Fractionation of Kraft lignin for production of alkyd resin coatings

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Renewable Resources & Biorefineries Conference, Brussels, Belgium

June 6, 2024

This project has received funding from the Bio-based Industries Joint Undertaking (JU) under the European Union's Horizon 2020 research and innovation programme under grant agreement No 101023342. The JU receives support from the European Union's Horizon 2020 research and innovation programme and the Bio-based Industries Consortium.

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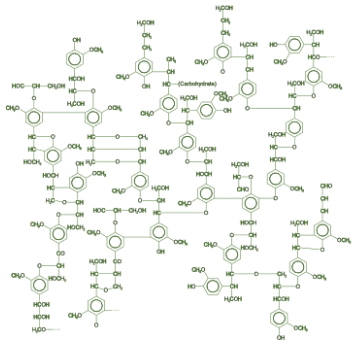
Lignin valorization for production of different bio-based coatings

LIGNIN



- Kraft Lignin
- Organosolv Lignin

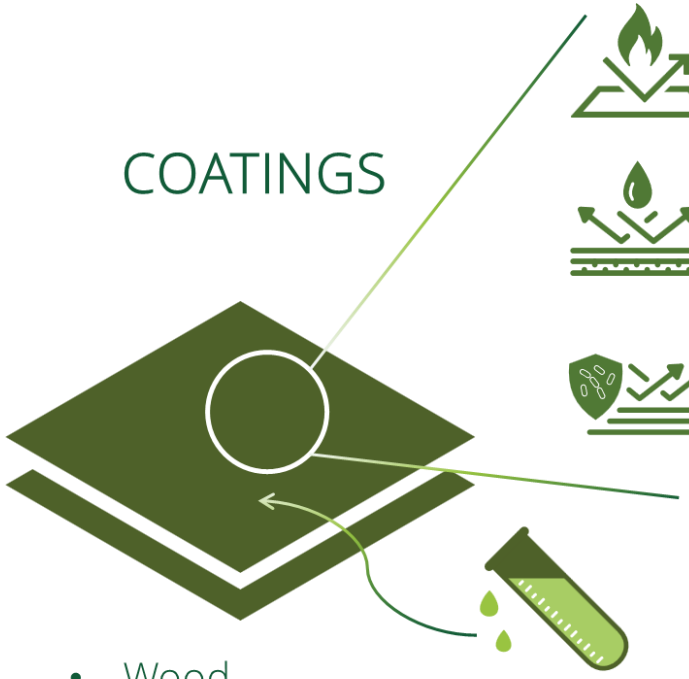
INTERMEDIATES

- Lignin Polyols
- Lignin Polyacids
- Epoxidized Lignin

RESINS

- Polyurethane
- Alkyd
- Epoxy

COATINGS



- Wood
- Metal

Fire protection

Anti-corrosion

Anti-microbial, anti-viral & VOCs degradation

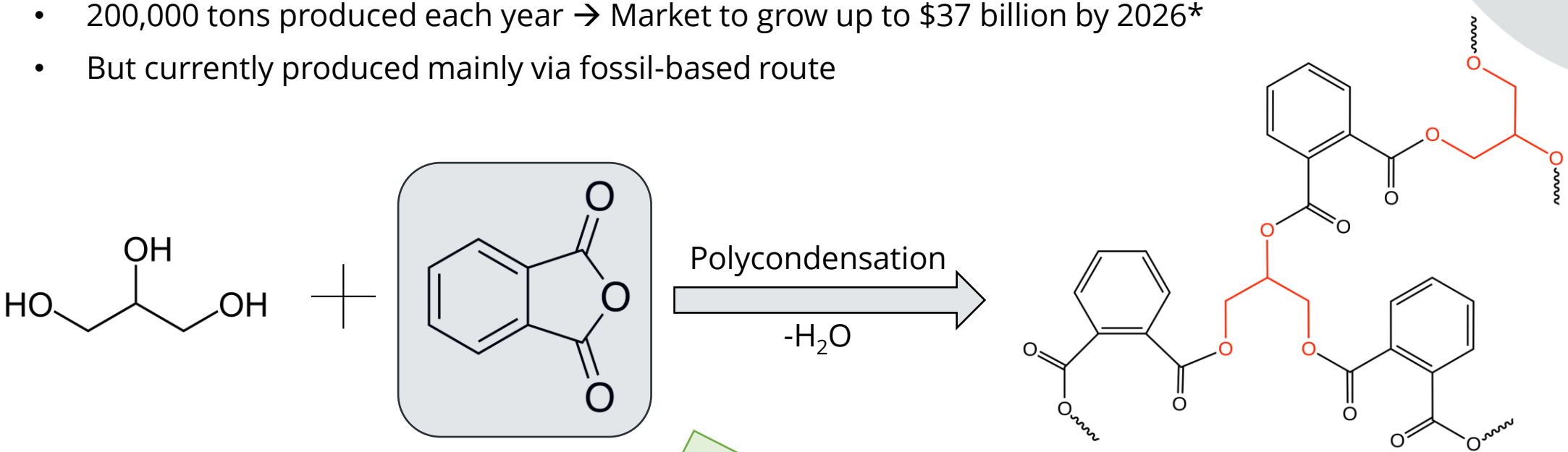
