Lignin Valorisation in a Thermochemical Biorefinery

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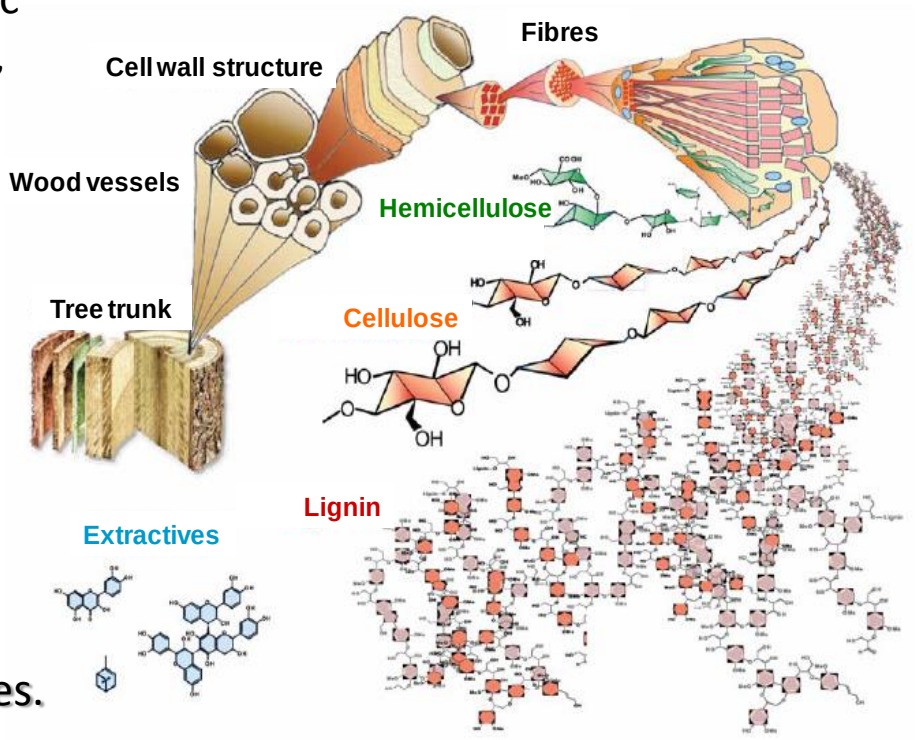
Lignin: structure, function and use

- Lignin is a complex and recalcitrant phenolic biopolymer that provides structural rigidity, flexibility and microbial protection in lignocellulosic biomass.
- Lignin is an abundant side stream from the pulp & paper industry and biorefineries and a source for renewable aromatics.
- Lignin is mainly used as low-value fuel for heat and power while there is a strong need for a cost-effective conversion into valuable products for profitable biorefineries.
- A dedicated pyrolysis technology was developed by ECN to convert lignin in biophenolics and biochar useful for a variety of value-added applications.



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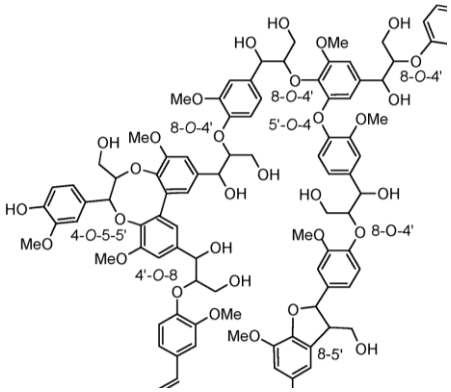
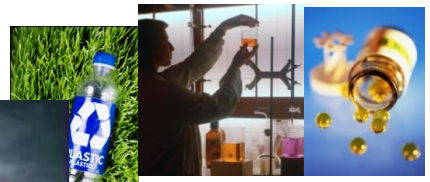
- Holladay et al., Top value added chemicals from biomass. *Volume II – Results of screening for potential candidates from biorefinery lignin. Produced by the staff at the Pacific Northwest National Laboratory (PNNL) and the National Renewable Energy laboratory (NREL) (2007).*
- Zakzeski, J., Bruijnincx, P.C.A., Jongerius, A.L., Weckhuysen, B.M., The Catalytic Valorization of Lignin for the Production of Renewable Chemicals. *Chem. Rev.* 110 (2010) 3552-3599
- P.J. de Wild, H. Reith, H.J. Heeres, Biomass pyrolysis for chemicals, Biofuels. 2 (2), 185 - 208 (2011)

