



VTT Technical Research Centre of Finland

## Fractionation of Kraft Lignin for Production of Alkyd Resin for Bio-Based Coatings: Characterization of Low Molecular Weight Kraft Lignin Products of Aqueous Ethanol Fractionation for Application in Alkyd Resins

Ghosh, Arpa; Ohra-aho, Taina; Kalliola, Anna

*Published in:*  
AIChE Annual Meeting 2024 Proceedings

Accepted/In press: 11/11/2024

*Document Version*  
Peer reviewed version

[Link to publication](#)

*Please cite the original version:*

Ghosh, A., Ohra-aho, T., & Kalliola, A. (in press). Fractionation of Kraft Lignin for Production of Alkyd Resin for Bio-Based Coatings: Characterization of Low Molecular Weight Kraft Lignin Products of Aqueous Ethanol Fractionation for Application in Alkyd Resins. In *AIChE Annual Meeting 2024 Proceedings* Article 687066 American Institute of Chemical Engineers (AIChE).

VTT  
<https://www.vttresearch.com>

VTT Technical Research Centre of Finland Ltd  
P.O. box 1000  
FI-02044 VTT  
Finland

By using VTT Research Information Portal you are bound by the following Terms & Conditions.

I have read and I understand the following statement:

This document is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of this document is not permitted, except duplication for research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered for sale.

**Full Paper Title:**

**Characterization of Low Molecular Weight Kraft Lignin Products of Aqueous Ethanol Fractionation for Application in Alkyd Resins**

Presentation Title: Fractionation of Kraft Lignin for Production of Alkyd Resin for Bio-Based Coatings

Presentation ID: 687066

Arpa Ghosh<sup>1\*</sup>, Taina Ohra-aho<sup>1</sup>, Anna Kalliola<sup>1</sup>

<sup>1</sup>VTT Technical Research Centre of Finland Ltd., P.O. Box 1000, FI-02044 VTT Espoo, Finland

\*Corresponding author. E-mail address of corresponding author: arpa.ghosh@vtt.fi

**Abstract**

We have recently demonstrated a new pathway of successful utilization of low molecular weight kraft lignin obtained from aqueous ethanol fractionation of kraft lignin in the synthesis of bio-based alkyd resins for anti-corrosion coatings. However, these lignin fractions generated foul odors during the synthesis of alkyd resins, which could not be explained by the reported characteristics of these lignin materials. The current literature does not focus on investigating the odor characteristics of the low molecular weight lignin fractions in realistic conditions of alkyd resin production, even though this information can be highly important in developing an efficient, safe, and sustainable bio-based formulation of alkyd resin. The thermal degradation profile obtained in realistic conditions of alkyd resin synthesis can help determine the release of volatile organic compounds generating odor and/or hazards during the resin synthesis. In addition, the solubility behavior of low molecular weight kraft lignin in an aqueous solution of varying pH is not typically reported in the literature, which also prevents researchers from understanding the applicability of these lignin fractions in water-borne formulations of alkyd resin in mildly alkaline/acidic conditions. In this work, the pH-dependent solubility and thermal degradation profiles of the low molecular weight fractions of softwood kraft lignin (MW < 3000 g/mol), produced by aqueous ethanol fractionation at pilot scale, were explored. The production of volatile organic carbons (VOCs) including odor-releasing sulfur compounds and lignin derivatives was analyzed by thermal desorption combined with a gas chromatography method simulated at the condition of alkyd resin synthesis. Overall, this study presents new insights into the feasibility, limitations, and areas of improvement in utilizing the low molecular weight kraft lignin fractions produced by ethanol/water fractionation, which in turn could help this technology to grow in the sustainable coating industry.

## 1. Introduction

Kraft lignin is an abundant, renewable, bio-based polyphenolic material that can serve as a promising feedstock for producing value-added, sustainable materials such as resins and coatings.<sup>1</sup> Due to its superior performance, low cost, versatility and ease of application, alkyd resin is predominantly used as a binder in the paint and coating industry.<sup>2</sup> These alkyd resins are produced by the reaction of polyacids such as phthalic anhydride, and polyols such as glycerol, which are often derived from fossil-based resources.<sup>2,3</sup> Alternatively, kraft lignin, which is rich in different hydroxyl groups and also contains carboxyl acid functionality, could potentially act as a bio-based, renewable substitute for fossil-based chemicals in the value chain of alkyd resins and thus, aid the decarbonization of the paints and coatings industry.<sup>4</sup>

