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

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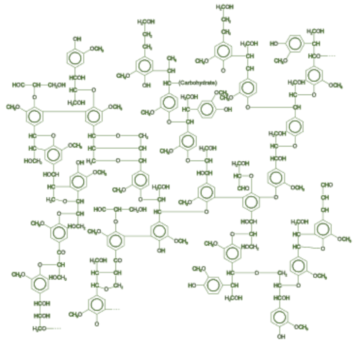
Lignin valorization for production of different bio-based coatings

LIGNIN



- Kraft Lignin
- Organosolv Lignin

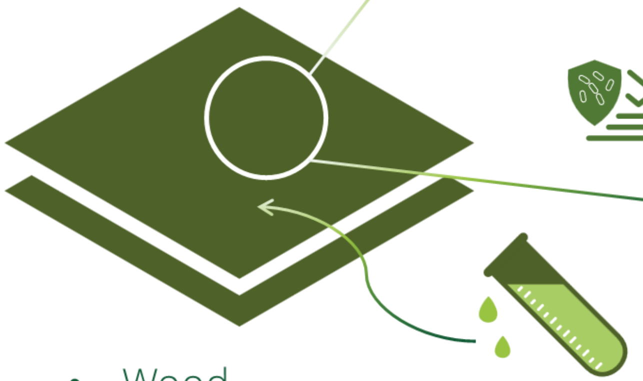
INTERMEDIATES

- 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

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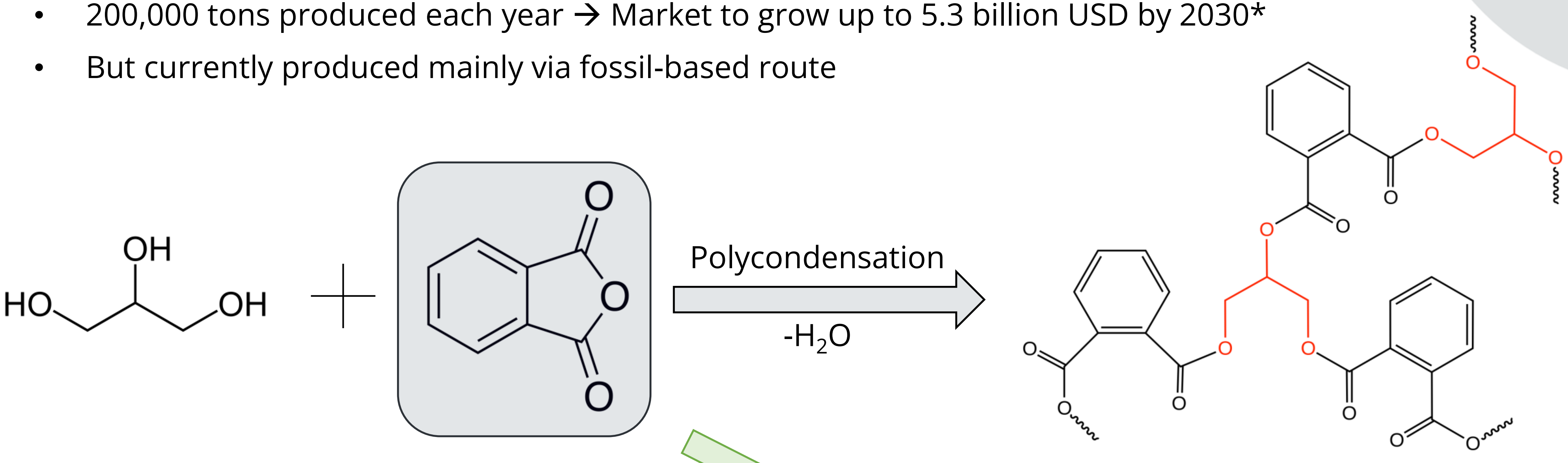
Bio-based alkyd resins from kraft lignin

Alkyd resins market:

- Dominate paint and coatings industry due to their superior performance
- 200,000 tons produced each year → Market to grow up to 5.3 billion USD by 2030*
- 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?

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Challenges of kraft lignin valorization for alkyd resin production

Kraft lignin as a drop-in raw material in resin formulations:

- Poor solubility/reactivity of kraft lignin:
  - Heterogeneous structure (wide Mw distribution, high dispersity)
  - Diverse functionalities (phenolic OH, aliphatic OH, COOH groups, branching etc.)

