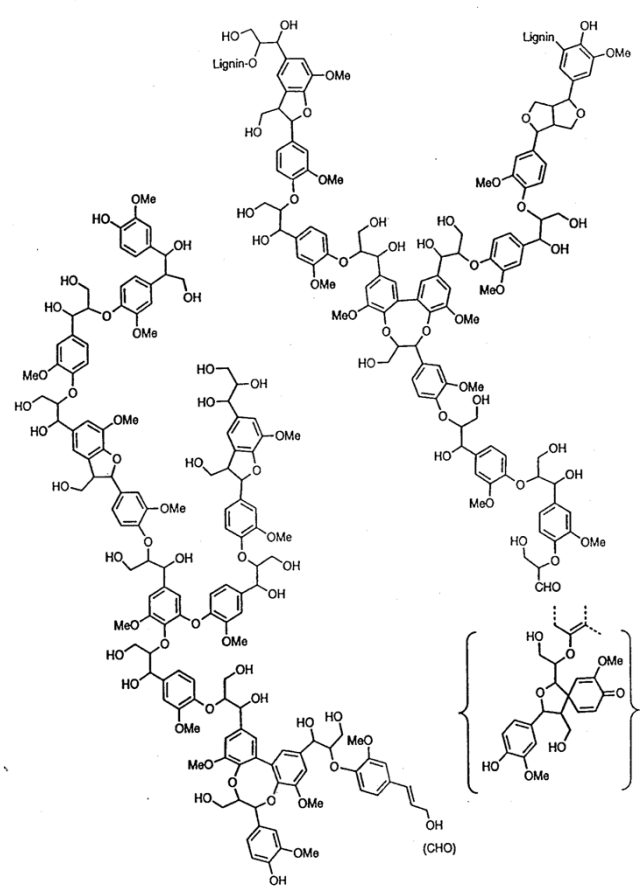
ProLignin - High-Value Products from Lignin Side-Streams of Modern Biorefineries



Tiina Liitiä

VTT Technical Research Centre of Finland

6th WoodWisdom-Net Research Programme Seminar
Hanover, Germany, November 11, 2014

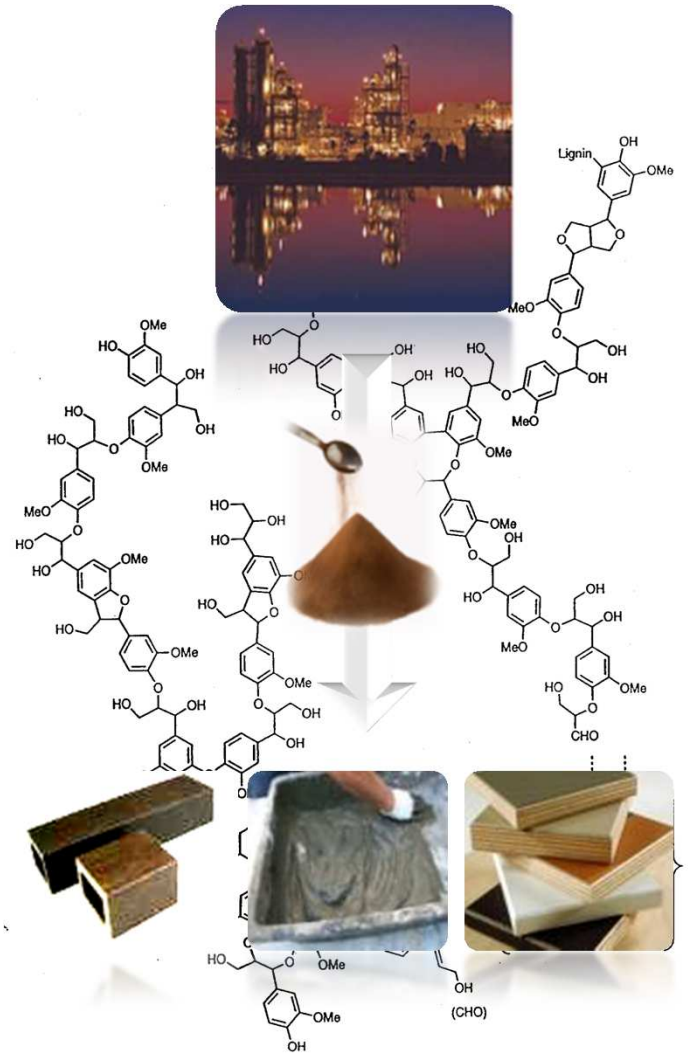
Background

- New biobased renewable fuels, chemicals and materials are required to replace the present oil based products
- For transportation, bioethanol is a potential substitute, but its high production costs inhibit rapid commercialisation
- Also traditional pulping industry is looking for new added value products
- Competitiveness of traditional pulp and bioethanol production processes could be increased by conversion of the side-stream lignins into new biobased high-value products instead of incineration
- For chemical industry, lignin is a valuable aromatic raw material available in high quantities