The diverse structure of kraft lignin, which is featured by high molecular weight, dispersity, and various functional groups imposes a great challenge to its industrial valorization to resins and coatings.<sup>5</sup> To overcome this heterogeneity of lignin, solvent fractionation can be applied to kraft lignin to upgrade it to (more homogeneous lignin fractions or) lignin intermediates, rich in phenolic polyols & polyacids.<sup>6</sup> This process typically uses an organic solvent, as pure or mixed with another solvent or water, to solubilize kraft lignin mostly at room temperature into different fractions.<sup>7,8</sup> The soluble fraction thus generated has significantly lower molecular weights (below 3000 g mol<sup>-1</sup>), more uniform physicochemical properties, and higher concentration of phenolic OH and COOH groups than the parent lignin, as desired for resin formulation.<sup>9,10</sup>

The soluble lignin generated from solvent fractionation can be upgraded to various phenolic resins and coatings including anti-corrosion polyurethane films.<sup>6</sup> Based on the structure-property-performance relationship reported in past studies, the lower the molecular weight of the soluble lignin fraction, the better its effectiveness as a lignin intermediate as reflected in the performance of the resins. Our recent work reports that alkyd resin synthesized with low molecular weight kraft lignin, produced via fractionation using aqueous ethanol, performs well against commercial standards.<sup>11</sup> Additionally, ethanol is a low-cost, bio-based, readily separable solvent with lower environmental impact.<sup>12-14</sup> Thus, aqueous ethanol fractionation of kraft lignin can potentially be developed into an efficient, economical, and sustainable pathway for producing bio-based alkyd resins.

Despite the promise of aqueous ethanol fractionation in valorizing kraft lignin into a highly effective lignin intermediate precursor for alkyd resins, some important aspects of this technology are still unknown, which can impede its growth. The solubility behavior of these low molecular weight kraft lignin fractions at different pH is not reported even though this information can help prepare waterborne alkyd resin formulations effectively. Furthermore, these low molecular weight kraft lignin generated by aqueous ethanol fractionation might undergo thermal degradation during the synthesis of alkyd resin, typically occurring at temperatures greater than 200°C,<sup>3</sup> and release volatile organic compounds (VOCs) causing an unpleasant odor, toxicity, and flammability issues, as reported for unmodified kraft lignin.<sup>15</sup> Despite these major concerns, the VOC release potential from low molecular weight kraft lignin products of ethanol/water fractionation has not been studied yet in the context of alkyd resin production.

This work explores the thermal degradation profile and pH dependence of the solubility of the low molecular weight lignin fractions from our previously developed aqueous ethanol fractionation process.<sup>11</sup> These characteristics were compared against unfractionated kraft lignin as a reference. A thermal desorption method combined with gas chromatography was applied to simulate the release of VOCs from low molecular weight lignin fractions under the same conditions of alkyd resin synthesis as used previously in our work.<sup>11</sup> The overall aim of this study was to gain new insights into the feasibility of integrating the low molecular weight kraft lignin of aqueous ethanol fractionation into alkyd resin formulations from the perspective of commercial product development to help advance the field of lignin-based coating industry.

## 2. Methods

### 2.1 Materials

The unfractionated lignin used in this work was dry industrial softwood kraft lignin kindly provided by Stora-Enso (Lineo™). Our recent publication presents the full compositional analysis of this kraft lignin feedstock.<sup>11</sup> Ethanol (purity min. 94 wt%), sodium hydroxide (NaOH) and 37 wt% hydrochloride acid (HCl), were procured from Anora Group Oyj, Merck and ThermoScientific, respectively. Reverse osmosis water used was supplied on-site.

### 2.2 Experiments

#### 2.2.1 Fractionation of kraft lignin using aqueous ethanol

Fractionation of kraft lignin was performed using aqueous ethanol at a pilot scale using our previously developed method.<sup>11</sup> The schematic of the processing steps followed by thermal desorption analysis of soluble lignin fraction can be seen in Figure 1. Lignin was added (17 kg dry weight) in 160 L of aqueous ethanol (50, 65, 80 vol% ethanol) and then the slurry was mixed at 25°C (or room temperature) for 2 hours in a 250 L reactor. After mixing, the slurry was filtered, and the solid residue on a filter or insoluble lignin fraction with high molecular weight was dried in an oven at 40°C and weighed. The insoluble lignin fraction was further upgraded to dispersants for special carbon black using alkali-O<sub>2</sub> oxidation.<sup>11</sup> The filtrate or soluble lignin fraction with low molecular weight was concentrated by evaporating the solvent using a rotary evaporator and then freeze-dried before weighing. The thermal desorption and solubility analysis performed on the low molecular weight kraft lignin fractions are described in detail in Section 2.3.1 and 2.3.2, respectively.