Solvent fractionation to improve the homogeneity of kraft lignin:

- Produces more uniform, lower MW lignin fractions rich in phenolic OH and COOH groups
- Structure-property relationships and coating applications of lignin fractions reported mostly at lab scale
- No applications in alkyd resin and coatings
- *Can low MW kraft lignin fractions be upgraded to alkyd resins for commercial application?*
  - *Solvent fractionation of kraft lignin by an efficient, economical, and sustainable pathway at large scale*
  - *High-performance alkyd resin and coating production using low MW kraft lignin fractions*
  - *Odor release and related hazards of using low MW kraft lignin in alkyd resin synthesis*
  - *Solubility of low MW kraft lignin in aqueous solution for alkyd resin formulation*

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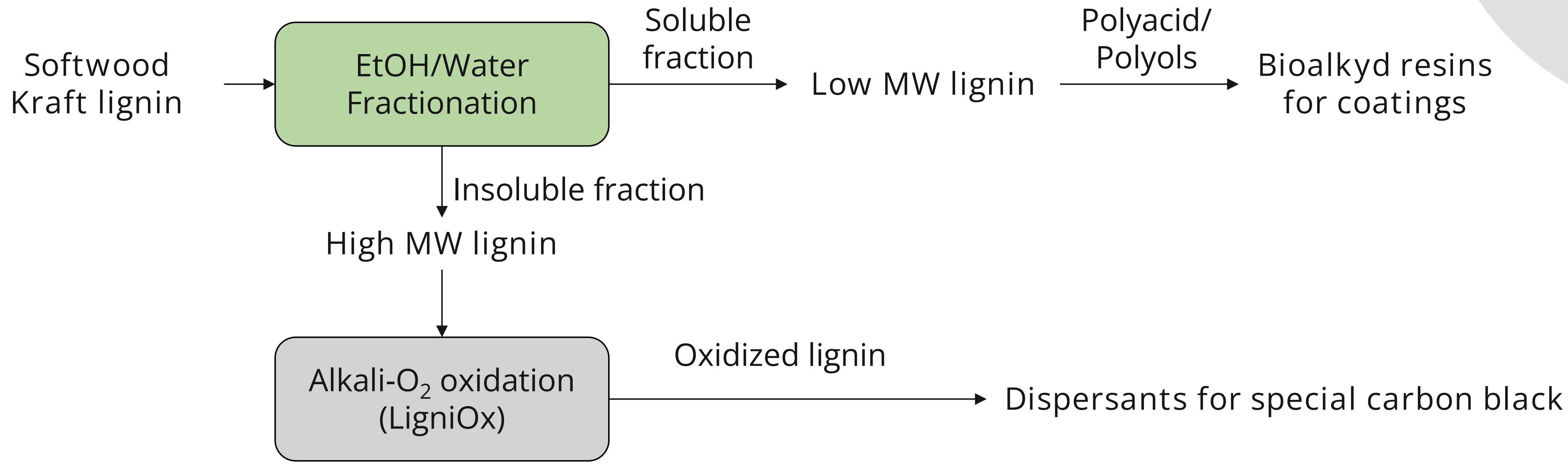
Solvent fractionation using EtOH for production of alkyd biocoatings



EtOH as a preferred solvent for technology scaleup
bio-based, low-cost, lower environmental impact, easy to recover from water (up to 85%)

