Electronic Supplementary Information

Influence of bio-based solvents on the catalytic reductive fractionation of birch sawdust

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A. Experimental procedures

Chemicals and materials

All commercial chemicals were analytical reagents and were used without further purification. 5% Pd on carbon, guaiacol (2-methoxyphenol, 98%), 4-*n*-propylguaiacol (>99%), syringol (2,6-dimethoxyphenol, 99%), 4-methylsyringol (>97%), methyl β-D-xylopyranoside (99%), 2-isopropylphenol (>98%), 1,4-dioxane (>99%), tetrahydrofuran (>99%) and glycerol (>99%) were purchased from Sigma Aldrich. 4-Ethylguaiacol (98%), 1-butanol (>99%), ethylene glycol (>99%) and 1,2-propanediol (99%) were purchased from Acros organics. Methanol (>99%), ethanol (>99%) and dichloromethane (>99%) were purchased from Fischer Chemical Ltd. 4-*n*-Propanolguaiacol (3-(4-hydroxy-3-methoxyphenyl)-1-propanol, >98%) was purchased from TCI chemicals. Isoeugenol (2-methoxy-4-propenylphenol, >98%) was purchased from Alfa Aesar. 2-Propanol was purchased from VWR International and hexane was purchased from Chem-Lab. Birch (*Betula pendula*) was obtained from a local sawmill (Ecobois, Ghent, Belgium).

Determination of the Klason lignin content

Product yields in lignin depolymerization literature are typically based on the amount of acid insoluble lignin, also called Klason lignin, in the lignocellulose sample. The determination of the Klason lignin content of birch, was based on a procedure from Lin & Dence.[1] The lignocellulose samples were sieved and the fraction of 0.25-0.50 mm was used for analysis. A Soxtec extraction was first executed to remove any extractives like fats, waxes, resins and terpenoids/steroids,[2] that can influence the Klason lignin determination. 10 g of oven dried substrate was therefore divided over 4 fritted glass extraction thimbles and extracted in a Soxtec 2055 Avanti with 4 times 70 mL of a 2:1 toluene:ethanol mixture. Prior to a 3 h standard extraction, a wet step was introduced for 15 min in which the samples were completely submersed in the toluene:ethanol solution to improve the speed of extraction and thus to reduce the total extraction time needed. After cooling, the samples were washed with ethanol and dried in an oven at 353 K for one night. Triplicate samples of extracted substrate (1 g) were transferred to 50 mL beakers after which 15 mL of a 72 wt% H_2SO_4-solution was added. The mixture was left at room temperature for 2 h while continuously stirred with a magnetic rod. Afterwards the content of each beaker was transferred to a round-bottom-flask which already contained 300 to 400 mL of water. The beakers were rinsed and additional water was added until a H_2SO_4 concentration of 3 wt% was reached. The diluted solution was boiled for 4 h under reflux conditions, to maintain a constant volume and acid concentration. After filtration of the hot solution, a brown lignin precipitate was retained. The precipitate was washed with hot water to remove any leftover acid and the obtained residue was dried in an oven at 353 K for one night. The reported Klason lignin content was determined relative to the oven dried substrate by averaging the measured weight of the residues and correcting for the amount of removed extractives.

Determination of the carbohydrate content and composition

The carbohydrate content and composition in birch sawdust as well as in the obtained carbohydrate pulps after hydrogenolysis were determined, using a standard total sugar determination procedure, adapted with hydrolysis conditions for cellulose-rich materials.[3-5] Samples of 10 mg were pre-hydrolyzed in a 13 M H_2SO_4-solution (1 mL) at RT for 2 h and subsequently hydrolyzed in a diluted 2 M H_2SO_4-solution (6.5 mL) at 373 K for 2 h. The resulting monosaccharides were reduced to alditols and acetylated to increase their volatility for GC analysis. First, internal standard (1 mL of a 1 mg/mL β-D-allose solution of 1:1 benzoic acid:water) was added to 3 mL of the hydrolyzed sample. NH_3 25% in water (1.5 mL) was added, as well as droplets of 2-octanol to avoid excessive foaming. Reduction was catalyzed with $NaBH_4$ (0.2 mL of a 200 mg $NaBH_4$/mL 2 M NH_3 solution) for 30 min at 313 K and the reaction was stopped by adding 0.4 mL acetic acid. At this point the procedure can be paused by placing the reaction tubes in a cold environment for 1 night. 1-Methylimidazole (0.5 mL) was added to 0.5 mL of the reduced samples to catalyze the formation of alditol acetates after addition of acetic acid anhydride (5 mL). After 10 min, 1 mL of ethanol was added and 5 minutes later, the reaction was quenched by adding 10 mL of water. The reaction vials were placed in an ice bath and bromophenol blue (0.5 mL of a 0.4 g/L water solution) as well as KOH (2 x 5 mL of a 7.5 M solution) were added to color the aqueous phase blue. The yellow ethyl acetate phase, containing the acetylated

monosaccharides, could then easily be separated with a Pasteur pipette and was dried with anhydrous Na_2SO_4 before transferring it into a vial. GC analysis was performed on a Supelco SP-2380 column with helium as carrier gas in a Agilent 6890 series chromatograph equipped with an autosampler, splitter injection port (split ratio 1:20) and flame ionization detector (FID). Separation was executed at 498 K with injection and detection temperatures at 543 K. Calibration samples, containing known amounts of the expected monosaccharides were included in each analysis. To calculate the carbohydrate content in the analyzed samples, a correction factor was used to compensate for the addition of water during hydrolysis. Each substrate was analyzed in threefold and the average values were used in the calculation of the carbohydrate retention and the sugar polyol yields.

Lignin hydrogenolysis on birch sawdust

In a typical catalytic hydrogenolysis experiment, 2 g of extracted (same conditions as for Klason lignin determination) birch sawdust (size 0.25-0.5 mm; *Betula pendula* from Ecobois, Ghent), 0.2 g Pd/C and 40 mL solvent were loaded into a 100 mL stainless steel batch reactor (Parr Instruments Co.). The reactor was sealed, flushed with N_2 and pressurized with 3 MPa H_2 at room temperature (RT). The mixture was stirred at 700 rpm and the temperature was increased to 473 K ($\sim$10 K.min^{-1}) at which the pressure reached ~7 MPa (~12 MPa at 523 K) and the reaction was started. After reaction, the autoclave was cooled in water and depressurized at RT.

In order to indicate the processability of wet birch chips, reaction was performed with 2 g of a larger fraction of non-extracted birch sawdust (size 1.5-5 mm), 2 g H_2O (to mimic the wet state), 0.2 g Pd/C and 40 mL ethylene glycol. Reaction was performed at 473 K for 3 h. Since 2.5 wt% extractives are present, the lignin oil yield and delignification was corrected[6] in order to avoid overestimation.

Lignin product analysis

For the 'volatile' solvents (bp. < 125 °C; H_2O, methanol, ethanol, 2-propanol, 1-butanol, tetrahydrofuran, 1,4-dioxane, hexane), the degree of delignification was determined by first evaporating the raw filtered product mixture. This way a brown oil was obtained, which was subjected to threefold liquid-liquid extractions using dichloromethane (DCM) and water to separate the soluble lignin- and sugar-derived products. Finally the DCM-extracted phase was dried to obtain the 'lignin oil'. The weight of the lignin oil is then used to determine the degree of delignification (based on Klason lignin weight).

In the case of ethylene glycol (197 °C bp.), the solvent could not be evaporated with a rotary evaporator. Therefore, after filtration of the product mixture, 150 mL of water was added to the ethylene glycol product phase. This homogeneous mixture is immiscible with dichloromethane and was subjected threefold liquid-liquid extractions with DCM. Analogous to above, the degree of delignification can be obtained from the weight of the dried lignin oil.

To analyze the lignin monomers after hydrogenolysis, a weighed amount of external standard (2-isopropylphenol) was added to the lignin oil after which the content was completely resolubilized in 10 mL methanol. A sample was then analyzed on a GC (Agilent 6890 series) equipped with a HP5-column and a flame ionization detector (FID). The following operating conditions were used: injection temperature of 573 K, column temperature program: 323 K (2 min), 15 K/min to 423 K, 10 K/min to 493 K and 20 K/min to 563 K (12 min), detection temperature of 573 K. Sensitivity factors of the products were obtained by calibration with commercial standards or obtained by ECN-based calculations[7] due to lack of commercial standards.

The dimer yield was analyzed in the same way as the monomer yield, yet a derivatization step was added to increase their volatility before GC analysis. Therefore, 0.2 mL of the resolubilized lignin oil with the internal standard 2-isopropylphenol, was dried under a N_2 flow and subsequently mixed with 0.5 mL of pyridine and 0.5 mL of *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide. The vial was sealed and put in an oven at 353 K for 30 min. After this the lignin products were quantified with GC analysis as described above.

Identification of the monomer and dimer signals was performed with GC-MS using an Agilent 6890 series GC equipped with a HP1-MS capillary column and an Agilent 5973 series Mass Spectroscopy detector. The following operating conditions were used: injection temperature of 523 K, column temperature program: 333 K (2 min), 10 K/min to 553 K (13 min), detection temperature of 563 K.

GC analysis of the gaseous phase was performed on an Interscience Trace GC equipped with HayeSep Q and RTX-1 columns and a FID and TCD detector.

To get more insight in the degree of lignin depolymerization, the distribution of the molar mass of the lignin products was investigated using gel permeation chromatography (GPC). Therefore a sample of the lignin oil was solubilized in THF (~ 2-5 mg/mL) and subsequently filtered with a 0.2 μm PTFE membrane to remove any particulate matter to prevent plugging of the column. GPC analyses were performed at 40 °C on a Waters E2695 equipped with a M-Gel column 3 μm (mixed), using THF as the solvent (1 mL/min) and a UV detection at 280 nm with a Walters 2988 Photodiode array detector.

In addition to GC/MS and GPC analyses, the structural features of the lignin oils were analyzed with NMR. ^{1}H, ^{13}C NMR spectra were acquired on a Bruker Avance 400 MHz. A sample of the lignin oil (100 mg) was dissolved in 0.7 mL of DMSO-d_6.

Structural analysis of the carbohydrate pulp after birch hydrogenolysis

Due to the large difference in the carbohydrate pulp volume after hydrogenolysis in methanol or ethyleneglycol at 250°C, scanning electron microscopy (SEM) was applied on the pulp to illustrate the structural differences at μm-scale for both solvents. After coating of the samples with gold using a JEOL JSC-1300 sputter, secondary electron images (SEI) were recorded on a JEOL JSM-6010 JV microscope with an accelerating voltage of 15 kV.