- Active compounds extracted from hop
- Enzyme encapsulation

This case study focuses on lignin-based alkyd resin coatings for metal surface

Bio-based alkyd resins from kraft lignin

Alkyd resins market:

- Dominate paint and coatings industry due to their superior performance
- 200,000 tons produced each year → Market to grow up to $37 billion by 2026*
- But currently produced mainly via fossil-based route



Glycerol
Vegetable oil sourced

Phthalic anhydride
Petroleum-sourced
Expensive (1800 € per ton)

Alkyd resin
Petroleum-based

Kraft lignin as a substitute of phthalic anhydride to increase the bio content alkyd resin?

Challenges of kraft lignin valorization for alkyd resin production

Problems with utilizing kraft lignin as a feedstock in resin formulations:

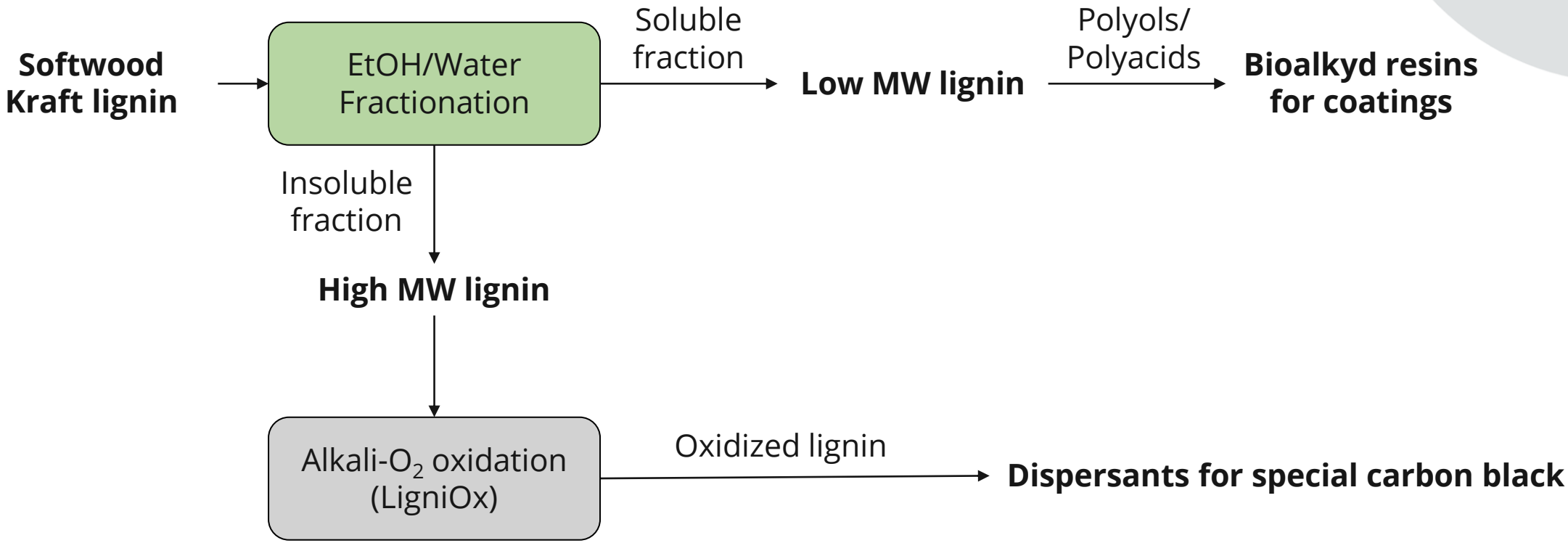
- Chemical characteristics of kraft lignin – poor solubility/reactivity
  - Heterogeneous polymeric structure (wide Mw distribution, high polydispersity)
  - Diverse functionalities (PhOH, aliphatic OH, COOH groups etc.)

