

Technical Note

Evaluation of Differences in Solubility in Organic Solvents of Softwood/Hardwood-Based Industrial Kraft Lignins Using Hansen Parameters and FTIR

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Abstract: Lignin is part of the lignocellulosic biomass found in hardwoods, softwoods, and herbaceous plants. It is isolated by fractionation and pulping processes, where it is considered a waste product and is mainly burned to generate electricity and heat. However, lignin is a biopolymer that can be a source of many chemicals of significant value after treatments of functionalisation or depolymerisation. The main processes for its valorisation require solubilisation in organic solvents, which may affect the process's mass balance and the biopolymer's chemical structure, as lignins are rarely completely soluble in organic solvents. In this research, two industrial Kraft lignins derived from softwood and hardwood were treated using different green organic solvents (2-methyl tetrahydrofuran, tetrahydrofuran, 1-methoxy-2-propanol, and acetone), measuring the soluble and insoluble content to determine the mass balance, and the solubility was evaluated using Hansen parameters and FTIR. The results showed that both lignins were more soluble in tetrahydrofuran and 1-methoxy-2-propanol. Also, tetrahydrofuran performed better than the 2-methyl tetrahydrofuran, which is considered the green alternative. The reason can be explained using the Hansen solubility parameters. Moreover, the solubilised fractions showed similar FTIR spectra. The same is the case for the insoluble parts. In conclusion, the two lignins studied showed different solubilities in absolute values in organic solvents, but the trends were similar.

Keywords: lignin; biopolymer; solubility; FTIR; organic solvents; green solvents; mass balance; biomass valorisation; Hansen solubility parameters; lignin isolation



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1. Introduction

Lignin is a highly branched biopolymer present in lignocellulosic biomasses and the most abundant natural source of aromatics on Earth [1,2]. Lignin can be extracted from biomass using several types of treatments [3] but, at industrial level, the main process is kraft pulping, used in Pulp and Paper mills to prepare cellulose fibres. Currently, the isolated lignin, called kraft lignin, is mainly burned for energetic reasons [4]. However, this aromatic biopolymer showed the potential to be used in a wide range of applications as a biomaterial and a source of platform chemicals [5,6]. Moreover, its elevated production (above 70 million tonnes) makes it a cheap renewable source [7]. The typical pathway for lignin valorisation is its modification/transformation after solubilisation in organic solvents, for example, for synthesising epoxy resins [8,9]. However, the chemical structure and, consequently, the properties and reactivity of lignin are strongly influenced by the original biomass (hardwood, softwood, and herbaceous plants) and extraction process. Furthermore, the same process class, such as kraft pulping, can generate lignin with different properties depending on the producers because they can apply changes in the process, such as the time and chemical loads [10,11]. Consequently, the solubility of kraft lignins from different providers can vary in organic solvents, making them more or less

suitable for specific chemical reactions [12–14]. Moreover, lignin is not a homogeneous polymer with a precise molecular weight, but it shows polydispersity, and it is reported in the literature that the soluble fractions show different molecular weights and functional group content with respect to the insoluble fractions [15]. Therefore, different lignins can generate soluble fractions with different reactivity using the same organic solvent for the solubilisation.

In this research, the solubility in organic solvents of two industrial kraft lignins from different providers were tested. Four organic solvents were selected: acetone, tetrahydrofuran (THF), 2-methyl tetrahydrofuran (2MeTHF), and 1-methoxy-2-propanol. The first two solvents were selected due to their use as solvents for lignin functionalisation reactions [8,9]. The 2MeTHF was selected because it is a greener alternative to the THF [16] already used in lignocellulosic biomass fractionation [17]. Therefore, it is interesting to consider whether it can replace the THF in the solubilisation of lignin for further valorisation.

The fourth solvent was chosen because it is a common industrial solvent that has already been tested in the solubilisation of lignin and because the presence of a free hydroxyl group offers the possibility of stronger hydrogen bonding compared to the other three solvents that are aprotic solvents [12].

In this article, the kraft lignins were solubilised in the four organic solvents. Afterwards, a mass balance considering the soluble and insoluble fractions, comparison of Hansen parameters of the solvents, and FTIR analysis were conducted to evaluate and compare the behaviours between the two target kraft lignins and detect similarities and differences. Several organic solvents, such as ethyl acetate, acetone, ethanol, and isopropanol, were already used and tested for lignin solubility for its functionalisation [18–24]. This aspect is important because the type of solubilised lignin affects the final properties of the final biomaterial [24,25]. However, as far as we know, only a few articles study Hansen parameters in correlation with the lignin solubility and the organic solvents [12–14,26–28]. These articles are further discussed in Section 3.2.