X-ray Diffraction (XRD) measurements were performed with an XeuSS X-ray camera (Xenocs, Sassenage, France), comprising a GeniX 3D Molybdenum ultra-low divergence X-ray beam delivery system (wavelength, λ = 0.71 Å) at a power of 50 kV – 1mA, a collimating assembly based on scatterless slits, a sample stage, a He flushed flight tube and a Mar345 image plate detector (MARresearch, Norderstedt, Germany). Pelletized samples were measured while being wrapped in aluminum foil. Scattered intensities were corrected for empty holder scattering, taking into account the sample and holder transmission. Transmissions were obtained by measuring the direct beam intensity with a photodiode placed downstream from the sample. The 2D WAXD data were azimuthally averaged using the ConeX program.[8] The scattering angles, 2θ, were calibrated using silver behenate and polyethylene standards. To facilitate comparison with literature data, the scattering angles were converted into values as if Cu Kα radiation (λ = 1.54 Å) would have been used. Cellulose I crystals have five different crystal planes: (101), (10ī), (021), (002) and (040).[9] The crystallinity indices were determined using the commonly used XRD peak height method developed by Segal et al.:[10]

$$CrI\ (\%) = (I_{002} - I_{AM}\ )\ /\ I_{002}\ \text{x}\ 100\%$$

where I_{002} represents the maximal intensity of the (002) reflection and I_{AM} represents the minimal intensity between the (002) and (101) reflections.

In addition to XRD-measurements, a crystallinity index was also defined, using solid-state ^{13}C CP-MAS NMR spectroscopy. This index is based on the partitioning of the C4 carbon signals in ordered cellulose (89 ppm) and disordered (hemi)cellulose (84 ppm) in the solid-state ^{13}C CP-MAS NMR spectrum.[11] Newman defined the crystallinity index as follows:[12]

$$CrI\ (\%) = A_{ord}\ /\ (A_{ord}\ + A_{disord}\ )\ \text{x}\ 100\%$$

where A_{ord} (ordered) and A_{disord} (disordered) represent the respective signal areas as obtained after deconvolution with Origin.

The degree of polymerization (DP) was measured by viscosimetry according to the NF G 06-037 norm. An amount of pulp containing about 0.125 g cellulose was dissolved in 50 ml of a 0.5 M cupriethylenediamine solution. The solution was stirred for 2 hours at room temperature. Viscosity data were determined in a UBBELOHDE thermostated capillary tube viscosimeter at 298 K. The DP was calculated according to the NF G 06-037 norm.

B. Tables

Table S1 Detailed overview of the phenolic monomer yields (%) of all reactions illustrated in the article in Figure 1a.[a]

Entry	4-*n*-propylguaiacol	isoeugenol	4-*n*-propanolguaiacol	4-ethylsyringol	4-*n*-propylsyringol	4-prop-1-enylsyringol	4-*n*-propanolsyringol	4-*n*-propanalsyringol	**Total monomers**	Selectivity PG+PS	Selectivity PohG+PohS
H$_2$O/water	0.1	0.1	7.9	0.2	3.2	0.0	31.6	0.4	**43.8**	8	91
Methanol	0.1	0.0	5.7	0.2	0.8	0.2	19.3	1.8	**28.1**	3	89
Ethylene glycol	0.1	0.0	5.2	0.2	0.8	0.2	18.6	1.9	**26.9**	3	88
Ethanol	0.0	0.0	4.1	0.1	0.6	0.0	11.8	0.7	**17.4**	3	92
2-Propanol	0.0	0.0	3.0	0.1	0.4	0.0	8.5	0.2	**12.2**	3	95
1-Butanol	0.0	0.0	2.8	0.1	0.3	0.0	7.4	0.3	**10.8**	3	94
Tetrahydrofuran	0.0	0.0	1.7	0.1	0.2	0.0	4.2	0.1	**6.2**	2	95
Dioxane	0.0	0.0	1.5	0.0	0.1	0.0	3.4	0.2	**5.1**	2	95
Hexane	0.0	0.0	0.4	0.1	0.1	0.0	1.3	0.0	**1.8**	0	95

[a] The reaction conditions are as follows: 2 g extracted birch sawdust (0.25-0.50 mm), 5% Pd/C, 40 mL solvent, 3 h reaction time, 200 °C and 30 bar H$_2$ at RT.

Table S2 Detailed overview of the phenolic monomer distribution/selectivity (%) of all reactions described in the article in Figure 1a.[a]

Entry	4-*n*-propylguaiacol	isoeugenol	4-*n*-propanolguaiacol	4-ethylsyringol	4-*n*-propylsyringol	4-prop-1-enylsyringol	4-*n*-propanolsyringol	4-*n*-propanalsyringol	% G in monomers	% S in monomers
H$_2$O/water	0.3	0.3	18.2	0.4	7.4	0.0	72.4	1.0	19	81
Methanol	0.5	0.0	20.1	0.8	2.9	0.6	68.6	6.5	21	79
Ethylene glycol	0.3	0.0	19.3	0.7	3.0	0.6	69.1	6.9	20	80
Ethanol	0.0	0.0	23.4	0.9	3.3	0.0	68.1	4.3	23	77
2-Propanol	0.0	0.0	24.9	1.0	3.0	0.0	69.6	1.4	25	75
1-Butanol	0.0	0.0	25.6	0.7	3.0	0.0	68.0	2.7	26	74
Tetrahydrofuran	0.0	0.0	27.6	1.1	1.7	0.0	67.2	1.7	28	72
Dioxane	0.0	0.0	28.9	0.0	2.5	0.0	65.9	3.5	29	71
Hexane	0.0	0.0	24.1	4.6	0.0	0.0	71.3	0.0	24	76

[a] The reaction conditions are as follows: 2 g extracted birch sawdust (0.25-0.50 mm), 5% Pd/C, 40 mL solvent, 3 h reaction time, 200 °C, 30 bar H$_2$ at RT.

Table S3 Detailed overview of the phenolic monomer yields (%) of all reactions illustrated in the article in Figure 4.[a]

Entry	Temperature (°C)	Reaction time (h)	4-n-propylguaiacol	isoeugenol	4-propanolguaiacol	4-ethylsyringol	4-n-propylsyringol	4-prop-1-enylsyringol	4-n-propanolsyringol	4-n-propanalsyringol	Total monomers	Selectivity PG+PS	Selectivity PohG+PohS
Methanol	200	3	0.1	0.0	5.7	0.2	0.8	0.2	19.3	1.8	**28.1**	3	89
Methanol	200	9	0.0	0.0	8.0	0.4	0.8	0.0	30.4	1.3	**41.3**	2	93
Methanol	200	24	0.2	0.0	9.1	0.8	1.3	0.1	34.0	0.9	**46.6**	3	93
Methanol	200	3	0.1	0.0	5.7	0.2	0.8	0.2	19.3	1.8	**28.1**	3	89
Methanol	225	3	0.2	0.2	8.4	0.8	1.1	0.0	30.0	0.7	**41.3**	3	93
Methanol	250	3	0.4	0.0	9.7	1.6	1.4	0.0	35.2	0.0	**49.0**	4	92
Ethylene glycol	200	3	0.1	0.0	5.2	0.2	0.8	0.2	18.6	1.9	**26.9**	3	88
Ethylene glycol	225	3	0.4	0.0	7.2	0.6	2.2	0.0	26.7	0.0	**37.8**	7	90
Ethylene glycol	250	3	1.0	1.0	9.5	0.7	2.0	0.0	32.3	0.0	**46.6**	7	90

[a] The reaction conditions are as follows: 2 g extracted birch sawdust (0.25-0.50 mm), 5% Pd/C, 40 mL solvent, 30 bar H_2 at RT.

Table S4 Detailed overview of the phenolic monomer distribution/selectivity of all reactions described in the article in figure 4.[a]

Entry	Temperature (°C)	Reaction time (h)	4-n-propylguaiacol	isoeugenol	4-propanolguaiacol	4-ethylsyringol	4-n-propylsyringol	4-prop-1-enylsyringol	4-n-propanolsyringol	4-n-propanalsyringol	% G in monomers	% S in monomers
Methanol	200	3	0.4	0.0	20.3	0.7	2.8	0.7	68.7	6.4	21	79
Methanol	200	9	0.0	0.0	19.4	1.0	1.9	0.0	73.6	3.1	20	80
Methanol	200	24	0.4	0.0	19.5	1.7	2.8	0.2	73.0	1.9	20	80
Methanol	200	3	0.4	0.0	20.3	0.7	2.8	0.7	68.7	6.4	21	79
Methanol	225	3	0.5	0.5	20.3	1.9	2.7	0.0	72.6	1.7	21	79
Methanol	250	3	0.8	0.0	19.8	3.3	2.9	0.0	71.8	0.0	21	79
Ethylene glycol	200	3	0.3	0.0	19.3	0.7	3.0	0.6	69.1	6.9	20	80
Ethylene glycol	225	3	1.1	0.0	19.0	1.6	5.8	0.0	70.6	0.0	20	80
Ethylene glycol	250	3	2.1	2.1	20.5	1.6	4.4	0.0	69.3	0.0	25	75

[a] The reaction conditions are as follows: 2 g extracted birch sawdust (0.25-0.50 mm), 5% Pd/C, 40 mL solvent, 30 bar H_2 at RT.

Table S5 Composition of the pulp after reductive fractionation in methanol (MeOH) and ethylene glycol (EG) and subsequent hot water extraction.[a]

	Birch sawdust	MeOH pulp	Hot water extraction of MeOH pulp	EG pulp	Hot water extraction of EG pulp
C6 sugar content (wt%)	41 (37)[b]	64 (55)	82 (67)	63 (54)	83 (68)
C5 sugar content (wt%)	21 (19)	28 (24)	7 (6)	20 (16)	7 (6)
Pd/C content (wt%)	(9)	(14)	(18)	(14)	(19)
Birch conversion (wt%)	/	39	55	40	57
C6 sugar retention (wt%)[c]	/	93	88	92	86
C5 sugar retention (wt%)[c]	/	81	15	54	15
Degree of polymerization (DP)[d]	/	/	375	/	355

[a] Reaction conditions for reductive catalytic fractionation: 2 g extracted birch sawdust (0.25-0.50 mm), 0.2 g 5% Pd/C, 40 mL solvent (MeOH or EG), 30 bar H_2 at RT, 250 °C, 3 h reaction time. Reaction conditions for hot water extraction: 0.6 g pulp (including catalyst), 20 mL water, 200 °C, 45 min. [b] The values outside the brackets indicate the composition of the birch sawdust or pulp without catalyst, the values inside the brackets indicate the composition of the birch wood or pulp + catalyst. [c] The C6 and C5 sugar retention are relative to the C6 and C5 content of the initial birch sawdust. [d] The degree of polymerization (DP) was measured by viscosimetry according to the NF G 06-037 norm.

