

Supporting information

Hydrothermal Depolymerization of Kraft Lignins with Green C₁-C₃ Alcohol-Water Mixtures[†]

Ming Guo, [†] Riku Maltari, [†] Rui Zhang, Jussi Kontro, Enlu Ma, and Timo Repo*

Department of Chemistry, University of Helsinki, A.I. Virtasen aukio 1, Post Office Box 55, FI-00140, Helsinki, Finland

*Corresponding author.

Timo Repo. E-mail: timo.repo@helsinki.fi

File S1 Thermal Analyzes

Thermogravimetric analysis (TGA) and Different Scanning Calorimetry (DSC) were both used in this experiment.¹ TGA measurements were performed with a NETZSCH Jupiter STA 449 F3. DSC measurements were performed with a Mettler 822e differential scanning calorimeter under nitrogen atmosphere. Typically, KL and KL residues samples were performed from 40 to 1200 °C at a heating rate of 20 °C/min under 20% air/80% nitrogen atmosphere. Differential scanning calorimetric analysis was carried out using a TA Instruments Q100 DSC with an aluminum hermetic pan. The measurement was made at a scan rate of 10 °C/min over a temperature range from 40 to 180 °C under a nitrogen atmosphere.

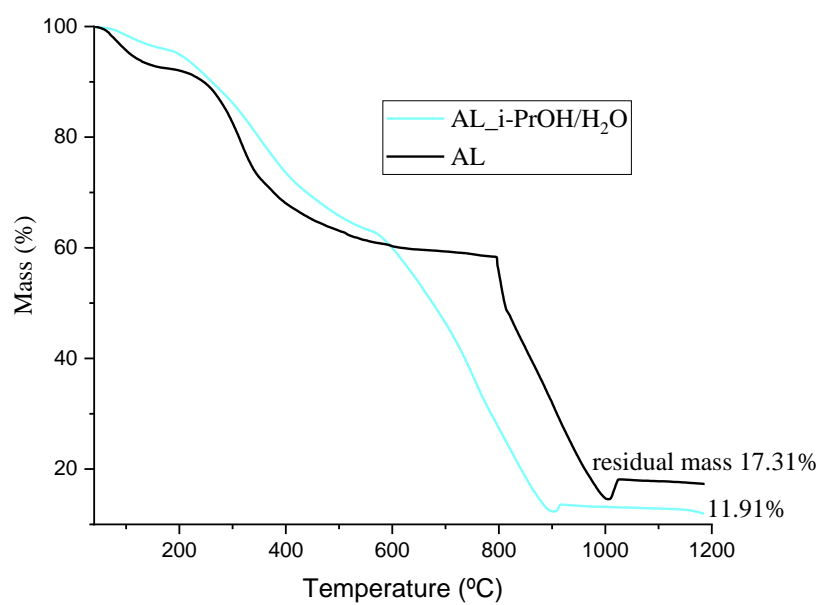
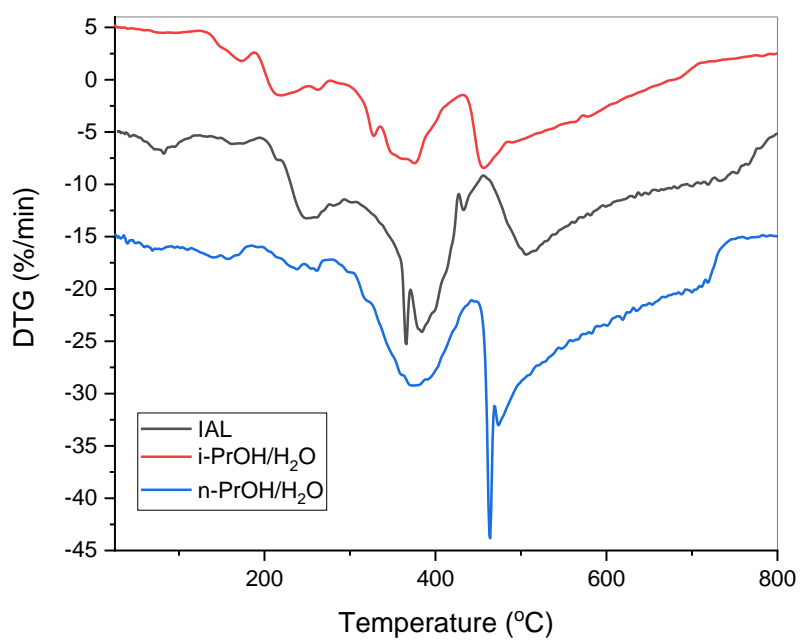
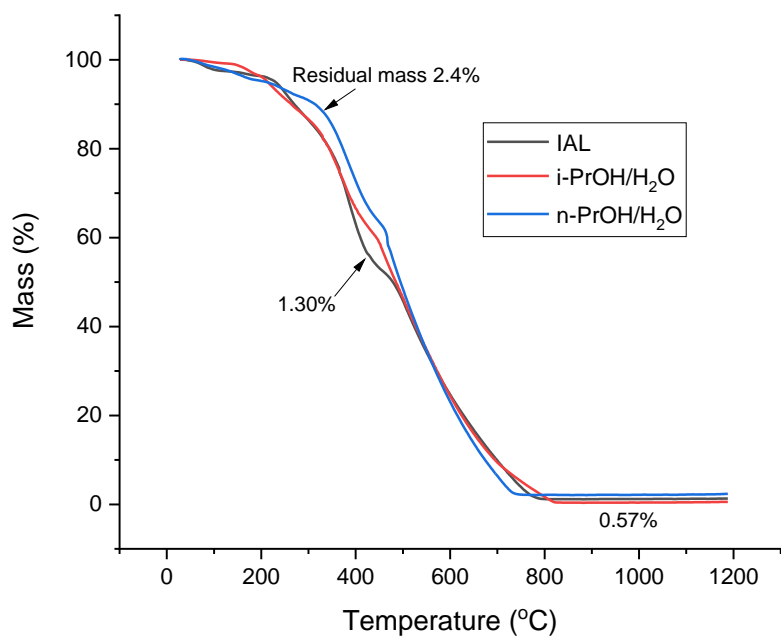


