Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information

OrganoSoxhlet: circular fractionation to produce pulp for textiles using CO_2 as acid source

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Contents

1. General consideration

All chemicals were purchased from Fischer chemicals, CCS Healthcare AB Sweden, Sigma-Aldrich, Honeywell, and VWR chemicals, and used as received. The Biomass feedstock Poplar "23.4" clone was used for the pulping experiments and was obtained from the Swedish University of Agricultural Sciences, Uppsala, Sweden. Sugar analysis was quantified by ^{1}H NMR recorded on a Bruker Advance (400 MHz) as a solution in D_2O. Chemical shifts are expressed in parts per million (ppm, δ). GC-MS and GC-FID analyses were conducted by a QP2020 system (SHIMADZU, Japan) equipped with two parallel HP-5MS columns (30 m × 0.25 mm × 0.25 µm). GPC analysis was performed on a Prominence-i, LC-2030C system (SHIMADZU, Japan) equipped with a UV detector at 280 nm. The IKA T-25 digital ULTRA-TURRAX® homogenizer was used for the pulp disintegration.

2. Substrate

The average composition of the wood meal consists of 43.2 wt% of glucans, 12.4 wt% of xylans, and 25.1 wt% of Klason lignin (AIL+ASL) with an S:G ratio of 1.6 and a β–O–4' content of 51%. Extractives accounted for 4.4 wt% while ashes residues 0.6 wt%. The biomass was dried overnight at 60 °C before being treated.

Figure S1 wood sawdust (left), wood sticks (centre) and wood chips (right) from Polar 23.4 clone.

3. OrganoSoxhlet reactor

The reactor consists of a 600 mL autoclave equipped with a gas valve, a thermocouple, and a cooling coil (Figure S2). The gas valve allows the loading of the reactor with positive pressure at room temperature. Inside the autoclave, two cups made of acid-resisting stainless steel are positioned one on top of each other: a collecting cup and on top of it an extraction cup equipped with a siphon that unloads directly into the collecting cup. The substrate, wrapped in a stainless-steel net with a mesh of 0.25 mm or in a cotton fabric cloth, is positioned in the extracting cup which finds space just below the cooling coil to let the drops produced by the condensation of the vapours drip directly on the substrate. Directly on the substrate are poured 200 mL of solvent. Part of it is discharged, with the help of the siphon, into the collecting cup leaving a soaked substrate and a filled collecting cup in contact with the heat source. The extraction cup allows the thermocouple to pass through and measure the temperature of the liquid contained in the collecting cup. The positive pressure allows a higher boiling point of the solvent. The role of the steam is both to provide fresh solvent for the pulping and to heat the extraction cup. Once the level of the condensed solvent reaches the top of the siphon, it is discharged into the collecting cup.

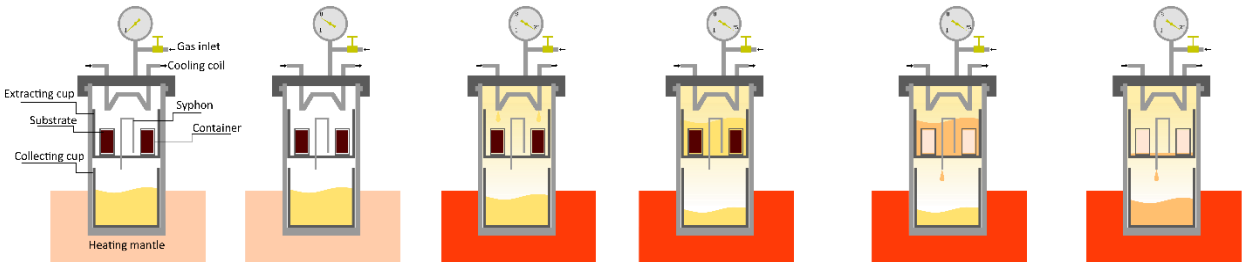


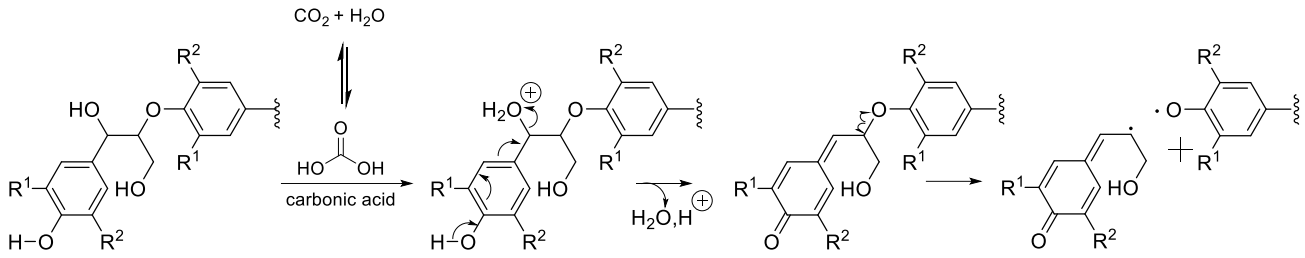
Figure S2 OrganoSoxhlet cycle.

Figure S3 Pictures of the reactor system. a) picture of the assembled reactor; b) heating unit; c) reactor head bearing the pressure valve, pressure gauge, burst valve, cooling coil, and thermowell; d) 600 mL reactor vessel and reactor head showing the PTFE white gasket; e) EC showing the syphon and the substrate wrapped in steel net; f) reactor head positioned on top of EC and CC simulating the assembled reactor.

4. General pulping procedure

Dry sawdust from poplar 23.4 was chosen as the initial substrate for its high surface area to weight ratio and consequently an expected higher reactivity, and higher density when compared to wood sticks or chips (Figure S1). The optimization reactions were performed on 5 g of wood sawdust as substrate. To optimize the pulping yields, the effect of the gas, water content, pulping time, and cooling flow rate were studied. In addition, different forms of the starting material were investigated to achieve dissolving grade quality pulp. The substrate was wrapped in a porous container made of either stainless steel net or cotton cloth, flushed with compressed air to remove the particles small enough to pass through the containers, and finally weighted. The containers filled with the substrate were positioned in the extraction cup. The solvent, 200 mL, was poured directly on the dry substrate to have it impregnated with solvent since the beginning of the reaction. The reactor was then closed and the atmosphere adjusted to proper pressure and composition, usually 8 barg of CO_2. The cooling system (cold tap water) was set to 1 L/min and the temperature was raised to 220 °C. After the appropriate amount of time, the reaction was stopped by removing the heating source and, once at room temperature, the reactor was vented and opened. The reacted substrate was removed from the extracting cup, washed with acetone, and dried. The mass loss of both the substrate and the containers was measured by weighing. The solid residue was then analysed to determine the amount of Klason lignin (ASL+AIL) and the sugar composition, i.e. glucose and xylose. As the aim of this study was to obtain dissolving grade quality pulp, we monitored the partial hydrolysis of cellulose using containers made of cotton cloth; only the experiments where the weight of the fabric clothes remained constant after the treatment were accepted and reported. In the case of RCF, 900 mg of Pd/C 5 wt% was added to the previously reported reaction conditions.

In the case of batch reactions 400 mg of Poplar 23.4 were reacted with 15 mL of H_2O:EtOH 3:1, in presence of CO_2 (8 barg) at 220 °C for 4 h. In the case of batch RCF, 70 mg of Pd/C 5 wt% was added to the previously reported reaction conditions.



Scheme S1 Proposed depolymerization pathway in presence of CO_2.

5. Pulping optimization

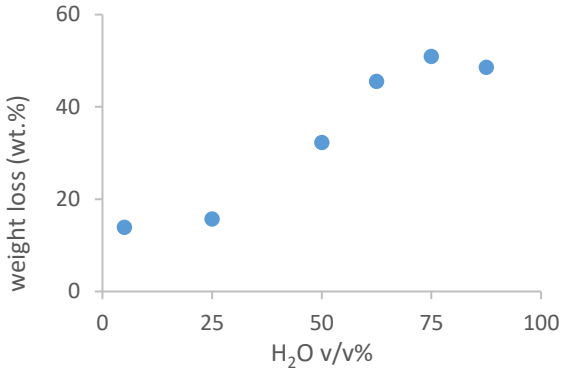


Figure S4 Mass loss versus solvent composition. Reaction conditions CO_2 (8 barg), substrate (poplar 23.4 sawdust 5 g), EtOH:H_2O 1:3 (200 mL), reaction time 4 h.

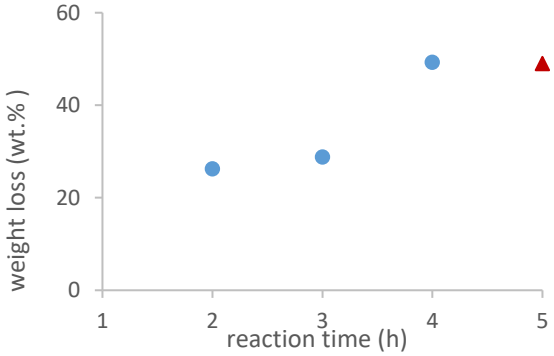


Figure S5 Mass loss versus reaction time. Reaction conditions CO_2 (8 barg), substrate (poplar 23.4 sawdust 5 g), EtOH:H_2O 1:3 (200 mL). The triangular dot represents a high degradation of fabric cloth (14 wt% mass loss).