The main objective of this work is to evaluate the solubility of industrial lignins in organic solvents that are of industrial interest by using Hansen parameters and FTIR for the evaluation.

2. Materials and Methods

2.1. Chemicals

Two types of kraft lignin were used: UPM BioPiva™ 395 (softwood, solid content > 95%, Ash content < 2%) was purchased by UPM Biochemicals, Helsinki, Finland and Protobind KW (hardwood, solid content > 95%, Ash content < 6%) was bought from PLT Innovations, Zürich, Switzerland. The solvents used were 2-methyl tetrahydrofuran ($\geq 99.0\%$), tetrahydrofuran ($\geq 99.8\%$), 1-methoxy-2-propanol ($\geq 99.5\%$), and acetone (99.5%), all sourced from Sigma Aldrich (Merck Life Science S.r.l, Milan Italy).

2.2. Solubilisation Tests

As shown in Figure 1, the solutions were prepared by adding lignin (2.5 g) separately to each solvent (25 mL). Then, they were stirred (1 h, 200 rpm) at room temperature. In the second stage, the solutions were transferred into labelled falcon tubes that were placed in a centrifuge (10 min, 5000 rpm). The supernatant was decanted into a flask, and the sediment was washed with distilled water, centrifuged, and transferred into a pre-weighted Petri dish. Both samples were dried in a vacuum oven (Kambič, VS-50 SCMHEX, Semič, Slovenia) at 3 h (30 °C, solvent vapour pressure) at first and then at 5 h (30 °C, 0 mbar) and weighed. A mass balance was prepared, considering the mass loss during the process. It was decided not to dry the solvents at higher temperatures because the possibility of modification of lignin structure when organic solvents, in particular, alcohols, are used is demonstrated in the literature [29]. In the case of 1-methoxy-2-propanol, 10 g of lignin was weighed, and 100 mL of solvent was used by the same procedure described above. Each experiment was performed twice.

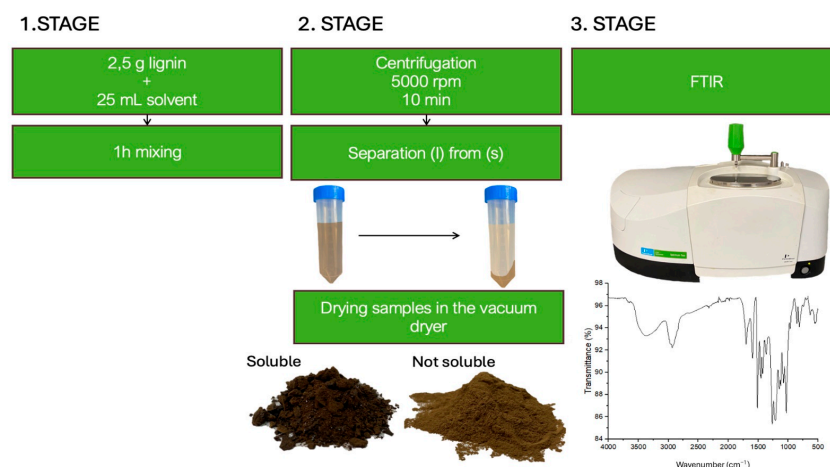


Figure 1. Solubility and mass ratio determination scheme.

In the third stage, FTIR analysis of sixteen samples was performed.

2.3. FTIR Analysis

The infrared analysis was performed using an infrared spectrometer (Spectrum Two FT-IR Spectrometer, PerkinElmer, Manchester, UK). Each sample was analysed with 16 scans in the wavenumber range between 500 and 4000 cm^{-1} , with a resolution of 4 cm^{-1} .

3. Results and Discussion

3.1. Solubility of Kraft Lignins in Organic Solvents: Mass Balance

In the first stage of this study, the mass balance of the solubilisation of the industrial lignin was performed. The weight percentages of soluble and non-soluble are reported in Figure 2. We also reported a third fraction called “lost” in Figure 2. It is a mass amount lost during the stirring, centrifugation, and drying activities due to the small amount of lignin used for the experiments. This mass loss is mainly from the non-soluble part but cannot be determined with certainty.

