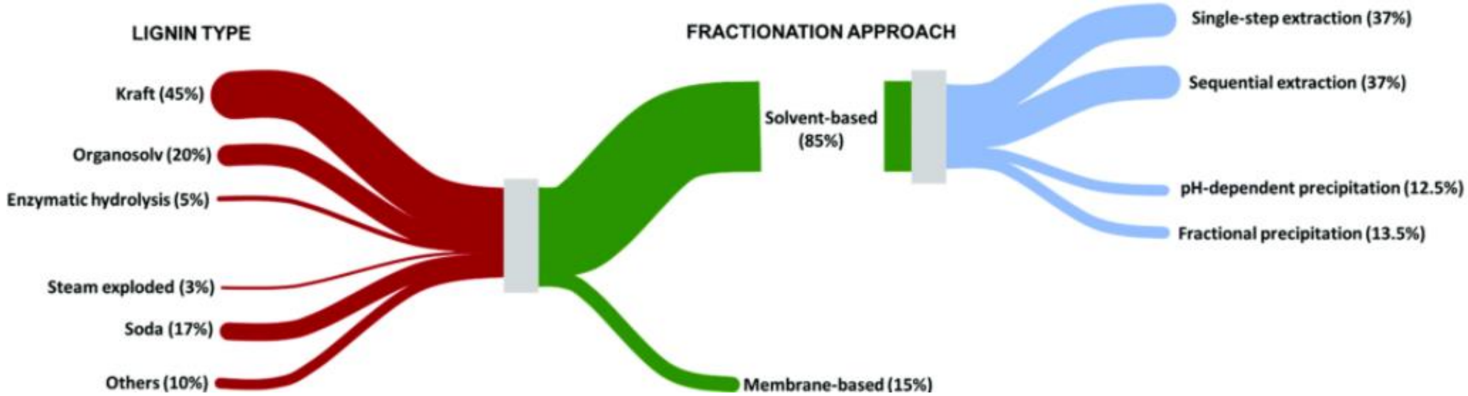


- We further develop this technology to get a 100% biobased resin
  - Production and modification to get a more reactive lignin
  - Biobased crosslinkers

Lignin Fractionation: powerful tool

- Fractionation is a useful method for purification and adjustment of lignin functionality

  - Different fractionation methods



  - More defined (homogeneous) lignin structures
  - Higher functionality
  - Added value application

Green Chemistry, 2020 (15), 4722
Green Chemistry, 2020 (22), 7448

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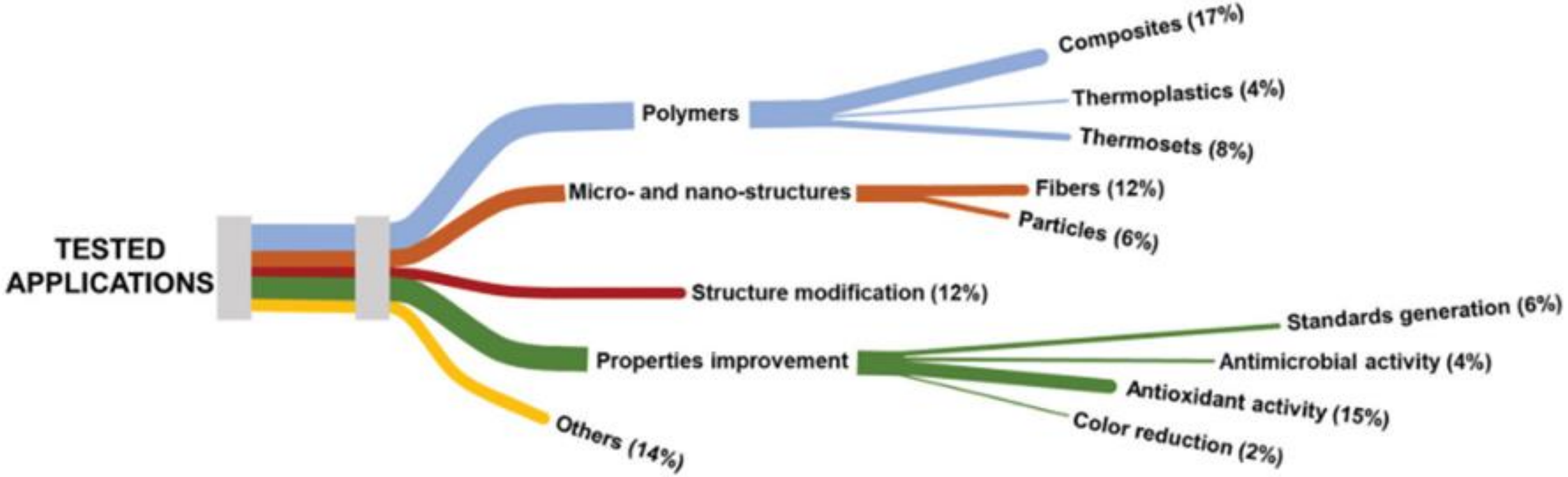
Uses of fractionated lignin