Fractionation of Kraft Lignin for Production of Alkyd Resin for Bio-based Coatings with Oxidized Lignin Dispersants as a Co-Product
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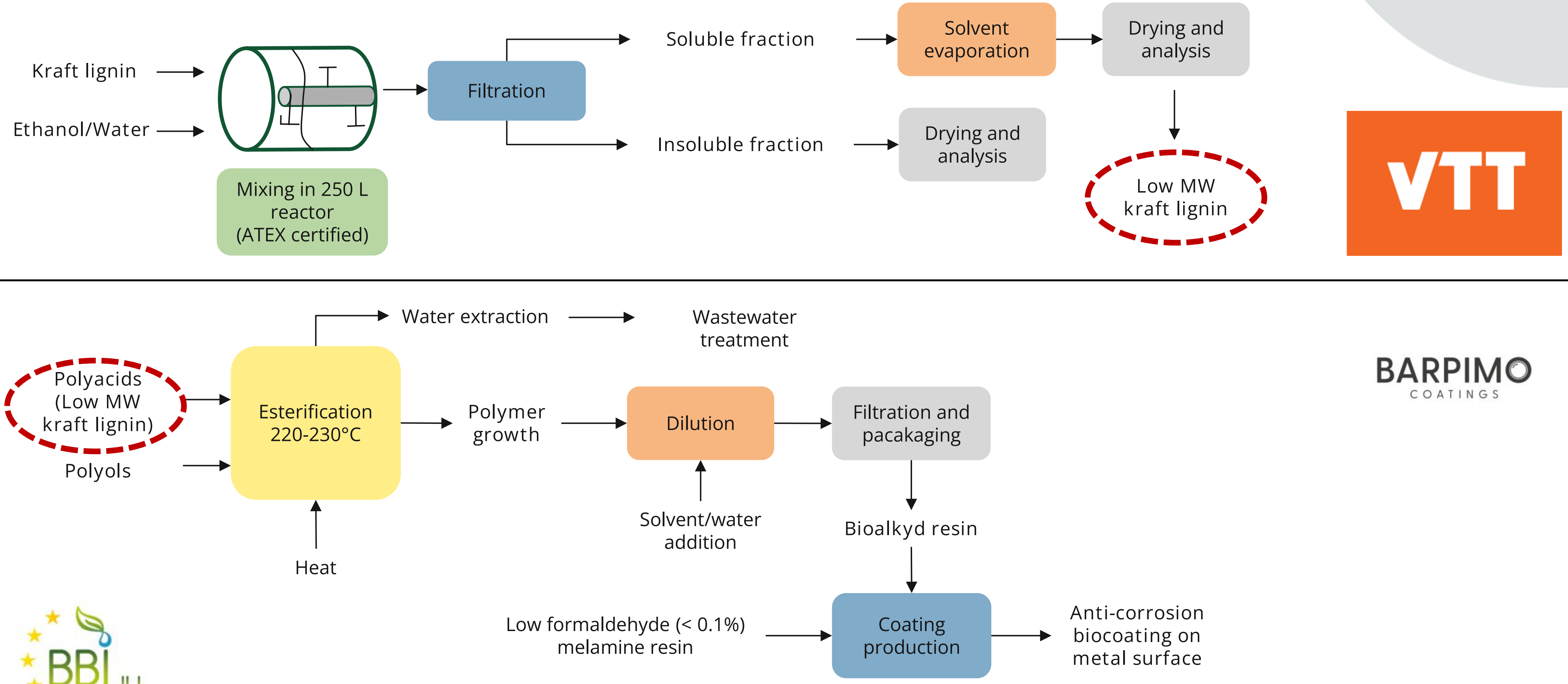
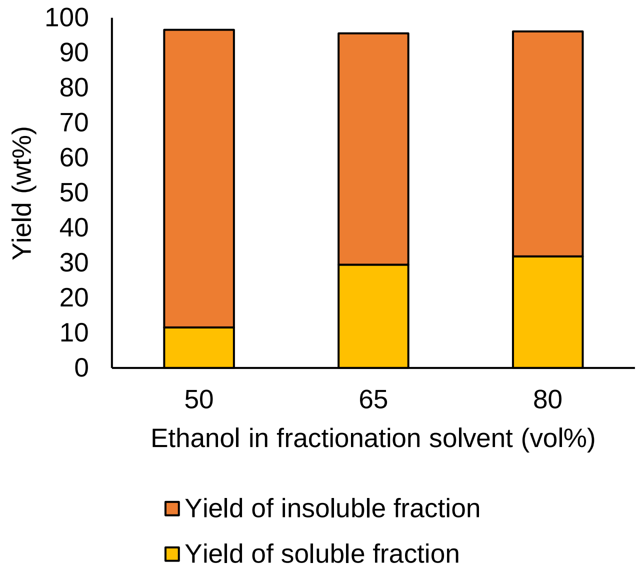
Pilot scale solvent fractionation and alkyd resin development for biocoating