Figure S6 Wrapping containers made of cotton fabric after reaction in optimized conditions (left) and the case of carbonisation, mass loss >10 wt% (right).

Figure S7 Poplar sawdust (left) after reaction in optimized conditions (centre) and the case of partial carbonization (right).

6. Reaction temperature and pressure over time

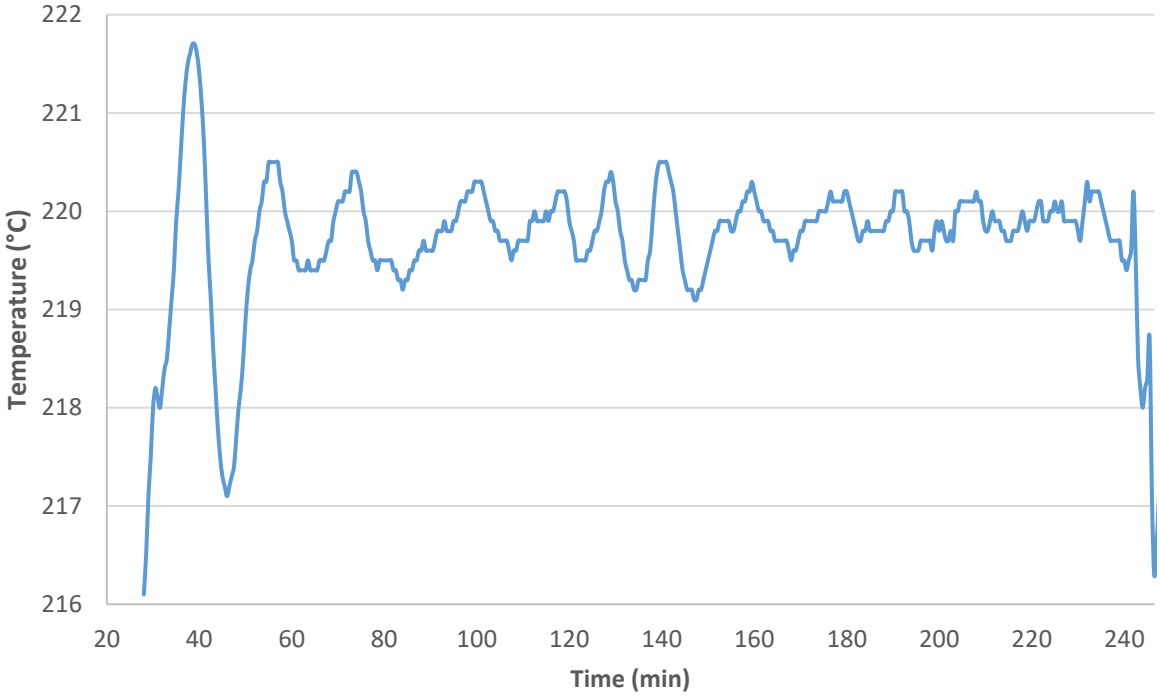


Figure S8 Reaction temperature measured in the CC over time showing 12 cycles. Sampling each 30 s. Reported T> 216 °C.

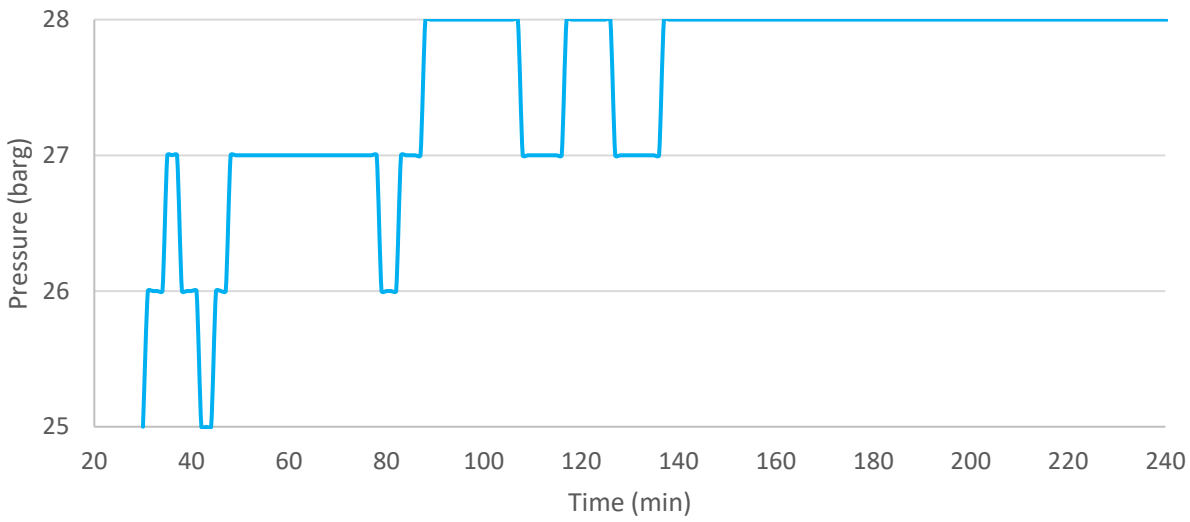


Figure S9 Reaction pressure measured in the reactor over time. Sampling each 60 s. Reported p> 25 barg.

7. Solvent recycling

The recycling study was performed by reacting different batches of wood using the same solvent. The reacted wood was removed from the reactors and weighed before and after drying to evaluate the amount of solvent left impregnated in the biomass. Approximately 20 mL of EtOH:H_2O 1:1 was added after each run to compensate for it.

Table S1 Solvent recycling study.

Entry	Mass loss [wt%]	Loading [g]	Lignin [wt%]	Glucose [wt%]	Xylose [wt%]	
1	48.3	9.7	4	94	2	control
2	48.2	10.2	4	94	2	I cycle
3	49.1	10.5	4	90	2	II cycle
4	47.1	11.4	6	89	4	III cycle

Reaction conditions: 220 °C, 4 h, cooling flow 1 L/min, 200 ml of EtOH: H_2O 1:3, 8 barg of CO_2 at RT.

8. Lignin oil isolation

The liquors collected in the collecting cup were merged with the liquid remaining in the extracting cup, filtrated over filter paper to determine the coking, and dried under vacuum to eliminate the solvents. The resulting lignin-containing oil was weighted and further analysed. For the batch reactions, the liquors were filtered through celite, collected and extracted with DCM, and dried with anhydrous $NaSO_4$. The solvent was removed under vacuum and the resulting lignin oil was weighted and further analysed.

9. GC-MS/FID analysis

The lignin oil was solubilized in 200 mL of EtOAc. 1 mL of the liquor was merged with 50 µL of dodecane (10.0 g/L solution) as internal standard and subjected to lignin monomer analysis by GC-MS/FID conducted on a QP2020 system (SHIMADZU, Japan) equipped with two parallel HP-5MS columns (30 m × 0.25 mm × 0.25 µm). Initial oven temperature 60 °C then as reported in Table S2, injector temperature 280 °C, injected volume 1 µL, carrier gas pressure 115.5 kPa, total flow 19.0 mL/min, column flow 1.46 mL/min, split ratio 1:10.0. No furans fragments (searched by fragmentation table 66.01 m/z) were found in any of the GC-MS chromatograms.

Table S2 GC oven temperature ramp.

Step	Rate (°C/min)	Final Temperature (°C)	Hold Time (min)
1		60.0	2.00
2	15.00	270.0	5.00
3	5.00	300.0	10.00

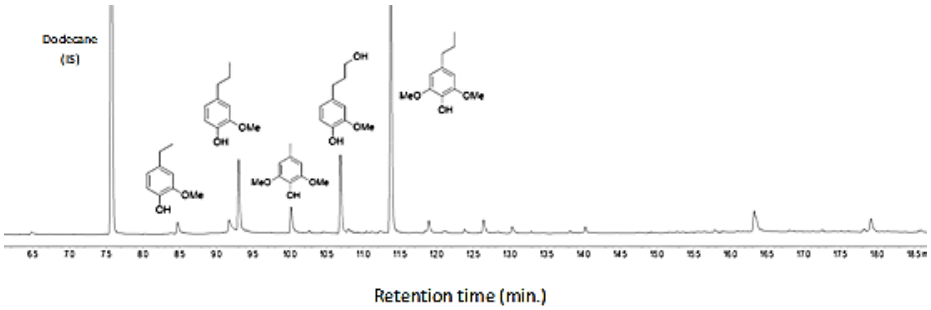
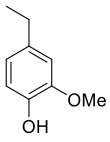
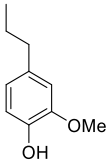
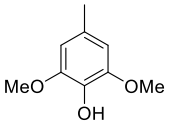
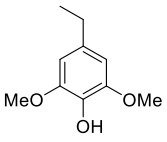
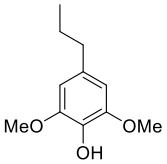


Figure S10 GC-FID chromatogram of upgraded lignin oil.

Table S3 Monophenolic distribution of upgraded lignin oil versus the initial amount of lignin.