Figure S1.1 TG of AL and AL residue.



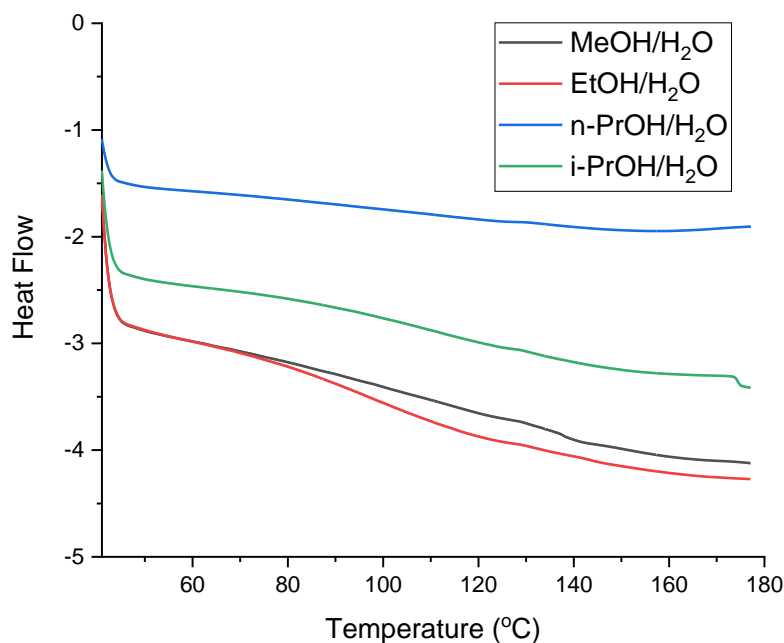


Figure S1.2 TG, DTG and DSC curves of IAL and its residues.

File S2 Elemental Analysis

Elemental analysis was conducted on an Elementar Analysensysteme (HANAU, Germany) model vario MICRO cube, operated in CHNS mode. Sulfanilamide was utilized as a standard.

The elements of lignin are carbon, hydrogen, oxygen. Other elements are nitrogen and sulfur which were mainly derived from mineral absorption and processing conditions. Chemical methods in biorefinery and extraction strategies lead to change the composition of lignin such as increasing the ash content. Carbon was the principal element in lignin compositions that accounts for the largest proportion. Lignin, with its higher carbon content than the proportion of carbon in carbohydrates, equates to higher purity as well as less carbohydrate residue.²

Table S2 Elemental Analysis of IAL, AL and Corresponding Residues

Sample	C	H	O*	N	S
IAL	63.2	5.7	28.2	0.8	2.1
IAL_ <i>i</i> -PrOH/H ₂ O	67.2	6.1	25.0	0.6	1.1
AL	47.8	4.5	43.3	0.1	4.3
AL_ <i>i</i> -PrOH/H ₂ O	47.7	4.9	43	0.1	4.3