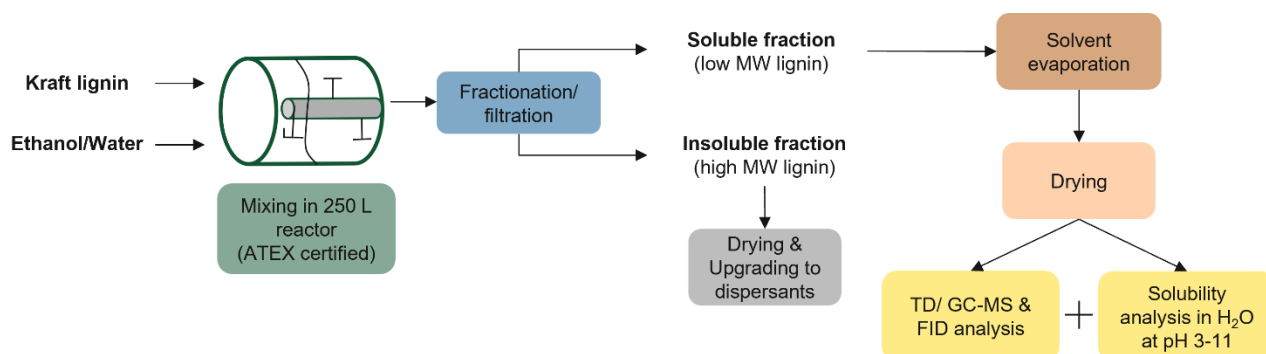


Figure 1. Schematic of ethanol/water fractionation of kraft lignin and subsequent thermal desorption and solubility analysis of the soluble lignin fraction (reproduced with modifications from Ref. 11).

### 2.3 Characterization

#### 2.3.1 Thermal desorption analysis of low molecular weight kraft lignin fractions

Thermal desorption was conducted on unfractionated kraft lignin and low molecular weight kraft lignin fractions in pyrolyzer (Pyrolab2000®, Sweden) connected to gas chromatography (Agilent GC 7890B) with a mass spectrometry (MS 5977A). Each sample was taken in a glass boat in the amount of 3 mg and thereafter transferred to the pyrolysis chamber. Each sample in pyrolyzer was heated at 180°C and 220°C and volatiles released by heating were led with constant helium flow (1 ml min<sup>-1</sup>) into the GC equipped with a mid-polar capillary column (J&W DB-1701: 30 m × 0.25 mm, film 1 μm) for separation. The oven was programmed as follows: initial temperature 40°C and held for 3 min, rate of increase 4 °C min<sup>-1</sup> to 280°C and held for 16 min at final temperature. The simultaneous FID and MS detection was achieved by allowing degradation products to be split in ratio of 2:1 via three-way splitter kit (Agilent G3440B). Two inert fused silica columns, one linked to FID (0.48 m, 0.18 mm i.d.) and other to MS (1.25 m, 0.15 mm i.d.), using outlet pressure of 3.8 psi was used. H<sub>2</sub> flow: 45 ml min<sup>-1</sup>; air flow: 450 ml min<sup>-1</sup>; make up (He) 50 ml min<sup>-1</sup> were used in the FID, which was operated at 300°C. Mass spectra were obtained using electron ionization (70 eV)

and having a full scan mode using mass range of 46–650 m/z. Peak areas of volatiles were integrated and normalized by the dry mass of the sample. At least two or three measurements were made for each sample and the average of peak areas were reported. Identification was done based on the previous publications.<sup>15</sup>

### 2.3.2 Determination of solubility of low molecular weight kraft lignin fractions as a function of pH

The solubility of unfractionated kraft lignin (reference) and low molecular weight kraft lignin fractions was determined in an aqueous solution of varying pH levels. The lignin sample was taken in a centrifuge tube (1.0 g dry matter) and mixed with 25 mL of alkaline water (prepared using 32% NaOH) under stirring overnight. Each lignin slurry was adjusted to the target pH of the solution. The range of pH used in this test varied between 3 to 11 and was adjusted using 32% NaOH. After overnight stirring, further adjustment of pH was performed by using water or 32% NaOH if required and the solutions were set aside for 2 h of mixing. The final pH of the solution was kept within +/- 0.2 of the target. As a next step, the solutions were centrifuged for 30 min, 14 000 xg, and the supernatant was removed. The wet solids were air-dried overnight in a freezer. Wash water solutions were prepared by adding mild NaOH or HCl to water to reach the same target pH levels as the lignin sample solutions. If a precipitate is obtained, the solids were washed with the wash water solution (at the same target pH levels) in the tube (approx. 20 mL) and then subsequently centrifuged for 30 min, 14 000 xg. The supernatant was discarded. The insoluble residue was freeze-dried for 2 days. The mass of dry, insoluble solids was recorded to determine the solubility of the lignin fraction.