- Fractions used as functional ingredients in various applications
  - Often for anti-oxidant properties
  - But also for insect repellent properties



Green Chemistry, 2020 (15), 4722
Composites Part C: Open Access 2020 (2), 100044

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Solvent fractionation

- Successive solvent fractionation with solvents of increasing Hansen solubility parameters (increasing polarity)
- First process with 4 solvents @ room temperature @ kg scale
    - Including solvent recovery
- Second process with 2 solvents only ethylacetate, ethanol

Soda Lignin fractions yields

Fraction	Code	Yield (% dry lignin)	Yield (% dry lignin)
Unfractionated	GV03		
Ethylacetate soluble (FB01)	GV03 FB01	31	32
Ethanol soluble (FB06)			34
Butanone soluble (FB02)	GV03 FB02	19	
Methanol soluble (FB03)	GV03 FB03	23	
Acetone/water soluble (FB04)	GV03 FB04	9	
Insoluble fraction (FB07)	GV03 FB05	17	34

Gosselink et al. Fractionation of technical lignin, WO2015/178771

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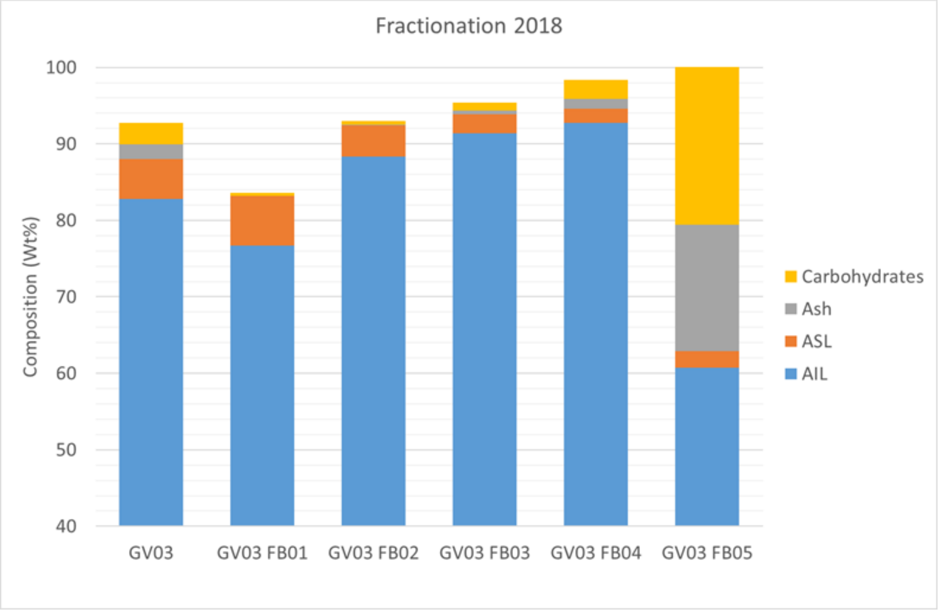
Solvent fractionation of GV03

