Electronic Supplementary Information (ESI)

Integrating lignin valorization and bio-ethanol production: on the role of Ni-Al_2O_3 catalyst pellets during *lignin-first* fractionation

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A. Experimental procedures

Chemicals and materials

All commercial chemicals were analytic reagents and were used without further purification. Ni-Al_2O_3 catalyst pellets (Ni-HTC500, trilobe 1.2 x 3 mm, 21% Ni-content) were purchased from Johnson Matthey, guaiacol (2-methoxyphenol, 98%), 4-*n*-propylguaiacol (>99%), syringol (2,6-dimethoxyphenol, 99%), 4-methylsyringol (>97%), 2-isopropylphenol (>98%), tetrahydrofuran (>99%), N-Methyl-N-(trimethylsilyl)trifluoroacetamide (>98.5%) were purchased from Sigma Aldrich. 4-Ethylguaiacol (98%) was purchased from Acros Organics. Methanol (MeOH)(>99%) and dichloromethane (>99%) were purchased from Fischer Chemical Ltd. Guaiacylglycerol-β-guaiacyl ether was purchased from GreenLignol, LLC. 4-*n*-propanolguaiacol (3-(4-hydroxy-3-methoxyphenyl)-1-propanol, >98%) was purchased from TCI chemicals. Isoeugenol (2-methoxy-4-propenylphenol, >98%) and coniferyl alcohol (>98%) were purchased from Alfa Aesar. 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 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.

Batch reaction

In a typical catalytic hydrogenolysis experiment, 2 g of pre-extracted (same conditions as for Klason lignin determination) birch sawdust (*Betula pendula* from Ecobois, Ghent), 0.2 g Ni-Al_2O_3 catalyst and 40 mL MeOH 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 750 rpm and the temperature was increased to 523 K (~10 $K.min^{-1}$) at which the pressure reached ~12 MPa and the reaction was started. After reaction, the autoclave was cooled in water and depressurized at RT. An analogous procedure was used for the reactions on coniferyl alcohol. Here, a 50 mL stainless steel batch reactor (Parr Instruments Co.) was used and loaded with 0.1 g Ni-Al_2O_3 powder, 0.05 g coniferyl alcohol and 20 mL MeOH.

Lignin product analysis

To determine the degree of delignification, the raw filtered MeOH product mixture was evaporated and a brown oil was obtained. This brown oil 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 lignin oil yield which also indicates the degree of delignification (based on Klason lignin weight). 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 DCM. 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 $K.min^{-1}$ to 423 K, 10 $K.min^{-1}$ to 493 K and 20 $K.min^{-1}$ 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 calculations3 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-FID 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 $K.min^{-1}$ to 553 K (13 min), detection temperature of 563 K.

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 columns. 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 $mL.min^{-1}$) and a UV detection at 280 nm with a Walters 2988 Photodiode array detector.

In addition with GC-MS and GPC analyses, the structural features of the lignin dimers and oligomers were analyzed with 2D HSQC NMR which 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. HSQC experiments had the following parameters: standard Bruker pulse sequence 'hsqcetgp' (double inept transfer, phase-sensitive), spectral width of 20 ppm in F2 (^{1}H dimension) by using 2048 data points for an acquisition time (AQ) of 128 ms, 219 ppm in F1 (^{13}C dimension) by using 512 increments (AQ of 11.6 ms), 24 scans with a 1.5 s interscan delay (D1). The base level of each HSQC spectra was corrected, using the aromatic $S_{2,6}$ signal (δ_C 102-108, δ_H 6.2-6.9 ppm) as an internal reference.

Theoretical maximum monomer yield

Lignin is a complex 3-dimensional irregular polymer with randomly cross-linked phenolic building blocks. To estimate the theoretical maximum monomer yield for a certain substrate, a simplified infinite linear lignin polymer is imagined, in which each building block is linked to two other units, either by a C-C bond or an ether-bond. In a hydrogenolysis reaction, the ether bonds are cleaved to depolymerize the lignin structure. When a unit is on both sides connected with an ether bond, the cleavage of the ether bonds will result in a monomer. Mathematically, the maximum amount of monomers coincides with the square of the fraction of ether bonds in the lignin structure.[4-6] Reported values for the ether content of birch lignin typically range around 67-76%,[7, 8] which implicates a theoretical maximum monomer yield, varying from 45% to 58% for birch. The here obtained monomer yields of around 50% are thus close to the theoretical maximum.

Determination of the carbohydrate content and composition

The carbohydrate content and composition in birch sawdust as well as in the obtained carbohydrate pulps after RCF were determined, using a standard total sugar determination procedure, adapted with hydrolysis conditions for cellulose-rich materials.[9-11] 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 NaBH4/mL 2 M NH3 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 Na2SO4 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.