## 3. Results

Our recent study demonstrated a new pathway for producing bio-based alkyd resins using low molecular weight kraft lignin intermediates generated via aqueous ethanol fractionation.<sup>11</sup> Table 1 below summarizes the yields and functional properties (molecular weight, dispersity, content of phenolic OH and COOH groups) of these kraft lignin fractions produced at the pilot scale. These results have been reproduced directly from our aforementioned publication and can be used as a reference for the rest of this study.

Table 1. Yields and properties of low molecular weight kraft lignin fractions used in alkyd resin formulation<sup>§</sup>

Kraft lignin fraction	Yield (wt%)	Mw (g/mol)	Mn (g/mol)	D	Phenolic OH (mmol/g)	COOH (mmol/g)
Unfractionated kraft lignin <sup>a</sup>	-	4230	1000	4.2	4.30	0.40
Unfractionated kraft lignin <sup>b</sup>	-	4270	470	9.2	3.76	0.36
50% EtOH soluble kraft lignin <sup>a</sup>	11.6	1930	470	4.1	4.20	0.55
65% EtOH soluble kraft lignin <sup>b</sup>	29.5	2239	395	5.6	4.66	0.51
80% EtOH soluble kraft lignin <sup>a</sup>	31.9	3000	546	4.1	4.41	0.47

§: Data reproduced from our previous publication<sup>11</sup>

a: Unfractionated kraft lignin a was used as raw material containing 94.2 wt% dry matter.

b: Unfractionated kraft lignin b was used as raw material containing 65.0 wt% dry matter.

As shown in Table, fractionation of kraft lignin using 50 – 80 vol% ethanol could produce lignin fractions of Mw ≤ 3000 g/mol and dispersity 4.1 – 5.6 at 11.6 – 31.9 wt% yields. These low molecular weight lignin fractions were rich in phenolic OH (4.20 – 4.66 mmol/g) and COOH (0.47 – 0.55 mmol/g) groups. The above structural characteristics contributed to the effective use of these lignin intermediates in the production of alkyd resin formulation.

## 3.1 Thermal desorption of low molecular weight kraft lignin fractions at alkyd resin synthesis condition

### 3.1.1 Products of thermal desorption of unfractionated kraft lignin

A wide range of volatile organic compounds were released from the thermal desorption of unfractionated kraft lignin at the coating process conditions. Figure 2 depicts that lignin-derived volatile compounds constitute most of the thermally degraded products of kraft lignin at the condition of alkyd resin synthesis. Additionally, sulfur-containing compounds and carbohydrate derivatives were found in these degradation products. Some compounds could not be classified as carbohydrate or lignin derivatives and were therefore termed as linear and cyclic based on their structures identified by the GC-MS system.