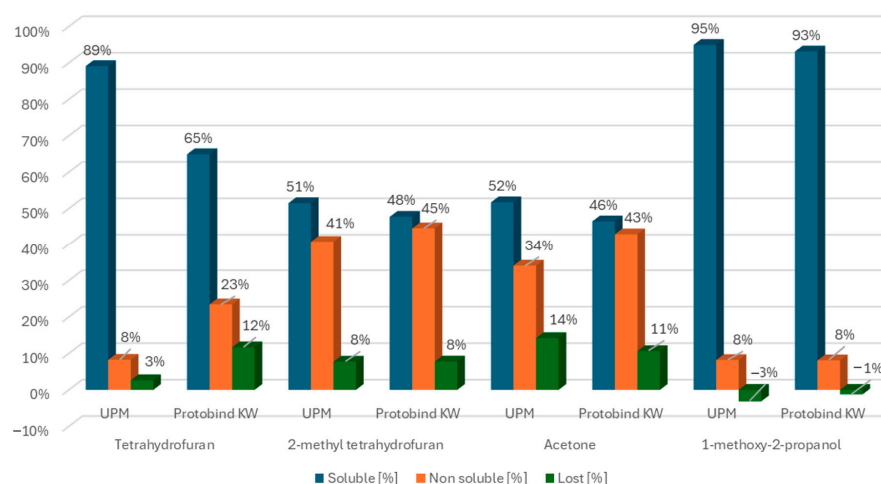


Figure 2. Weight percentages of industrial lignins in the four solvents.

Based on Figure 2, the solubility behaviours of the two industrial kraft lignins are similar: 1-methoxy-2-propanol > THF > 2MeTHF \approx Acetone. This similarity can be correlated to the fact that both industrial lignins are obtained from the kraft process. In this case, the different origins (softwood and hardwood) look like less relevant parameters. The main difference in quantitative analysis can be observed in the case of THF, where UPM

BioPiva™395 is more soluble than Protobind KW. This is discussed in the next section, considering the Hansen parameters.

3.2. Solubility of Kraft Lignins in Organic Solvents: Hansen Parameters

In this section, Hansen parameters are used to discuss the solubilisation of the two different lignins in the four organic solvents. This approach has already been used in the literature for acetone, THF, and 1-methoxy-2-propanol, but not for 2MeTHF, as far as we know [12,13,26,27]. All the values are adopted from the website <https://www.stevenabbott.co.uk/> (accessed on 2 August 2024) [30] because it has a database of Hansen parameters for most solvents. The values of the organic solvent of interest are reported below in Table 1.

Table 1. Hansen parameters of the four organic solvents.

Organic Solvent	Dispersion δ_D (MPa ^{1/2})	Polar δ_P (MPa ^{1/2})	Hydrogen-Bonding δ_H (MPa ^{1/2})
Acetone	15.5	10.4	7
THF	16.8	5.7	8
2MeTHF	16.9	5	4.3
1-methoxy-2-propanol	15.6	6.3	11.6

The Hansen solubility parameters are a valuable approach to study and evaluate the solubility of lignin in organic solvents because they allow us to consider the dispersion, the polarity, and the hydrogen-bonding properties [31,32]. The four solvents considered show similar δ_D values. In this case, the δ_D is not discriminant. The main differences can be observed in the other two parameters. In fact, the two solvents that showed lower lignin solubility, acetone, and 2MeTHF, showed the highest value of δ_P and the lowest δ_H . Considering the four solvents studied in this research, it is possible to ponder that a high δ_P and a low δ_H value reduce the lignin solubility. This observation can be correlated with the structure of lignin. This biopolymer contains several apolar “sites” and aromatics; so, a too-polar solvent risk is incompatible. At the same time, lignin has a high content of hydroxyl groups. Therefore, a solvent that can “break” the resulting hydrogen bonding (high δ_H) would enhance the lignin solubility [4].

When the results are compared with the literature, the complexity of lignin solubility can be further understood. In 2016, Duval et al. [26] studied the solubility of a softwood KL obtained from the Lignoboost process. This lignin showed a solubility of around 66% in acetone. In 2019, Kwok et al. [27] studied the solubility of lignin extracted from hardwood using sulphur dioxide. In this case, the lignin solubility in THF was above 90%. In 2020, Dastpak et al. [12] explored the solubility of two lignins, softwood kraft lignin, UPM BioPiva™ 190, and a pilot-scale hardwood organosolv lignin (Fraunhofer CBP). Both lignins showed a solubility in 1-methoxy-2-propanol above 80%. Also in 2020, Ribeiro et al. [13] studied the solubility of kraft lignin from *Eucalyptus urograndis* by Suzano. This lignin showed solubility of >88% in acetone and >95% in THF. In 2022, Ruwoldt et al. [14] worked on several lignins, including the UPM BioPiva™ 395, searching to determine the Hansen parameters of the lignins. The solubility values of UPM BioPiva™ 395 were $\delta_D = 17.6$, $\delta_P = 12.6$ and $\delta_H = 15.95$. In this case, the calculated δ_D is close to the experimental values of THF and 1-methoxy-2-propanol obtained in this work. However, the other two calculated parameters show a significant deviation from the experimental data of this work. A possible explanation could be the way the parameters were calculated. The method is based on an Excel workbook where the solvents are classified as “good” (score 1) and “bad” solvents (score 0) [33]. Therefore, there is an uncertainty associated with the selection of “good” and “bad” solvents by the scientists.