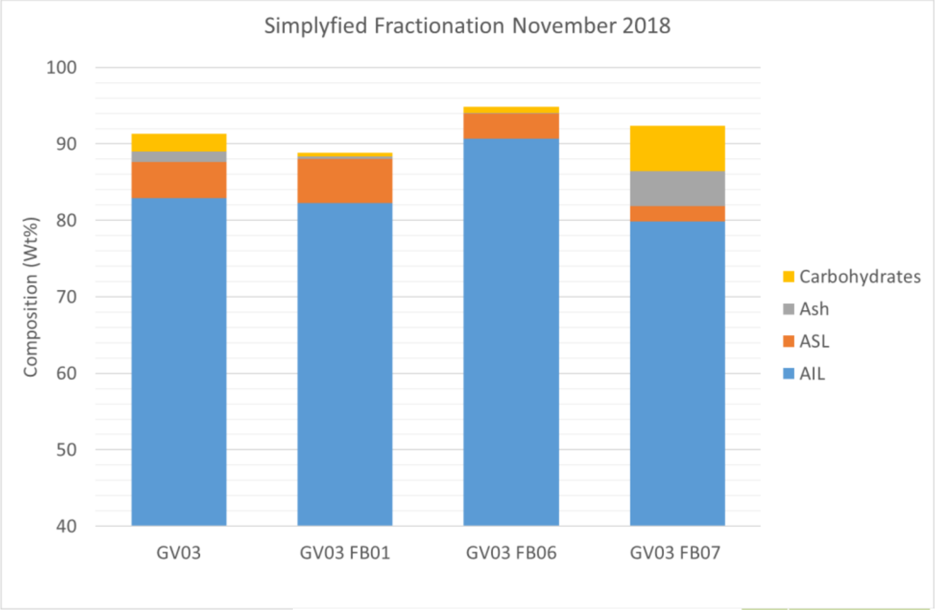
4 solvents fractionation versus 2 solvents fractionation

Lignin ethylacetate fractions (FB01) are comparable in composition and molar mass

Ethanol fraction (FB06) is rather pure, but a higher molar mass

Residual 2nd fractionation (FB07) has a higher yield and less impurities





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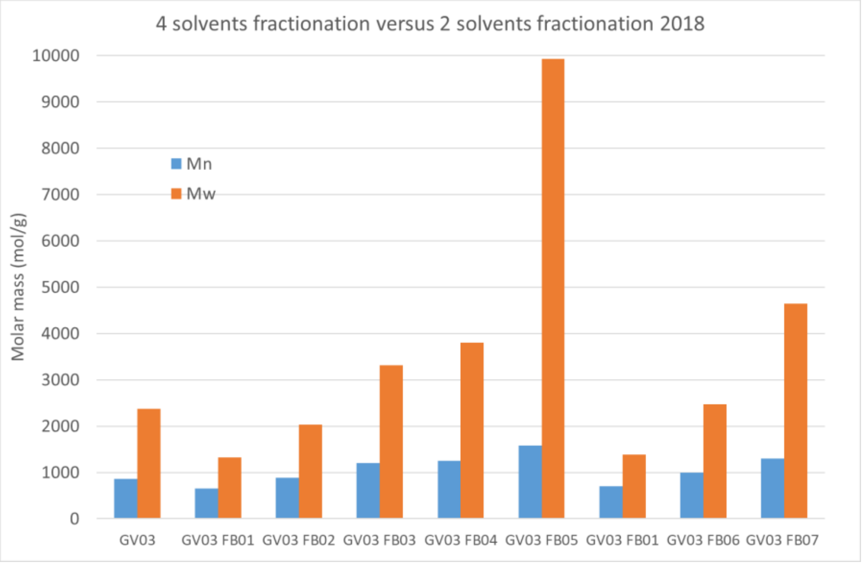
ZELCOR
Zero Waste Ligno-Cellulosic Bio-Refineries