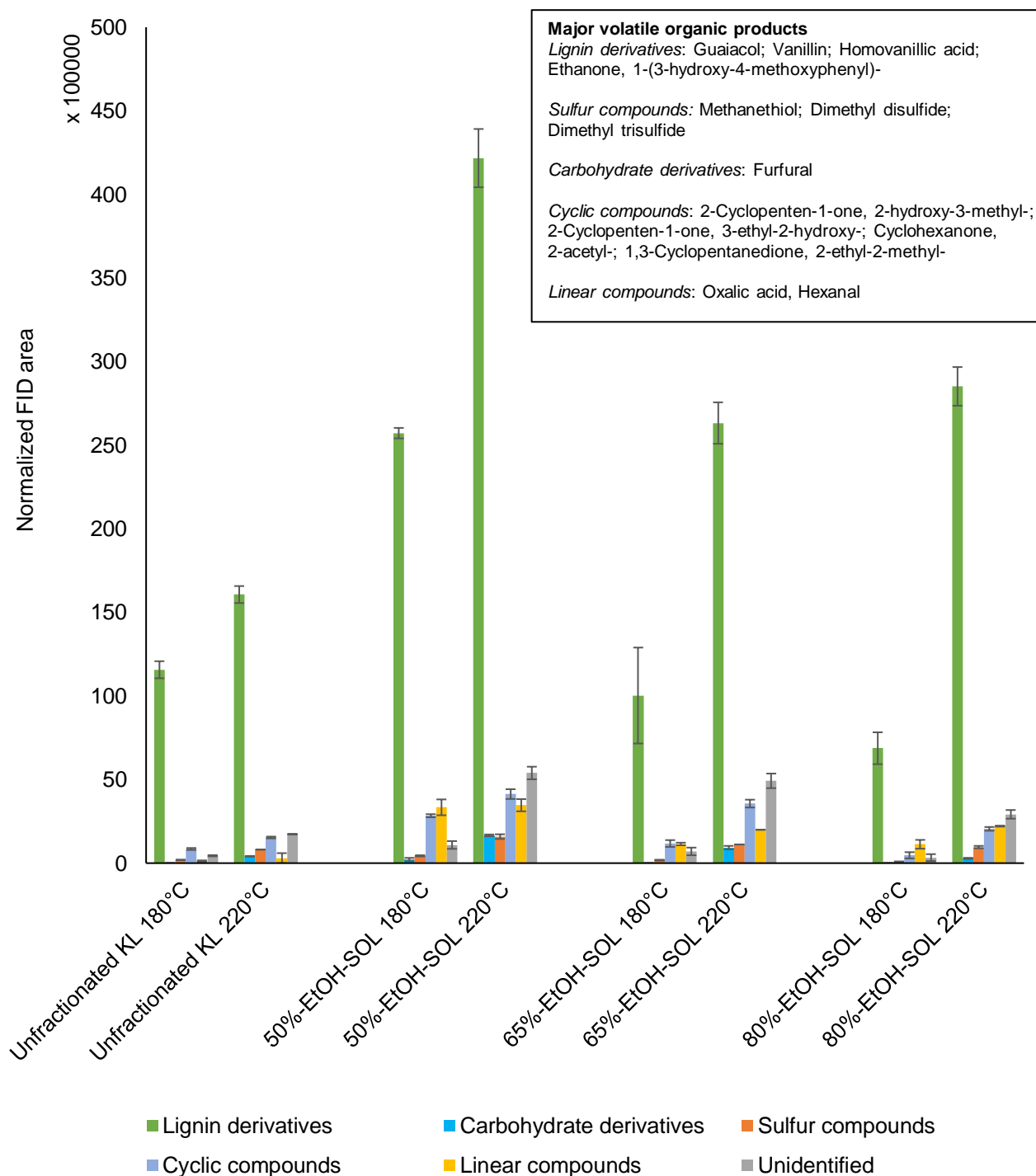


Figure 2. GC-FID areas of volatile organic compounds released at 180°C and 220°C during the thermal desorption of unfractionated kraft lignin (KL) and ethanol soluble kraft lignin (EtOH-SOL) fractions obtained at different EtOH/water ratios used in pilot scale fractionation.

The sulfur compounds released were mainly, methanethiol, dimethyl disulfide, and dimethyl trisulfide. Major lignin derivatives present in the product distribution were guaiacol, vanillin, homovanillic acid, ethanone, 1-(3-hydroxy-4-methoxyphenyl)- and other phenolic monomers. Some of the thermal desorption products of lignin were unidentified by the GC-MS/NIST library. These compounds were mostly relatively higher in molecular weight including aromatic oligomers. On the other hand, the main carbohydrate-derived volatile product found in the thermal degradation of kraft lignin was furfural. The prominent cyclic compounds identified in the above thermal desorption test were 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy- and 1,3-Cyclopentanedione, 2-ethyl-2-methyl- while the major linear compounds found in these tests included oxalic acid and hexanal, etc.

The temperature showed a significant effect on the product distribution of volatile organic compounds as shown in Figure 2. The total amount of VOCs released was significantly higher at 220°C with lignin derivatives still being the main component. Noticeably, the increase in lignin-derived VOCs and sulfur compounds was 1.39 and 4.16 times, respectively, as the temperature was increased from 180°C to 220°C.

### *3.1.2 Products of thermal desorption of low molecular weight kraft lignin*

The composition of volatile organic compounds released during the thermal desorption of low molecular weight kraft lignin was largely like that observed for unfractionated lignin under the simulated conditions of alkyd resin production. As shown in Figure 2, all low molecular weight kraft lignin fractions or EtOH-soluble lignin fractions, generated by different mixing ratios of ethanol/water in the fractionation process, showed lignin derivatives to be the largest component of the VOCs released during their thermal desorption. Other major volatile products were sulfur compounds, carbohydrate derivatives, cyclic, linear, and unidentified compounds as observed in the case of unfractionated lignin. However, using different ethanol/water ratios in fractionation resulted in some differences in the product distribution of these VOCs of the low molecular weight kraft lignin materials. Generally, the content of volatile compounds especially those derived from lignin, carbohydrates, and sulfur-containing molecules, was larger in the 50 vol% soluble lignin as compared to 65 – 80 vol% EtOH soluble lignin.