There is need for viable lignin upgrading routes for value added products

Project Objectives

- Create more sustainable products by substitution of the oil based raw materials with the industrially available lignin residues
  - ***Resins (PF, PU, epoxy)*** → *adhesives, foams, coatings*
  - ***Thermoplastics*** → *composites*
  - ***Dispersants*** → *fluid control*
- Evaluate the application potential of industrial lignins of different origin
  - ***Feedstock*** *(SW, HW, wheat straw, bagasse)*
  - ***Process technology*** *(kraft, soda, soda-AQ, organosolv, steam explosion)*



Partners globally troughout the value chain

Finland
VTT
UH
Stora Enso
Valmet
Momentive

Latvia
LSIWC

Germany
FhG-ICT
UniHH
Rampf E & G

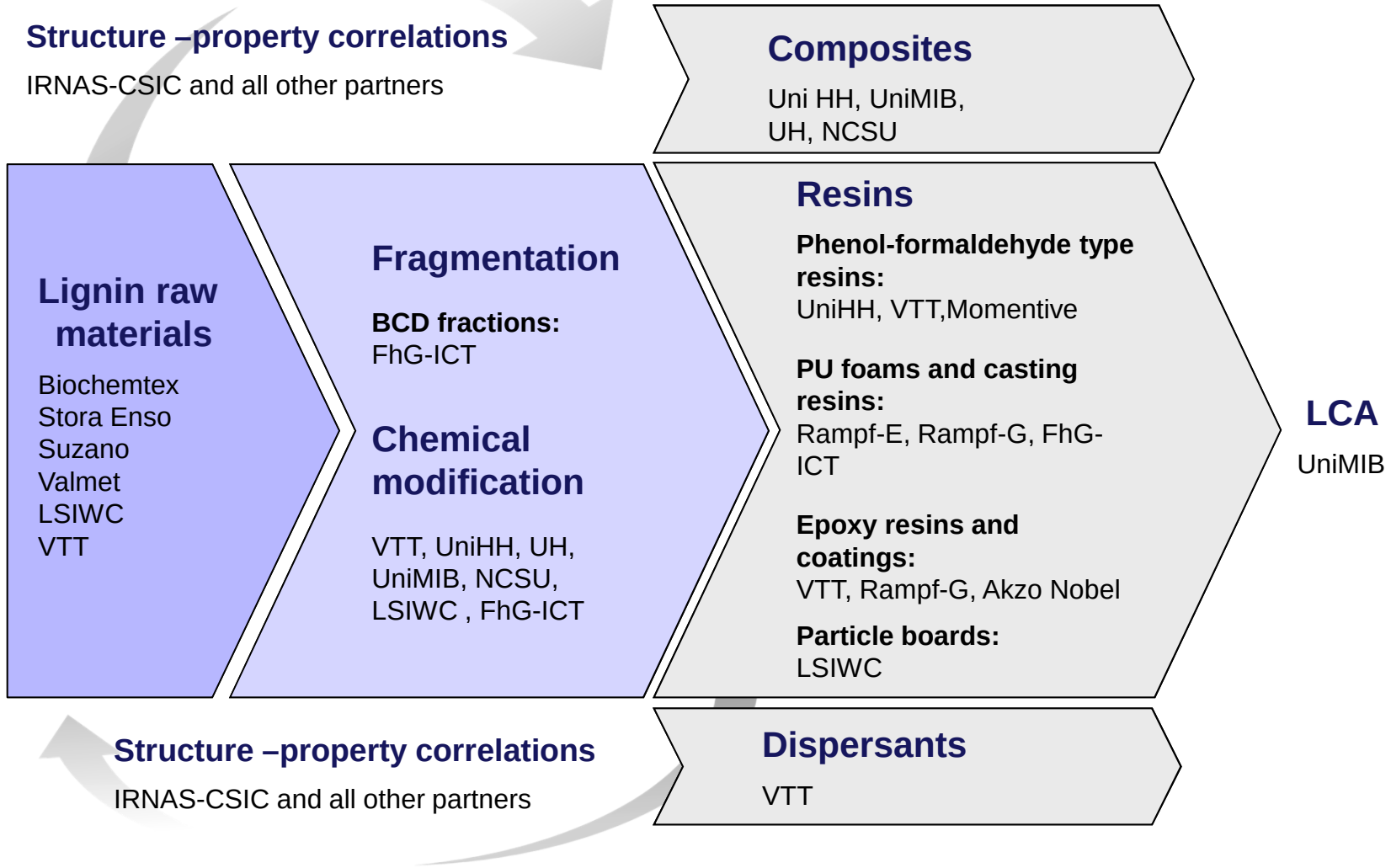
Italy
UNIMIB
Biochemtex

Spain
CSIC-IRNAS

USA
NCSU
AkzoNobel

Brazil
Suzano

Project structure - Role of partners in value chain



Lignins studied

Wide selection of lignins produced with distinct characteristics and application potential