Applications for lignin products

low volume - high value market 10000 €/t

Example of an oligomeric fragment from the pyrolysis of lignin

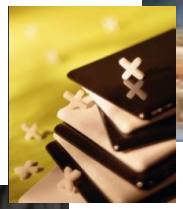




specialty chemicals for food, fragrance and pharmaceuticals

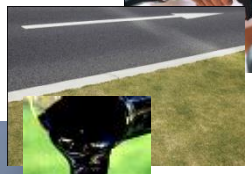
bio-plastics

bio-resins for wood-adhesives

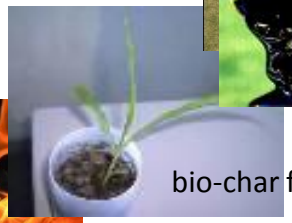


additives for flooring material

activated carbon, carbon-fibres and carbon-black



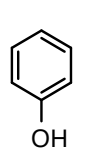
fuel-additives



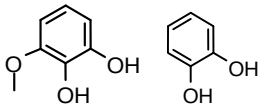
bio-bitumen for green asphalt

bio-char for soil improvement

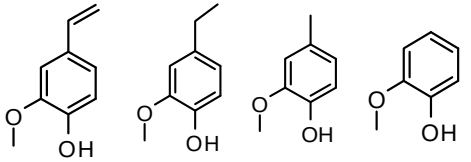
bio-fuel for CHP



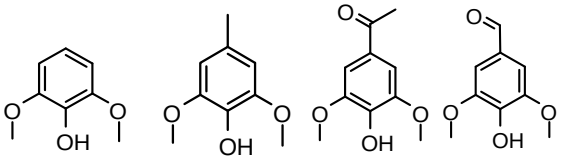
alkylphenols



catechols



guaiacols



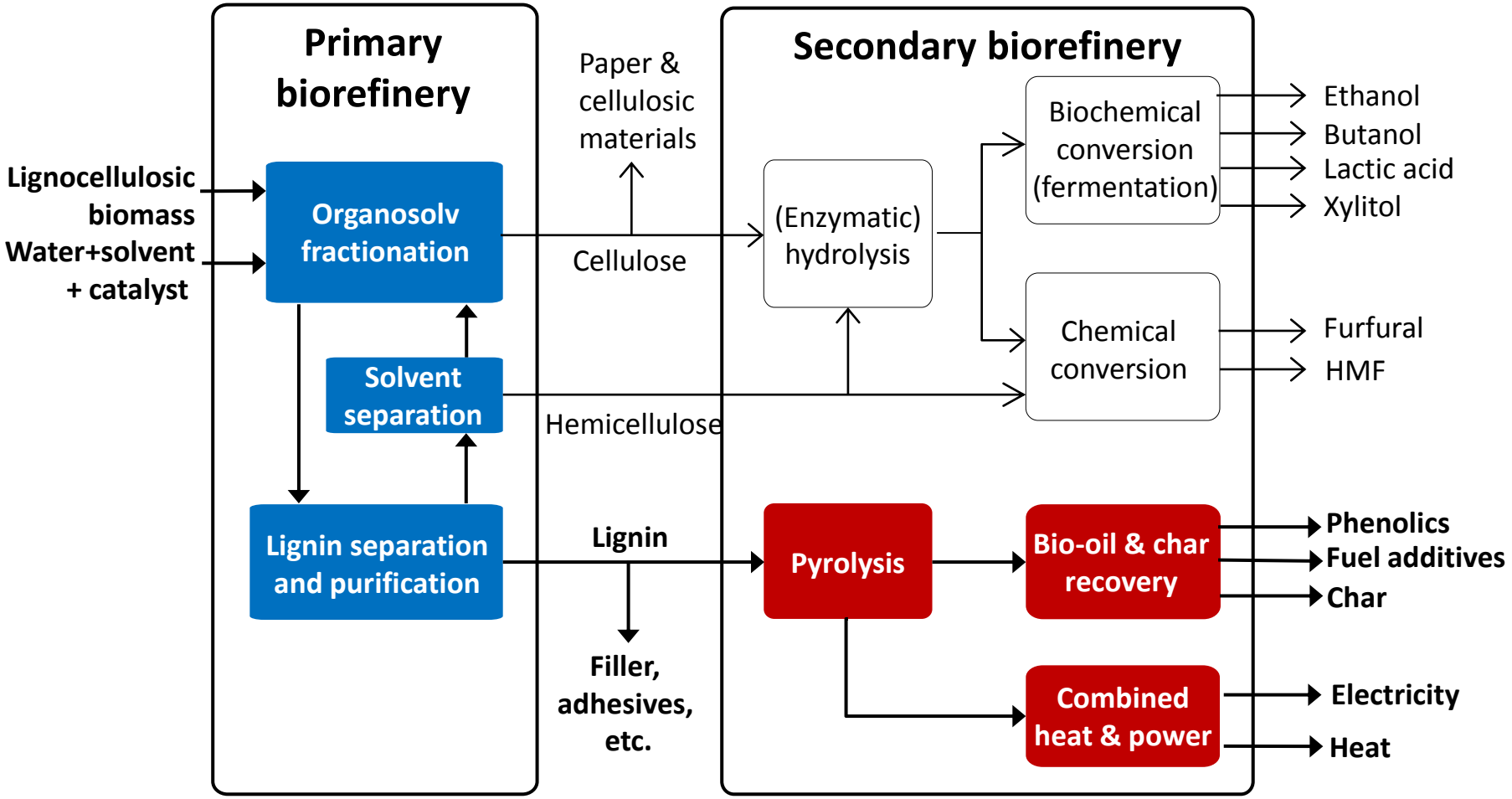
syringols

high volume - low value market 100 €/t

Selection of 12 major monomeric phenols from the pyrolysis of lignin

Lignocellulose biorefinery

Organosolv fractionation and lignin valorisation via pyrolysis

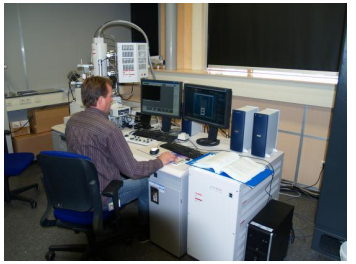