Table S6 Catalytic results for the Pd/C-H_2WO_4-catalyzed conversion of the ethylene glycol pulp and ball-milled cellulose to ethylene glycol [a]

Product yields (wt%)	Ethylene glycol pulp	Ball-milled cellulose
Ethylene glycol	26.3	34.6
Propylene glycol	4.1	4.3
1,2-Butanediol	1.1	2.9
Sorbitol	3.1	6.1
Glucose	0.0	2.9
Sorbitans	1.1	1.8
Erythritol	0.6	3.0
Glycerol	0.7	1.4
Total yield (wt%)	**37**	**57**

[a] Reaction conditions: Ethylene glycol pulp: 0.7 g (containing 0.1 g 5 wt% Pd/C, 0.38 g C6 sugars and 0.12 g C5 sugars), 1 g H_2WO_4, 40 mL H_2O, 245 °C, 4.5 MPa H_2 (RT), 1 h. Yield is based on the C6 and C5 sugar content of the pulp. Ball-milled cellulose: 0.5 g cellulose (Avicel cellulose after a 2 h ball-milling procedure), 0.1 g 5 wt% Pd/C, 1 g H_2WO_4, 40 mL H_2O, 245 °C, 4.5 MPa H_2 (RT), 1 h.

Table S7 Gas phase composition and loss of solvent into gaseous and liquid products after birch processing in methanol and ethylene glycol at 250 °C.

	MeOH	EG
Composition of the gas phase (vol%)		
H_2	94.2	94.6
N_2	4.05	4.1
CH_4	0.22 (0.013)[a]	0.05 (0.002)
C_2H_4/C_2H_6	< 0.01	0.05 (0.004)
CO	0.86 (0.055)	1.01 (0.042)
CO_2	< 0.01	0.15 (0.006)
Solvent degradation products in the liquid phase		
Methanol		(0.03)
Ethanol		(0.04)
Loss of solvent into gaseous compounds (C%)[a]	**0.07**	**0.054**
Loss of solvent into liquid compounds (C%)[a]		**0.07**

[a] The values in brackets indicate the C% of the gaseous or liquid compound relative to the initial amount of solvent. The sum of these values represents the loss of solvent into carbonaceous gasses, suggested that the solvent is the only source of these gasses

C. Figures
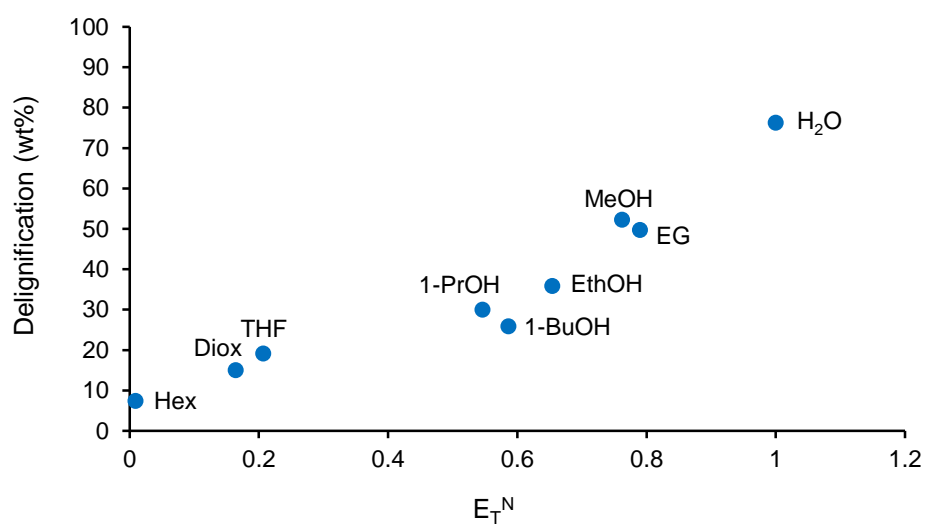
Figure S1 Birch delignification *versus* the solvent polarity as described by the Reichardt parameter (E_T^N). Reaction conditions: see Figure 1.
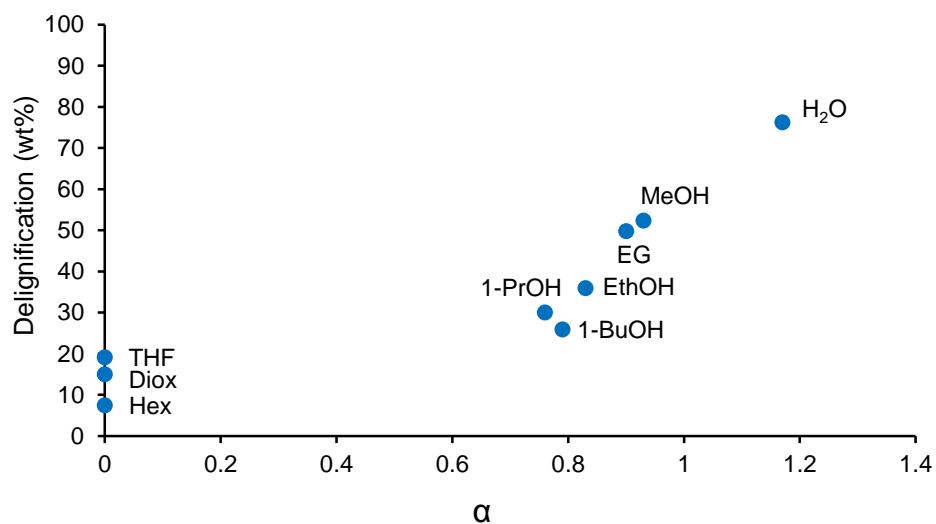
Figure S2 Birch delignification *versus* the solvent Kamlet-Taft parameter for the hydrogen bond donating ability (α). Reaction conditions: see Figure 1.
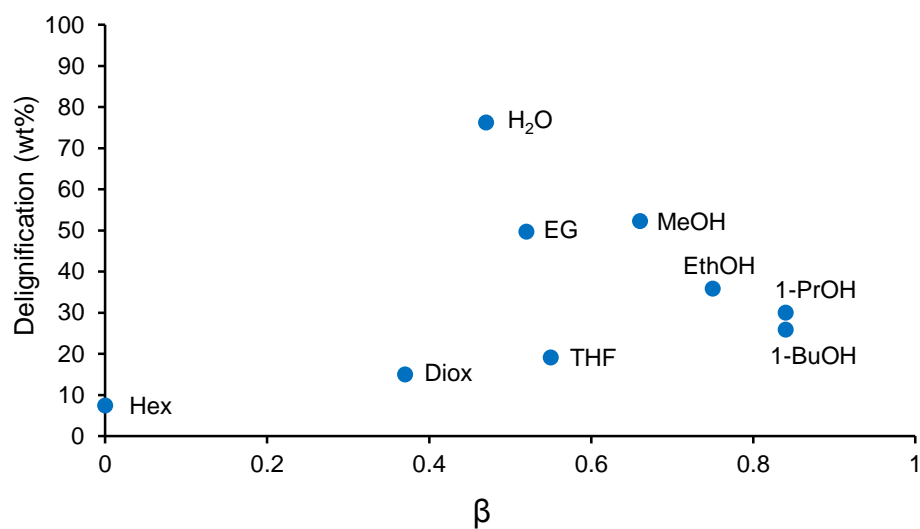
Figure S3 Birch delignification *versus* the solvent Kamlet-Taft parameter for the hydrogen bond acceptor ability (β). Reaction conditions: see Figure 1.
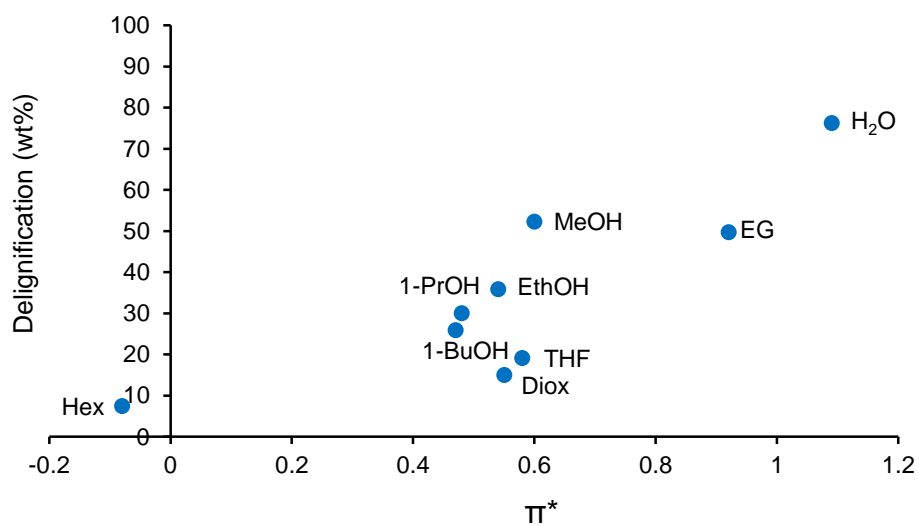
Figure S4 Birch delignification *versus* the solvent Kamlet-Taft parameter for the dipolarity/polarizability (π^*). Reaction conditions: see Figure 1.
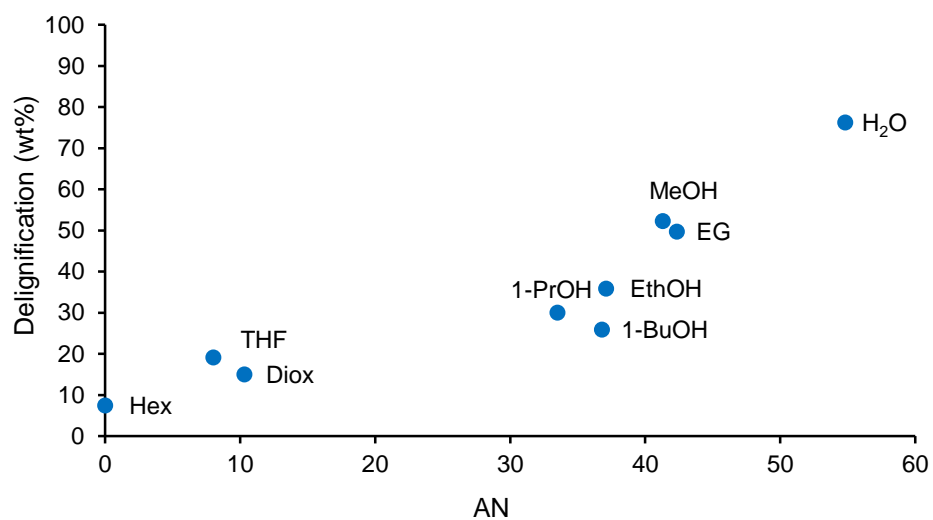
Figure S5 Birch delignification *versus* the Lewis acidity of the solvent as described by the acceptor number (AN). Reaction conditions: see Figure 1.
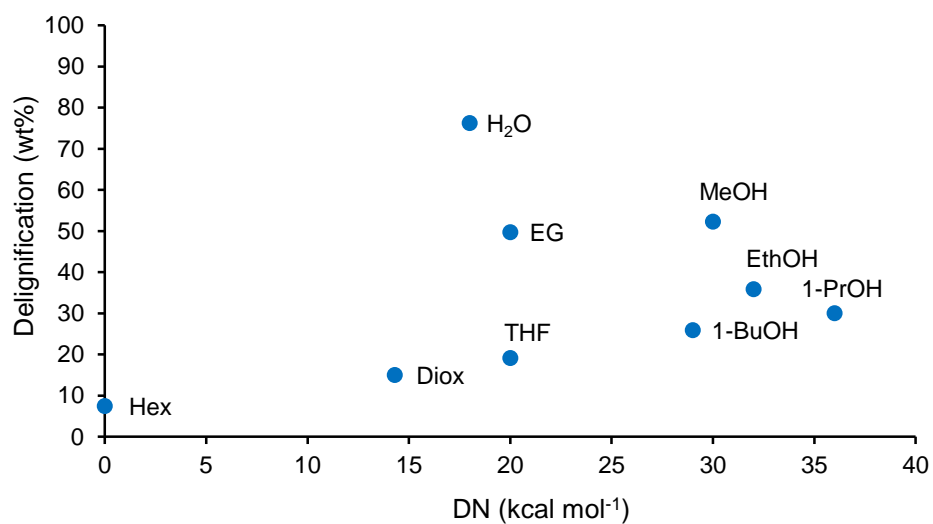
Figure S6 Birch delignification *versus* the Lewis basicity of the solvent as described by the donor number (DN). Reaction conditions: see Figure 1.
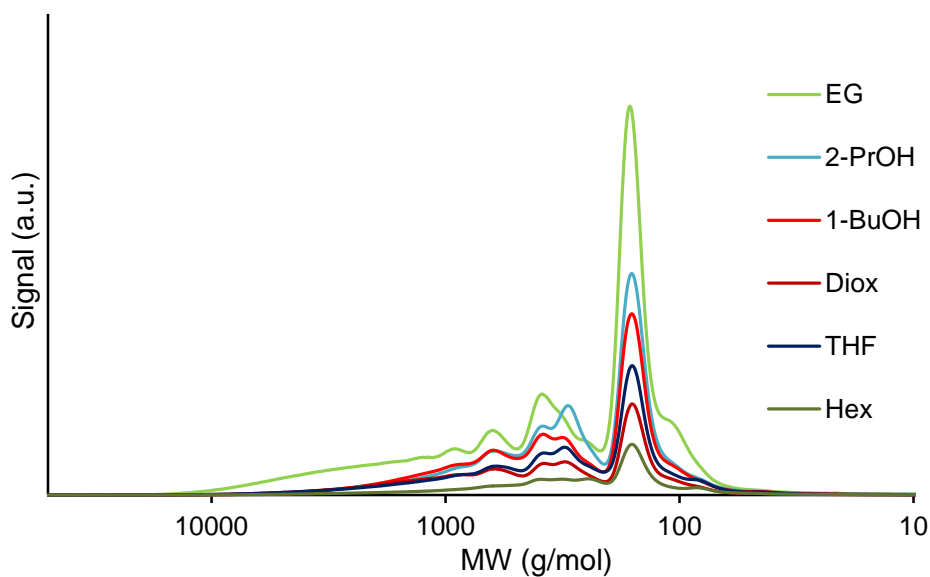
Figure S7 Molecular weight distribution of the lignin oils obtained from birch processing in ethylene glycol (EG), 2-propanol (2-PrOH), 1-butanol (1-BuOH), 1,4-dioxane (Diox), tetrahydrofuran (THF) and hexane (Hex) measured by gel permeation chromatography (calibration with polystyrene standards). Reaction conditions: see Figure 1
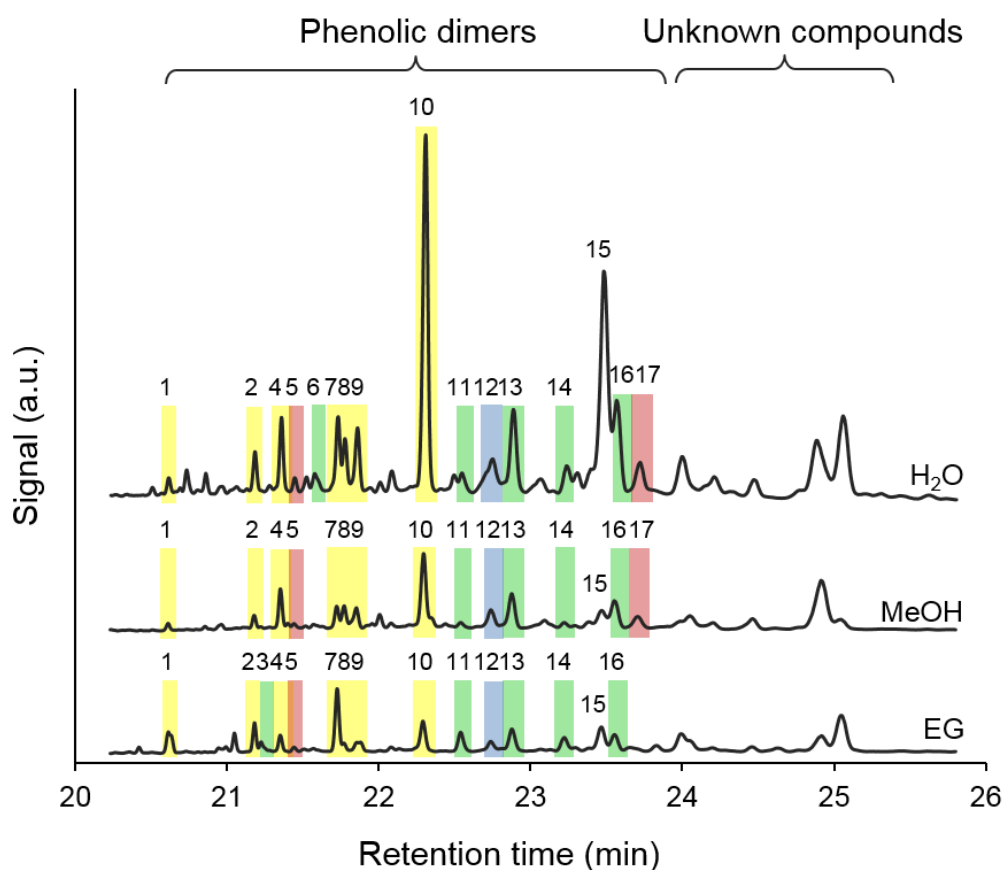
**Figure S8** Gas chromatograms of the trimethylsilylated lignin dimer product obtained from birch processing in water (H_2O), methanol (MeOH) and ethylene glycol (EG). In support of this figure (also presented in the article as Fig. 3 c), the corresponding mass spectra for each peak are provided below, as well as the chemical structure of each identified dimer. The peak identification was confirmed by literature.[13-17]