Solvent fractionation of GV03

Lignin fractions (FB01) comparable in Mw

FB06 (ethanol) higher in Mw than FB02 (MEK)

FB07 lower in Mw than FB05



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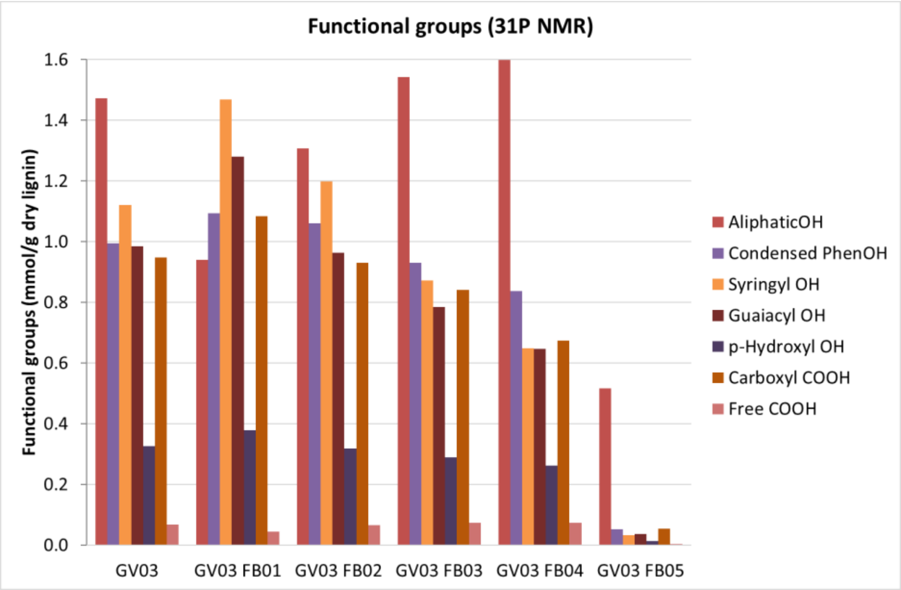
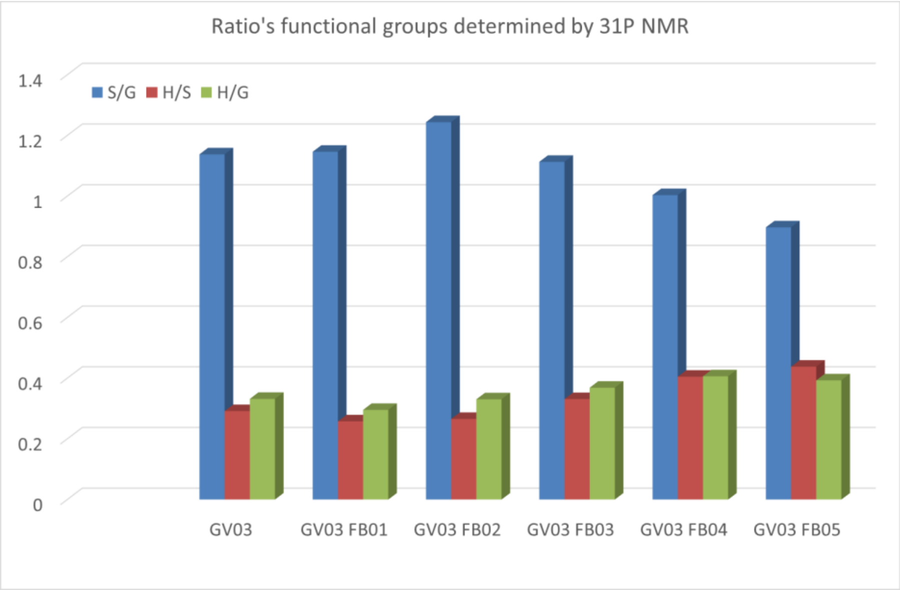
ZELCOR Zero Waste Ligno-Cellulosic Bio-Refineries