Wild, P.J. de, Huijgen, W.J.J., Heeres, H.J. (2012). Pyrolysis of wheat straw-derived organosolv lignin. Journal of Analytical and Applied Pyrolysis 93, 95-103.

Lignin pyrolysis experiments

- Feedstocks
  1. Straw derived lignin (Biolignin™)
     acid-organosolv fractionation (CIMV)
  2. Softwood derived lignin (Kraft)
     Kraft - pulping
  3. Hardwood derived lignin (Alcell™)
     EtOH / water organosolv fractionation

- Test facilities
  - Atmospheric Bubbling fluidised bed reactor (1 kg/hr, 5 kW_{th})
  - On-line (ND-IR) and off-line (GC/MS/FID, Karl-Fischer, gravimetry) product analysis (condensables, non-condensables,aerosols)
  - Electron microscopy of the chars (Hitachi – SU-70 HR-SEM, 1 nm resolution at 15 kV, Char micrographs at 5000x.



- Comparative tests different lignins
  - 150 g dry feedstock, 500°C, 8 sec vapour residence time
  - Co-feeding with 10 wt% of a proprietary additive

Pyrolysis reactor set-up

1 kg/hr bubbling fluidised bed Reactor

Cyclone & particle filter

Ash

Products

Gas conditioning & analysis (CO, CO_2, C_xH_y)