Dimer 1: β-1 (EG-G)

Dimer 2: β-1 (EG-S)

Dimer 3: β-5 (EG-PG)
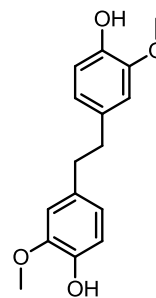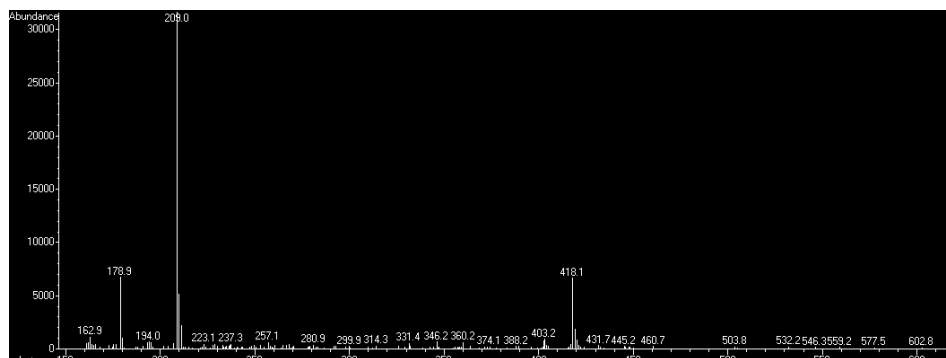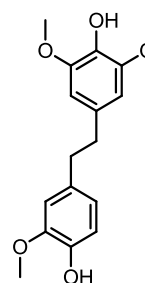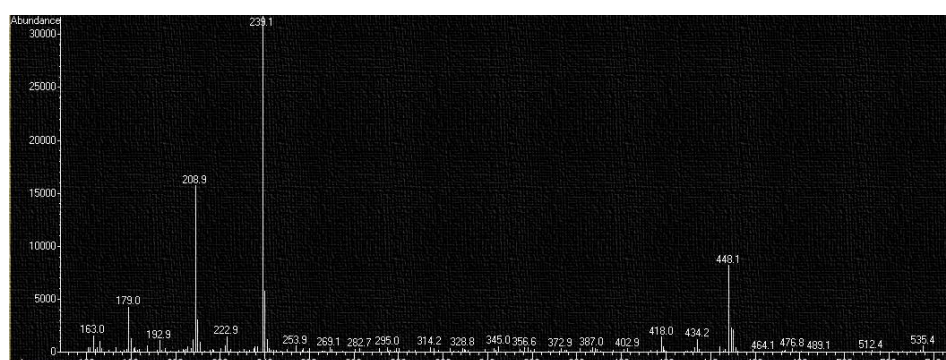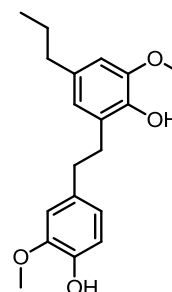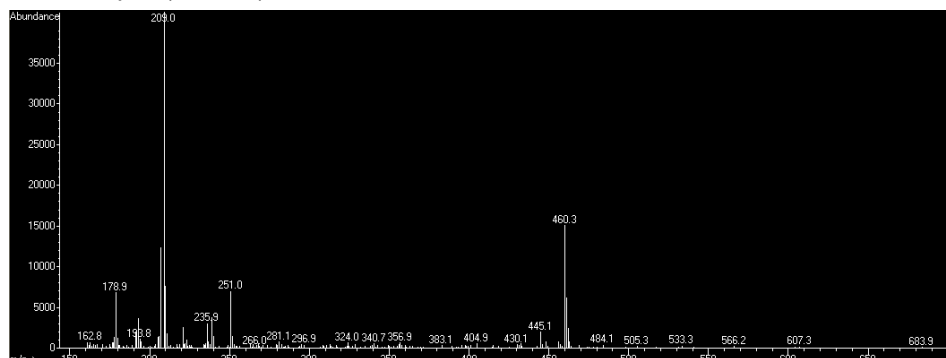
Dimer 4: β-1 (PohG-G)
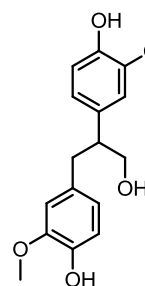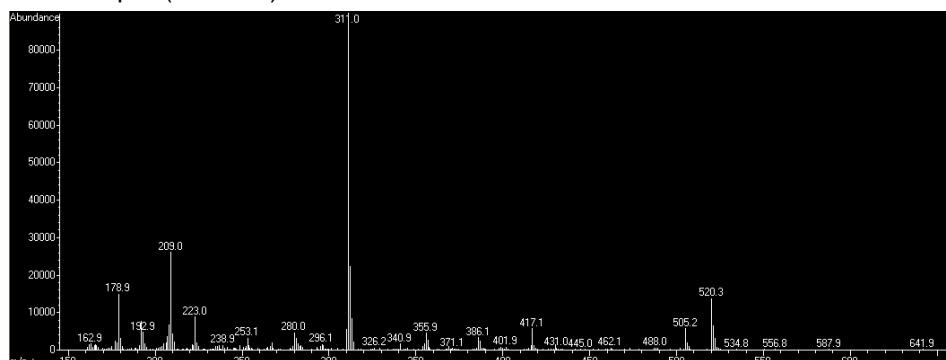
Dimer 5: β-β (PS-PS,α-O-γ₂) (syringaresinol)