						Sum
monophenols vs lignin [wt%]	0.6	1.5	0.5	1.6	3.7	7.9

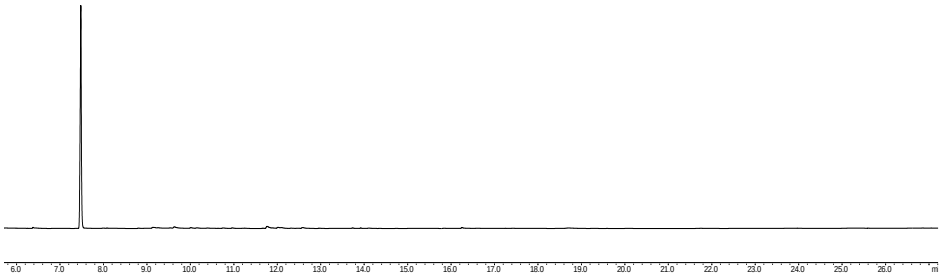


Figure S11 GC-FID chromatogram of lignin oil produced in batch showing only the peak produced by the IS (dodecane).

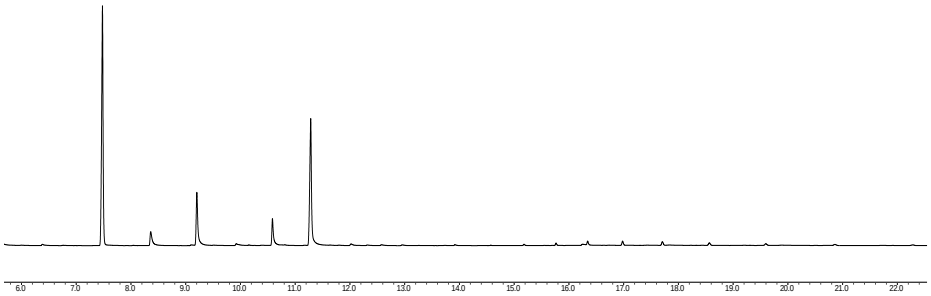
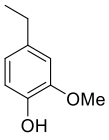
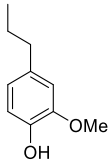
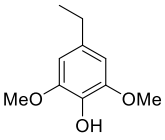
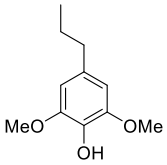


Figure S12 GC-FID chromatogram of upgraded lignin oil produced in batch.

Table S4 Monophenolic distribution of upgraded lignin oil in batch.

					Sum
monophenols vs lignin [wt%]	1.2	3.7	2.4	10.3	17.6

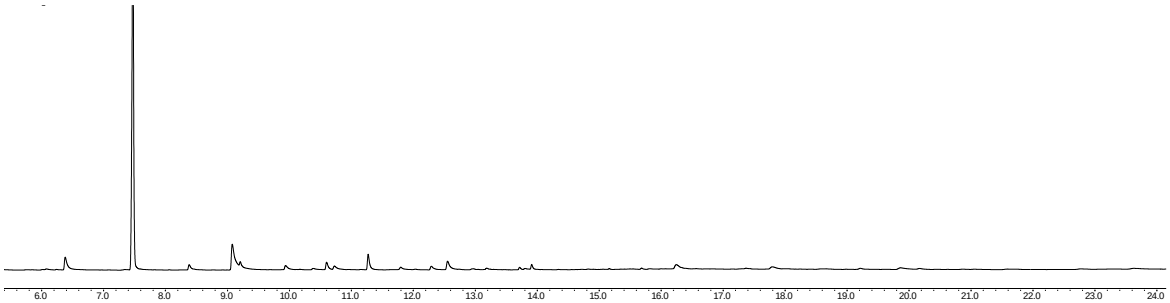


Figure S13 GC-FID chromatogram of upgraded lignin oil produced by reacting OrganoSoxhlet lignin oil with Pd in batch. Reaction conditions: 0.5 g lignin oil, 70 mg Pd/C, 15 mL (H_2O:EtOH/3:1), CO_2 (8 barg), 220°C, 4h

Table S5 Monophenolic distribution of upgraded lignin oil produced by reacting OrganoSoxhlet lignin oil with Pd in batch versus the initial amount of lignin.

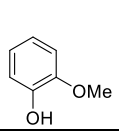
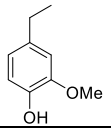
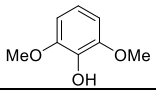
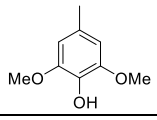
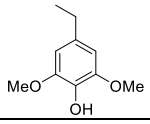
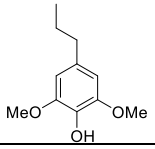
							Sum
Monophenols vs lignin [wt%]	0.2	0.1	0.6	0.1	0.1	0.1	1.2

Table S2 Contribution of Effective Carbon Number (ECN).[1]

Atom/Group	ECN contribution
Oxygen/Ether	-1
Oxygen/Phenol	-1
Carbon/Aromatic	1
Carbon/Aliphatic	1

Lignin monomer yield was calculated according to a previously reported procedure.[2] Integrated peak area of each monomer, internal standard, and effective carbon number were taken into consideration for calculation. Use Eq.[1-3] to calculate the yield of each monomer.

$$N_{monomer} = \frac{A_{monomer}}{A_{dodecane}} \times n_{dodecane} \times \frac{ECN_{dodecane}}{ECN_{monomer}} \quad \text{[Eq.1]}$$

$$m_{monomer} = n_{monomer} \times MW_{monomer} \quad \text{[Eq.2]}$$

$$Yield_{monomer} = \frac{m_{monomer}}{m_{biomass} \times \text{Klason lignin content (AIL)} \times \text{moisture content}} \times 100\% \quad \text{[Eq.3]}$$

n (moles), A (integrated area of the peak), ECN (effective carbon number), MW (molecular weight), and m (mass).

10. GPC analysis

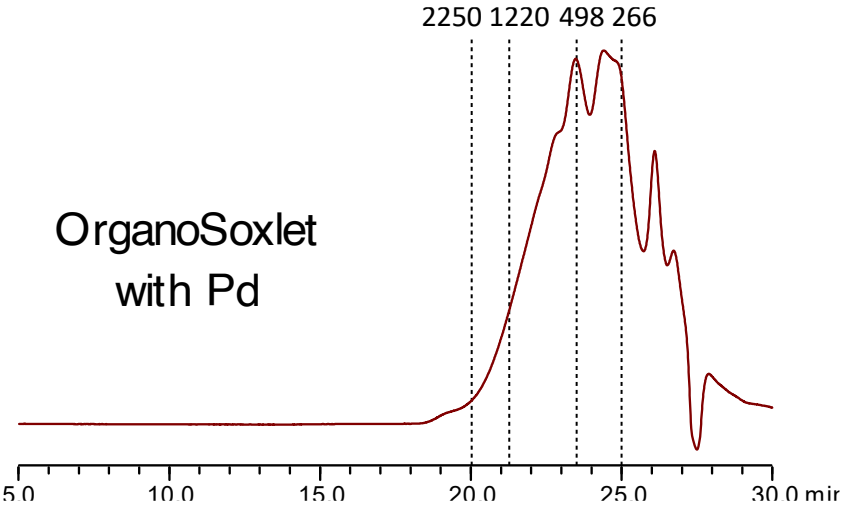


Figure S14 GPC chromatogram of upgraded lignin oil produced by OrganoSoxhlet procedure.

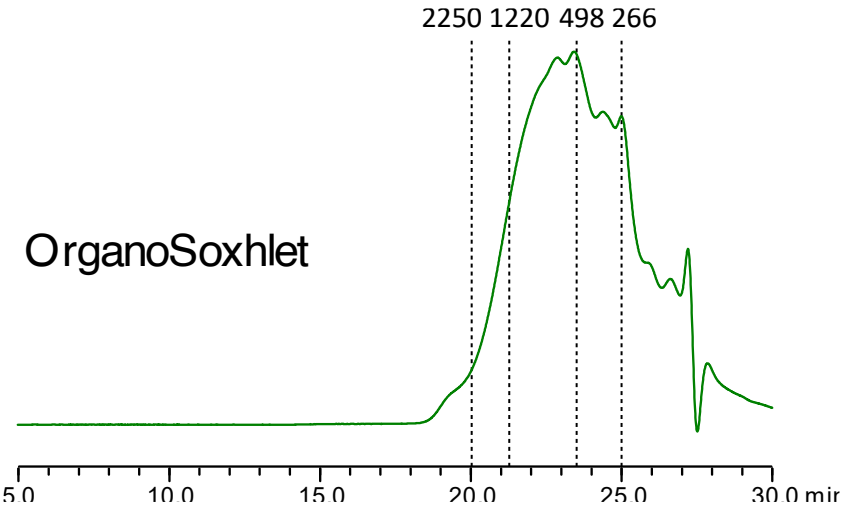


Figure S15 GPC chromatogram of lignin oil produced by OrganoSoxhlet procedure.