These results confirm that every lignin from different suppliers must be studied separately. In other words, it is not possible to use “a” kraft lignin as standard for all kraft lignins. For completeness, in 2024, Ma et al. [28] reported in a review the limitations in

the calculation of the lignin Hansen parameters due to the complex molecular structure of this biopolymer.

In conclusion, comparing THF and 2MeTHF, it is possible to consider that 2MeTHF is probably not the best green alternative for THF due to the difference in δ_H , at least for these lignins. In terms of molecular structure, it is possible to correlate this difference in lignin solubility property to the presence of a methyl group in 2MeTHF, which causes an increase in branching level in comparison to THF. In future research, testing lignins from different extraction and fractionation processes (i.e., organosolv, soda, and acid hydrolysis) to confirm this result would be useful.

3.3. Solubility of Kraft Lignins in Organic Solvents: FTIR Analysis

The FTIR spectra of the original lignins are reported in Figure 3. The main differences can be observed at 1710 cm^{-1} , where the band of UPM BioPiva™ 395 is more intense than that of Protobind KW and in the range $1300\text{--}1000\text{ cm}^{-1}$. The first band can be correlated to the unconjugated carbonyl stretching [34]. Instead, the broad area $1300\text{--}1000\text{ cm}^{-1}$ cannot be correlated to a specific band because both vibrations aliphatic C–H bonds and C–O are present there [35]. These differences can be ascribed to the different types of wood (softwood and hardwood) and possible variations between the kraft processes. It is further proof that each industrial lignin has its fingerprint.

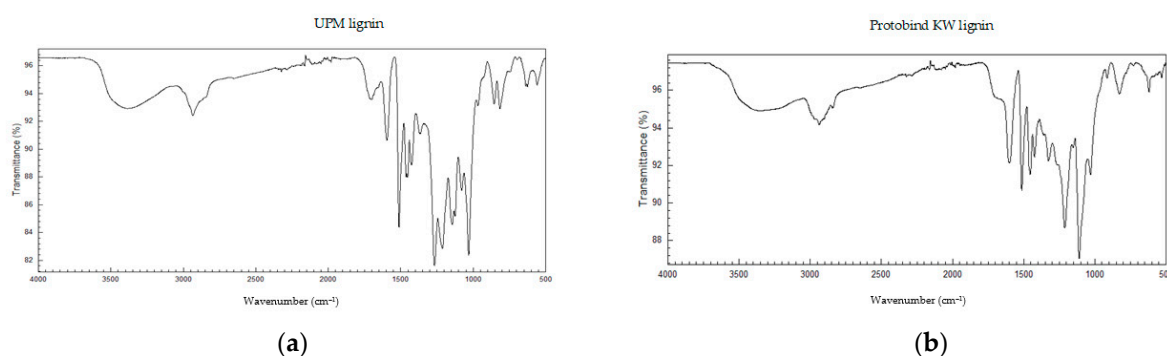


Figure 3. FTIR scheme: (a) UPM lignin; (b) Protobind KW lignin.

The FTIR of the soluble and insoluble fractions of UPM BioPiva™ 395 are reported in Figure 4. It is possible to observe that the corresponding fingerprints of the spectra from soluble fractions are similar, independent of the solvents. The same can be observed for the spectra of the insoluble fractions. Instead, two main differences are observed when the soluble and insoluble spectra are compared. The bands at 1710 cm^{-1} and 1075 cm^{-1} are more intense in the soluble fractions than in the insoluble fractions. As reported above, the band at 1710 cm^{-1} corresponds to unconjugated carbonyl stretching. The band at 1075 cm^{-1} can be correlated to the C–O vibrations of secondary alcohols and ether bonds [4,35]. This difference can be correlated to the fact that lower molecular weight lignin fractions, which contain higher contents of C=O and C–O, are more soluble in organic solvents than the high molecular weight lignin fractions [19,36,37].