Dimer 6: β-5 (PohG-PG)

Dimer 7: β-1 (ES-S)

Dimer 8: β-1 (PohS-G)

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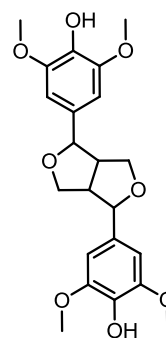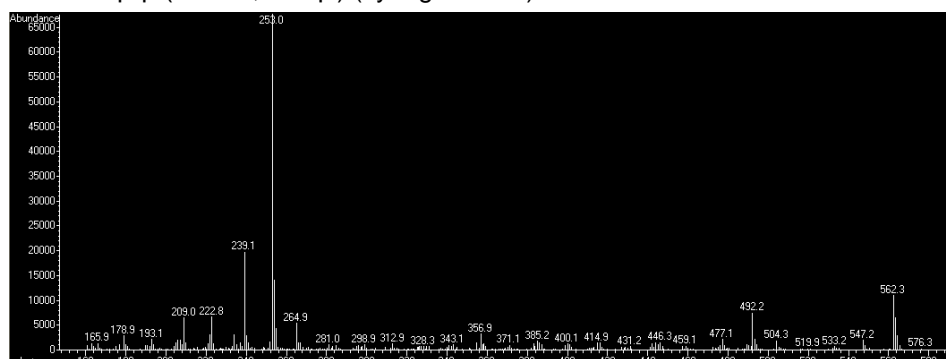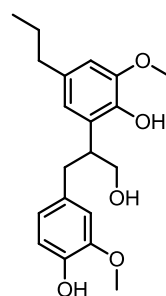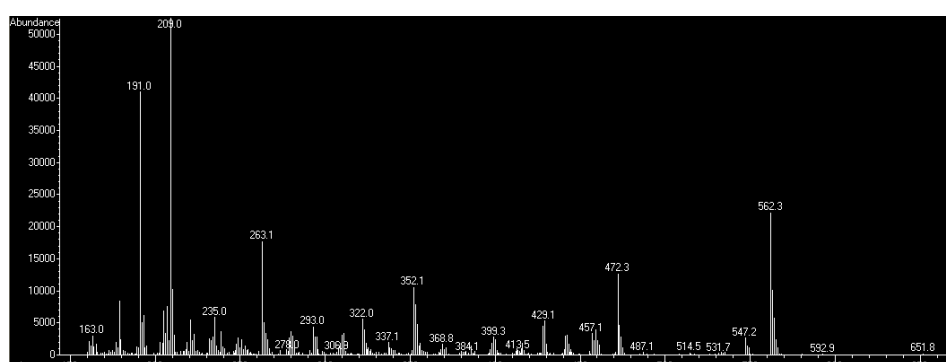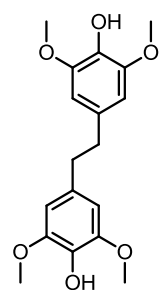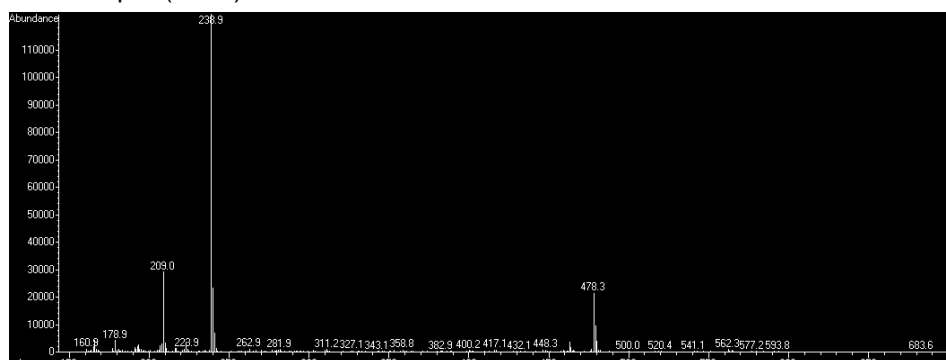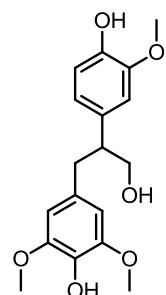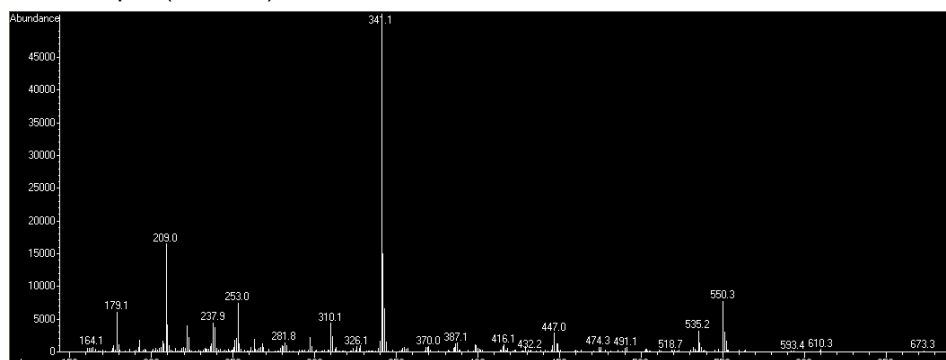
Dimer 9: β-1 (PohG-PS)
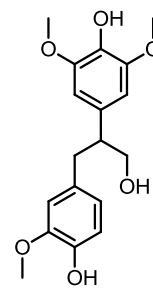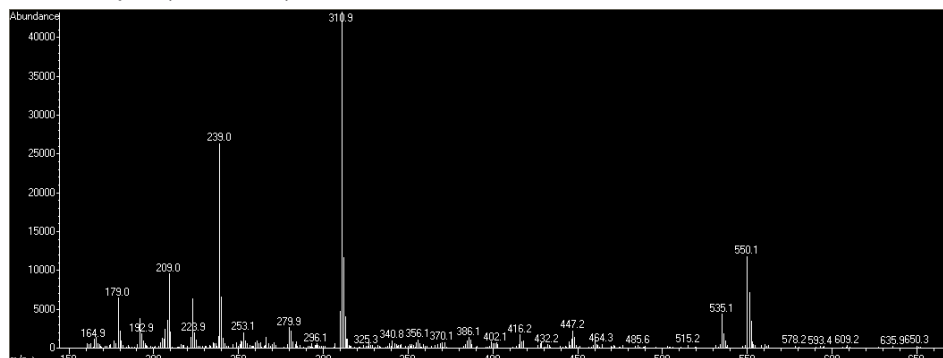
Dimer 10: β-1 (PohS-S)
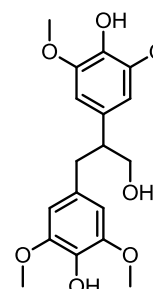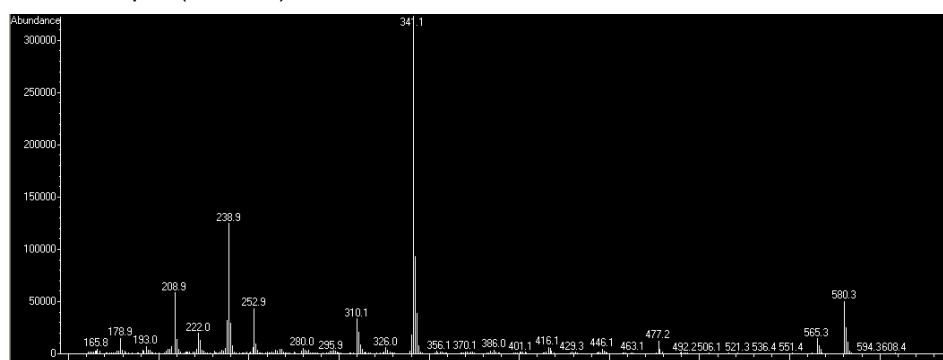
Dimer 11: β-5 (EG-PohG)
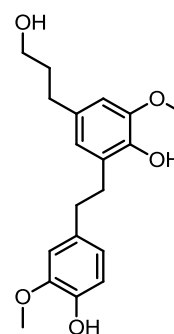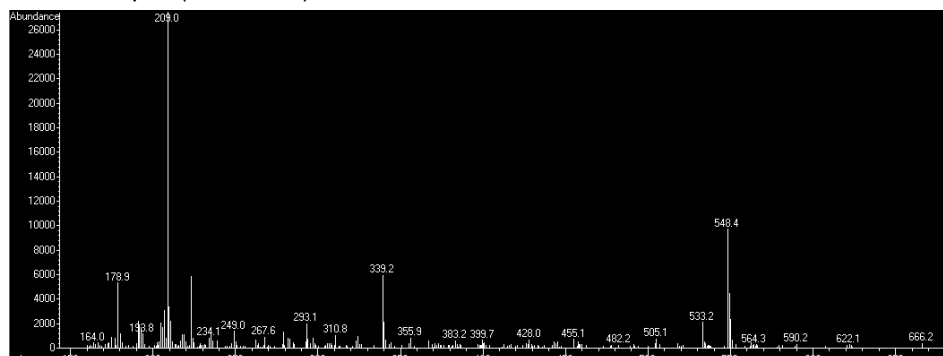
Dimer 12: 5-5 (PohG-PohG)
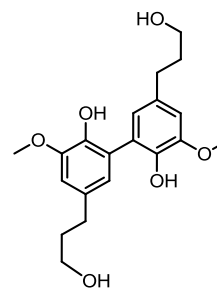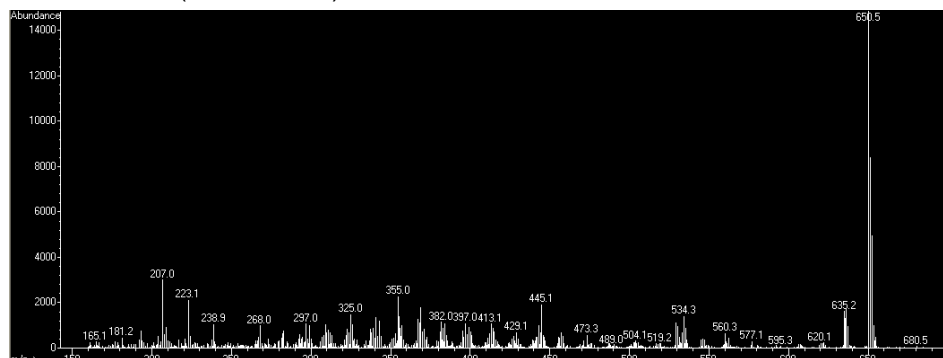
Dimer 13: β-5 (PohG-PohG)
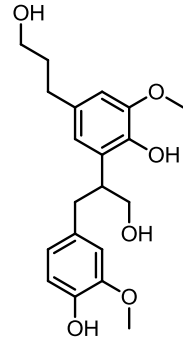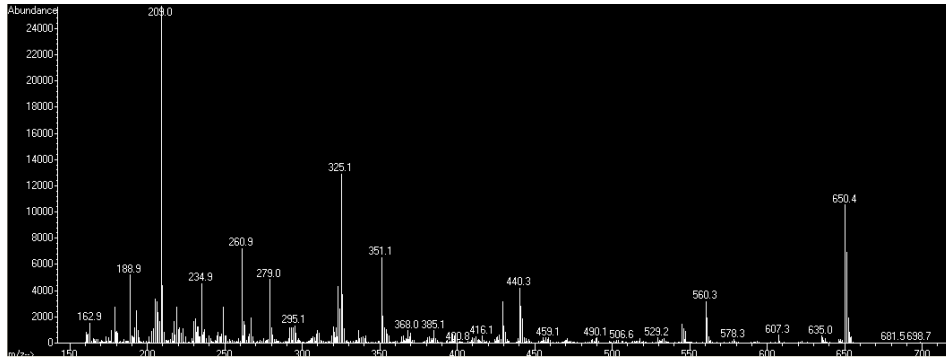
Dimer 14: β-5 (ES-PohG)
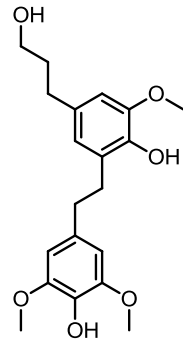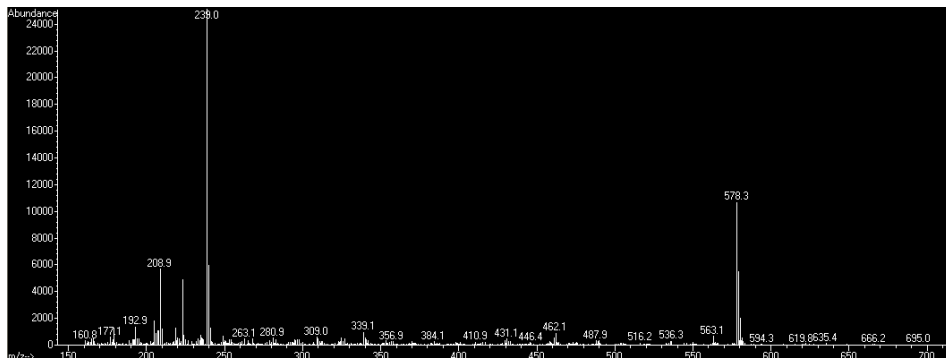