Methods

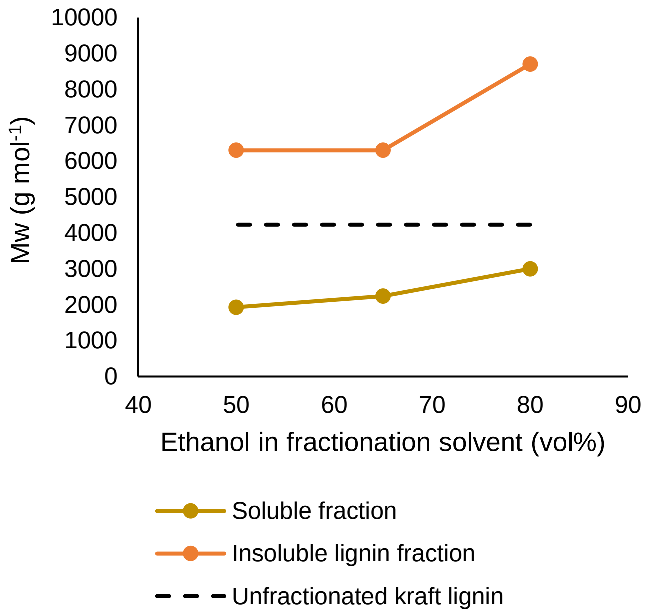


Yields and Mw of lignin from pilot scale EtOH/water fractionation

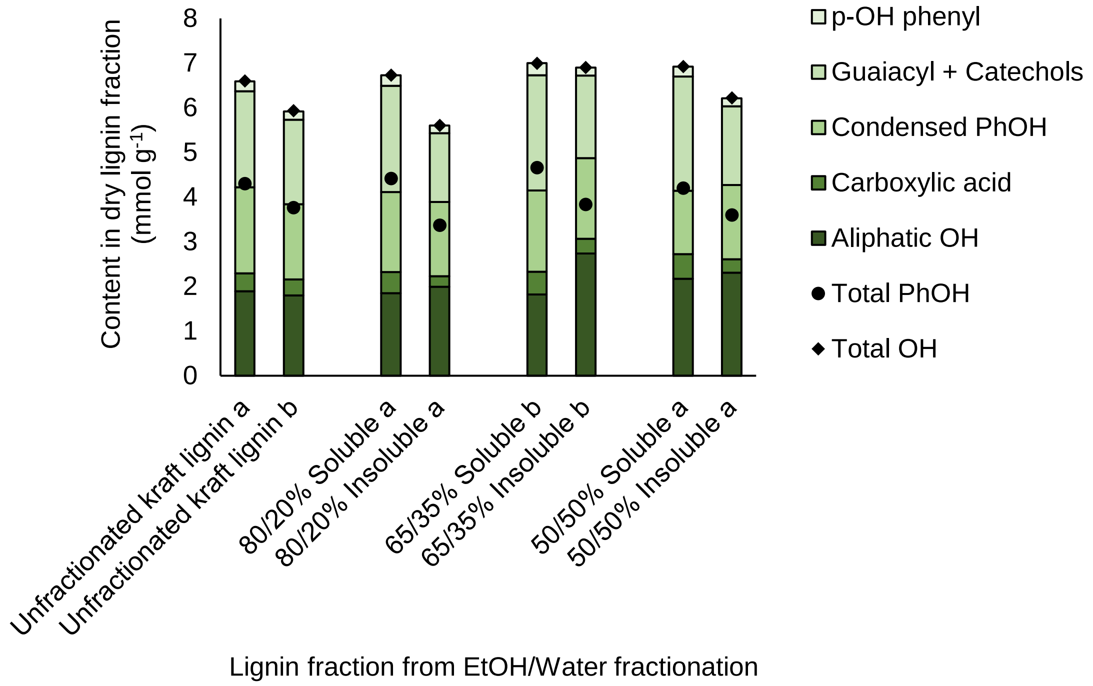
Soluble lignin with Mw ≤ 3000 g mol^{-1} and enriched in Phenolic OH and COOH groups produced using 50 – 80 vol% EtOH



Yields of soluble and insoluble fractions of kraft lignin



Average molecular weights of soluble and insoluble fractions of kraft lignin



Amounts of different hydroxyl groups ($mmol\ g^{-1}$) in dry lignin fractions

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Properties of lignin-based alkyd resin & coating

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

Alkyd resin and coating prepared with low MW kraft lignin fractions performed well against commercial standards

Characteristics	Commercial standard alkyd coating	Lignin-based alkyd coating
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)

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Lignin-based anti-corrosion alkyd coating 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

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Thermal degradation analysis of low MW kraft lignin by TD/GC-MS

Methodology:

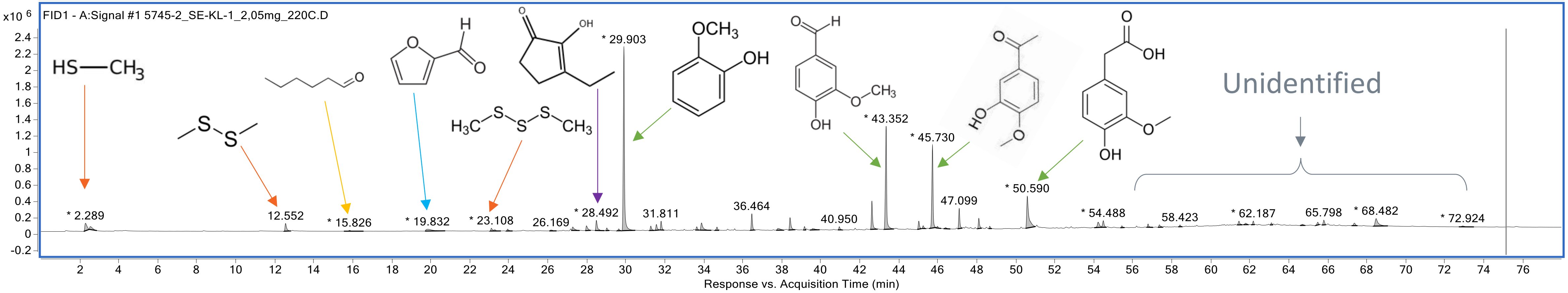
Thermal desorption (TD) in a Pyrolyzer unit connected to a GC-MS/FID system was used to identify the VOCs (by MS spectra) and their relative % (by FID peak area) from lignin materials

- **Temperature range**: 180°C (Low) and 220°C (High) – *to simulate alkyd resin synthesis conditions*
- **Kraft lignin materials:** Unfractionated and Low MW kraft lignin fractions
- **Low MW kraft lignin fractions:** *Lignin substrates used in alkyd resin*
    - 50 vol% EtOH soluble lignin
    - 65 vol% EtOH soluble lignin
    - 80 vol% EtOH soluble lignin

TD/GC-MS analysis of unfractionated kraft lignin

VOCs released from TD of kraft lignin are characterized by GC-MS/NIST library

- Sulfur compounds (methanethiol, dimethyl disulfide, dimethyl trisulfide)
- Linear (oxalic acid, hexanal etc.)
- Carbohydrate-derived (furfural etc.)
- Cyclic (2-cyclopenten-1-one, 3-ethyl-2-hydroxy-; 1,3-cyclopentanedione, 2-ethyl-2-methyl-)
- Lignin-derived (guaiacol, vanillin, homovanillic acid, ethanone, 1-(3-hydroxy-4-methoxyphenyl)-)
- Unidentified



The sulfur compounds and major lignin-derived VOCs (guaiacol) detected in TD/GC-MS of lignin have strong odor at ppb level!