Solvent fractionation as a promising scalable process to valorize kraft lignin for resin production:

- Produces uniform, lower Mw lignin fractions rich in PhOH groups
- **State-of-the-art**:
  - *Structure-property relationships of lignin fractions developed with some coating applications at lab scale*
  - *No applications for production of alkyd coatings from kraft lignin – lab or pilot scale*
- **Roadblocks**:
  - *Use of biorenewable, cheap, green, safe, easy-to-recover solvents like EtOH still not developed beyond lab scale*
  - *Gap in knowledge – can kraft lignin fractions be used in alkyd resin formulation?*
  - *Full valorization of kraft lignin is often ignored – uneconomical for scaleup*

Solvent fractionation using EtOH for production of alkyd biocoatings

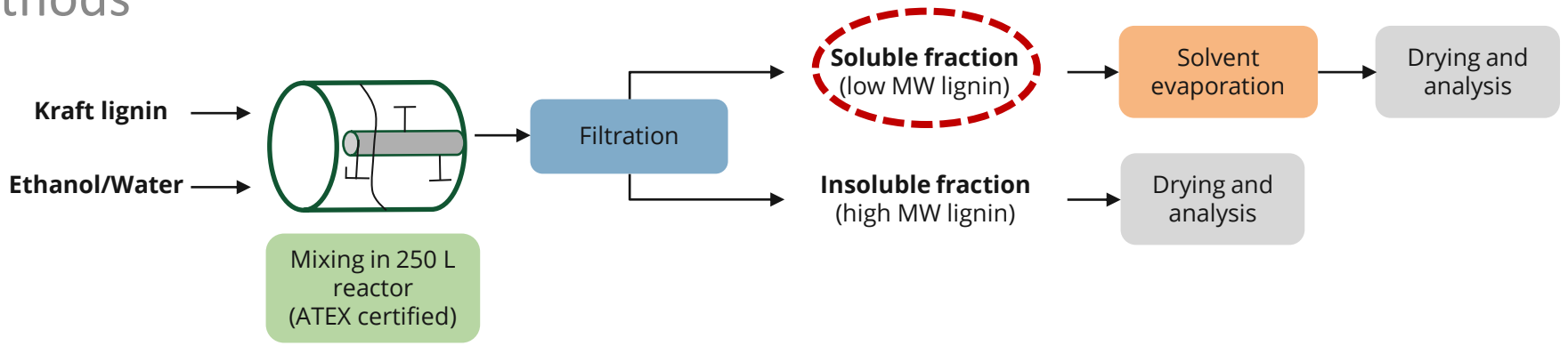
Process concept

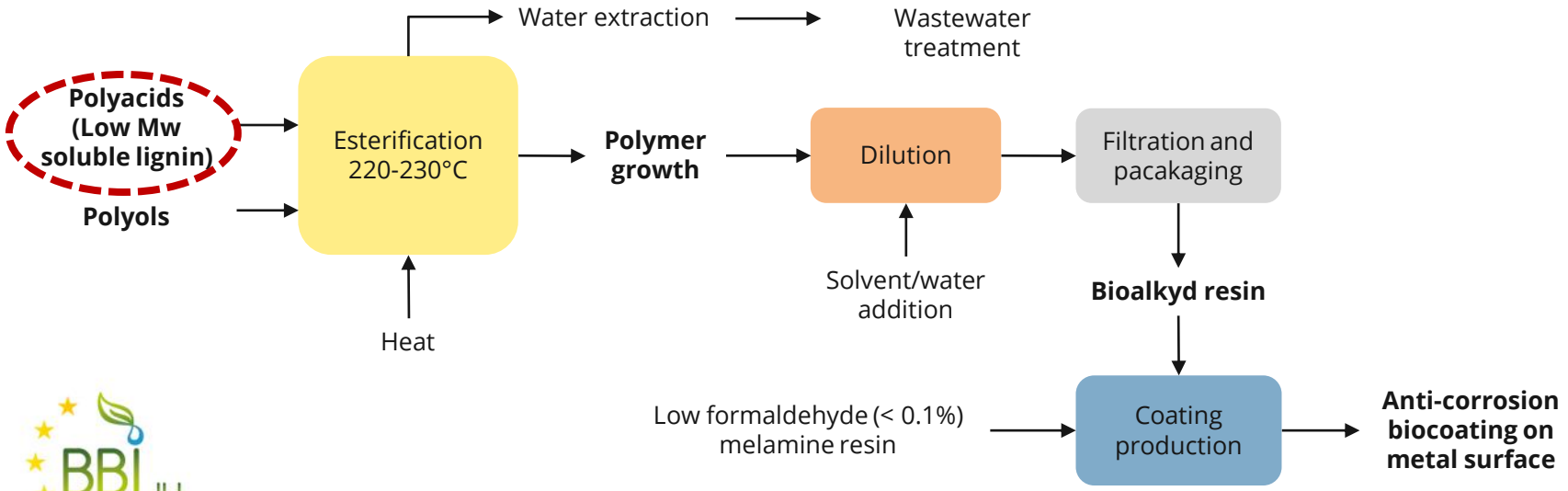


Poster: P37
Title: Production of Dispersants for Special Carbon Black by Oxidization of Fractionated Kraft Lignin
Presenting Author: Anna Kalliola, VTT