Dimer 15: Unknown compound (M•⁺: 708)
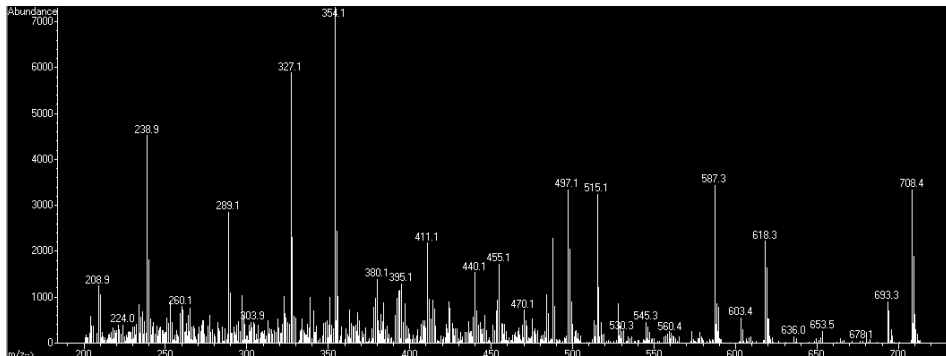
Dimer 16: β-5 (PohS-PohG)
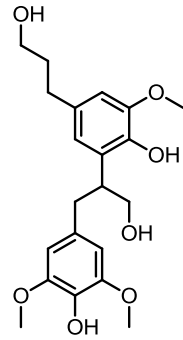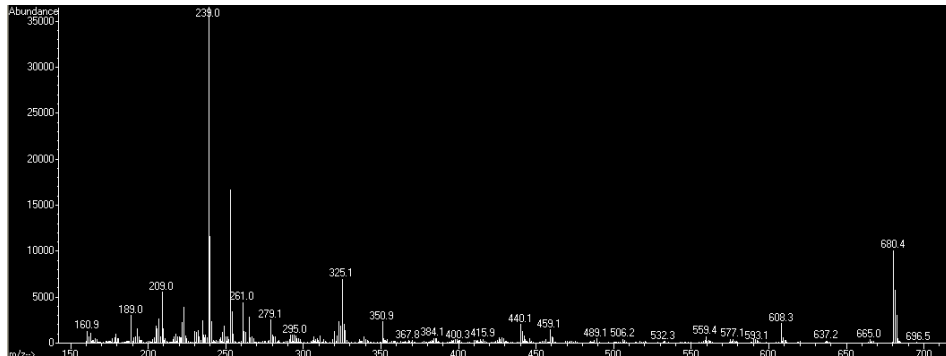
Dimer 17: β-β (PohS-PohS)
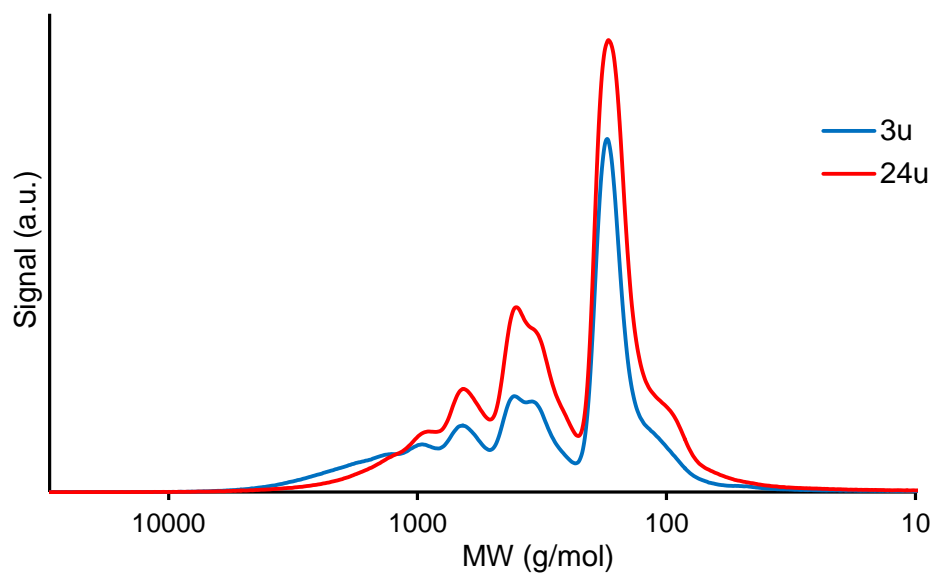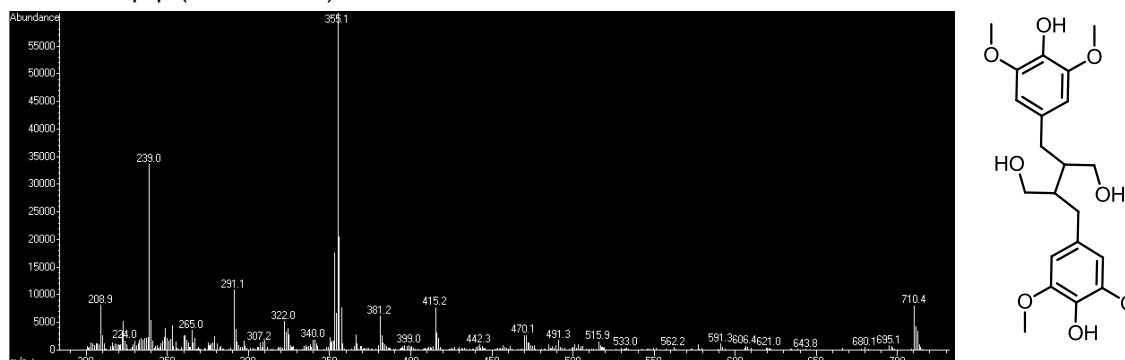
Figure S9 Molecular weight distribution of the lignin oils obtained from birch processing in methanol at 200 °C for 3 and 24 h, measured by gel permeation chromatography (calibration with polystyrene standards). Reaction conditions: see Figure 1.
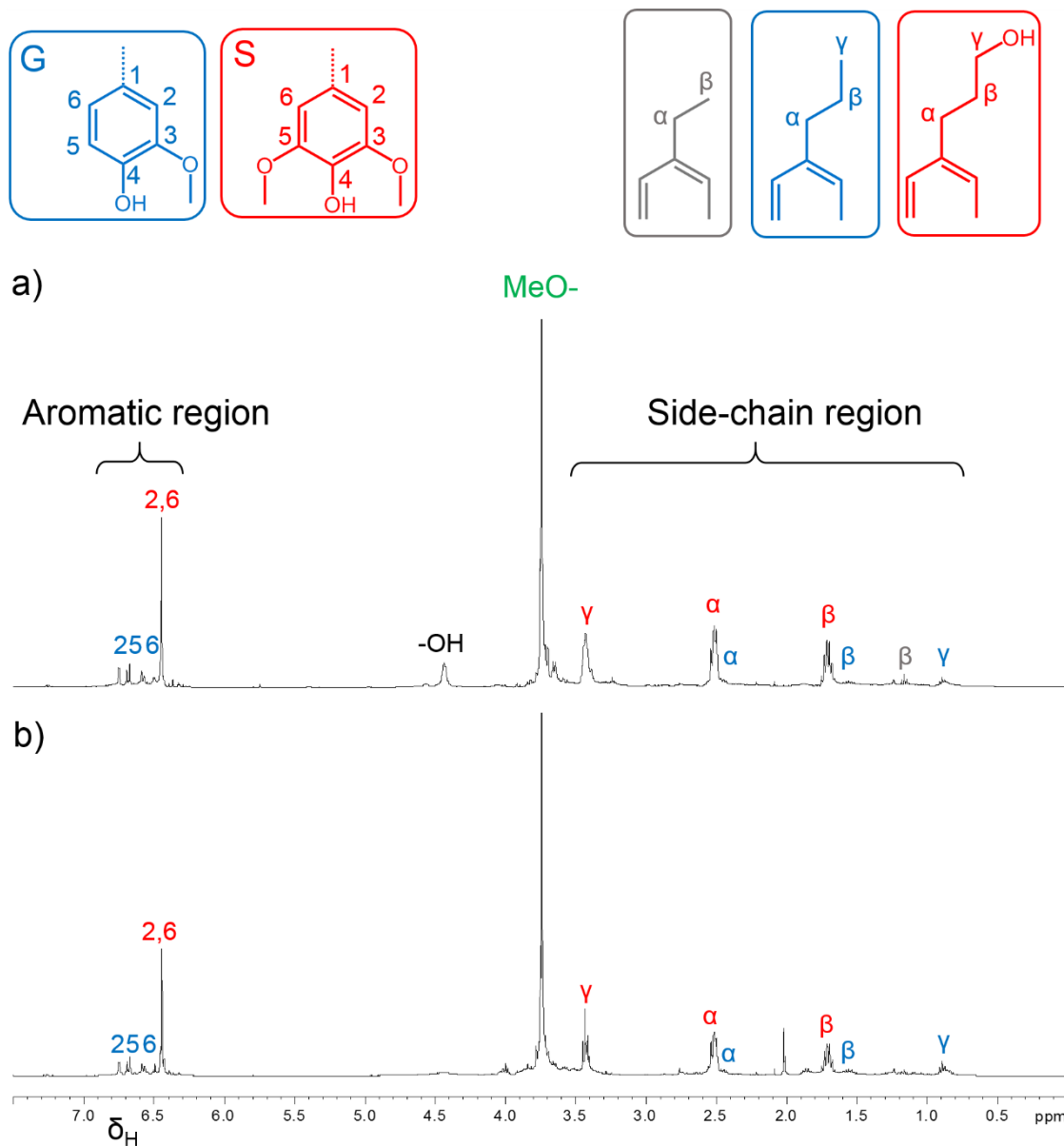
Figure S10 ^{1}H NMR spectra of the lignin oils obtained from birch processing in a) methanol and b) ethylene glycol at 250 °C. The signals from propanol side-chains are prominent in the side-chain region of both spectra.
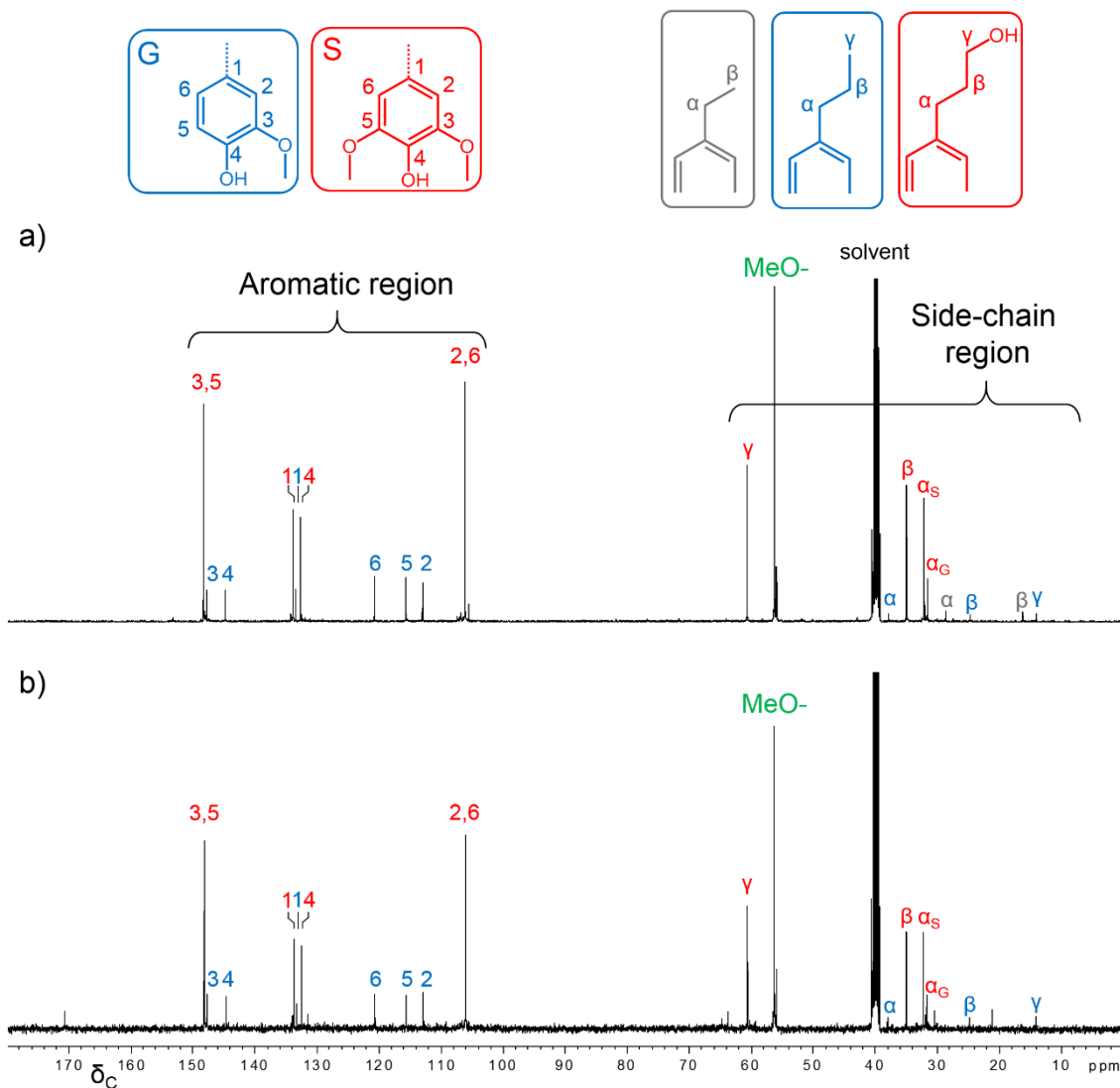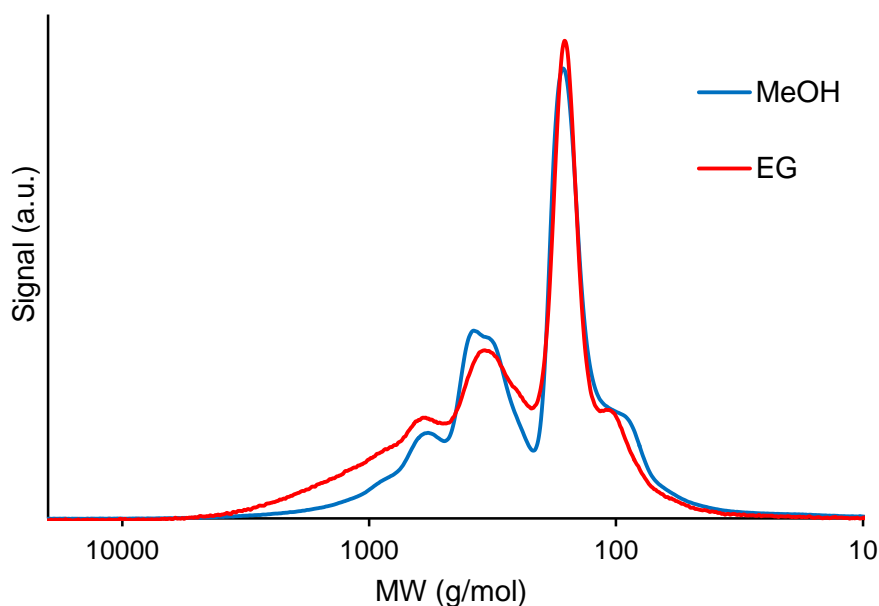
Figure S11 ^{13}C NMR spectra of the lignin oils obtained from birch processing in a) methanol and b) ethylene glycol at 250 °C. The signals from propanol side-chains are prominent in the side-chain region of both spectra.