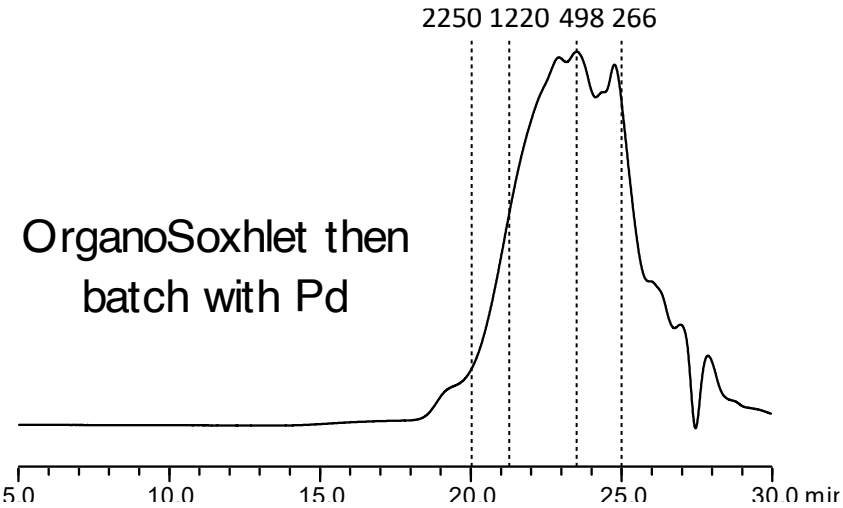


Figure S16 GPC chromatogram of upgraded lignin oil produced by reacting OrganoSoxhlet lignin oil with Pd in batch.

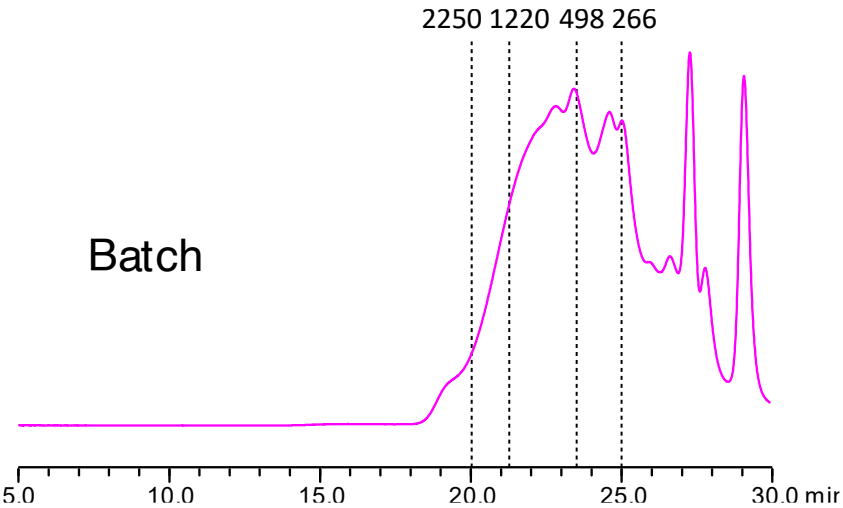


Figure S17 GPC chromatogram of lignin oil produced by the batch procedure.

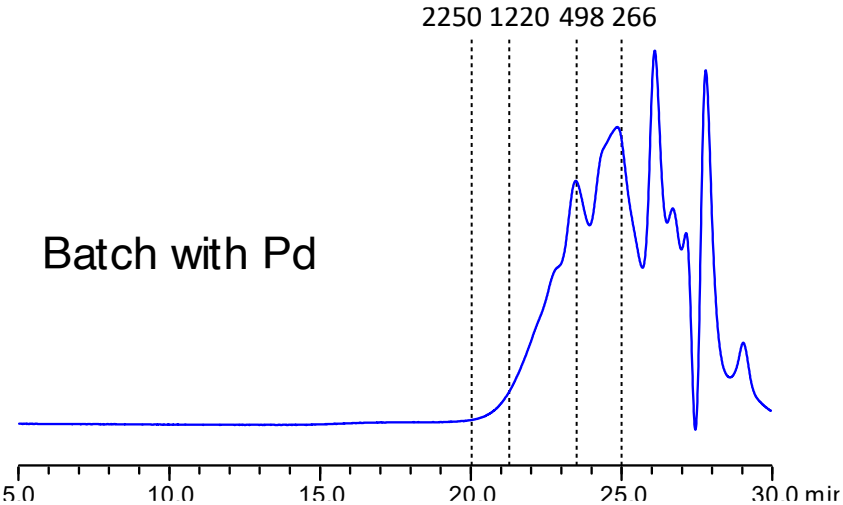


Figure S18 GPC chromatogram of upgraded lignin oil produced by the batch procedure.

11. NMR analysis

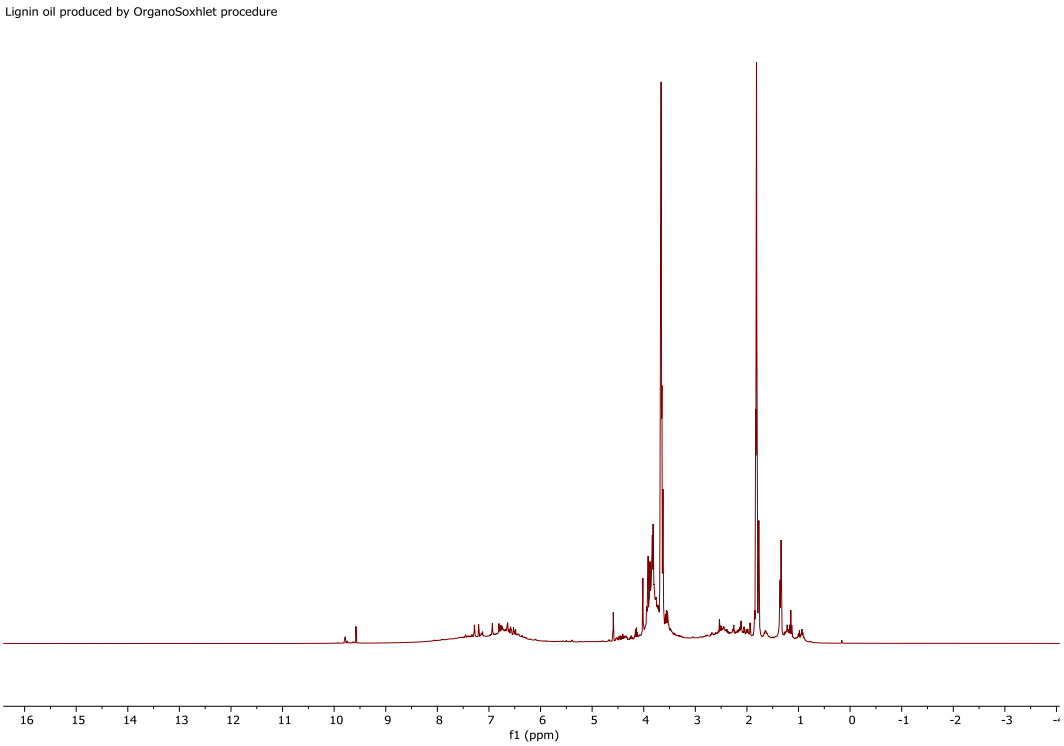


Figure S19 ^{1}H NMR spectrum of lignin oil produced by OrganoSoxhlet procedure.

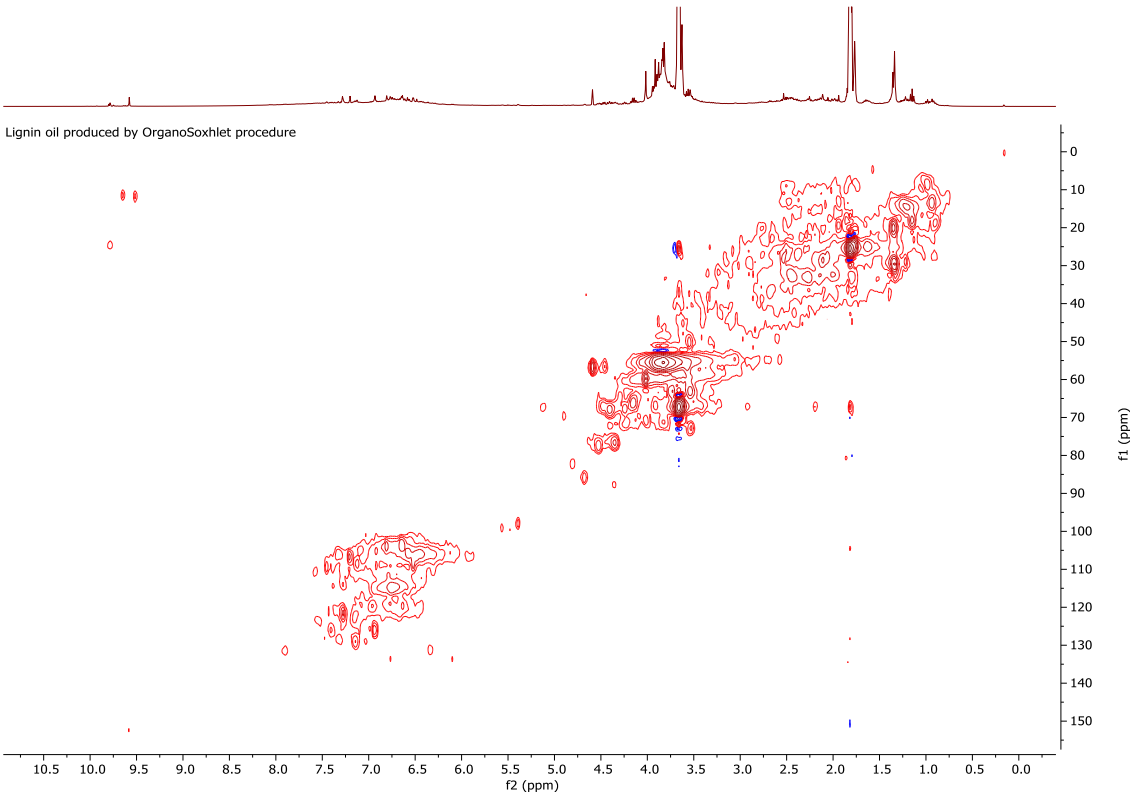


Figure S20 ^{1}H ^{13}C HSQC NMR spectrum of lignin oil produced by OrganoSoxhlet procedure.