Pilot scale solvent fractionation and alkyd resin development for biocoating

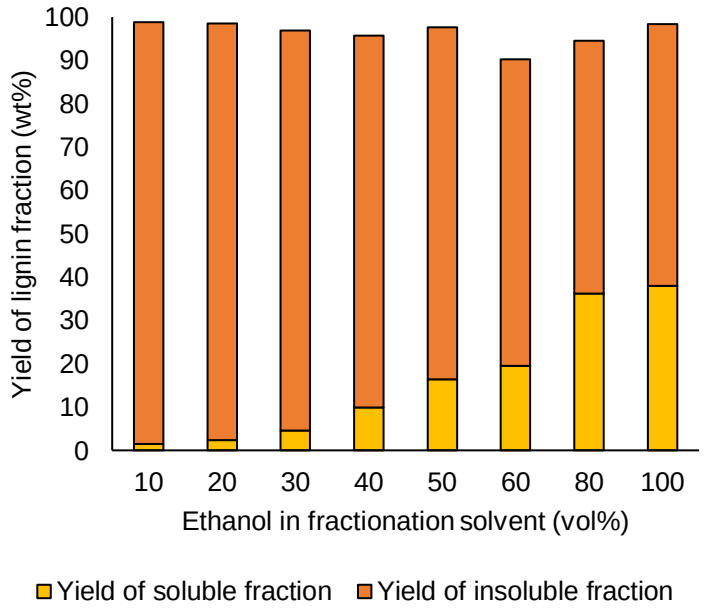
Methods



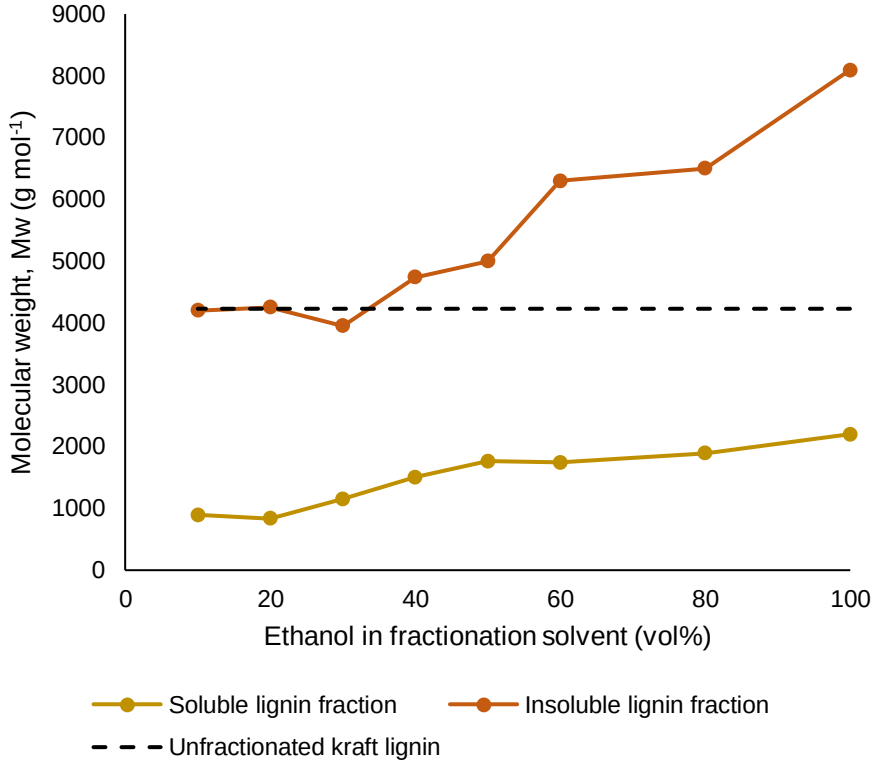


Yields and Mw of lignin from lab scale EtOH/water fractionation

Increasing yield of soluble lignin but also steadily increasing Mw with greater vol% of EtOH in solvent