Off-gas

Batch sampling with impinger train

Off-gas

Continuous sampling with condensers, ESP and filters in series

Off-gas

Lignin feed

Hot sand bed 500°C

Reactor feeding screw

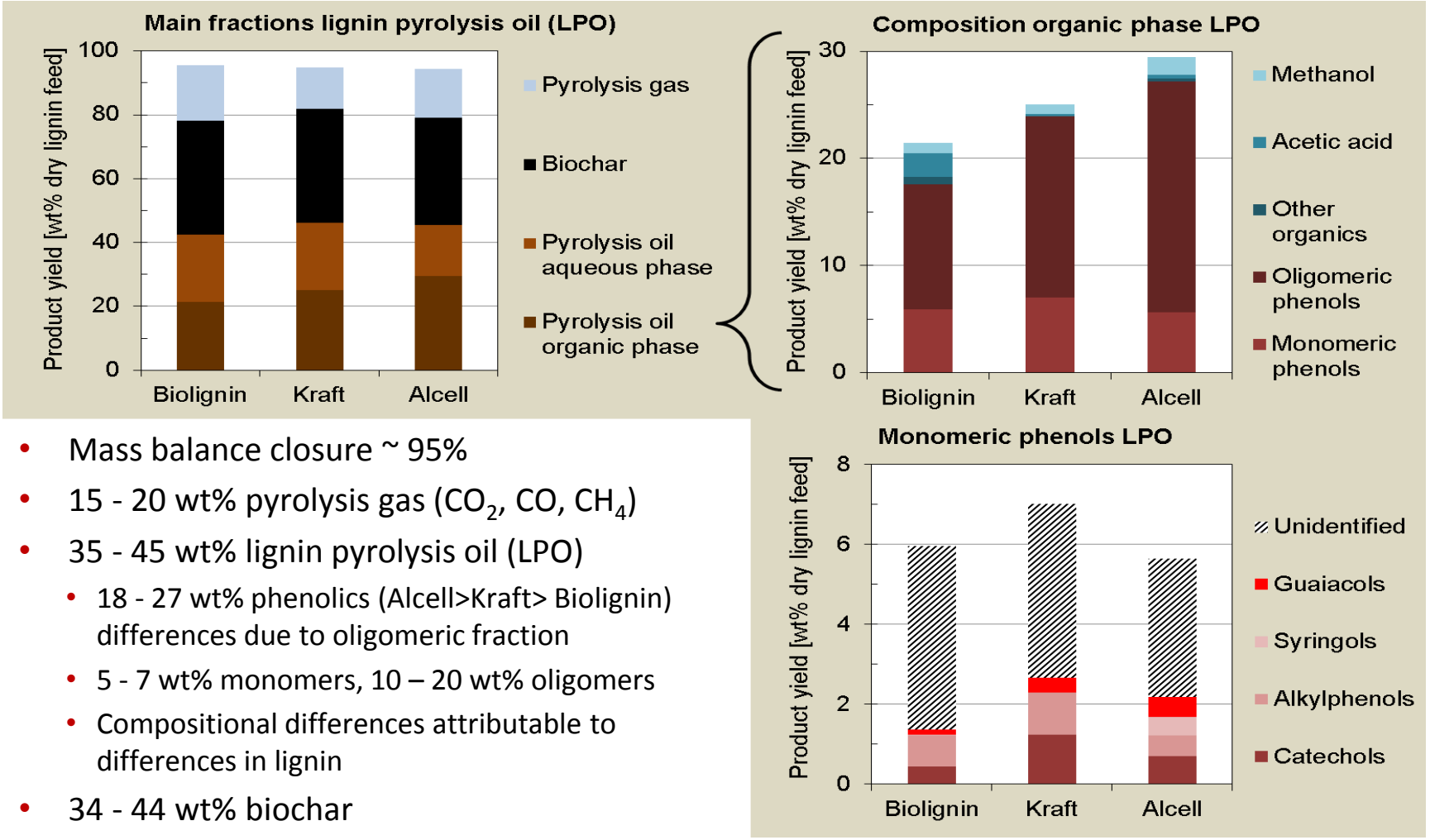
Pre-heated fluidisation gas

Lignin biochar

Lignin bio-oil

Comparative pyrolysis results

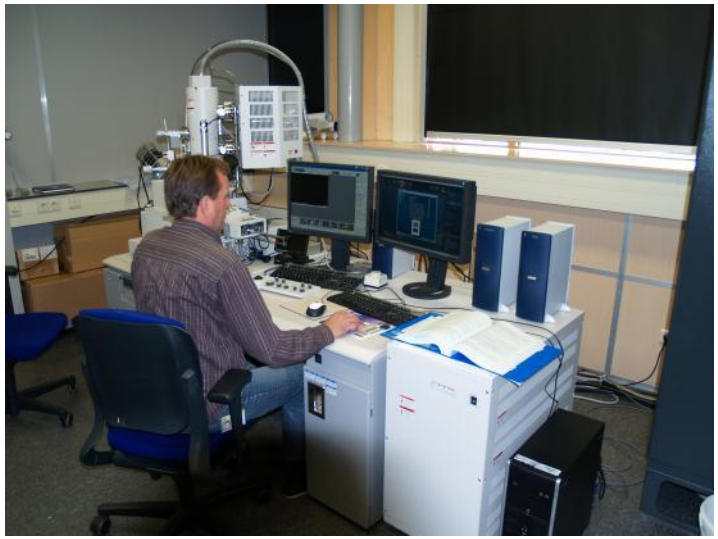
Major product fractions and lignin pyrolysis oil composition for Biolignin, Kraft and Alcell



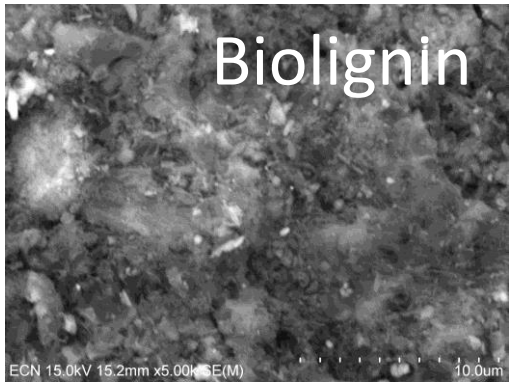
- Mass balance closure ~ 95%
- 15 - 20 wt% pyrolysis gas (CO_2, CO, CH_4)
- 35 - 45 wt% lignin pyrolysis oil (LPO)
  - 18 - 27 wt% phenolics (Alcell>Kraft> Biolignin) differences due to oligomeric fraction
  - 5 - 7 wt% monomers, 10 – 20 wt% oligomers
  - Compositional differences attributable to differences in lignin
- 34 - 44 wt% biochar