The temperature of thermal desorption marked the differences between the low molecular weight kraft lignin and the unfractionated even more clearly. The product distribution of thermal desorption of low molecular weight kraft lignin fractions had some interesting, distinguishable features in comparison to the unfractionated lignin. Firstly, the total amount of VOCs released from the low molecular weight kraft lignin fractions at 220°C was at least double that of the VOCs generated from unfractionated lignin under the same condition, reaching a maximum of  $5.8 \times 10^7$  FID area in the case of 50 vol% EtOH soluble lignin. The total amount of VOCs released from 50 vol% EtOH soluble lignin at 180°C was significantly higher as compared to unfractionated lignin. On the other hand, at 180°C, the total amount of VOCs released from 65 vol% EtOH soluble lignin and unfractionated lignin were nearly comparable. Further, the amount of VOCs released from 80 vol% EtOH soluble lignin fraction was even lower than that produced from the unfractionated lignin. At both temperatures, the total amount of VOCs was inversely proportional to the ethanol/water ratios of fractionation with the most drastic reduction seen between 50 to 65 vol% EtOH soluble lignin.

The highest amount of sulfur compounds of  $1.58 \times 10^7$  (FID area) was found in 50 vol% EtOH soluble lignin during the thermal desorption at 220°C. The release of sulfur compounds could, however, be lessened by increasing ethanol/water ratios of fractionation as well as lowering the temperature of thermal desorption. In fact, the amount of sulfur compounds released from 50 vol% EtOH soluble lignin analyzed at 220°C could be reduced to 60.4% (by FID area) of its original value by switching to 80 vol% EtOH soluble lignin material. The sulfur compounds could further be reduced to 4.6% (by FID area) of the original amount by conducting the thermal desorption of 80 vol% EtOH soluble lignin at 180°C. Qualitatively, this indicates that the release

of sulfur compounds and thus odor and other related hazards can be limited by carefully optimizing the fractionation solvent mixture and/or lowering the temperature of alkyd resin synthesis.

To explain these behaviors of low molecular weight kraft lignin fractions as a function of ethanol/water ratios of fractionation, the structural and chemical characteristics could be considered. Lower molecular weight, richer content of Phenolic OH and COOH, and higher carbohydrate content could together be attributed to the higher thermal degradability of 50 vol% EtOH soluble lignin as compared to 80 vol% EtOH soluble lignin. This could also help explain the enhanced release of VOCs at the low temperature of 180°C due to the larger share of low molecular weight compounds present in 50 vol% EtOH soluble lignin in contrast to other lignin fractions obtained at a higher ratio of ethanol to water during fractionation.

### 3.2 Solubility characteristics of low molecular weight kraft lignin fractions for alkyd resin formulation

The solubility of low molecular weight kraft lignin fraction obtained by fractionation using 65 vol% ethanol was determined in aqueous solutions of different pH levels and was compared with the solubility of unfractionated kraft lignin at similar conditions as shown in Figure 3.

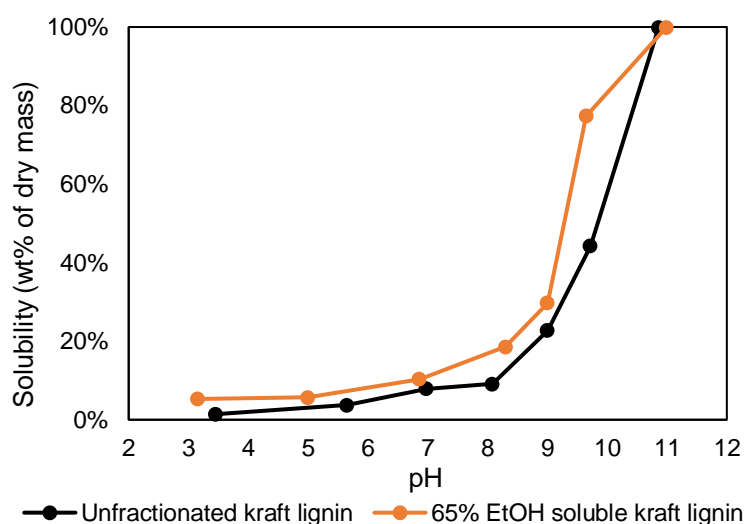


Figure 3. Solubility of the unfractionated and low molecular weight kraft lignin fraction obtained by 65 vol% ethanol fractionation as a function of pH of aqueous solution.