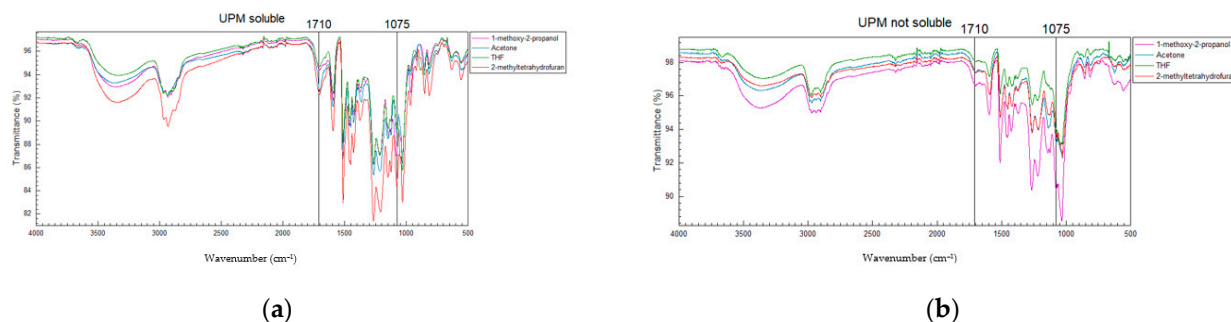


Figure 4. FTIR scheme of UPM lignin with different solvents: (a) FTIR spectra of soluble part of UPM lignin; (b) FTIR spectra of not soluble part of UPM lignin.

In the case of the Protobind KW soluble and insoluble fractions, the spectra are reported in Figure 5. The main difference observed in this case is at the band 1710 cm^{-1} . For the rest, the spectra are quite similar. In the case of the insoluble fraction from 1-methoxy-2-propanol, the bands at around 1600 cm^{-1} , around 1300 cm^{-1} , and below 1000 cm^{-1} are more intense, with respect to the other organic solvents. This deviation will require further studies to be interpreted, but it is possible to make the hypothesis that the impurities were more visible in this specific insoluble residue. The Protobind KW contains three times more ashes than UPM BioPiva™ 395. Moreover, the insoluble content for 1-methoxy-2-propanol is around 8% compared to the other three solvents, with an insoluble content between 23 and 45% (Figure 2). Consequently, the insoluble ashes become more visible because most of the lignin was solubilised. Kraft lignin can contain inorganic salts of sodium sulphide and sodium carbonate [7]. These salts show transmittance at wavelengths around 1300 cm^{-1} and below 1000 cm^{-1} [38]. For completion, the band at around 1600 cm^{-1} can also be correlated to residual water (O–H vibration).

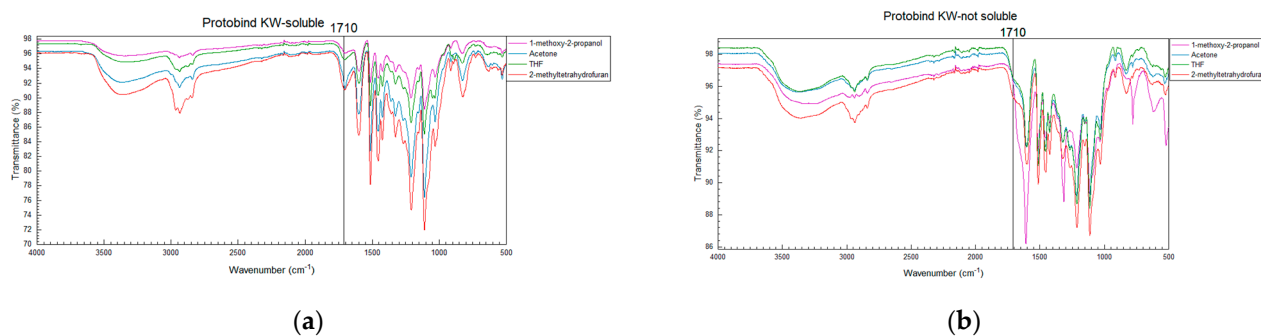


Figure 5. FTIR scheme of Protobind KW lignin with different solvents: (a) FTIR spectra of soluble part of Protobind KW lignin; (b) FTIR spectra of not soluble part of Protobind KW lignin.