Solvent fractionation of GV03

- Functional group distribution upon fractionation determined by ^{31}P NMR





- In ethylacetate fraction (FB01) phenOH ↑ aliphOH ↓

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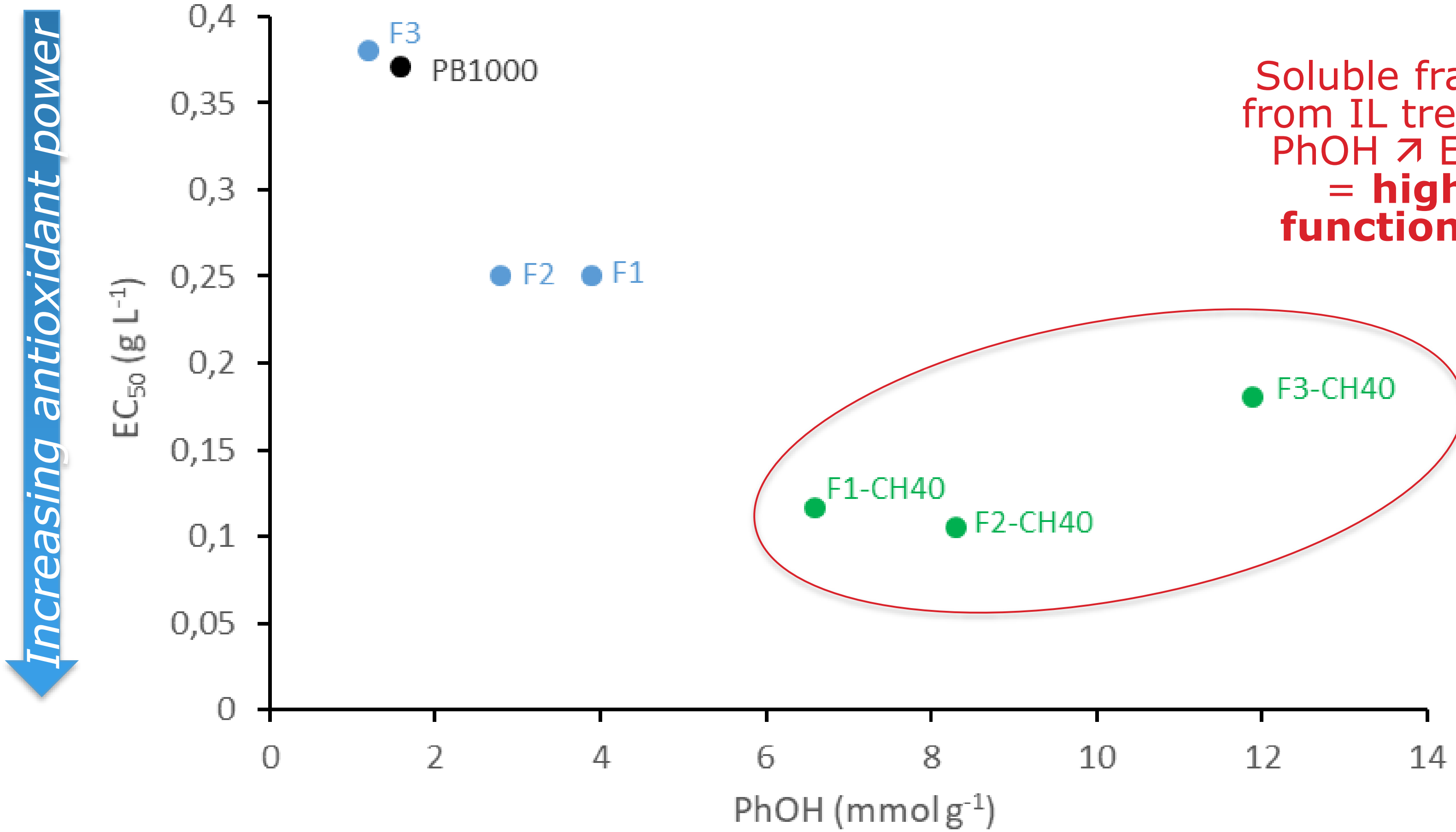
Antioxidant versus phenOH content