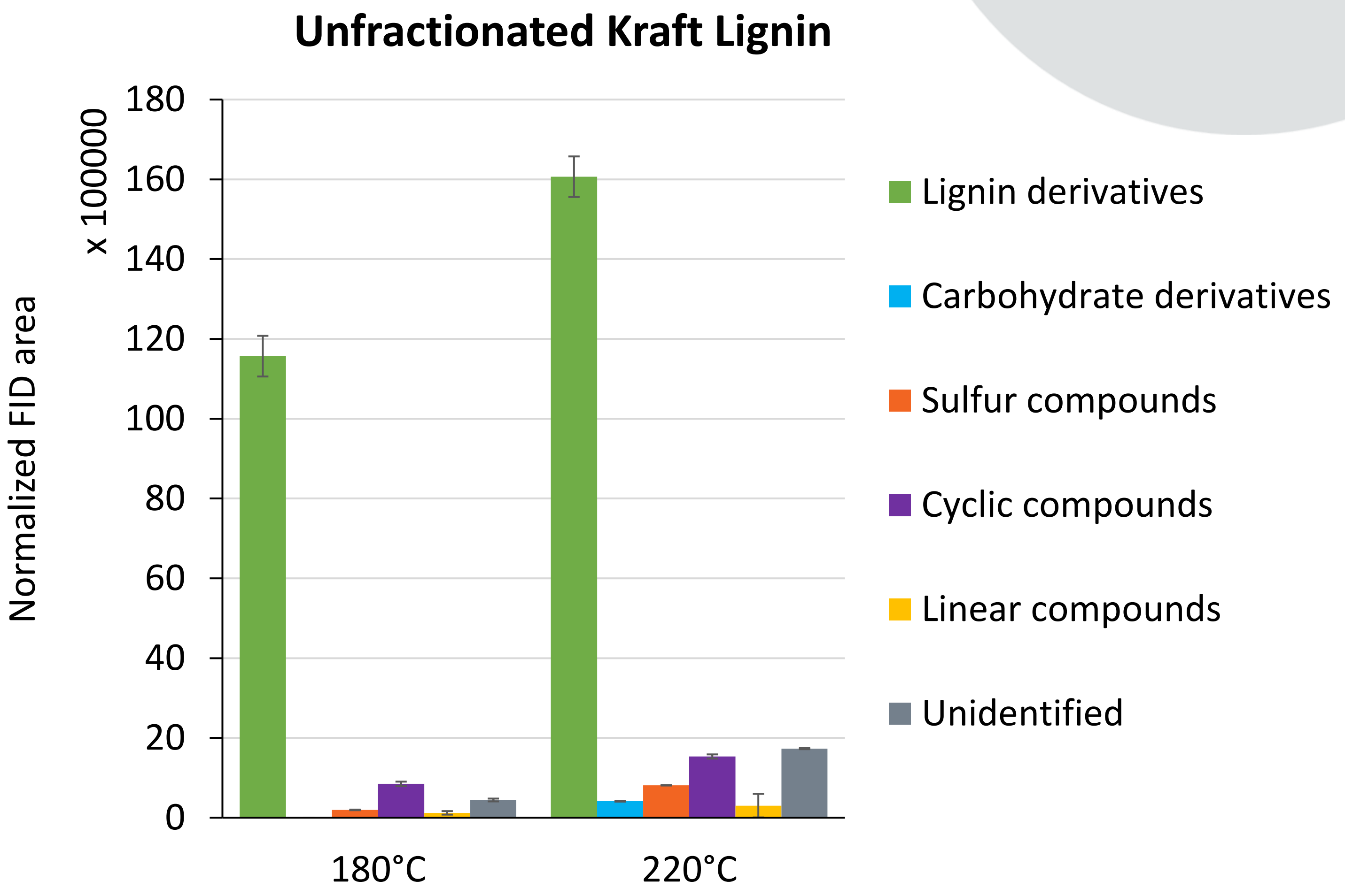
TD/GC-MS analysis of unfractionated kraft lignin

Product distribution:

- Mostly lignin-derived VOCs
- Sulfur compounds prominent
- Other products:
  - Carbohydrate-derived (e.g. furfural), Cyclic, Linear products

Effect of temperature:

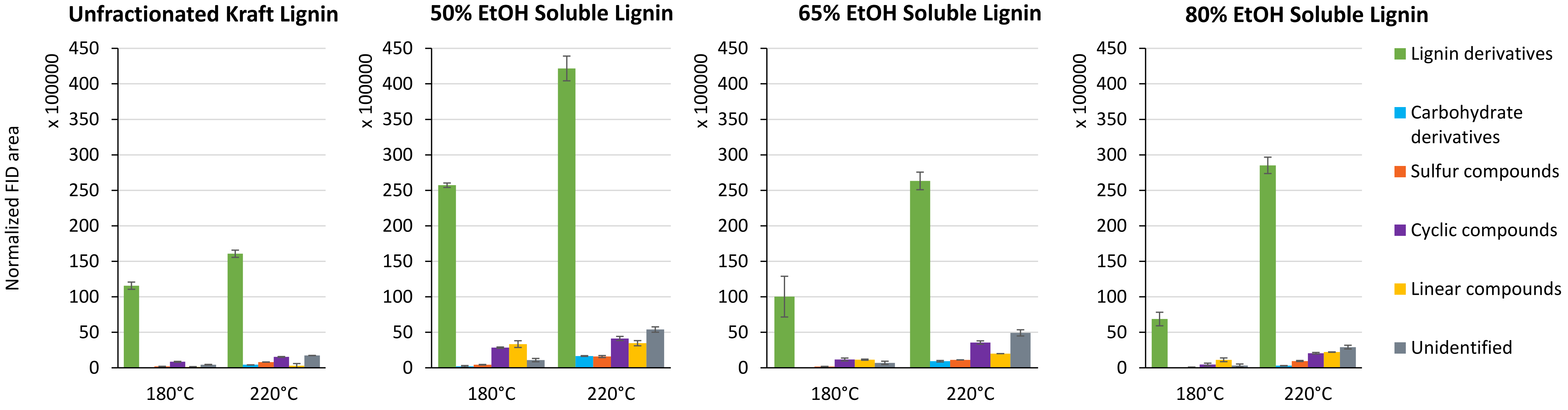
- All VOCs released more at 220°C
- Increase in lignin-derived VOCs and Sulfur-compounds is 1.39 and 4.16 times with temperature increase



TD/GC-MS of different low MW kraft lignin fractions

Total VOCs from low MW vs unfractionated kraft lignin:
- Lower for 65 – 80% EtOH soluble lignin at 180°C
- Higher for 50% EtOH soluble lignin at 180°C
- Higher for all EtOH soluble lignin at 220°C

Total VOCs from low MW kraft lignin as a function of EtOH/water ratio:
- Lower for higher EtOH% soluble lignin at 180-220°C
- Similar trend for lignin derivatives and S-compounds



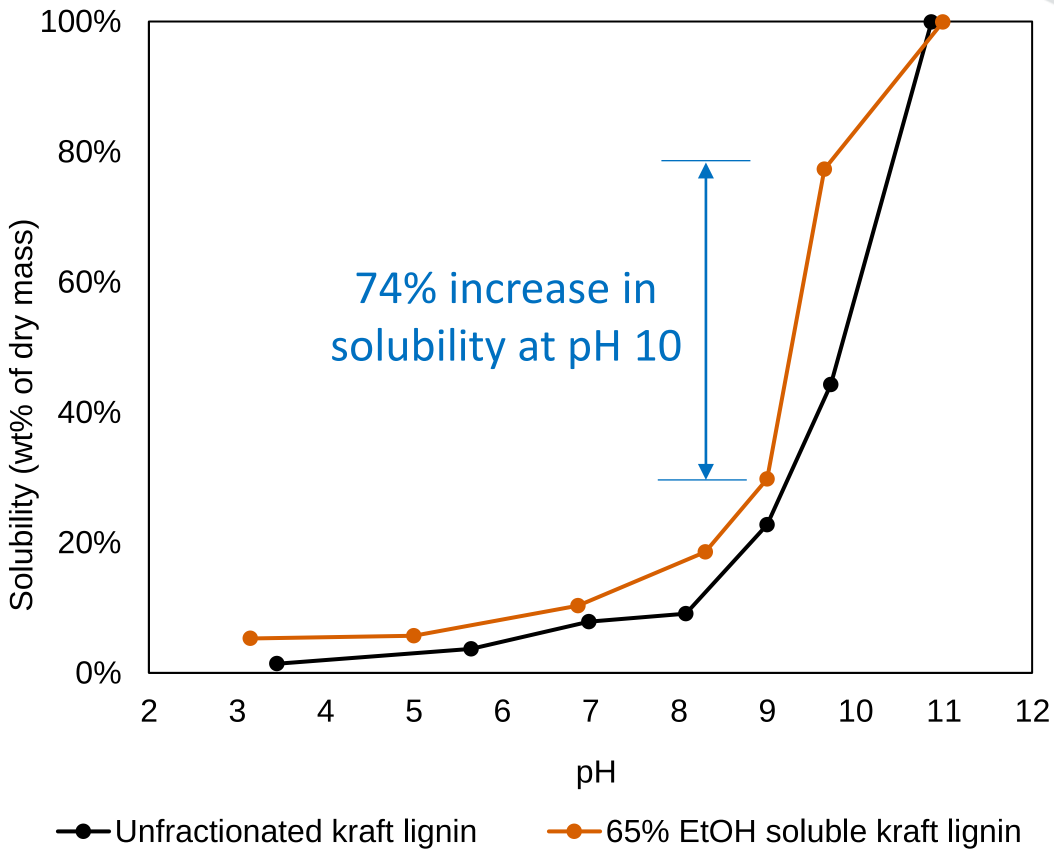
Release of VOCs including Lignin derivatives and Sulfur compounds can be reduced by using A/ B/ both
(A) Higher EtOH% in fractionation of kraft lignin (B) Lower temperature in alkyd resin synthesis