The different spectra reported in this work show close similarities that do not allow us to enter more into detail in the discussion the correlation of the chemical structure of the two industrial lignins with their solubility in organic solvents. A more in-depth study of the correlation of the molecular structure of the two lignins and their different solubilities will require the use of two additional techniques, SEC and NMR, to study the molecular weight and determine quantitatively the functional groups (mainly hydroxyl and carboxylic groups) [15,39].

4. Conclusions

The solubility of the two industrial lignins can be summarised as 1-methoxy-2-propanol > THF > 2MeTHF \approx Acetone. The results show that 2MeTHF is not the best green alternative to THF for lignin solubilisation. At the same time, 1-methoxy-2-propanol looks like an interesting green solvent for further studies on lignin solubilisation for functionali-

sation reactions to prepare biomaterials because it is already used on an industrial scale for several applications [12] and shows high lignin solubility (>93%). These differences between lignin solubilities can be correlated to the hydrogen-bonding Hansen parameter and the different branching levels of the organic solvents. Instead, comparing the behaviours of the two lignins, they show similar trends (FTIR spectra and mass balance), probably because both lignins are produced by the kraft process. For further studies, a more in-depth analysis on the chemical structure of the lignin fractions requires the use of further techniques such as NMR and SEC and should use additional organic solvents such as alcohols.

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Data Availability Statement: The data that support the findings of this study are available from the corresponding author (Giorgio Tofani) upon reasonable request.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Deuss, P.J.; Barta, K. From Models to Lignin: Transition Metal Catalysis for Selective Bond Cleavage Reactions. *Coord. Chem. Rev.* **2016**, *306*, 510–532. [[CrossRef](#)]
2. Rabiei, Z.; Simons, A.; Folkmanova, M.; Vesela, T.; Uhlik, O.; Kozliak, E.; Kubátová, A. Stability and Reactivity of Guaiacylglycerol- β -Guaiacyl Ether, a Compound Modeling β -O-4 Linkage in Lignin. *Separations* **2024**, *11*, 59. [[CrossRef](#)]
3. Bouaziz, F.; Abdeddayem, A.B.; Koubaa, M.; Barba, F.J.; Jeddou, K.B.; Kacem, I.; Ghorbel, R.E.; Chaabouni, S.E. Bioethanol Production from Date Seed Cellulosic Fraction Using *Saccharomyces Cerevisiae*. *Separations* **2020**, *7*, 67. [[CrossRef](#)]
4. Tofani, G.; Cornet, I.; Tavernier, S. Separation and Recovery of Lignin and Hydrocarbon Derivatives from Cardboard. *Biomass Convers. Bioref.* **2022**, *12*, 3409–3424. [[CrossRef](#)]
5. Monaci, S.; Minudri, D.; Guazzelli, L.; Mezzetta, A.; Mecerreyes, D.; Forsyth, M.; Somers, A. Lignin-Derivative Ionic Liquids as Corrosion Inhibitors. *Molecules* **2023**, *28*, 5568. [[CrossRef](#)]