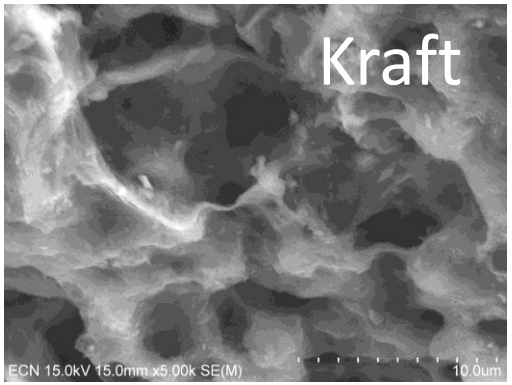
Results comparative pyrolysis tests

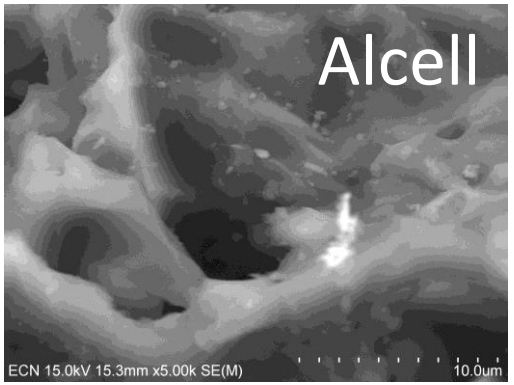
SEM characterisation biochars



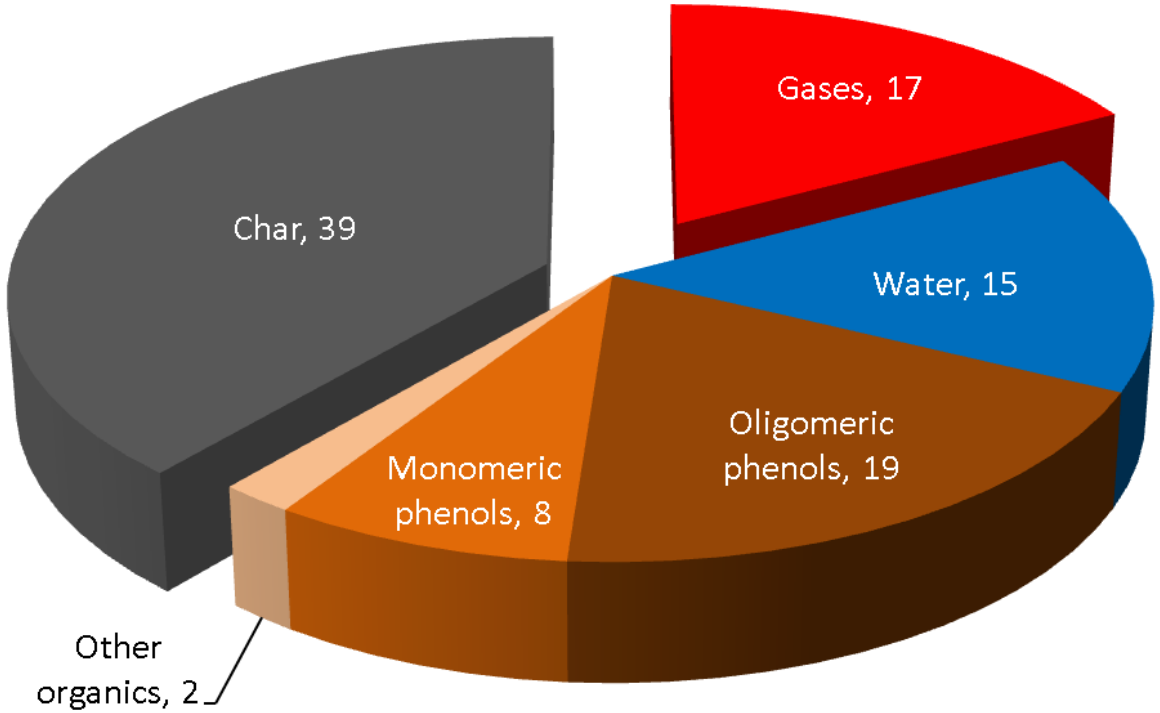
- Hitachi – SU-70 HR-SEM,
  1 nm resolution at 15 kV
- Char micrographs at 5000x magnification
- Clear evidence for melting phenomena with Kraft and Alcell lignin. Less clear for Biolignin







Lignin pyrolysis oil from pure Biolignin™



- Ultimate analysis results dry oil:
  - Heating value ~31 MJ/kg
  - 70% C, 20% O, 8% H, 2% N
  - Negligible ash content
- Pyrolysis oil composition:
  - Complex bio-oil composition
  - Various phenolic monomers, guaiacols, alkylphenols and catechols are the major phenols
  - The unidentified oligomeric phenols constitute the major fraction
  - Acetic acid is the main non-phenolic organic (~1.6 wt% based on lignin)

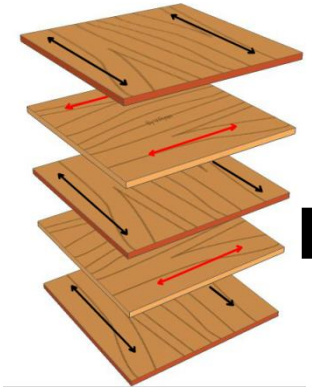
Lignin pyrolysis oil is usable for e.g. resins,
biochar can be used as soil improver or as precursor for carbon-black

Plywood panels production with lignin pyrolysis oil as phenol substitute

Veneers-odd number, cross bonding – face to face

10 wt% substitution of phenol by lignin pyrolysis oil is easily possible without compromising final product quality