Yields of soluble and insoluble fractions of kraft lignin produced in lab scale

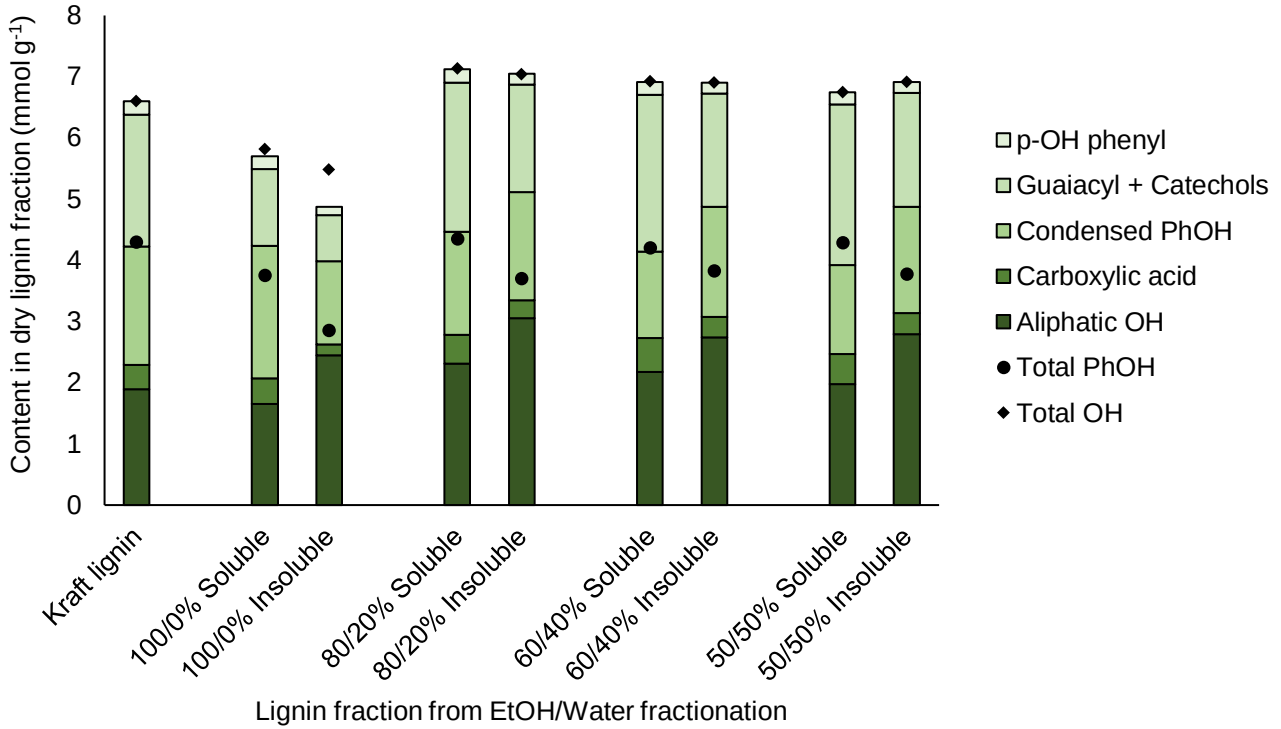


Average molecular weights of soluble and insoluble fractions of kraft lignin produced in lab scale

Chemical functionalities in lignin from lab scale EtOH/water fractionation

Features of soluble vs insoluble lignin fractions:

- Higher content of Total PhOH and COOH groups in soluble lignin fractions
- Lower content of aliphatic OH groups in soluble lignin fractions



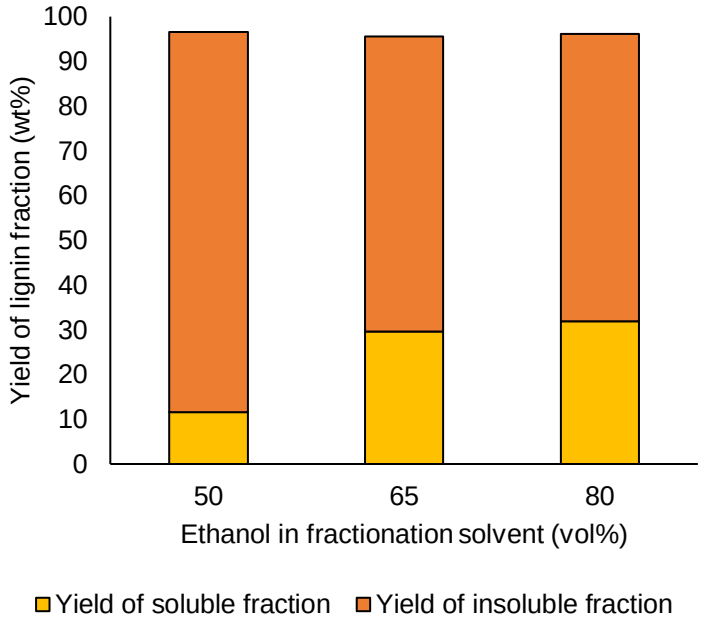
Amounts of different hydroxyl group species (mmol g^{-1}) in dry lignin fractionated by different EtOH/Water vol% in laboratory scale

Changes of features of soluble and insoluble lignin with EtOH vol%:

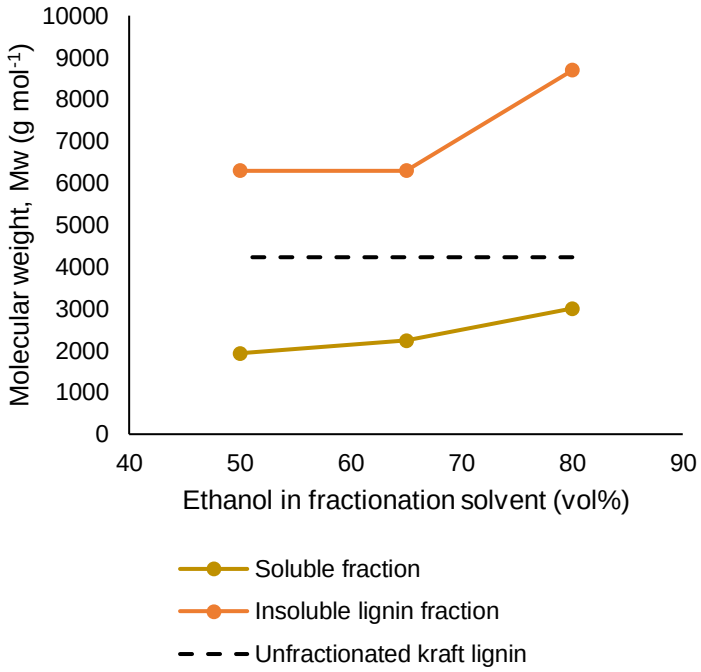
- 100 vol% ethanol produces lignin fractions with low Total PhOH and COOH groups
- No major differences in distribution of chemical groups for 50 – 80 vol% EtOH conditions

Yields and Mw of lignin from pilot scale EtOH/water fractionation

32 wt% yield of soluble lignin with Mw of 3000 g mol^{-1} using 65 – 80 vol% EtOH



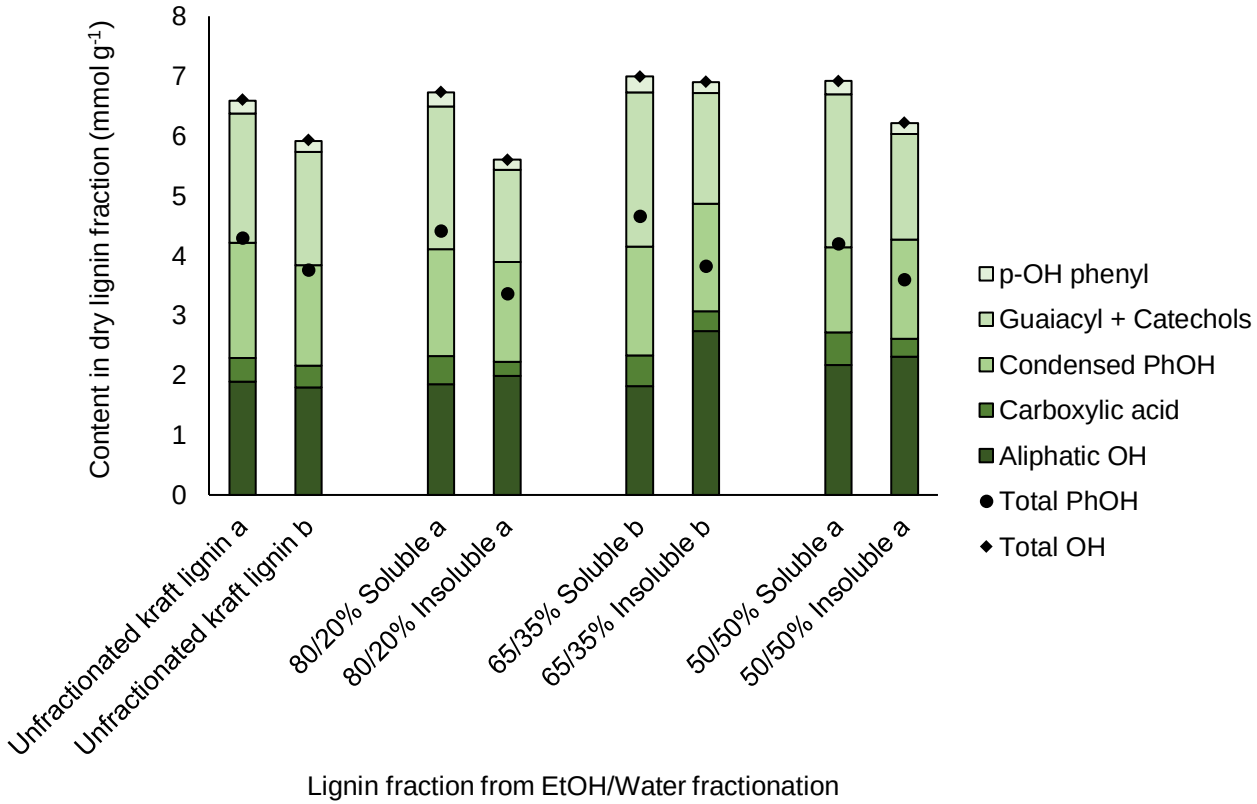
Yields of soluble and insoluble fractions of kraft lignin produced in pilot scale