Figure S12 Molecular weight distribution of the lignin oils obtained from birch processing in methanol and ethylene glycol at 250 °C for 3 h, measured by gel permeation chromatography (calibration with polystyrene standards). Reaction conditions: see Figure 1.
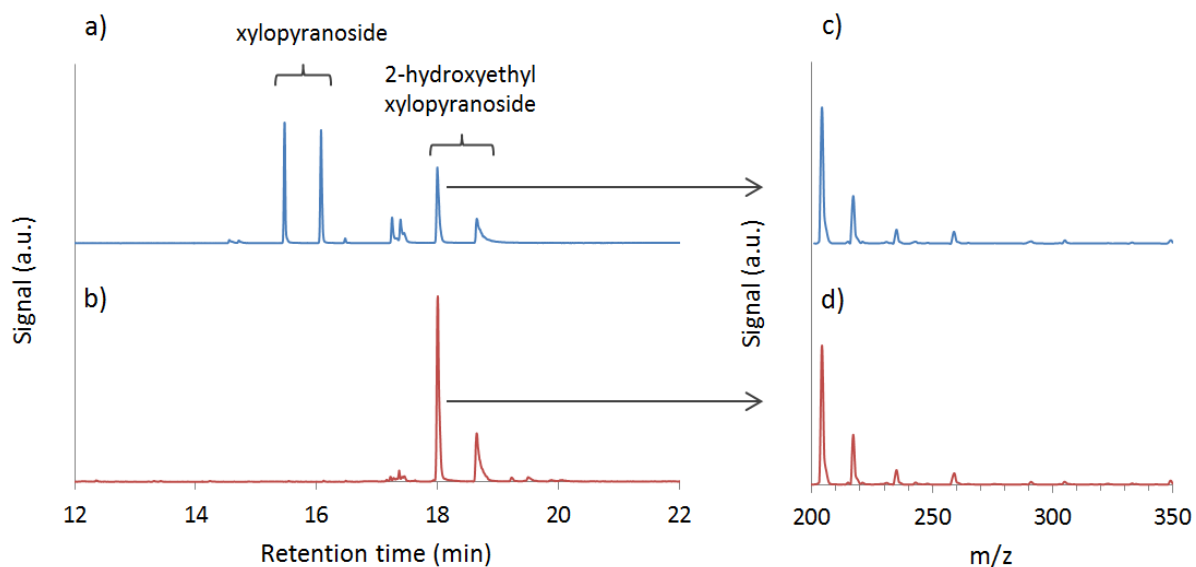
Figure S13 a) Gas-chromatograms of the product mixture after a condensation reaction with 0.5 g xylopyranoside in 5 mL ethylene glycol (EG) with 0.2 g amberlyst 15(H) as an acid catalyst at 100°C for 1.5 h. As a similar reaction was described in literature, this reaction is expected to produce 2-hydroxyethyl xylopyranoside[18] b) Gas-chromatogram of the sugar-derived product fraction after reductive catalytic processing of birch wood in EG (reaction 3, table S1). Next to the α- and β- anomer of the xylopyranoside substrate, the main products of this coupling reaction of EG and xylopyranoside have the same retention times (18 and 18.6 min) as the main two products of the sugar-derived products after fractionation. This is already a first indication that the produced sugar is 2-hydroxyethyl xylopyranoside. In addition, the MS-spectra of the 18 min. peak in a) and b) are shown in c) and d) respectively. Although the MS-spectra of sugar derived products are typically very similar, the spectra in c) and d) indicate again a xylose substructure.
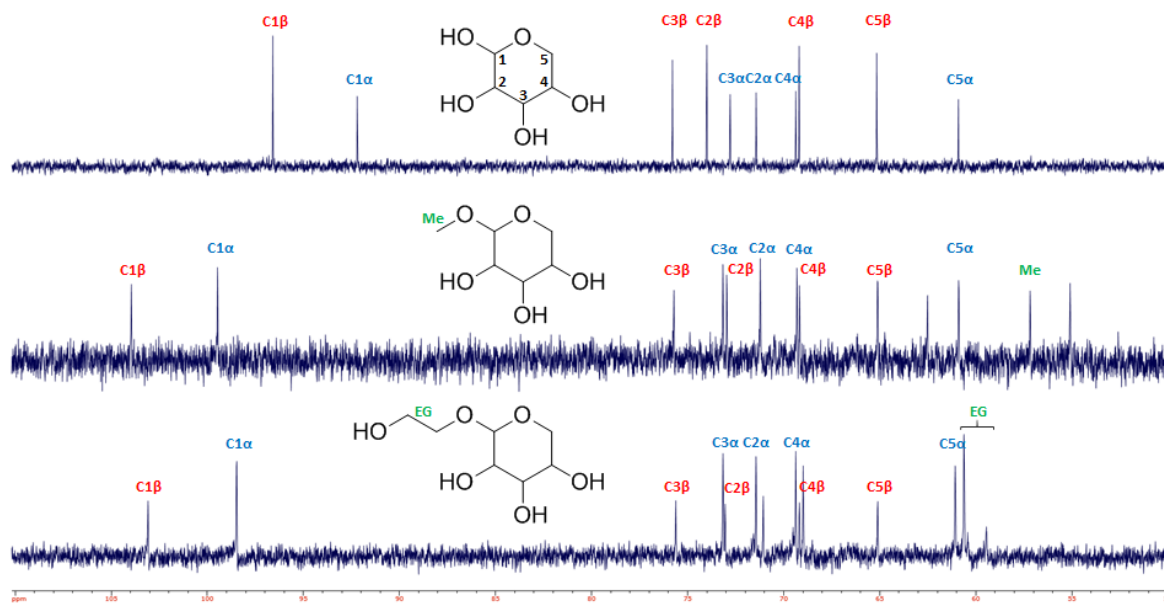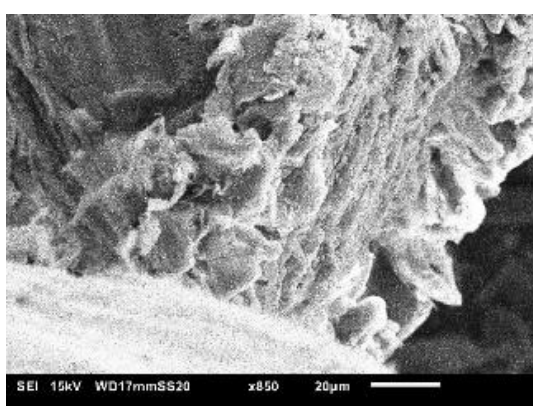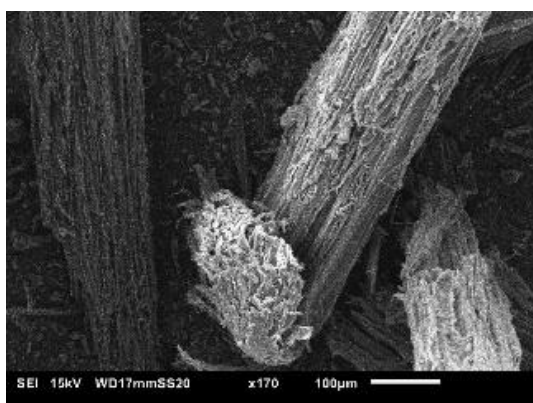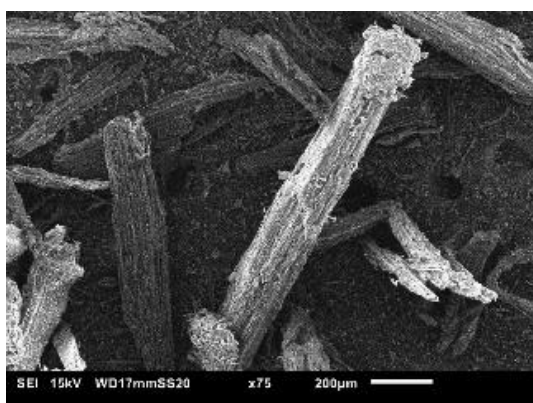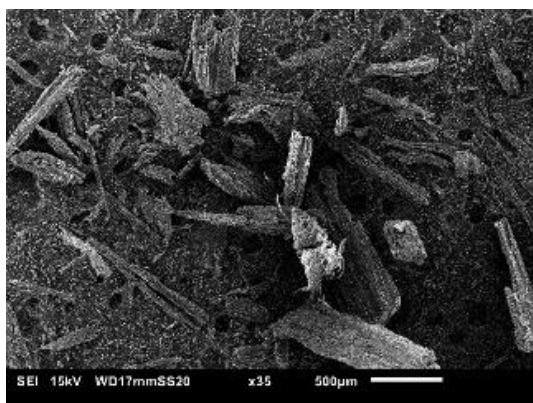
Figure S14 ^{13}C NMR spectra of xylopyranoside (top), methyl xylopyranoside (middle) and the sugar derived product fraction after reductive catalytic processing of birch wood in EG, reaction 3, table S1 (bottom). The bottom spectra confirms the indications from Figure S13 that the main sugar derived product is 2-hydroxyethyl xylopyranoside.