*Calculated by removing other elements. (Ash not considered)

File S3 Antioxidant Activity

The UV–VIS absorption measurements were performed on a Hewlett Packard 8453 instrument using 1.0 cm plastic cuvettes at room temperature. DPPH (2,2-diphenyl-1-picrylhydrazyl) radical was utilized to detect the antioxidant activity of lignin samples.^{3,4} Six solutions with different concentrations of lignin residues and bio-oil (after *i*-PrOH/H₂O solvolysis) were made for each sample. The solutions had concentrations ranging from 2.5 to 35 mg/L. They were dissolved in a mixture consisting of 25 mg/L of DPPH in 90% dioxane-water. In addition, a control sample was measured, consisting of 25 mg/L of DPPH. After 2 h incubation in a dark room at ambient temperature, the UV-VIS absorbance of all samples was measured and compared to 90% dioxane:water (v/v) solution at 517 nm. Experiments were performed in triplicate.

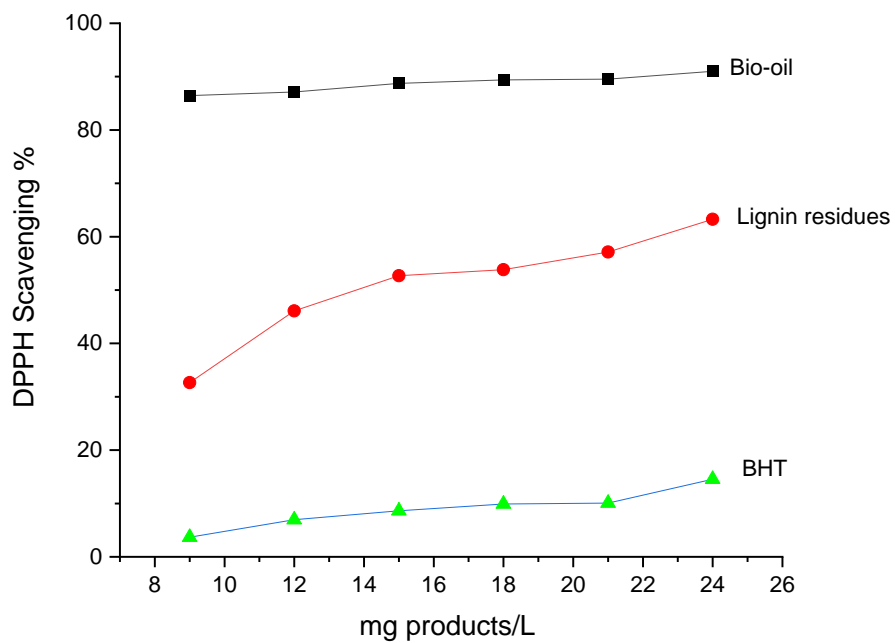


Figure S3 Antioxidant activity of *i*-PrOH/H₂O released IAL oil and residue.

File S4 IR

IR (Infrared Spectroscopy) spectra were recorded on a Bruker Alpha-P Fourier transform infrared spectrometer in the range of 4000-375 cm⁻¹ with a resolution of 4 cm⁻¹ and 64 scans.

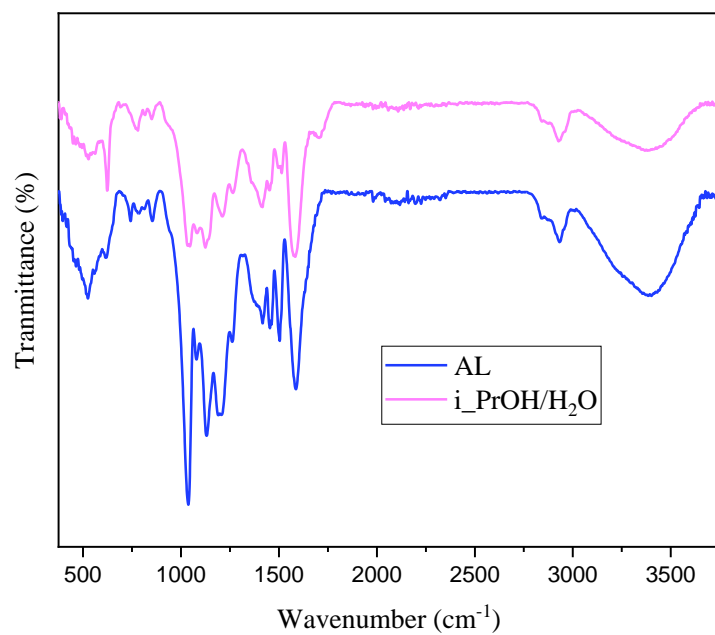


Figure S4.1 FT-IR spectrum of untreated AL and *i*-PrOH/H₂O treated residue.