6. Liu, Q.; Sang, Y.; Bai, Y.; Wu, K.; Ma, Z.; Chen, M.; Ma, Y.; Chen, H.; Li, Y. Catalytic Conversion of Kraft Lignin into Platform Chemicals in Supercritical Ethanol over a $\text{Mo}(\text{OCH}_2\text{CH}_3)_x/\text{NaCl}$ Catalyst. *Catal. Today* **2023**, *408*, 204–210. [[CrossRef](#)]
7. Argyropoulos, D.D.S.; Crestini, C.; Dahlstrand, C.; Furuşjö, E.; Gioia, C.; Jedvert, K.; Henriksson, G.; Hulteberg, C.; Lawoko, M.; Pierrou, C.; et al. Kraft Lignin: A Valuable, Sustainable Resource, Opportunities and Challenges. *ChemSusChem* **2023**, *16*, e202300492. [[CrossRef](#)]
8. Asada, C.; Fujii, M.; Suzuki, A.; Nakamura, Y. Cured Epoxy Resin Synthesized Using Acetone-Soluble Lignin and Ligno-p-Cresol Obtained from Steam-Exploded Wheat Straw. *Biomass Convers. Bioref.* **2023**, *13*, 10495–10504. [[CrossRef](#)]
9. Scarica, C.; Suriano, R.; Levi, M.; Turri, S.; Griffini, G. Lignin Functionalized with Succinic Anhydride as Building Block for Biobased Thermosetting Polyester Coatings. *ACS Sustain. Chem. Eng.* **2018**, *6*, 3392–3401. [[CrossRef](#)]
10. Tofani, G.; Cornet, I.; Tavernier, S. Estimation of Hydrogen Peroxide Effectivity during Bleaching Using the Kappa Number. *Chem. Pap.* **2021**, *75*, 5749–5758. [[CrossRef](#)]
11. Wang, Z.; Deuss, P.J. The Isolation of Lignin with Native-like Structure. *Biotechnol. Adv.* **2023**, *68*, 108230. [[CrossRef](#)]
12. Dastpak, A.; Lourençon, T.V.; Balakshin, M.; Farhan Hashmi, S.; Lundström, M.; Wilson, B.P. Solubility Study of Lignin in Industrial Organic Solvents and Investigation of Electrochemical Properties of Spray-Coated Solutions. *Ind. Crops Prod.* **2020**, *148*, 112310. [[CrossRef](#)]
13. Ribeiro, W.C.O.; Lobosco, V.; Martinez, P.F.M. Solubility Parameters Analysis of Eucalyptus Urograndis Kraft Lignin. *BioResources* **2020**, *15*, 8577–8600. [[CrossRef](#)]
14. Ruwoldt, J.; Tanase-Opedal, M.; Syverud, K. Ultraviolet Spectrophotometry of Lignin Revisited: Exploring Solvents with Low Harmfulness, Lignin Purity, Hansen Solubility Parameter, and Determination of Phenolic Hydroxyl Groups. *ACS Omega* **2022**, *7*, 46371–46383. [[CrossRef](#)] [[PubMed](#)]
15. Salanti, A.; Orlandi, M.; Lange, H.; Ferruti, F.; Zoia, L. Phenolic Group Distribution as a Function of Molecular Weight in Lignins and Their Fractions. *ACS Sustain. Chem. Eng.* **2022**, *10*, 11680–11691. [[CrossRef](#)]
16. Pace, V.; Hoyos, P.; Castoldi, L.; Domínguez de María, P.; Alcántara, A.R. 2-Methyltetrahydrofuran (2-MeTHF): A Biomass-Derived Solvent with Broad Application in Organic Chemistry. *ChemSusChem* **2012**, *5*, 1369–1379. [[CrossRef](#)]
17. Holtz, A.; Weidener, D.; Leitner, W.; Klose, H.; Grande, P.M.; Jupke, A. Process Development for Separation of Lignin from OrganoCat Lignocellulose Fractionation Using Antisolvent Precipitation. *Sep. Purif. Technol.* **2020**, *236*, 116295. [[CrossRef](#)]