Soluble fractions from IL treatment
PhOH ↗ EC$_{50}$ ↘
= **higher functionality**

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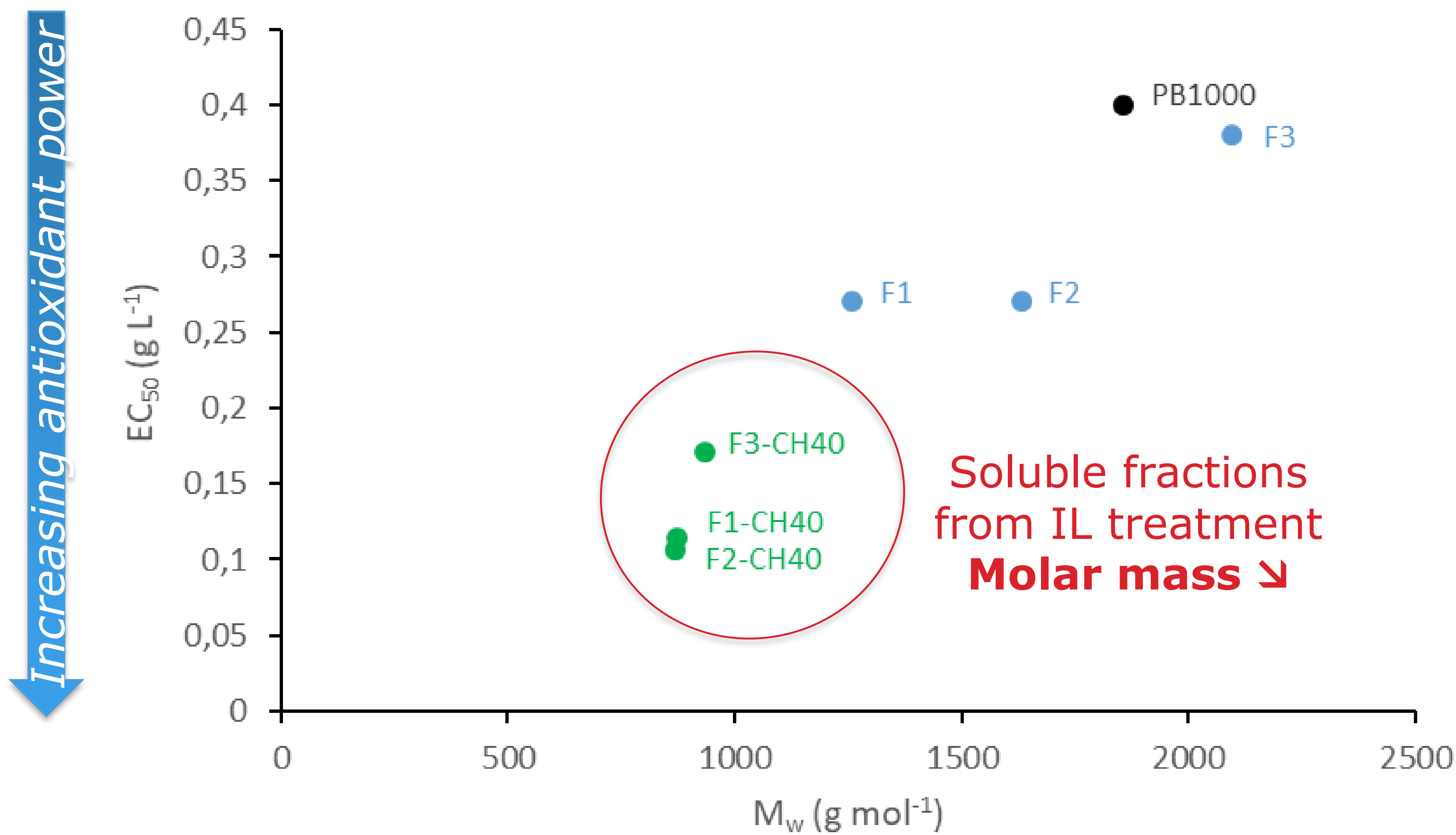
(Majira et al., 2019)