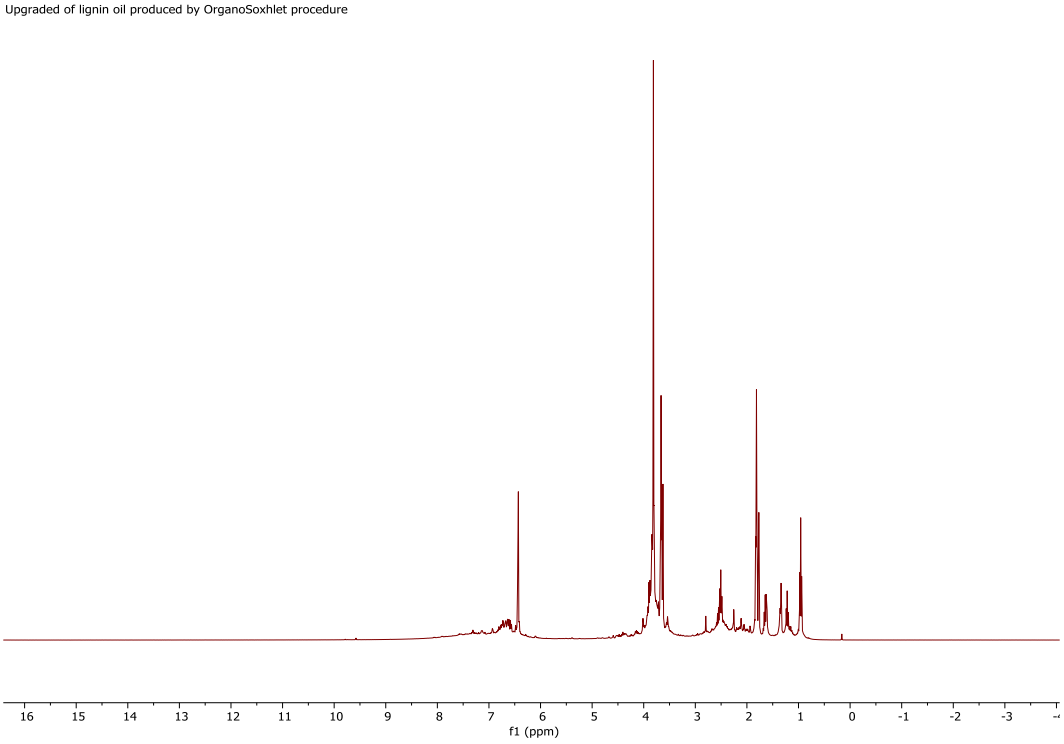


Figure S21 ^{1}H NMR spectrum of upgraded lignin oil produced by OrganoSoxhlet procedure.

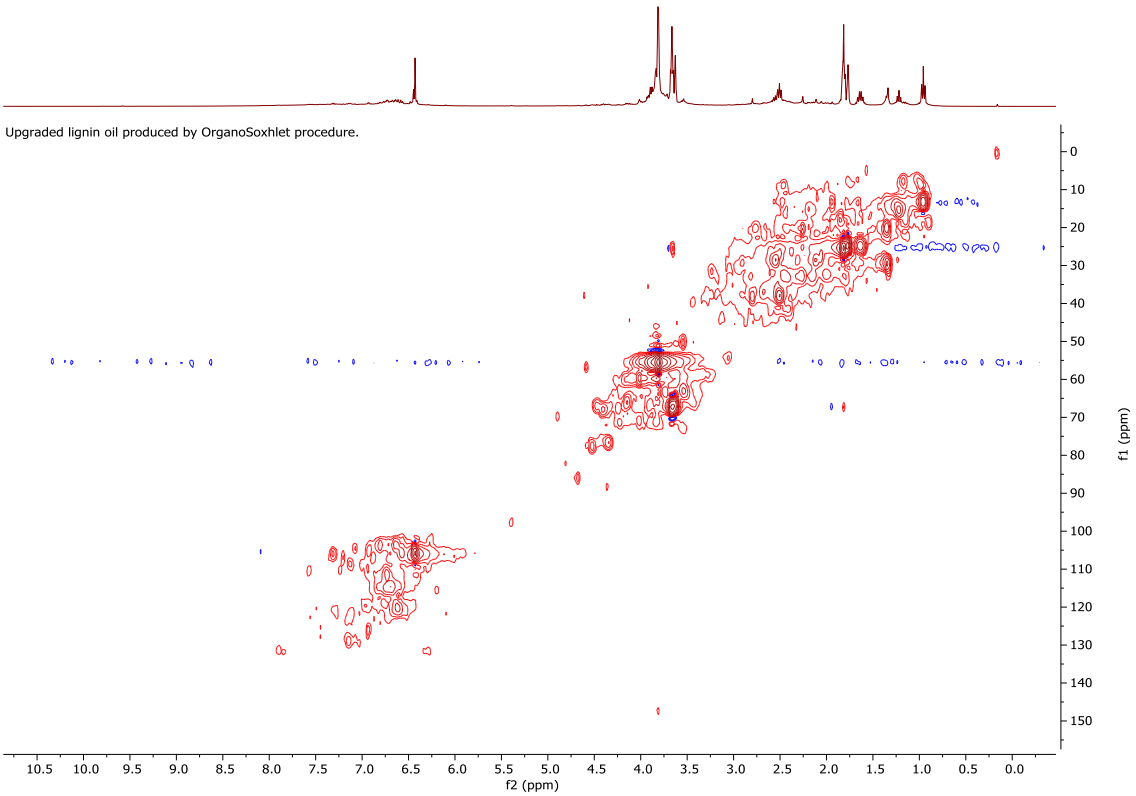


Figure 22 ^{1}H ^{13}C HSQC NMR spectrum of upgraded lignin oil produced by OrganoSoxhlet procedure.

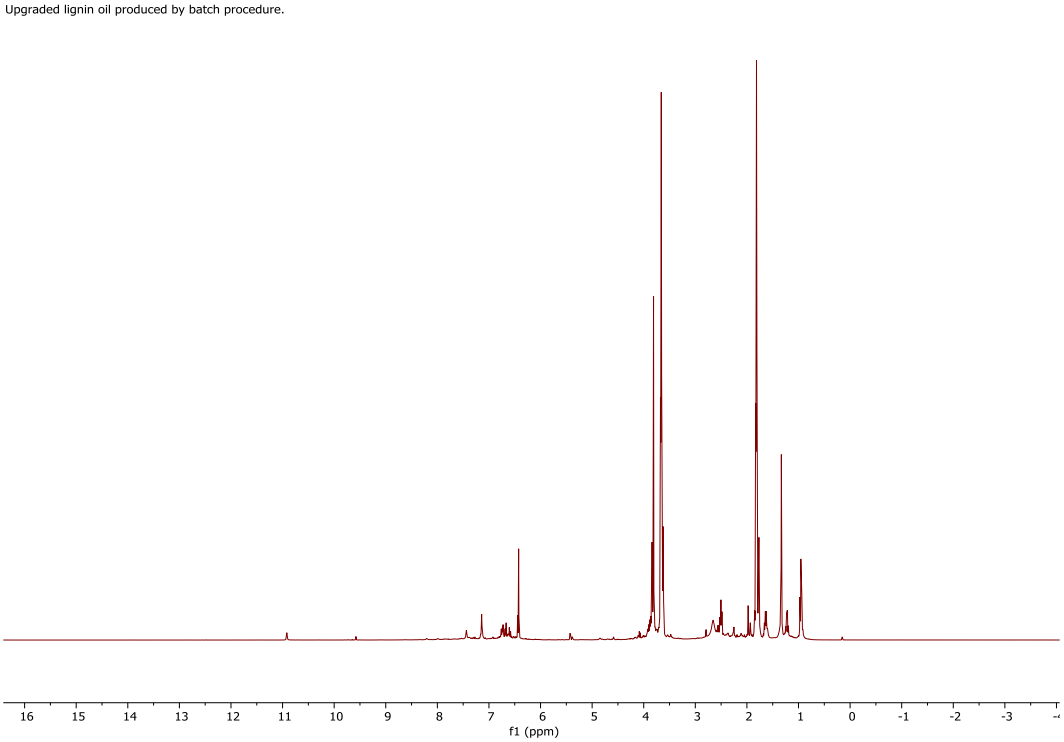


Figure S23 ^{1}H NMR spectrum of upgraded lignin oil produced by the batch procedure.