18. Ponnudurai, A.; Schulze, P.; Seidel-Morgenstern, A.; Lorenz, H. Effect of Feed Concentration in Solvent/Anti-Solvent Precipitation Fractionation of Lignin: Impact on Lignins Structure-Property Correlations. *Sep. Purif. Technol.* **2024**, *337*, 126343. [CrossRef]
19. 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. [CrossRef] [PubMed]
20. Zhou, N.; Yang, J.; Lu, X.; Xin, Z.; Xu, C.; He, Q. Microwave-Assisted Depolymerization of Lignin and a Biphasic Extraction Method for the Recovery of Bio-Oil and Phenolic Monomers. *J. Anal. Appl. Pyrolysis* **2022**, *161*, 105403. [CrossRef]
21. Zou, S.-L.; Xiao, L.-P.; Li, X.-Y.; Yin, W.-Z.; Sun, R.-C. Lignin-Based Composites with Enhanced Mechanical Properties by Acetone Fractionation and Epoxidation Modification. *iScience* **2023**, *26*, 106187. [CrossRef]
22. Izaguirre, N.; Robles, E.; Llano-Ponte, R.; Labidi, J.; Erdocia, X. Fine-Tune of Lignin Properties by Its Fractionation with a Sequential Organic Solvent Extraction. *Ind. Crops Prod.* **2022**, *175*, 114251. [CrossRef]
23. Ghaffari, R.; Almqvist, H.; Idström, A.; Sapouna, I.; Evenäs, L.; Lidén, G.; Lawoko, M.; Larsson, A. Effect of Alkalinity on the Diffusion of Solvent-Fractionated Lignin through Cellulose Membranes. *Cellulose* **2023**, *30*, 3685–3698. [CrossRef]
24. Silau, H.; Melas, A.; Dam-Johansen, K.; Wu, H.; Daugaard, A.E.; Høj, M. Solvent Fractionation and Depolymerization Provide Liquid Lignin Fractions Exploited as Bio-Based Aromatic Building Blocks in Epoxies. *ACS Sustain. Chem. Eng.* **2023**, *11*, 1591–1597. [CrossRef]
25. Gioia, C.; Lo Re, G.; Lawoko, M.; Berglund, L. Tunable Thermosetting Epoxies Based on Fractionated and Well-Characterized Lignins. *J. Am. Chem. Soc.* **2018**, *140*, 4054–4061. [CrossRef]
26. Duval, A.; Vilaplana, F.; Crestini, C.; Lawoko, M. Solvent Screening for the Fractionation of Industrial Kraft Lignin. *Holzforschung* **2016**, *70*, 11–20. [CrossRef]
27. Kwok, T.T.; Bright, J.R.; Realf, M.J.; Bommarius, A.S. Pretreatment Efficacy and Lignin Solubility of Organic Solvents on Juvenile Slash Pine Chips for Lignin Value Prior to Pulping. *BioResources* **2019**, *14*, 5988–6003. [CrossRef]
28. Ma, Q.; Yu, C.; Zhou, Y.; Hu, D.; Chen, J.; Zhang, X. A Review on the Calculation and Application of Lignin Hansen Solubility Parameters. *Int. J. Biol. Macromol.* **2024**, *256*, 128506. [CrossRef] [PubMed]
29. Wang, Z.; Zhang, Z.; Wang, H.; Deuss, P.J. Tuning Lignin Properties by Mild Ionic-Liquid-Mediated Selective Alcohol Incorporation. *Chem Catal.* **2022**, *2*, 1407–1427. [CrossRef]
30. HSP Basics. Available online: <https://www.stevenabbott.co.uk/practical-solubility/hsp-basics.php> (accessed on 25 June 2024).
31. Novo, L.P.; Curvelo, A.A.S. Hansen Solubility Parameters: A Tool for Solvent Selection for Organosolv Delignification. *Ind. Eng. Chem. Res.* **2019**, *58*, 14520–14527. [CrossRef]
32. Giummarella, N.; Lindgren, C.; Lindström, M.E.; Henriksson, G. Lignin Prepared by Ultrafiltration of Black Liquor: Investigation of Solubility, Viscosity, and Ash Content. *BioResources* **2016**, *11*, 3494–3510. [CrossRef]
33. Díaz De Los Ríos, M.; Hernández Ramos, E. Determination of the Hansen Solubility Parameters and the Hansen Sphere Radius with the Aid of the Solver Add-in of Microsoft Excel. *SN Appl. Sci.* **2020**, *2*, 676. [CrossRef]
34. Yang, H.; Yoo, C.G.; Meng, X.; Pu, Y.; Muchero, W.; Tuskan, G.A.; Tschaplinski, T.J.; Ragauskas, A.J.; Yao, L. Structural Changes of Lignins in Natural Populus Variants during Different Pretreatments. *Bioresour. Technol.* **2020**, *295*, 122240. [CrossRef]
35. Lu, Y.; Lu, Y.-C.; Hu, H.-Q.; Xie, F.-J.; Wei, X.-Y.; Fan, X. Structural Characterization of Lignin and Its Degradation Products with Spectroscopic Methods. *J. Spectrosc.* **2017**, *2017*, 8951658. [CrossRef]
36. Boeriu, C.G.; Fițigău, F.I.; Gosselink, R.J.A.; Frissen, A.E.; Stoutjesdijk, J.; Peter, F. Fractionation of Five Technical Lignins by Selective Extraction in Green Solvents and Characterisation of Isolated Fractions. *Ind. Crops Prod.* **2014**, *62*, 481–490. [CrossRef]
37. Pang, T.; Wang, G.; Sun, H.; Sui, W.; Si, C. Lignin Fractionation: Effective Strategy to Reduce Molecule Weight Dependent Heterogeneity for Upgraded Lignin Valorization. *Ind. Crops Prod.* **2021**, *165*, 113442. [CrossRef]
38. Tofani, G.; de Nys, J.; Cornet, I.; Tavernier, S. Alternative Filler Recovery from Paper Waste Stream. *Waste Biomass Valor* **2021**, *12*, 503–514. [CrossRef]
39. Sosa, F.H.B.; Abranches, D.O.; da Costa Lopes, A.M.; Coutinho, J.A.P.; da Costa, M.C. Kraft Lignin Solubility and Its Chemical Modification in Deep Eutectic Solvents. *ACS Sustain. Chem. Eng.* **2020**, *8*, 18577–18589. [CrossRef]

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