Industrial kraft lignins:

- Softwood **(*Kraft-SW*)** - Stora Enso
- Hardwood, eucalypt **(*Kraft-HW*)** - Suzano Pulp and Paper

Industrial soda lignin:

- Wheat straw (***Soda-WS***), commercial Green Value

Industrial hydrolysis residue:

- Wheat straw (***HL-WS***) after SSF from pilot plant

Steam exploded lignins:

- Wheat straw (***SE-WS*)**, Birch (***SE-birch)***, Grey alder (***SE-GA***)

Organosolv lignin:

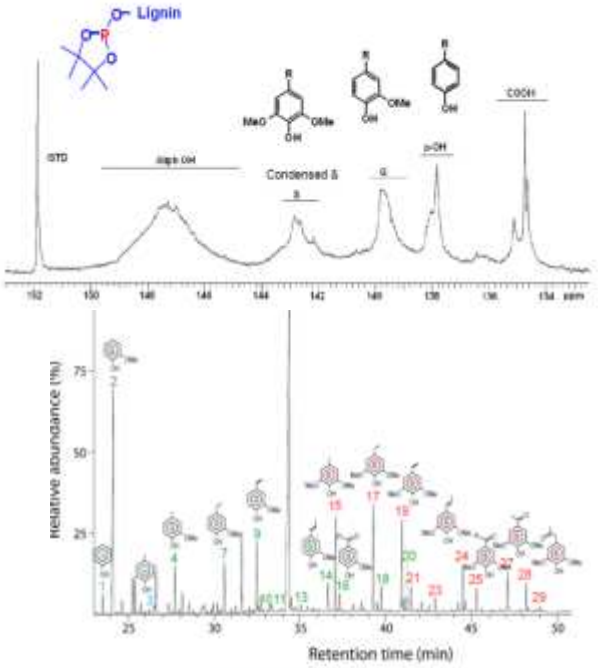
- *E. globulus* (***LGF-OS-HW***),
- VTT lignofibre (LGF) with ethanol/water solvent

Soda-AQ lignin:

- Bagasse (***SAQ-B***) - Valmet

Lignin characterization

Structural information on effect of biomass pretreatment process and feedstock for evaluation of lignin applicability in target products



Purity and composition

- ✓ Klason and acid soluble lignin
- ✓ Carbohydrate composition
- ✓ Ash content
- ✓ Elemental analysis

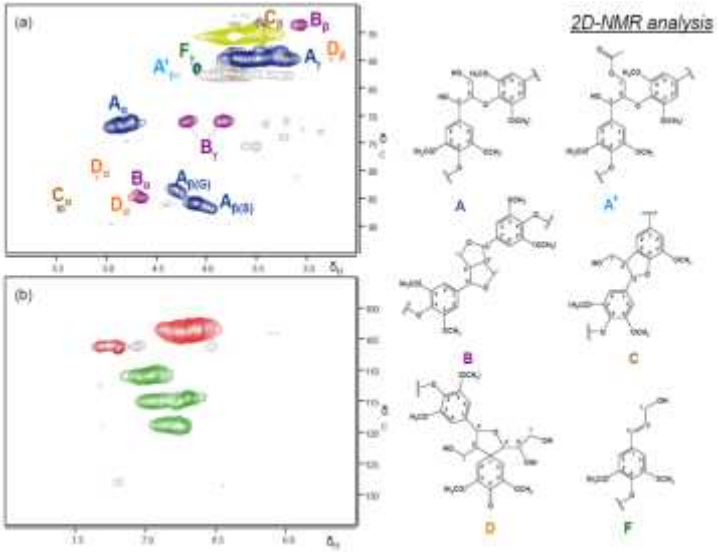
Aromatic subunits S/G/H (Py-GC/MS, NMR)