ZELCOR Zero Waste Ligno-Cellulosic Bio-Refineries

Antioxidant versus molar mass



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(Majira et al., 2019)

ZELCOR
Zero Waste Ligno-Cellulosic Bio-Refineries

Cascading approach conclusions

- Combined fractionation and IL treatment lead to fractions with higher functionality
- Adjustment of molar mass, purity, phenolic OH groups
- Antioxidant properties increased with factor 3-5
- Proof of concept achieved
- Valorization of lignin towards added value applications
- TRL 2-3
- Scalability

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ZELCOR Zero Waste Ligno-Cellulosic Bio-Refineries

Development of new applications

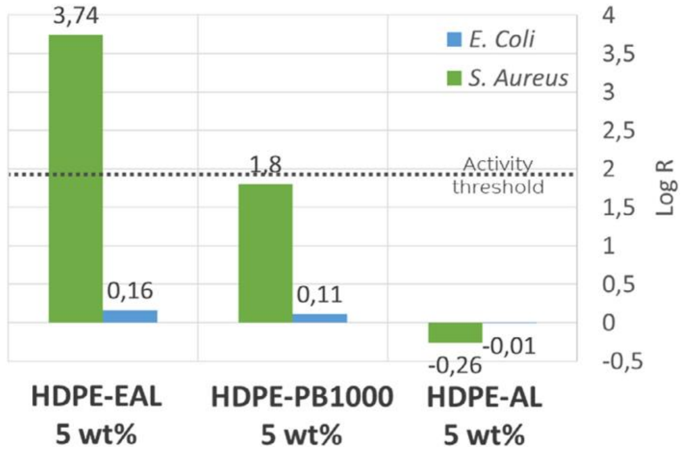
- As functional component in polymers

ZELCOR Zero Waste Ligno-Cellulosic Bio-Refineries

- Lignin shows antioxidant, antimicrobial, insect repellent properties to HDPE films
- Higher phenol content enhance the lignin antioxidant and antimicrobial effects
- Insect repellence is obtained at 2 wt % lignin ethyl acetate extract in HDPE
- Lignin ethyl acetate extract is a good candidate for food protection packaging

Insect repellence results on *Sitophilus oryzae* measured as the number of insects in the treated zone.

Sample code	N-insects	Effect
HDPE ref	4.2[a]	No repellence (4-6)
HDPE-AL 2 wt%	6.7	Attractant (>6)
HDPE-PB1000 2 wt%	4.55[a,b]	No repellence (4-6)
HDPE-EAL 2 wt%	3.2	Repellence (<4)



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Vachon et al. Use of lignin as additive in polyethylene for food protection: insect repelling effect of an ethyl acetate phenolic extract, 2020

Lignin fraction for wood preservation

- Application to preserve (***alum treated***) archaeological wood
- Ethyl acetate fraction (lower molar mass; higher functionality)
- Non-aqueous solvent (no leaching salts)