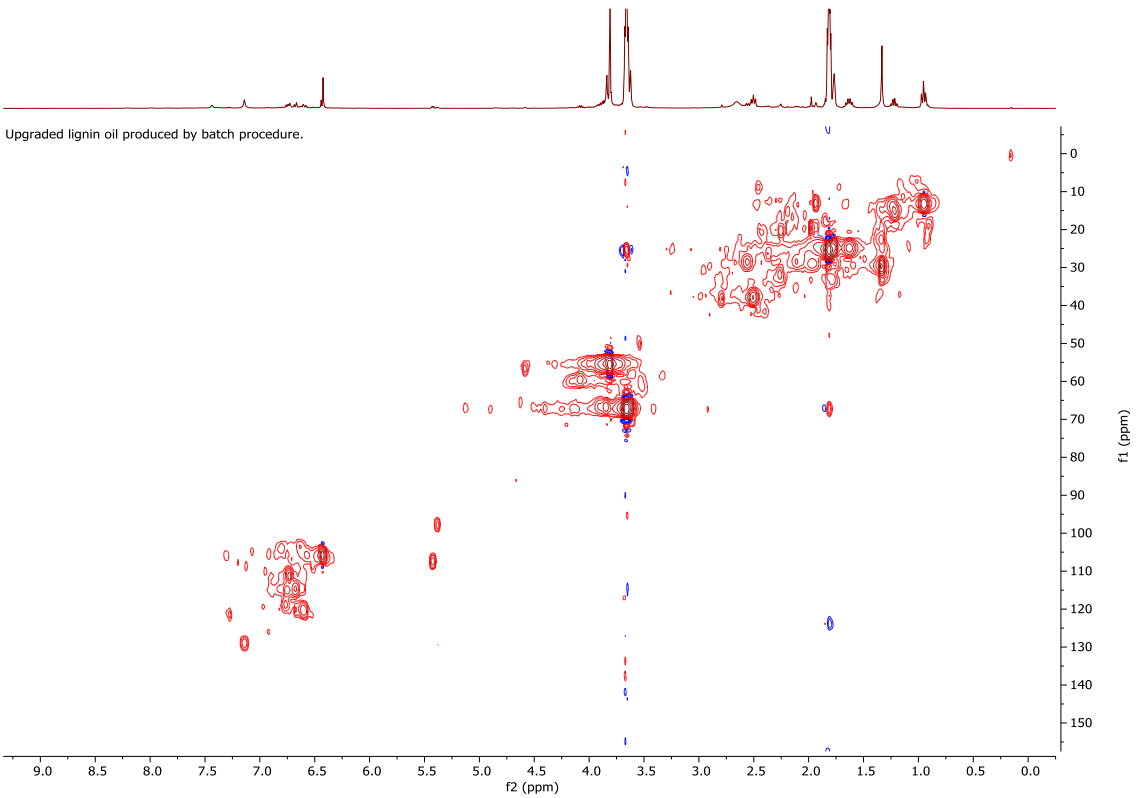


Figure S24 ^{1}H ^{13}C HSQC NMR spectrum of upgraded lignin oil produced by the batch procedure.

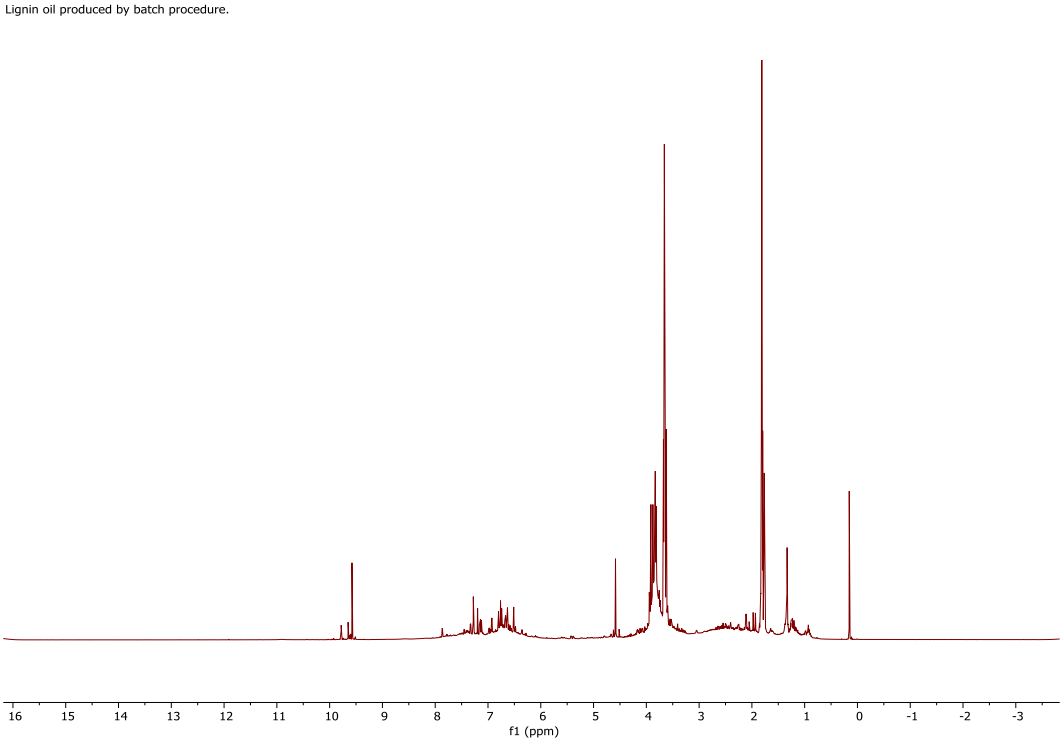


Figure S25 ^{1}H NMR spectrum of lignin oil produced by the batch procedure.

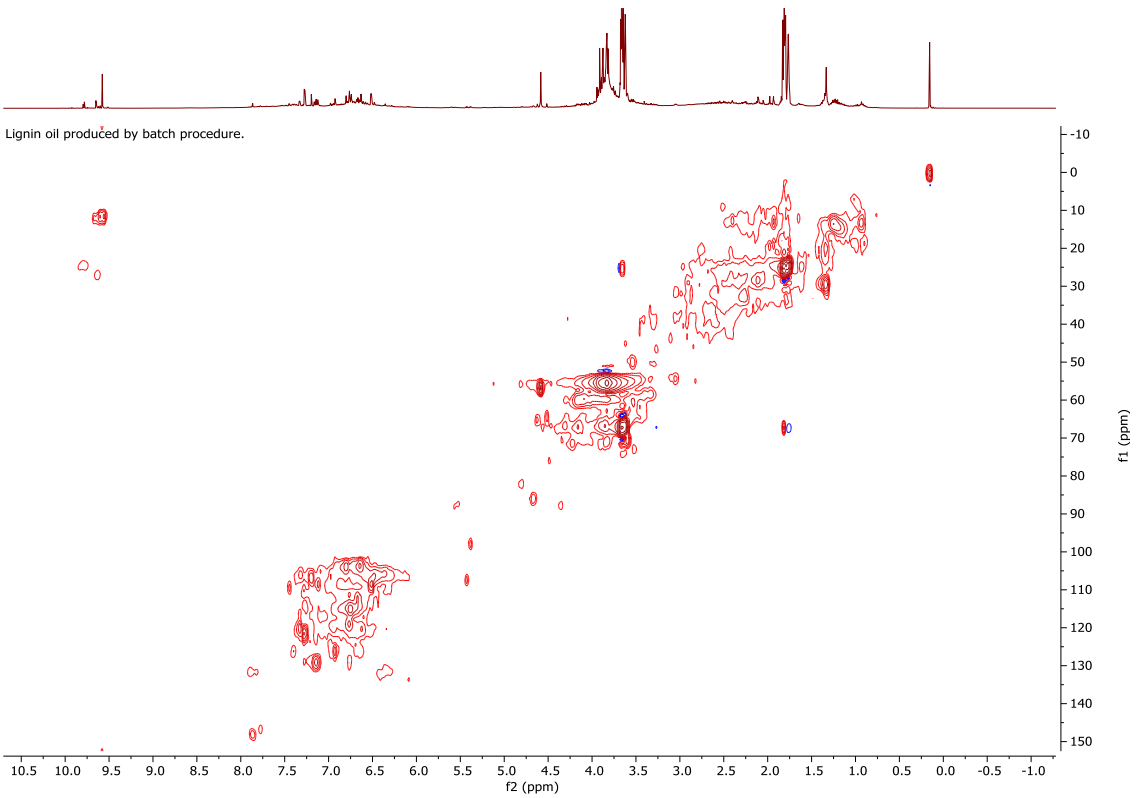


Figure S26 ^{1}H ^{13}C HSQC NMR spectrum of lignin oil produced by the batch procedure.