Functionalities - aliphatic and phenolic OH, COOH (^{31}P NMR)

Inter-unit linkages (2D ^{1}H-^{13}C HSQC NMR)

Molar mass distributions (alkaline SEC)

Thermal properties - Tg (DSC)



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Chemical characteristics of industrial lignins

Hydrolysis residue

SE lignins

- **High molar mass and low phenolic content** due to non-dissolving and less degrading pretreatment
  - *Enhanced cleavage of aryl ether linkages and condensation reactions in more drastic steam explosion conditions*
- **Carbohydrate, protein and ash residues** after SSF affecting solubility and reactivity (high aliph-OH)

Spent liquor lignins

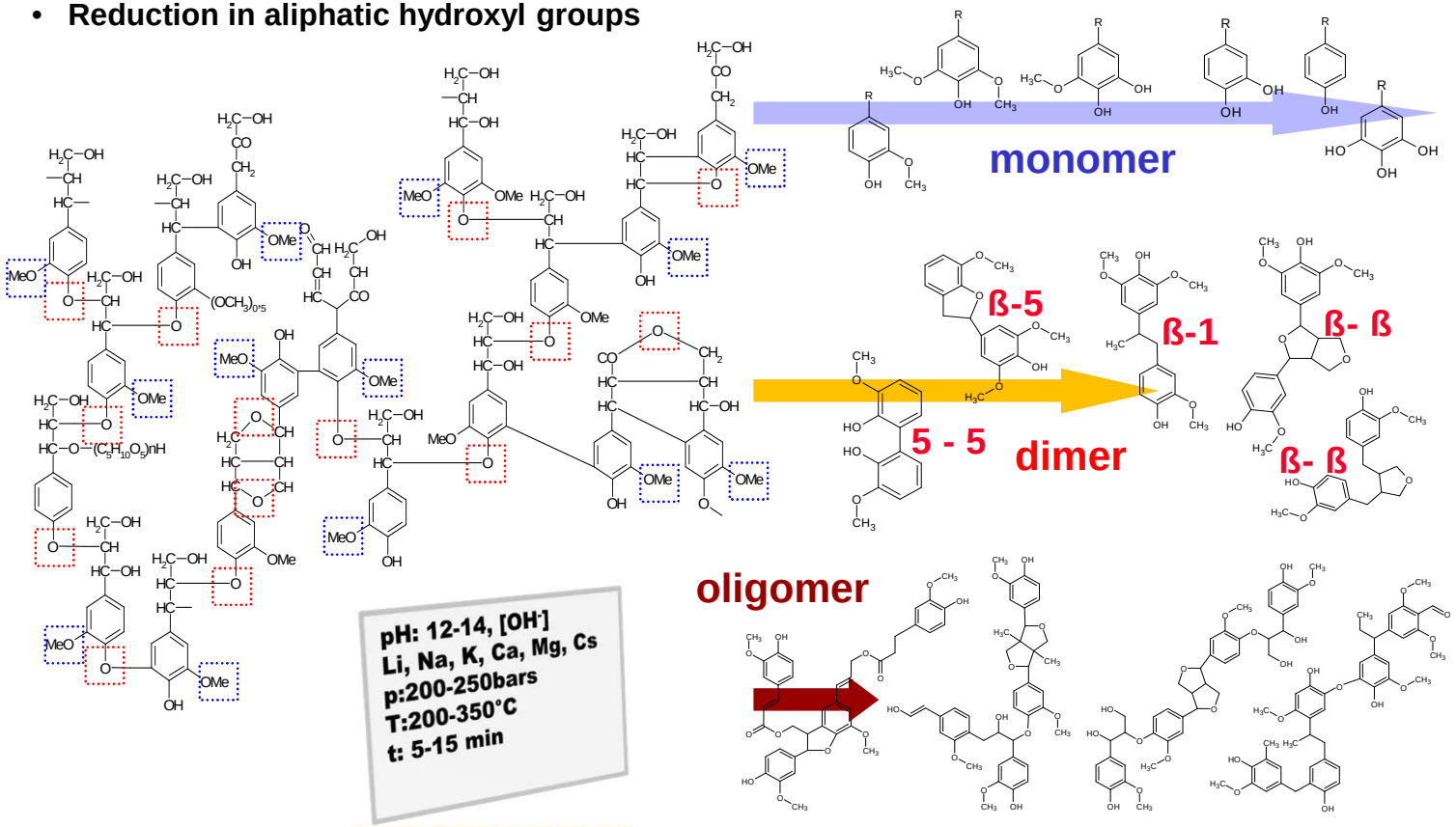
Kraft (SW, HW)
Soda (WS)
SAQ (bagasse)
LGF-OS (HW)