Acid digestion of the carbohydrate pulp for ICP-AES analysis

To determine the Ni-content in the carbohydrate pulp, obtained after reductive catalytic fractionation of birch wood, an acid digestion procedure was performed on the pulps,[12] prior to ICP-AES analysis. A weighed amount (0.2 g) of oven-dry pulp was transferred into a 20 mL screw cap glass vial together with 2 mL of a 1:1 HNO_3 solution. The suspension was heated for 15 minutes at 90-95 °C in an oil bad (no boiling should occur), after which the vials were removed from the oil bad and allowed to cool. Next, 1 mL of concentrated HNO_3 (65%) was added and the vials were again heated for 30 minutes. After cooling, this step was repeated. Next, 0.4 mL of deionized water and 0.6 mL of 30% H_2O_2 was added to each vial. When heated, the samples now begin to effervesce. Heating was allowed until the effervescence subsided. After cooling, 0.2 mL of 30% H_2O_2 was added and the solution was heated again until effervescence subsides. This step was repeated until the appearance of the acid digest was unchanged, or until a total volume of 2 mL of 30% H_2O_2 was added. Concentrated HCl (1 mL) was added next, together with 2 mL of deionized water and the vials were heated for 15 minutes. Once cooled, the samples were filtered and the filtrate was diluted with deionized water to reach a final volume of 20 mL. The final solution was analyzed as such on a Varian 720 ES ICP emission spectrometer.

Physicochemical characterization of the Ni-Al_2O_3 catalyst

CO-chemisorption was used to determine the Ni-dispersion. For this 15 mg of Ni-Al_2O_3 was placed in a fixed bed set-up and pretreated at 250°C for 1 h (at a heating rate of 5 $K.min^{-1}$) under a constant H_2-flow. To ensure a good packing of the catalyst bed, the pellets (1.2 x 3 mm) were mildly crushed and sieved to obtain a smaller pellet size (0.25-0.50 mm). Next, the sample was cooled to room temperature and saturated with He. CO-pulses were provided at regular time intervals and the amount of adsorbed CO on the catalyst was calculated from the CO-concentration in the effluent, quantified by mass spectrometry. Nickel dispersion is calculated as the amount of available surface Ni-atoms over the total amount of Ni-atoms (21 wt% of Ni in the Ni-Al_2O_3 pellets), assuming the chemisorption of 1 CO molecule on 1 surface Nickel atom.

N_2-physisorption were used to determine the porosity of the Ni-Al_2O_3 catalyst. Measurements were performed on a Micromeritics Instruments Tristar 3000 at 77 K. 35 mg of catalyst was degassed overnight at 573 K under a constant N_2 flow prior to analysis. Pore volumes were determined by the t-plot method on the desorption branch.

B. Tables

Table S1 Detailed phenolic monomer yields of all reactions described in table 1 and figure 5 in the main article.[a]

Entry	Ni-Al_2O_3 catalyst	Reaction time (h)	4-ethyl-G/S	4-propenyl-G/S	4-propyl-G/S	4-propanal/one-G/S	4-methoxypropyl-G/S	4-propanol-G/S (Poh-G/S)	4-methoxypropenyl-G/S	Coniferyl/sinapyl-alcohol	other	**Total monomers (C%)**	% S-monomers	Selectivity Poh-G/S (%)	Lignin oil yield (wt%)
1	Powder[b]	3	1.1	1.1	6.0	1.1	2.1	29.3	0.0	1.9	1.5	**44.2**	81	66	87
2	Pellets[c]	3	1.2	1.2	6.2	0.9	3.1	22.8	0.2	1.5	1.3	**38.2**	83	60	91
3	Pellets[d]	3	1.3	1.2	5.2	0.9	3.6	21.1	0.2	1.7	1.2	**36.4**	82	58	84
4	Blank[e]	3	0.2	3.3	0.1	1.9	0.4	0.5	0.3	0.6	1.3	**8.5**	80	6	84
5	Blank[f]	3	0.1	3.9	0.1	1.9	0.3	0.6	1.0	0.7	1.2	**9.8**	79	6	80
6	Blank[g]	3	0.1	3.5	0.4	1.8	0.3	0.5	1.5	1.3	0.7	**10.1**	81	5	82
7	Two-step[h]	3	1.4	0.4	3.7	0.5	0.9	1.9	0	0.5	1.2	**10.6**	85	18	64
8	Blank[e]	0	0.0	0.5	0.0	0.3	0.1	0.1	0.5	2.6	0.3	**4.4**	75	1	28
9	Blank[e]	0.5	0.0	1.6	0.1	1.1	0.1	0.3	2.0	3.5	0.6	**9.5**	78	4	65
10	Blank[e]	3	0.2	3.3	0.1	1.9	0.4	0.5	0.3	0.6	1.3	**8.5**	80	6	84
11	Blank[e]	6	0.6	2.2	0.0	1.4	0.4	0.3	0.1	0.1	1.6	**6.8**	86	5	85
12	Powder[b]	0	0.1	0.8	0.0	0.4	0.4	9.8	0.1	6.0	0.2	**17.7**	75	55	39
13	Powder[b]	0.5	0.3	1.1	1.2	0.9	1.1	20.3	0.1	4.6	0.7	**30.4**	80	67	68
14	Powder[b]	3	1.1	1.1	6.0	1.1	2.1	29.3	0.0	1.9	1.5	**44.2**	81	66	87
15	Powder[b]	6	2.1	0.6	9.1	0.5	2.4	34.1	0.0	1.4	1	**51.2**	80	67	94