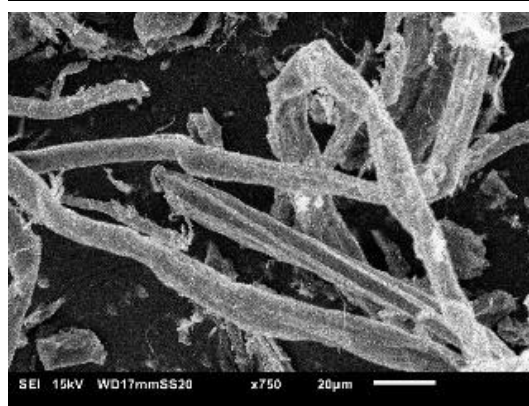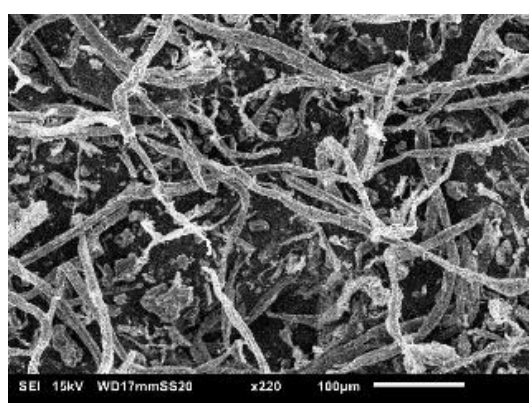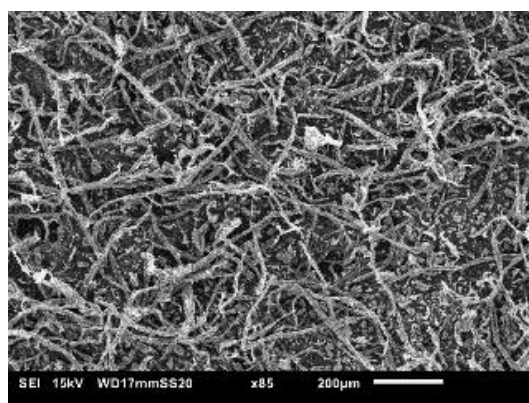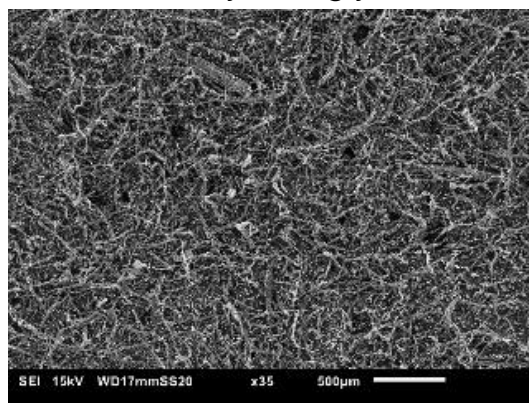methanol   ethylene glycol

Figure S15 Scanning electron microscopy (SEM) images at various magnifications of the pulps obtained by birch processing in methanol and ethylene glycol at 250 °C with Pd/C.

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