- **High phenol content and lower molar mass** from delignifying processes
  - *Highest phenol content in kraft lignins for resins and chemical modifications in general*
  - *Most C5 or C3 unsubstituted phenols in SW, bagasse and wheat straw lignins for PF resins*
- **Highest COOH content** in soda WS for dispersants
- **Lowest Tg** in LGF-organosolv for thermoplastic composites or coatings

Base catalysed degradation (BCD)

Non-acidified HW kraft	*Oligomeric BCD tar*	*More reactive fragments*
Hydrolysis lignin	*Monomer rich BCD oil*	*for resin applications*

- New phenolic units
- Demethylation / demethoxylation
- Reduction in aliphatic hydroxyl groups

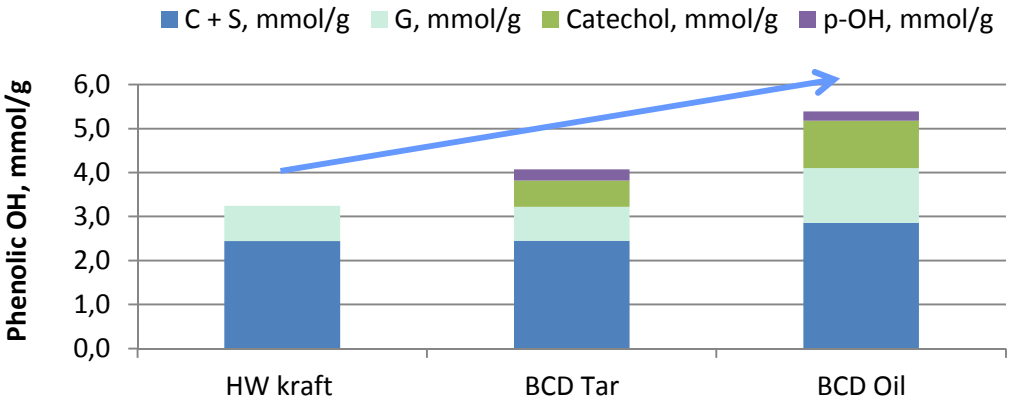


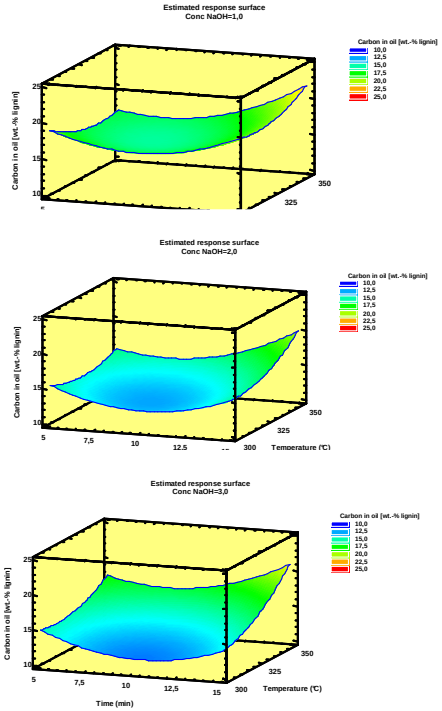
Characteristics of BCD fractions

Optimised reaction conditions for production of BCD oil and tar fractions for maximal yield were identified and structural features characterised

- Native lignin inter-unit linkages efficiently cleaved and new phenolic functionalities formed for resin applications
- Demethylation and demethoxylation further enhancing reactivity towards PF resins
- Reduced content of aliphatic OH-groups for PU resins

Next step: Adjustment of conditions to meet the desired properties





BCD-oil-Yield via Carbon balance (z-axis: 10 - 25%) vs. process parameters (y-axis):
T: 300-350 °C ,
τ: 5-15 min,
[NaOH]: **1%**, **2%, 3%**

Thermoset resin products

- Both lignins and smaller molecular BCD fragments were used
- Reactivity and performance were further adjusted by chemical modification

Target products:

- ✓ **PF resins** for wood products (particle boards, plywood)
  …and as alternative self-binding particle boards without resins
- ✓ **PU foams and casting resins** for insulation and automotive industry
- ✓ **Resin based coatings** for food/beverage cans