Solubility analysis of low MW kraft lignin at different pH of water

Low MW weight kraft lignin in solubility test → Soluble lignin generated by 65 vol% EtOH fractionation

Solubility of low MW weight kraft lignin:

- Increases sharply from 10 wt% to 77 wt% as pH changes from 7 to 10
- Increased by 74% at pH 10 compared to unfractionated kraft lignin
- Generally higher at all pH levels tested compared to unfractionated kraft lignin
- Easier to mix low MW kraft lignin in aqueous or mildly alkaline solution



Conclusions

- Fractionation by aqueous ethanol can be an efficient, economical, and sustainable process to convert softwood kraft lignin into a more homogenous, soluble fraction, with low Mw and high content of phenolic OH and COOH groups

- Low MW kraft lignin can serve as a polyacids substitute for fossil-derived phthalic anhydride (partially) in alkyd resin production to prepare bio-based, high-performance anti-corrosion coatings

- Odor and related hazards of VOC release can be linked to sulfur compounds and some lignin-derivatives generated during the thermal degradation of low MW kraft lignin in alkyd resin synthesis

- Release of VOCs can be lowered by using higher EtOH% in fractionation of kraft lignin and/or lower temperature in alkyd resin synthesis

- Low MW kraft lignin has satisfactorily high solubility in water of pH 8 – 10 making it a more desirable material for alkyd resin production than unfractionated kraft lignin

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Acknowledgment

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Thank you!

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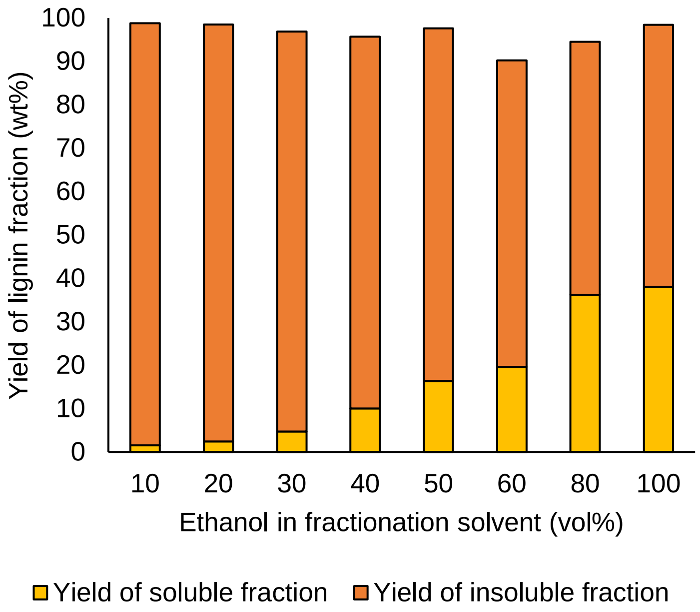
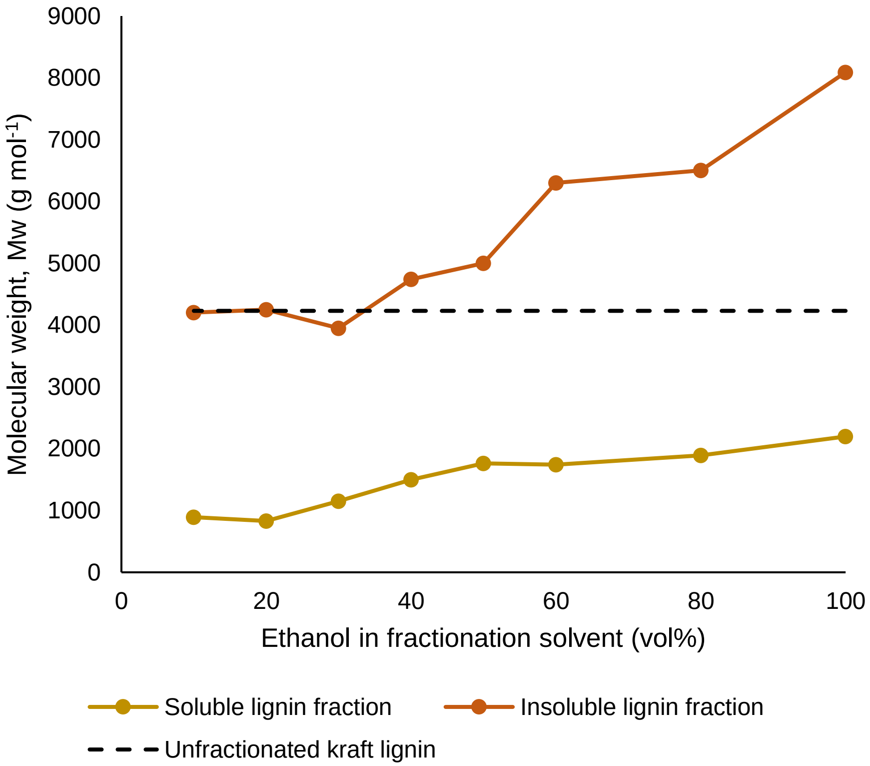
Supplementary Materials