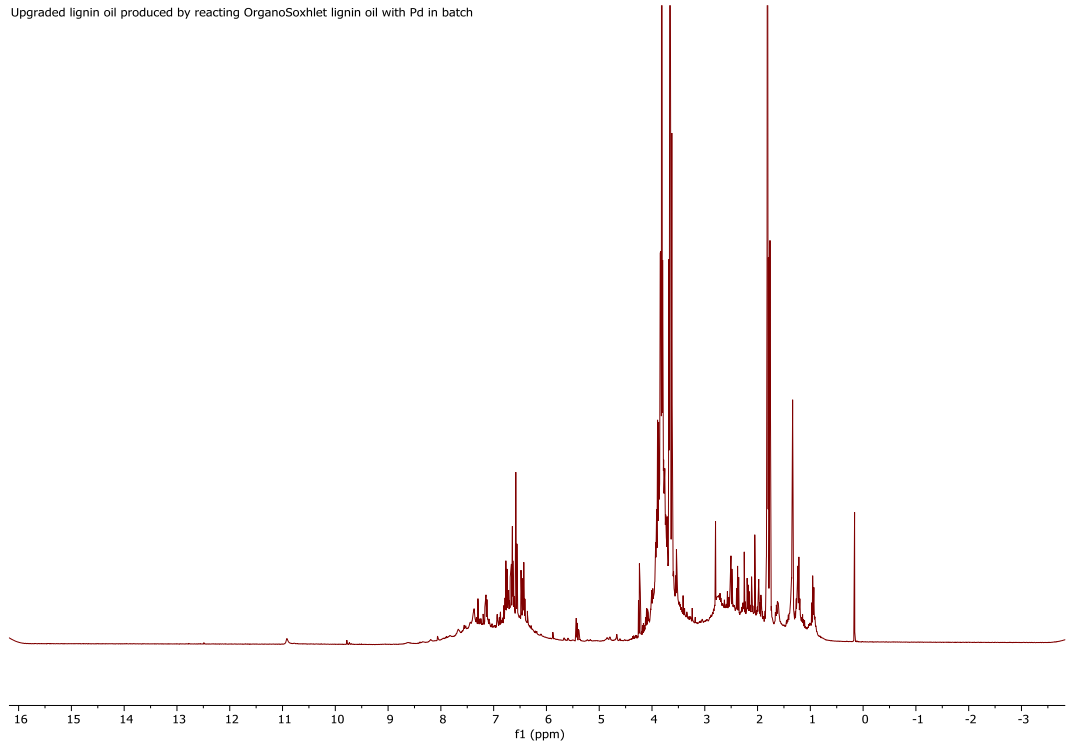


Figure S27 ^{1}H NMR spectrum of upgraded lignin oil produced by reacting OrganoSoxhlet lignin oil with Pd in batch.

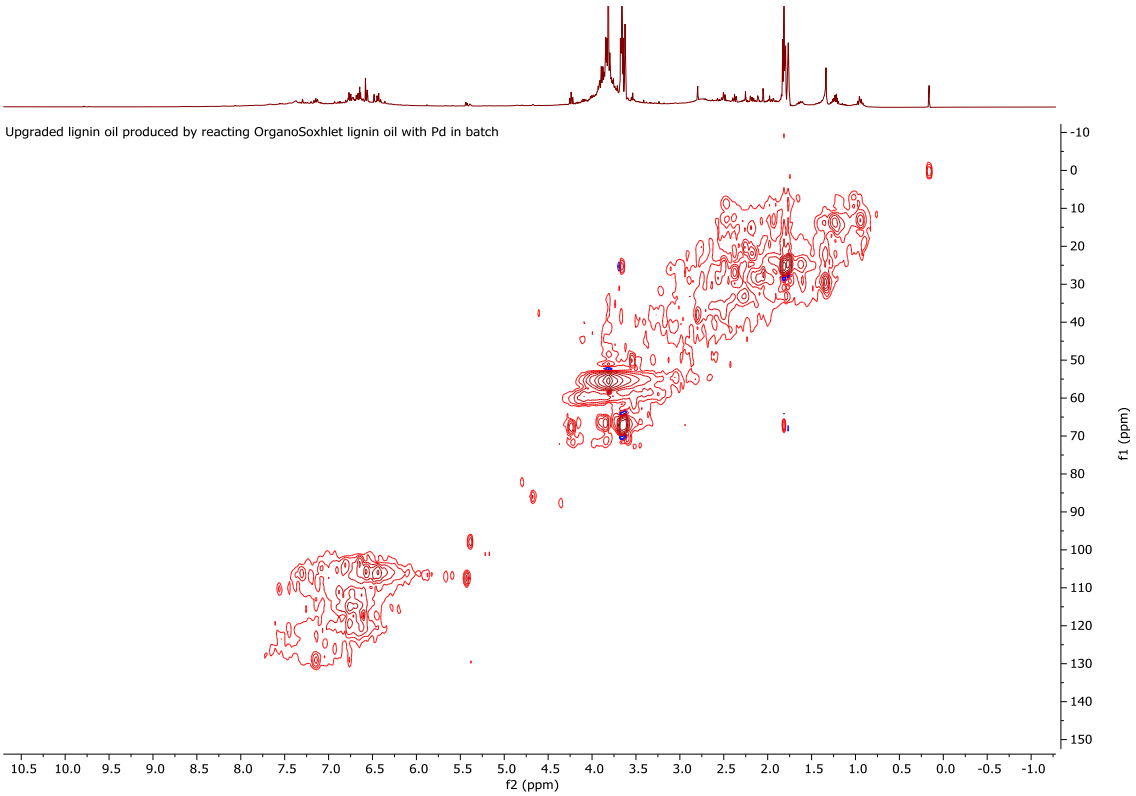


Figure S28 ^{1}H ^{13}C HSQC NMR spectrum of upgraded lignin oil produced by reacting OrganoSoxhlet lignin oil with Pd in batch.

12. Chemical composition of biomass by two-steps acid hydrolysis

A slightly modified procedure from the standard protocol from NREL (Determination of Structural Carbohydrates and Lignin in Biomass) was performed.[3] 300 mg of biomass was transferred into a 100 mL pressure bottle. 3 mL of H_2SO_4 72 wt% was added dropwise over biomass. The pressure bottle was shaken in an incubator at 30 °C for 1 h. The acid concentration was adjusted to 4% by adding 84 mL deionized water. The bottle was placed in an autoclave at 120 °C for 1 h. After the completion of the reaction, the mixture was cooled in an ice bath. The solid residues were recovered through filtration by the means of a pre-weighed filter paper and 20 mL of the aqueous solution was collected into a vial for acid-soluble lignin analysis. The solid residues were rinsed with water and dried overnight at 60 °C. The weight was reported as acid-insoluble lignin (AIL). For acid-soluble lignin (ASL) content analysis, 1 mL of the previously collected aqueous solution was taken and diluted in 4 mL distilled water. The resulting solution was analysed by UV-vis spectrophotometer at λ_{max} = 240 nm to obtain UV absorbance, which was applied in the calculation [Eq. 4] to get ASL content. Ash content was determined by placing 200.00 mg of biomass in a pre-weighed crucible and treating it in a furnace at 575 °C for 6 h. After completion, the ash content was measured by gravimetric analysis.

Acid-soluble lignin (ASL) content calculation:

$$\%\ ASL = \frac{\mathbf{UV_{abs}} \times \mathbf{Volume}_{\mathbf{filtrate}} \times \mathbf{Dilution}}{\boldsymbol{\varepsilon} \times \mathbf{m}_{\mathbf{biomass}} \times \mathbf{Pathlength}} \times 100\% \qquad \text{[Eq.4]}$$

Where: $\mathbf{UV_{abs}}$ = UV absorbance measured at λ = 240 nm, $\mathbf{Volume}_{\mathbf{filtrate}}$ = 87.0 mL, **Dilution** = 5, **ε** = Absorptivity of biomass at specific wavelength = 25, $\mathbf{m}_{\mathbf{biomass}}$ = Oven dried weight of biomass, **Pathlength** = 1 cm.

13. Sugar content of biomass and pulp by NMR

The hydrolysis procedure is similar to the above mentioned, where deuterated solvents were used instead of H_2O and H_2SO_4, and the scale was reduced by 10 times. 30.0 mg of biomass was placed in a microwave vial. 0.3 mL of D_2SO_4/D_2O 72 wt% was added to the biomass. The reaction was performed at 30 °C for 1 h. 9 mL of D_2O was added afterward and the temperature was adjusted to 120 °C for 1 h. After completion, the reaction mixture was cooled in an ice bath. 0.2 mL of dimethyl malonic acid (20.0 mg/mL solution) was added to the reaction mixture as the internal standard. 1 mL of the resulting reaction mixture was filtered, and subjected to NMR (Bruker Advance 400 MHz, ^{1}H NMR, D_2O, 256 scans, 6 s delay). Monomeric sugars were quantified with respect to the ratio of known concentration of the internal standard (dimethyl malonic acid). The signals of alpha ($\delta_{H\text{-}\alpha}$) and beta protons ($\delta_{H\text{-}\beta}$) of both glucose and xylose were integrated $\delta_{H\text{-}\beta}$ 4.97 (d, *J* = 3.8 Hz, 1H)/ $\delta_{H\text{-}\alpha}$ 4.39 (d, *J* = 7.9 Hz, 1H) and $\delta_{H\text{-}\beta}$ 4.93 (d, *J* = 3.7 Hz, 1H)/ $\delta_{H\text{-}\alpha}$ 4.32 (d, *J* = 7.9 Hz, 1H (Figure S29). Where internal standard protons signal was presented at δ_H 1.19 (s, 6H). Thus, the ratio signal of internal standard and monomeric sugars were obtained and monomeric sugar yield can be calculated.