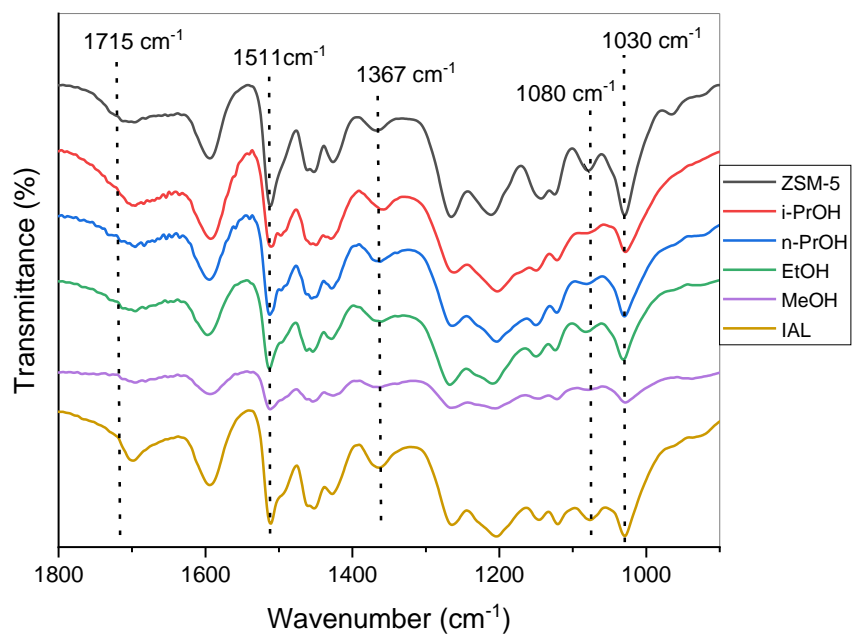


Figure S4.2 FT-IR spectrum of original IAL and IAL residues.

File S5 Extraction of bio-oil

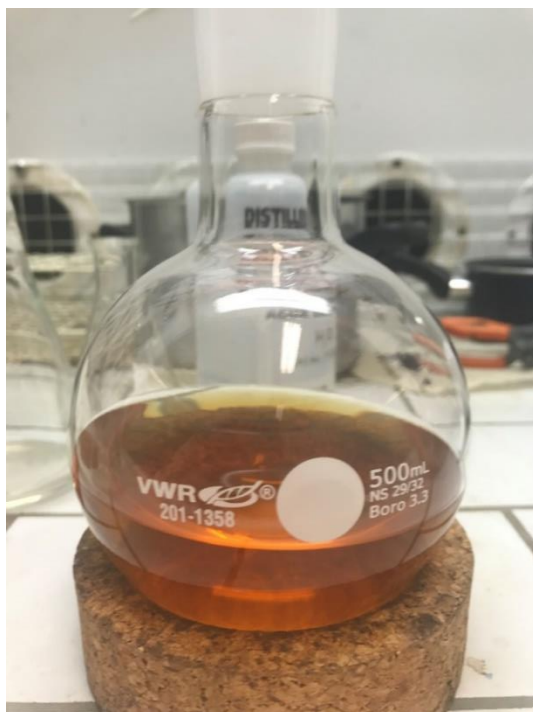


Figure S5.1 Petroleum ether extraction.



Figure S5.2 DCM extraction after evaporation (heavy oil).