- Impregnation
- Physical properties
- Acid induced crosslinking

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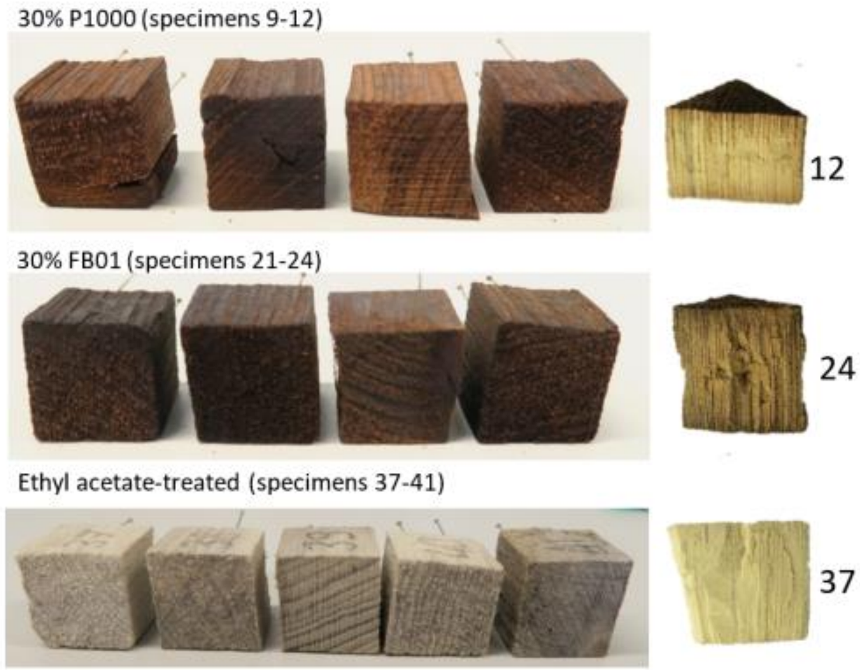
Łucejko, J.J. Forests 2021, 12, 911.

Lignin fraction for wood preservation

- Impregnation



- More in-depth impregnation with ethylacetate fraction
- Lignin gives a harder wood object
- Potential to develop a wood consolidant based on lignin

Łucejko, J.J. Forests 2021, 12, 911.

Conclusions

- Lignin has large potential to be used in materials and for chemicals
- Only using it for energy hampers its full potential
- Need for larger volume lignin production
    - Constant quality at reasonable costs
- Focus both on bulk and niche applications
    - Need for demonstration projects / products

- Short-medium term options: in materials such as bio-asphalt, resins, additives for polymers/composites

- Longer term options: archaeological wood preservation, bio-aromatics

Acknowledgements

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- All partners from the Zelcor project

- All partners from the Oseberg project

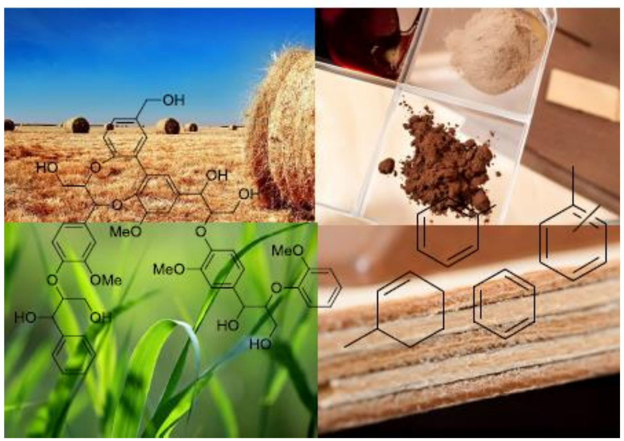
- Partners from the bio-asphalt projects: AKC, H4A, Roelofs, NTP, University of Utrecht and others

Thank you for your attention

Lignine

Groene grondstof voor chemicaliën en materialen

Jan van Dam, Paulien Harmsen, Harriëtte Bos,
Richard Gosselink



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