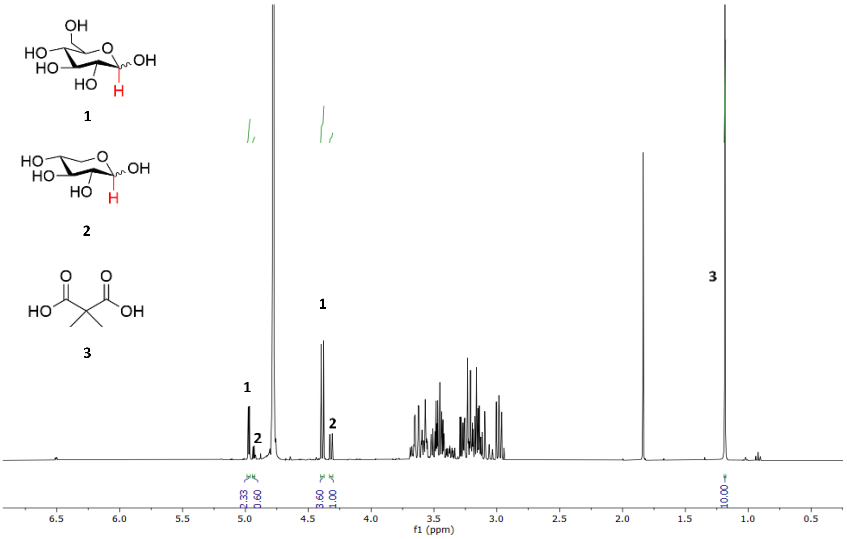


*Figure S29 ^{1}H NMR spectrum of sugars mixture (**1** and **2**) obtained after acid hydrolysis of biomass vs internal standard (**3**).*

14. β-O-4' content by thioacidolysis

The thioacidolysis solution was prepared by adding 20 mL of dioxane in a round-bottom flask followed by 2.5 mL of EtSH (97%) and 0.7 mL of $BF_3{\cdot}OEt_2$ (1.0 M in THF). The total volume was adjusted to 25 mL by the addition of 1.8 mL of dioxane. 40 mg of biomass was added into a 20 mL microwave vial followed by 4 mL of the thioacidolysis solution. The reaction was performed at 100 °C for 4 h. After completion, the mixture was cooled in an ice bath. Saturated $NaHCO_3$ was added to the reaction mixture followed by HCl 1M until pH <3 was reached. The mixture was extracted by DCM/brine. The organic fraction was dried using anhydrous Na_2SO_4 and filtered; then the solvent was removed under vacuum. 5 mL of EtOAc was used to dissolve the resulting crude. 0.5 mL of the crude solution and 0.1 mL tetracosane (5.0 mg/mL solution) as the internal standard were merged in a 10 mL vial. The solvent was then removed under vacuum. 0.1 mL of pyridine and 0.1 mL of BSTFA were added into the vial and the reaction mixture was kept at 60 °C for 30 min. After completion, the solution mixture was subjected to GC-MS/FID conducted by a QP2020 system (SHIMADZU, Japan) equipped with two parallel HP-5MS columns (30 m × 0.25 mm × 0.25 µm) and β-O-4' content was reported. The chromatogram from the GC-FID in Figure S30 shows G and S monomer base peaks at 17.7 and 18.5 min, respectively. The procedure and response factor of 1.44 and 1.51 for G and S derived monomer reported from literature was followed and applied in the calculation.[4]

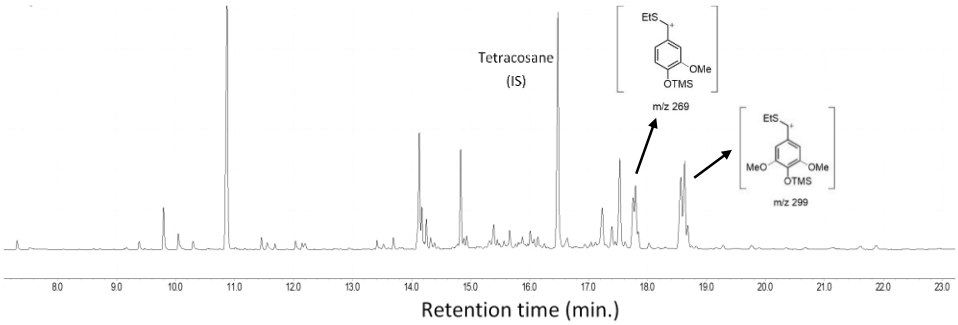


Figure S30 Chromatogram of lignin-derived thioacidolysis monomers from GC-FID.

15. Reacted wood disintegration

The obtained reacted wood sticks were washed with aqueous ethanol which was at the same concentration of ethanol as the original pulping liquor. The solvent washes were drained away and the wood material was transferred into a 2 L beaker which contains 1 L distilled water and was disintegrated into a homogeneous pulp by using T-25 digital ULTRA-TURRAX® Homogenizer with 20.4 X 1000 rpm for 15 min. The solvent was drained and the pulp was oven-dried to yield 44 wt% of unbleached pulp.

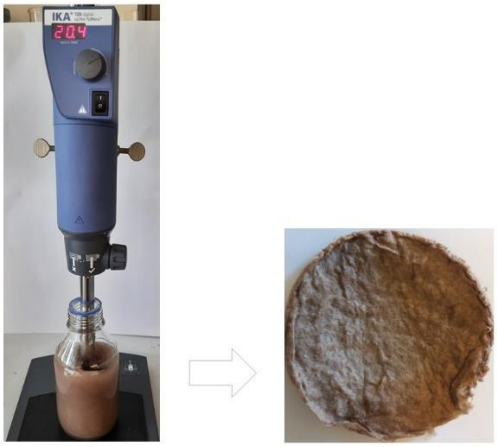


Figure S31 (a) Disintegration of cooked wood sticks; (b) Unbleached pulp.

16. Bleaching

The above poplar "23.4" pulp (10 g) was bleached with a 1:1 ratio of 1.7% aq. $NaClO_2$ and the mixture of 2.7% aq. NaOH, 7.5% acetic acid at 85 °C for 2h with 1 % pulp consistency.[5] The lignin was liberated from the brown pulp under these conditions and the pulp turned into white pulp after single-stage bleaching. The obtained pulp was vacuum filtered and washed with distilled water three times (500 mL water in each wash). Finally, the bleached pulp was dried at room temperature for 2 days and stored in a sealed cover for further analysis.

17. Preparation of pulp sheet

The bleached pulp was used for making a pulp sheet by vacuum filtration of 800 ml of 0.5% suspension over Whatman filter paper (Pore size number 3mm and 90 mm diameter) at 1.0 bar. The cellulose cake was placed between Whatman filter papers under 30 N load at room temperature for 30min. This process was repeated with fresh Whatman filter papers until the cellulose filter cake became dry. The cake was allowed to dry at room temperature for a day. In the end, a 50 N load was applied to it for 2 days to keep the pulp sheet wrinkle-free. Finally, the obtained wrinkle-free pulp sheet (Figure S32) had 3 mm thickness and a diameter of 5 cm, suitable for ISO brightness measurement.

Figure S32 Bleached pulp sheet for brightness test.

18. ISO–brightness test

The ISO–brightness test was performed on a poplar "23.4" pulp sheet (Figure S32) by using *Minolta Spectrophotometer CM–3630* with standard method *ISO 2470-1* which gave the brightness value of 91.3%.

19. Intrinsic viscosity measurements

The viscosity test performed on bleached "23.4" pulp using standard method *ISO 5351:2010* which is found to be η=442 mL/g and the degree of polymerization (DP) value is 610 according to method *SCAN-C 15:62*.

20. Determination of α–cellulose in 23.4 bleached pulp

The cellulose insoluble in 17.5 % sodium hydroxide is called α–cellulose which is one of the quality parameters of dissolving pulp. To determine the α–cellulose content in "23.4" bleached pulp, we followed a previously reported method.[6,7] In this experiment we used 2 g of bleached pulp torn into small pieces and then soaked into 50 mL of 17.5% NaOH solution (freshly prepared and carbonate free). The mixture was thoroughly mixed by using an overhead PTFE stirrer for 10 min. The pulp solution was stored at 20 °C for 60 min. The alkali-soluble fraction was filtered off and the insoluble fraction (*i.e.* α–cellulose) was collected and washed with distilled water 2 x 50 mL, 1 % acetic acid 2x 100 mL, again with distilled water 2 x 50 mL and finally with acetone 2 x 50 mL. The washed material was oven-dried at 60 °C for 12 h to obtain α–cellulose in 90.58 % (1.81 g) for "23.4" pulp.

21. Ash content

Table S6 Ash content of biomass along the process.

	Wood sticks	Reacted wood sticks	Pulp	Bleached pulp
Ash content (wt%)	0.40	0.10	<0.01	<0.01

22. References

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