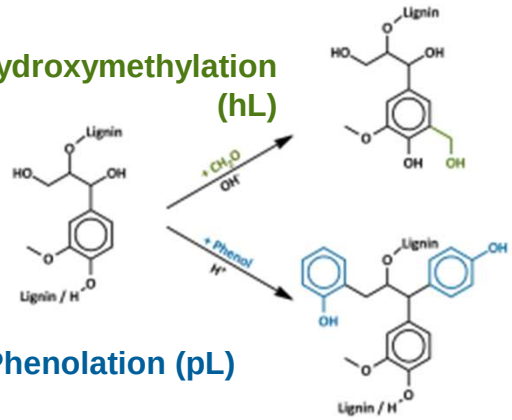
www.call2010.woodwisdom.net | www.eranetbioenergy.net

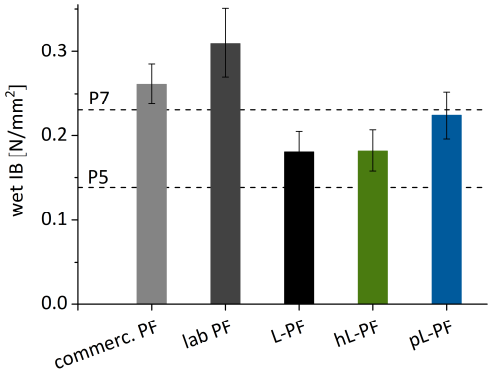
LPF resins for particle boards and plywood

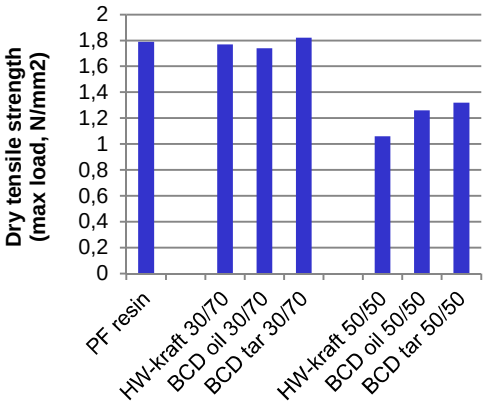
- With unmodified lignins 20-30 wt% phenol substitution possible in particle boards for dry and humid environment
  - ✓ Wood bonding efficiency best for lignins with low methoxyl content
- Lignin activation by phenolation improved performance for heavy load-bearing applications in humid environment
  - ✓ Aliph-OH and purity important for the degree of phenolation
- Performance of BCD fractions at high 50% replacement level better than with original HW-kraft – although yet lower compared to commercial PF resin

Hydroxymethylation (hL)

Phenolation (pL)



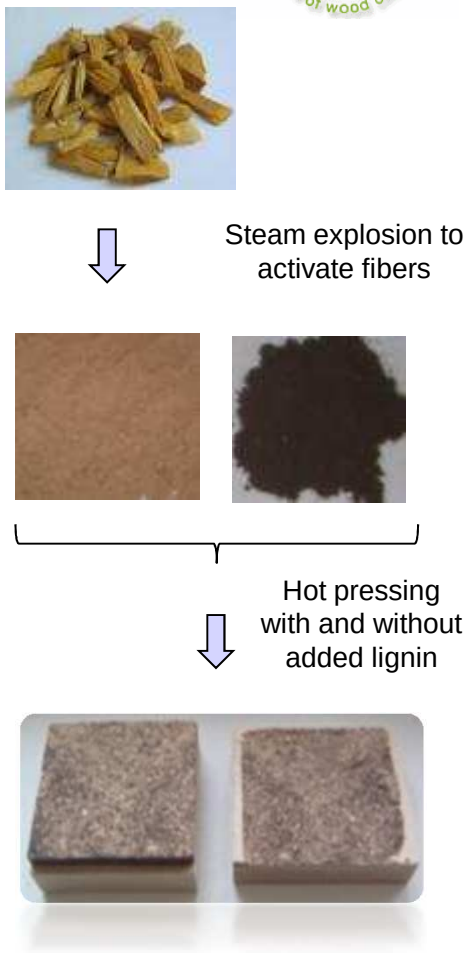




Self binding particle boards

Steam explosion (SE) is a potential pretreatment method to produce self-binding particle boards without any synthetic resins

- Improved bonding ability of steam exploded fibers/particles due to formation of new phenolic groups in fiber lignin and enhanced tendency to condensate during hot pressing
- Bonding ability can be further improved by addition of lignin
- Properties of produced boards in many cases comparable with the conventional commercial boards for dry-use in interior grades

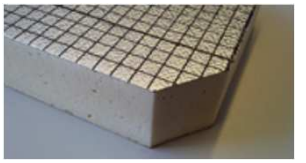


Self binding particle boards

Polyurethane resins for foams and casting resins

Lignin can be used in industrial PU resin formulations up to 40 % depending on target product