The low molecular weight kraft lignin fraction (i.e. 65 vol% EtOH-soluble lignin) exhibited a 74% increase in solubility at pH between 8 to 10 compared to unfractionated kraft lignin. This could be attributed to a lower molecular weight, and high content of phenolic and carboxylic acid groups of the soluble lignin product of fractionation with 65 vol% ethanol in comparison to unfractionated kraft lignin. These solubility characteristics indicate that the low molecular weight kraft lignin produced by 65 vol% ethanol/water can be more suitable as a substrate for alkyd resin formulation, prepared especially at lower alkaline pH, than the unfractionated kraft lignin.

### 3.3 Outlook and Prospects

Volatile organic compounds in low molecular weight kraft lignin are mainly lignin-derived phenolic molecules such as guaiacol or reduced sulfur compounds formed during wood kraft pulping. The odor threshold values of these VOCs are extremely low. For example, methanethiol has an odor threshold of 0.002 ppm while guaiacol in water solution can have an odor threshold from 3 to 21 ppb. The problem of odor can become unavoidable when alkyd resin synthesis is in progress as this process can initiate thermal degradation of these lignin intermediates releasing the above types of VOCs in significant quantities. In addition, these volatile products can be highly flammable at high concentrations and can pose health



hazards. Therefore, reducing the VOC release from low molecular weight kraft lignin will be highly important to advance the industrialization of alkyd resin production from these lignin materials. Interestingly, using a high ethanol-to-water ratio (e.g. 80 vol% EtOH) greatly helps in lowering the content of lignin-derived and sulfur-containing VOCs when the temperature is 180°C. In fact, at this condition, the sulfur compounds released are less than that produced due to the thermal degradation of unfractionated kraft lignin. Using EtOH-rich solvent becomes less effective at higher temperatures (220°C) though a higher EtOH/water ratio still shows more reduced release of the VOCs, especially, for sulfur compounds. Hence, one way to limit the release of hazardous VOCs from low molecular weight lignin could involve using a lower temperature during alkyd resin synthesis and/or a higher ratio of ethanol/water as the fractionation solvent.

As a path forward, it can be useful to investigate other types of lignin feedstocks, such as sulfur-free lignin from soda pulping or organosolv fractionation process to understand if the chemical structure of different lignin material can have an impact on the release of VOCs in the synthesis of alkyd resin. Additionally, O<sub>2</sub> oxidation of low molecular weight kraft lignin at alkaline pH could also be applied to oxidize sulfur compounds to decrease the release of VOCs.<sup>15</sup> Future research may focus on these directions to help develop a safer and more environment-friendly fractionation process to produce lignin-based alkyd resins.

#### 4. Conclusion

Low molecular weight kraft lignin obtained by fractionation using aqueous ethanol was characterized for its thermal desorption properties and solubility at varying pH, which are essential characteristics to evaluate its feasibility to be used as an intermediate to alkyd resin. Odor can be linked to sulfur compounds and some lignin-derived VOCs released during the thermal degradation of low molecular weight kraft lignin during alkyd resin production. The origin of sulfur compounds in these lignin fractions can be attributed to kraft pulping. The release of ppb level of sulfur compounds from thermal degradation of these low molecular weight kraft lignin fractions can contribute to very bad odor, health hazards and flammability issues. Nevertheless, the release of the VOCs could be lessened by applying lower temperatures during alkyd resin synthesis and/or using a higher ratio of ethanol/water such as 80 vol% in the fractionation process. Solubility of low molecular weight kraft lignin (65 vol% EtOH soluble lignin) can be satisfactorily high at pH 9 to 10 making it more desirable over unfractionated kraft lignin for alkyd resin applications.

#### Acknowledgment

This research work was conducted as part of the LIGNICOAT project, which has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation program 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. The authors gratefully acknowledge the above funding support for this project. The authors sincerely thank the LIGNICOAT consortium members for the helpful discussions and their feedback in this research study. The authors also thank Stora Enso for supplying the kraft lignin feedstock used in this study. Further, the authors are thankful to the VTT technicians, Atte Mikkelsen, Riitta Alander, Pia Willberg-Keyriläinen, Liisa for their help skillful and vital contribution in conducting laboratory tests and analytics.

#### References

- (1) Li, T.; Takkellapati, S. The Current and Emerging Sources of Technical Lignins and Their Applications. *Biofuels, Bioproducts and Biorefining* **2018**, *12* (5), 756–787. <https://doi.org/10.1002/bbb.1913>.
- (2) Jones, F. N.; Nichols, M. E.; Pappas, S. P. Alkyd Resins. In *Organic Coatings: Science and Technology*; Wiley, 2017; pp 213–227. <https://doi.org/10.1002/9781119337201.ch15>.