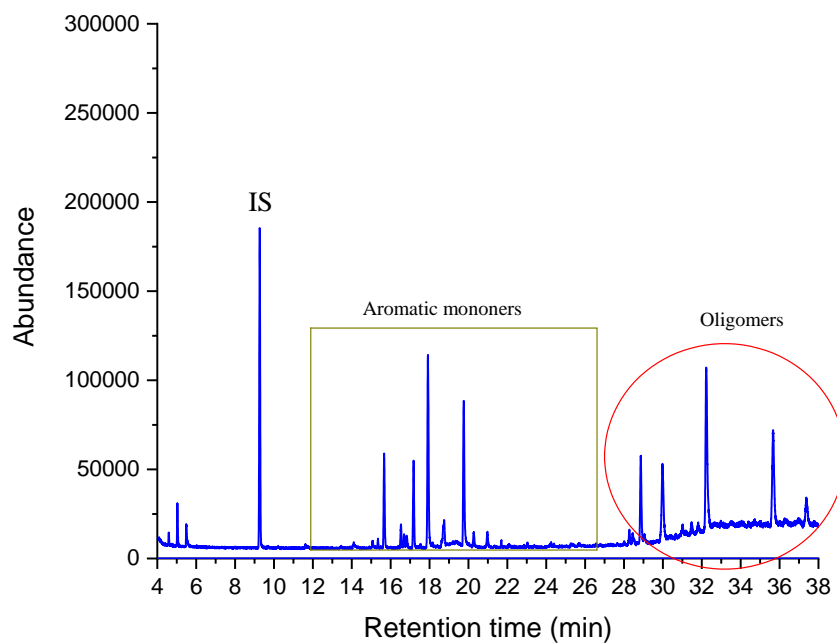
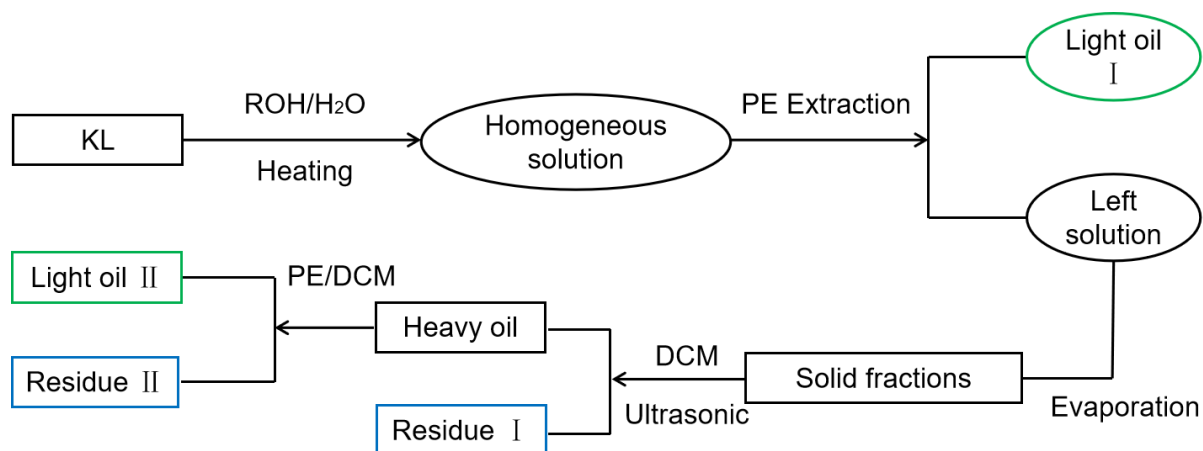


Figure S5.3 GC-MS analysis of solid-liquid extraction.

a) IS: Internal standard.

Scheme I. Another Light oil and Residue Fraction Processing Procedure



GC-MS quantification

1 g of acetophenone was dissolved in 500 mL of ethyl acetate, concentration on 2.0 mg/mL as the internal standard (IS) solution for further use. Different commercial aromatic monomers were weighed in 20 mL volumetric flask to be stock solution. Internal standard curves ($y = ax \pm b$) were measured by adding a fixed concentration of acetophenone (0.1 mg/mL) together with different concentrations of monomers ranging from 0.1 mg/mL-1.0 mg/mL in 10 mL volumetric flask. Herein, x axis is the peak area ratio of samples and IS and y-axis stands for the different concentration of samples. With obtained SD oil, based on their mass, we dissolved it in designated volume (V) by adding a constant IS. Every sample has its unique retention time, we can attain the x value of each sample by dividing its peak area into the peak area of IS, then substitute it into each linear equation to calculate the corresponding concentration value.

General formula:

$$\text{SD yield (wt\%)} = \frac{(ax \pm b) * V * 100 \text{ (mg)}}{m \text{ (mg)}}$$

$$\text{Lignin residue yield (wt\%)} = \frac{(m - m1) * 100}{m1}$$

*m (mg) is the starting material mass; m1 (mg) is the dried lignin residue.