- Rigid PU foams with similar properties can be produced with lignin concentrations up to 40 %
- In soft foams 20% lignin increased hardness and improved compression recovery
- In casting resins 10 % lignin increased hardness, and improved elasticity and tensile strength
- Only high purity lignin (no ash/carbohydrate residues) provides good surface quality of foams
- Additional modification needed for BCD tar to increase aliph-OH



Future challenges:

- Low storage stability and viscosity increase limiting the amount of lignin
- Strong odour limiting the applications - not for automotive, or mattresses

Resin based coatings for food/beverage contact

Lignin is a potential major component for resin based coatings (with food/beverage contact)

AkzoNobel
Tomorrow's Answers Today

Requirements:

- Solubility in common organic solvents and/or water for application on metal surface
- Good cure providing solvent resistance, hardness, and blush resistance – also flexibility
- Low/no flavor and extracted components into foods and beverages

Achievements:

- Kraft, soda, and organosolv lignins are soluble in glycol ethers and water
- Good reactivity as such with phenolic, melamine formaldehyde, and epoxy resin formulations for curing
- Coatings have good hardness, solvent resistance, adhesion, and blush resistance, but poor flexibility
- Flexibility can be improved by partial esterification of lignin

(patent filed)

Future challenges:

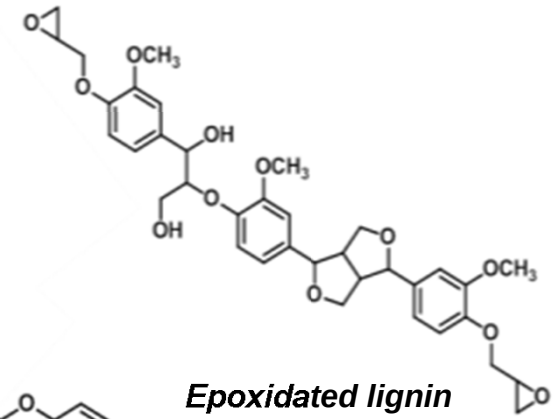
- Meeting extraction requirements for FDA approval, and effects of low molecular weight components

Lignin based epoxy resins

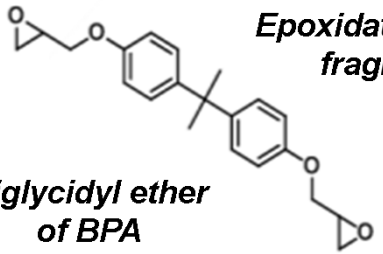
Epoxy resins provide versatile application potential in metal coatings, electrical insulators, fibre-reinforced plastics, structural adhesives

Novel epoxidation methods to epoxidize lignin and BCD fractions without epichlorohydrine have been developed

- ✓ Less toxic chemicals, no hydrolysable chlorine
- ✓ Easier to control
- ✓ Means to replace diglycidyl ether of Bisphenol-A
- ✓ Can be utilised also in composites to improve compatibility



Epoxidated lignin fragment

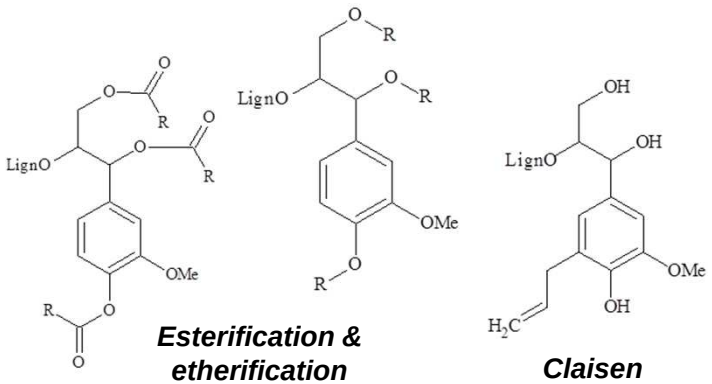


Diglycidyl ether of BPA

Thermoplastic lignin for composites

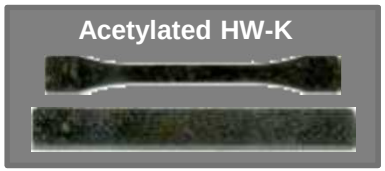
For composite applications lignin thermoplasticity and compatibility was adjusted by means of chemical modification

- Effect of substituent chain length (C2-C16), bulkiness (benzyl) and DS level on thermal properties revealed
- Novel chemical modification routes developed to improve compatibility through epoxy, hydrosilyl, or allyl groups
- Applicability as a major polymeric component as such and in PE blends evaluated