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

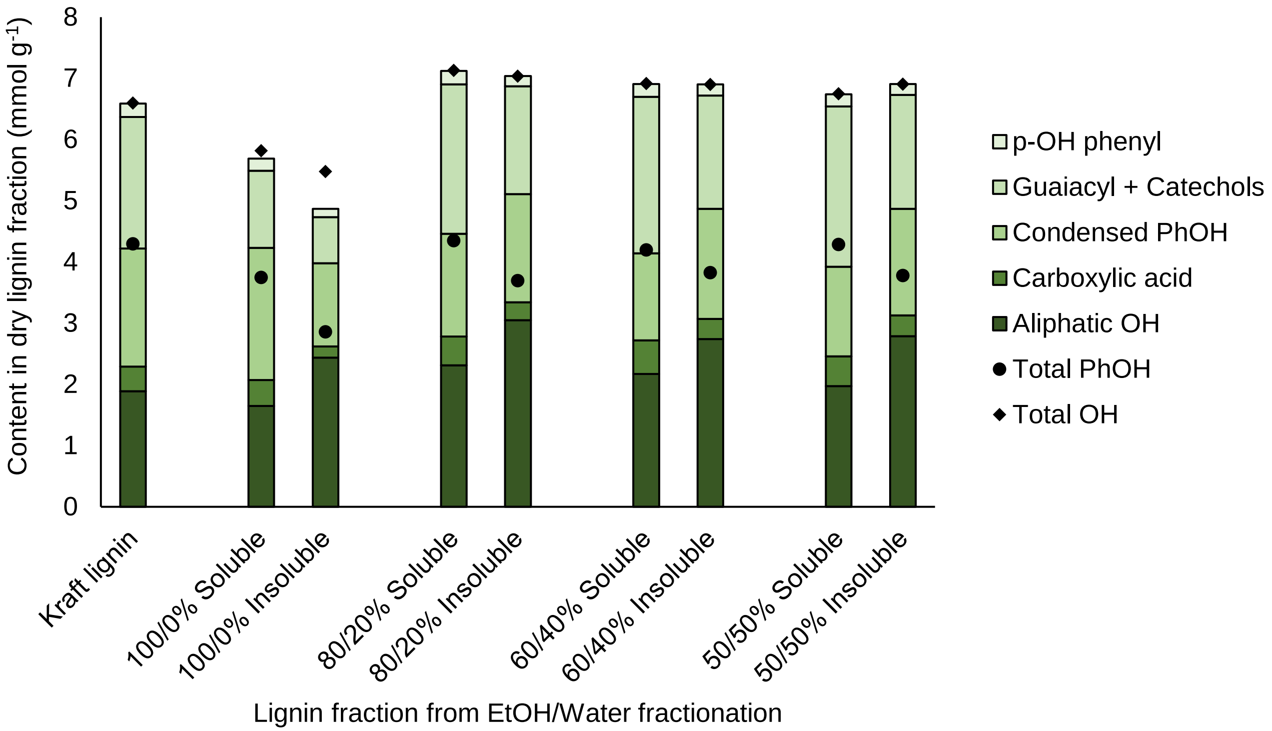


Average molecular weights of soluble and insoluble fractions of kraft lignin produced in lab scale

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

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

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Odor in alkyd resin synthesis

- Odor can be linked to sulfur compounds and some lignin-derived VOCs released during the thermal degradation of soluble lignin in coating process
- Origin of sulfur compounds in EtOH soluble lignin can be linked to kraft pulping
- Release of <u>ppb level of sulfur compounds</u> from thermal degradation of EtOH soluble lignin can contribute to <u>very bad odor, health hazards and flammability</u>!

- Recommendations for path forward:
  - *Develop alkyd coating process at lower temperatures?*
  - *Pre-process kraft lignin before/after fractionation to neutralize/oxidize sulfur compounds?*
  - *Organosolv lignin as a feedstock?*

<u>Methanethiol</u>

Odor threshold
1 ppb

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