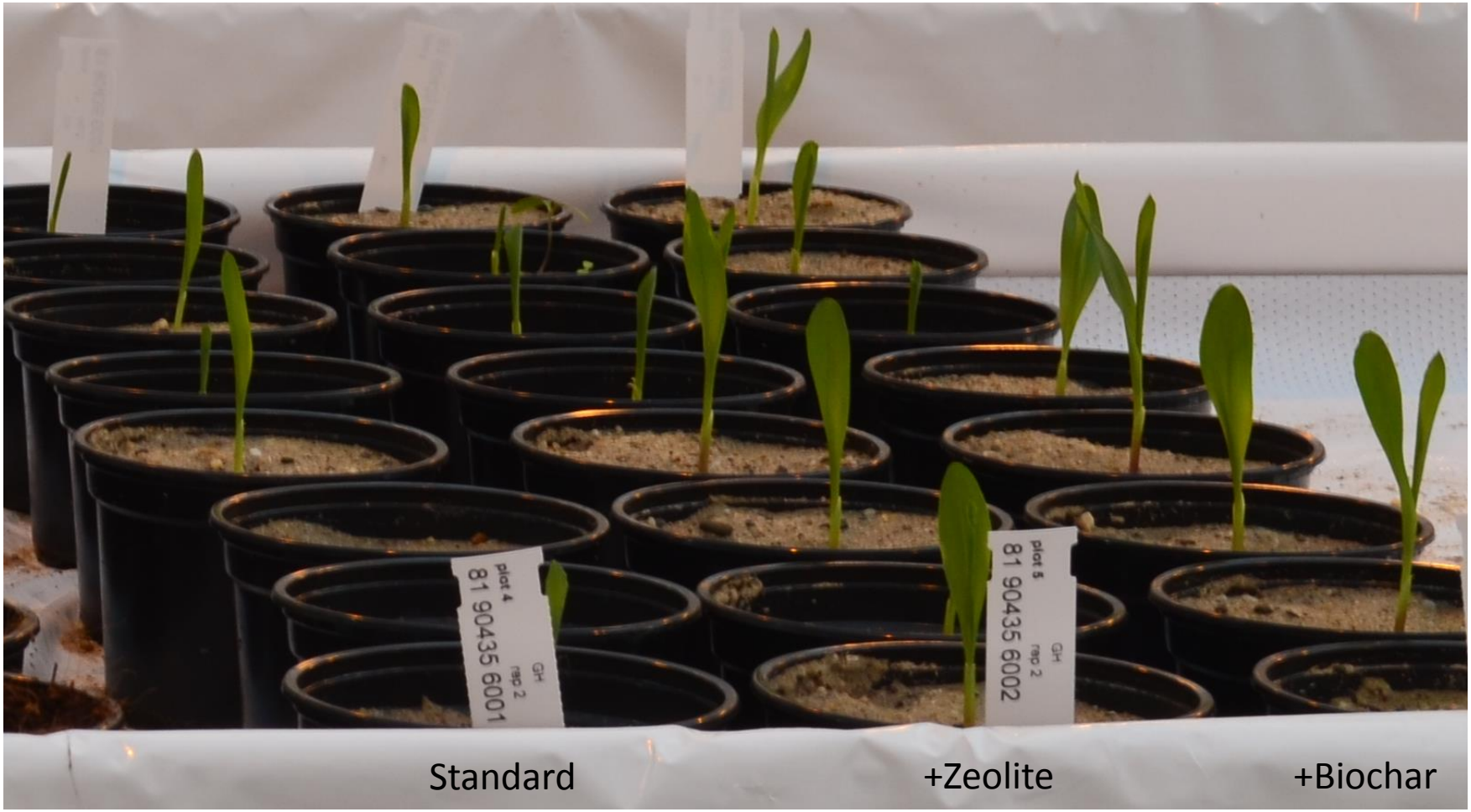
Hand spreading



Machine spreading

Chimar Hellas S.A.

Lignin char as growth enhancer



Lignin char to replace carbon-black in tyres

Conclusions / outlook

- Lignin valorisation is a key-issue for a profitable biorefinery.
- Lignin can be pyrolysed into a complex phenolic bio-oil and biochar. The bio-oil contains monomeric and oligomeric phenolics and its yield and composition depend on process conditions and lignin type.
- Although the complexity of the lignin pyrolysis oil presents a challenge for the economic recovery of individual phenols, the whole oil can be used as a substitute for phenol in a variety of applications.
- Valorisation of lignin by pyrolysis has economic potential.
  The challenge remains to increase the phenolics yield and to identify valorisation routes for the biochar.

Thank you for your attention!

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the 7th framework Integrated Project BIOCORE


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