Esterification & etherification

Claisen rearrangement



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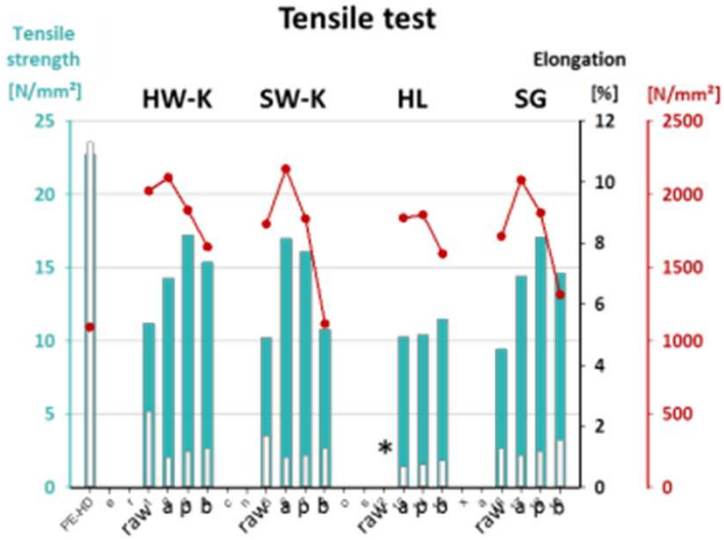
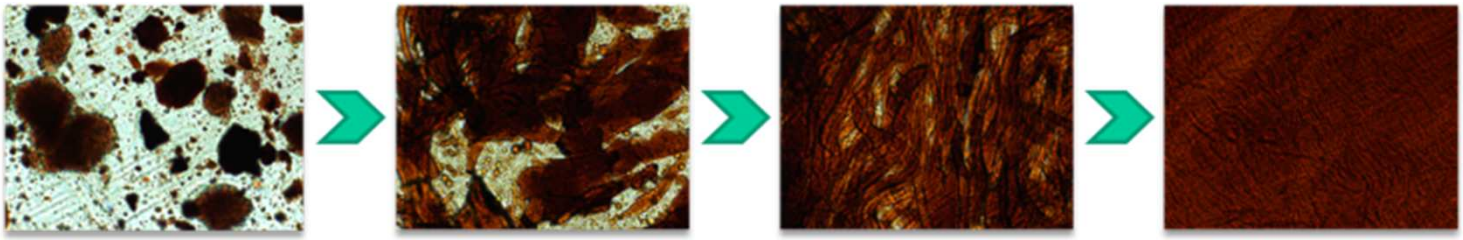
Lignin-Polyethylene Blends as Matrix Material for Fibre-Reinforced composites

- Esterification improves miscibility of lignin and polyethylene
- Increasing the substituent length (C2 → C4)
  - ✓ enhances the compatibility of lignin and PE-HD
  - ✓ enables injection moulding at decreasing temperatures
  - × increases the affinity to the metal surface of the casting moulds
- Chemical modification more important than lignin origin for mechanical properties (impurities affect)
- Highest strengths observed for propionated blends





raw lignin
168 °C

acetylated lignin
168 °C

propionated lignin
162 °C

butyrated lignin
160 °C

Lignin based dispersants

Cost efficient lignin modification method has been developed to adjust lignin water solubility and molar mass for dispersants to replace lignosulphonates and synthetic polycarboxylates

- Better concrete plasticizing performance compared to commercial lignosulphonates, and comparable with some commercial polycarboxylates

(patent filed)

Conclusions

Lignin upgrading routes have been developed to produce lignin based

- ✓ **PF resins** with improved reactivity through phenolation and base catalysed degradation
- ✓ **Self-binding particle boards** by wood steam explosion pretreatment and lignin additives in hot pressing for dry interior grades
- ✓ **PU foams and casting resins** providing good mechanical properties at low replacement levels
- ✓ **Resin coatings for metal packages** with good adhesion and strength properties
- ✓ **Composite materials** utilising thermoplastic lignin with good compatibility
- ✓ **Concrete plasticizers** with better performance than commercial lignosulphonates, and comparable to some commercial synthetic polycarboxylates

…although further research is still needed to further improve the performance !

Benefits of transnational collaboration

- Competencies of partners complemented each other, covering the whole value chain from the biomass fractionation, modification and characterisation, to the development of lignin based new product formulations.
- Special asset was the strong commitment and involvement of the industrial partners.

Thank you !