Average molecular weights of soluble and insoluble fractions of kraft lignin produced in pilot scale

Chemical functionalities in lignin from pilot scale EtOH/water fractionation

- Soluble fractions richer in Total PhOH and COOH groups
- Insoluble fractions rich in aliphatic OH



Amounts of different hydroxyl group species (mmol g^{-1}) in dry lignin fractionated by different EtOH/Water vol% in pilot scale

Properties of lignin-based alkyd resin

Resin properties	Standard alkyd resin	Lignin-based alkyd resin
Molecular weight and polydispersity of resin		
Mw (g mol^{-1})	4650	4110
Mn (g mol^{-1})	1660	1430
PD	2.8	2.9
Dry time test characteristics		
Set-to-touch time (min)	20	22
Dust-free time (min)	25	31
Tack-free time (min)	126	143
Dry through time (hours)	72	87
Gloss test characteristics (ASTM 3928)		
Gloss 60° (gloss)	89	90
Persoz hardness test characteristics (ASTM 4366-16)		
Persoz hardness after 1 week of drying (sec)	63	55

Performance of lignin-based alkyd resin as a function of resin ratio

Resin ratio (bioalkyd to melamine)	Persoz Hardness (sec)/ Gloss (GU)					
	140°C		150°C		160°C	
	30 min	60 min	30 min	60 min	30 min	60 min
8.8	99	143	136	158	137	160
7.5	87	136	132	169	157	180
6.9	106/ 82	151/ 76	140/ 77	**180/ 72**	166/ 73	**188/ 67**

Performance of lignin-based alkyd biocoating

Characteristics	Commercial standard coating	Lignin-based biocoating
Viscosity (Cup-Ford 4 at 20°C, sec)	55 ± 5	> 150
pH	8.2-8.5	8.2
Solids (wt%)	50 ± 5	47
Volatile organic compounds (% VOC)	5	1.66
Biocontent (%)	5	10.8
Gloss (%)	> 60	72
Physical Tests	OK	OK
Thickness (µm)	30-40	30-40
Persoz hardness (sec)	180	180
Salt Spray Test	120 h (OK)	120 h (OK)

Lignin-based alkyd biocoating on metal surface

Carbon steel panel with biocoating produced using lignin-based alkyd resin

After application of biocoating by spray gun

After physical tests of adhesion, impact, blending and cupping

After salt spray test

<u>Coating preparation</u>

Bioalkyd to melamine resin ratio of 6.9 and curing at 150°C, 60 min

Conclusions

- Fractionation by aqueous ethanol can be an economical and sustainable process to convert softwood kraft lignin into a **uniform, soluble fraction, with low Mw and high content of PhOH and COOH groups**
- Soluble lignin serves as a **polyacids substitute of petroleum-derived phthalic anhydride in alkyd resin** formulation for coatings
- Biocoatings applied on metal surfaces using lignin-based alkyd resin **performs well against commercial standard**
- **Full valorization of kraft lignin possible** by producing sustainable coatings (soluble lignin) and dispersants for special carbon black (insoluble lignin) via solvent fractionation

Publication in preparation

Fractionation of Kraft Lignin for Production of Alkyd Resin Formulation for Bio-based Coatings

Arpa Ghosh, Olesya Fearon, Melissa Agustin, Susanna Alonso, Estefania Camara, Saulo Franco, Anna Kalliola, *To be submitted to ACS Sustainable Chemistry & Engineering, 2024*

Thank you!

Questions?

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