- (3) Ifijen, I. H.; Maliki, M.; Odiachi, I. J.; Aghedo, O. N.; Ohiocheoya, E. B. Review on Solvents Based Alkyd Resins and Water Borne Alkyd Resins: Impacts of Modification on Their Coating Properties. *Chemistry Africa* **2022**, *5* (2), 211–225. <https://doi.org/10.1007/s42250-022-00318-3>.
- (4) Dizman, C.; Cerrahoğlu Kaçakgil, E. Alkyd Resins Produced from Bio-Based Resources for More Sustainable and Environmentally Friendly Coating Applications. *Turk J Chem* **2023**, *47* (1), 1–23. <https://doi.org/10.55730/1300-0527.3511>.
- (5) Argyropoulos, D. D. S.; Crestini, C.; Dahlstrand, C.; Furusjö, E.; Gioia, C.; Jedvert, K.; Henriksson, G.; Hulteberg, C.; Lawoko, M.; Pierrou, C.; Samec, J. S. M.; Subbotina, E.; Wallmo, H.; Wimby, M. Kraft Lignin: A Valuable, Sustainable Resource, Opportunities and Challenges. *ChemSusChem* **2023**, *16* (23), e202300492. <https://doi.org/10.1002/cssc.202300492>.
- (6) Gigli, M.; Crestini, C. Fractionation of Industrial Lignins: Opportunities and Challenges. *Green Chemistry* **2020**, *22* (15), 4722–4746. <https://doi.org/10.1039/D0GC01606C>.
- (7) Ponnuchamy, V.; Gordobil, O.; Diaz, R. H.; Sandak, A.; Sandak, J. Fractionation of Lignin Using Organic Solvents: A Combined Experimental and Theoretical Study. *Int J Biol Macromol* **2021**, *168*, 792–805. <https://doi.org/10.1016/j.ijbiomac.2020.11.139>.
- (8) Jääskeläinen, A.-S.; Liitiä, T.; Mikkelsen, A.; Tamminen, T. Aqueous Organic Solvent Fractionation as Means to Improve Lignin Homogeneity and Purity. *Ind Crops Prod* **2017**, *103*, 51–58. <https://doi.org/10.1016/j.indcrop.2017.03.039>.
- (9) Ajao, O.; Jeaidi, J.; Benali, M.; Abdelaziz, O. Y.; Hulteberg, C. P. Green Solvents-Based Fractionation Process for Kraft Lignin with Controlled Dispersity and Molecular Weight. *Bioresour Technol* **2019**, *291*, 121799. <https://doi.org/10.1016/j.biortech.2019.121799>.
- (10) Passoni, V.; Scarica, C.; Levi, M.; Turri, S.; Griffini, G. Fractionation of Industrial Softwood Kraft Lignin: Solvent Selection as a Tool for Tailored Material Properties. *ACS Sustain Chem Eng* **2016**, *4* (4), 2232–2242. <https://doi.org/10.1021/acssuschemeng.5b01722>.
- (11) Ghosh, A.; Fearon, O.; Agustin, M.; Alonso, S.; Balda, E. C.; Franco, S.; Kalliola, A. Fractionation of Kraft Lignin for Production of Alkyd Resin for Bio-Based Coatings with Oxidized Lignin Dispersants as a Co-Product. *ACS Omega* **2024**. <https://doi.org/10.1021/acsomega.4c07187>.
- (12) Bušić, A.; Marđetko, N.; Kundas, S.; Morzak, G.; Belskaya, H.; Ivančić Šantek, M.; Komes, D.; Novak, S.; Šantek, B. Bioethanol Production from Renewable Raw Materials and Its Separation and Purification: A Review. *Food Technol Biotechnol* **2018**, *56* (3), 289–311. <https://doi.org/10.17113/ftb.56.03.18.5546>.
- (13) Byrne, F. P.; Jin, S.; Paggiola, G.; Petchey, T. H. M.; Clark, J. H.; Farmer, T. J.; Hunt, A. J.; Robert McElroy, C.; Sherwood, J. Tools and Techniques for Solvent Selection: Green Solvent Selection Guides. *Sustainable Chemical Processes* **2016**, *4* (1), 7. <https://doi.org/10.1186/s40508-016-0051-z>.
- (14) Karimi, S.; Karri, R. R.; Tavakkoli Yarak, M.; Koduru, J. R. Processes and Separation Technologies for the Production of Fuel-Grade Bioethanol: A Review. *Environ Chem Lett* **2021**, *19* (4), 2873–2890. <https://doi.org/10.1007/s10311-021-01208-9>.
- (15) Kalliola, A. K.; Savolainen, A.; Ohra-aho, T.; Faccio, G.; Tamminen, T. Reducing the Content of VOCs of Softwood Kraft Lignins for Material Applications. *Bioresources* **2012**, *7* (3), 2871–2882.