File S6 Hansen solubility parameters

The solubility of lignin to mixture solvents is also related to dispersion force (δ_d), polar interactions (δ_p) and hydrogen bonding (δ_h), expressed as follows: $\delta = \delta_d^2 + \delta_p^2 + \delta_h^2$.⁵⁻⁷ It was suggested in the literature that good solvents for lignin substrates have δ values that are close to 22.5 MPa^{1/2}. This was one of the reasons motivating the selection of the aforementioned solvent mixtures. The solvent mixtures showed a better dissolution performance than pure constituents. It can be seen

that increasing the water fraction of *i*-PrOH led to higher solubility. The reason is likely due to an increased formation of hydrogen bonds between the hydrates and lignin in mixtures. Generally, polymers such as lignin exhibit a maximum solubility in solvents with a δ -value close to their own. In addition, the lignin dissolving property increases as the hydrogen bonding capacity of the solvent increases when it is an optimal δ -value. The properties of solvents calculated are referred from Hansen solubility parameters (Table S6). The δ value of *i*-PrOH/water is near to IAL resulted in less char formation and higher SD oil yield.

Table S6. Hansen Solubility Parameters for Solvent Mixtures and KL Used

Entry	Alcohol with 30% water/KL	δ_d	δ_p	δ_h	δ
1	MeOH	15.22	13.41	28.3	34.82
2	EtOH	15.71	10.96	26.27	32.51
3	<i>n</i> -PrOH	15.85	9.56	24.87	31.00
4	<i>i</i> -PrOH	15.71	9.07	24.17	30.22
5	IAL	16.7	13.7	11.7	24.6

File S7 Different *i*-PrOH to water ratios effect

Table S7. Different Volumetric Ratios of *i*-PrOH and Water in IAL Depolymerization^a

Entry	Co-solvent ratio	SD oil yield (wt%) ^b	Lignin residue (wt%) ^c	Char (wt%) ^c
1	<i>i</i> -PrOH	56	/	38.6
2	<i>i</i> -PrOH/H ₂ O (7:3)	36.3	62.4	/
3	<i>i</i> -PrOH/H ₂ O (5:5)	20.5	78.3	negligible
4	<i>i</i> -PrOH/H ₂ O (3:7)	9.0	69.7	20.8 (unreacted)
5	H ₂ O	trace	20-30 (recovered by acetone)	70-80

^aReaction conditions: IAL (1.2 g), 200 mL of *i*-PrOH/H₂O (v/v), and 1500 rpm at 220 °C for 48 h.

^bExtracted with PE (40-60 °C).

^cAfter 24 hours drying in 105 °C.

Reference

- (1) Sevastyanova, O.; Helander, M.; Chowdhury, S.; Lange, H.; Wedin, H.; Zhang, L.; Ek, M.; Kadla, J. F.; Crestini, C.; Lindström, M. E. Tailoring the Molecular and Thermo-Mechanical Properties of Kraft Lignin by Ultrafiltration. *J. Appl. Polym. Sci.* **2014**, *131* (18), 9505–9515. <https://doi.org/10.1002/app.40799>.
- (2) Jiang, Z.; Zhang, H.; He, T.; Lv, X.; Yi, J.; Li, J.; Hu, C. Understanding the Cleavage of Inter- and Intramolecular Linkages in Corncob Residue for Utilization of Lignin to Produce Monophenols. *Green Chem.* **2016**, *18* (14), 4109–4115. <https://doi.org/10.1039/c6gc00798h>.
- (3) Bokhary, A.; Leitch, M.; Liao, B. Q. Liquid–Liquid Extraction Technology for Resource Recovery: Applications, Potential, and Perspectives. *J. Water Process Eng.* **2021**, *40* (October 2020), 101762. <https://doi.org/10.1016/j.jwpe.2020.101762>.
- (4) Ajao, O.; Benali, M.; El Mehdi, N. Experimental and Computer Aided Solubility Quantification of Diverse Lignins and Performance Prediction. *Chem. Commun.* **2021**, *57* (14), 1782–1785. <https://doi.org/10.1039/d0cc04228e>.
- (5) 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. <https://doi.org/10.1021/acs.iecr.9b00875>.
- (6) Kouris, P. D.; Van Osch, D. J. G. P.; Cremers, G. J. W.; Boot, M. D.; Hensen, E. J. M. Mild Thermolytic Solvolysis of Technical Lignins in Polar Organic Solvents to a Crude Lignin Oil. *Sustainable Energy Fuels* **2020**, *4*, 6212–6226. <https://doi.org/10.1039/d0se01016b>.
- (7) Hansen, C. M.; Björkman, A. The Ultrastructure of Wood from a Solubility Parameter Point of View. *Holzforschung* **1998**, *52*, 335–344. <https://doi.org/10.1515/hfsg.1998.52.4.335>.