[a] Reaction conditions: 2 g extracted birch sawdust, 40 mL MeOH, 523 K and 3 MPa H_2 at RT. [b] 0.2 g Ni-Al_2O_3 powder (<0.25 mm). [c] 0.2 g Ni-Al_2O_3 pellets (1.2x3 mm trilobe) without catalyst basket. [d] 0.2 g Ni-Al_2O_3 pellets (1.2x3 mm trilobe) in catalyst basket. [e] no catalyst and 0.1 MPa N_2 at RT. [f] no catalyst and 3 MPa N_2 at RT. [g] no catalyst and 3 MPa H_2 at RT. [h] Reaction on brown oil (from blank reaction, entry 4) with 0.2 g Ni-Al_2O_3 powder (<0.25 mm).

Table S2 Detailed phenolic monomer yields of all reactions described in fig. S4 in the ESI.[a]

Entry	Ni-Al_2O_3 catalyst	Reaction time (h)	4-ethyl-G/S	4-propeyl-G/S	4-propyl-G/S	4-propanal/one-G/S	4-methoxypropyl-G/S	4-propanol-G/S (Poh-G/S)	4-methoxypropenyl-G/S	Coniferyl/sinapyl-alcohol	other	**Total monomers (C%)**	% S-monomers	Selectivity Poh-G/S (%)	Lignin oil yield (wt%)
1	Pellets	0	0.1	0.8	0.3	0.5	0.4	3.4	0.3	6.8	0.3	**12.7**	76	27	37
2	Pellets	0.5	0.4	1.0	1.7	0.9	1.7	12.3	0.5	4.7	0.8	**24.0**	80	51	68
3	Pellets	1.5	0.8	1.5	3.4	0.8	2.9	17.8	0.3	2.0	1.0	**30.6**	82	58	80
4	Pellets	3	1.3	1.2	5.2	0.9	3.6	21.1	0.2	1.7	1.2	**36.4**	82	58	84
5	Pellets	6	1.9	0.8	7.1	0.7	4.0	22.6	0.0	0.9	1.5	**39.3**	83	57	93
6	Pellets	16	2.4	0.5	7.8	0.6	4.4	23.7	0.0	0.7	1.3	**41.4**	81	57	99

[a] Reaction conditions: 2 g extracted birch sawdust, 40 mL MeOH, Ni-Al_2O_3 pellets (1.2x3 mm trilobe) in catalyst basket, 523 K and 3 MPa H_2 at RT.

Table S3 Detailed phenolic monomer yields of all reactions described in fig. 6a and 6b in the main article.[a]

Entry	Weight Ni-Al_2O_3 pellets (g)	Stirring speed (rpm)	4-ethyl-G/S	4-propenyl-G/S	4-propyl-G/S	4-propanal/one-G/S	4-methoxypropyl-G/S	4-propanol-G/S (Poh-G/S)	4-methoxypropenyl-G/S	Coniferyl/sinapyl-alcohol	other	**Total monomers (C%)**	% S-monomers	Selectivity Poh-G/S (%)	Lignin oil yield (wt%)
1	0.2	0	1.2	1.2	5.0	0.8	3.9	15.3	0.2	1.4	1.3	**30.2**	83	51	84
2	0.2	250	1.5	1.3	6.0	0.9	3.6	15.0	0.1	1.2	1.8	**31.4**	82	48	80
3	0.2	500	1.5	1.4	5.1	0.8	3.7	19.0	0.2	1.7	1.1	**34.4**	82	55	87
4	0.2	750	1.3	1.2	5.2	0.9	3.6	21.1	0.2	1.7	1.2	**36.4**	82	58	84
5	0.2	900	1.5	1.3	5.4	0.8	3.3	21.2	0.2	1.4	1.1	**36.0**	81	59	85
6[b]	0.2	250	1.7	1.0	6.7	0.9	3.6	16.0	0.1	1.4	1.7	**33.2**	81	48	85
7[b]	0.2	750	1.2	1.2	6.2	0.9	3.1	22.8	0.1	1.5	1.3	**38.2**	83	60	91
7[c]	0 (blank)	750	0.2	3.3	0.1	1.9	0.4	0.5	0.3	0.6	1.3	**8.5**	80	6	84
8	0.1	750	1.2	1.9	5.1	1.4	3.3	17.5	0.2	1.8	1.9	**34.4**	82	51	90
9	0.2	750	1.3	1.2	5.2	0.9	3.6	21.1	0.2	1.7	1.2	**36.4**	82	58	84
10	0.5	750	1.0	0.5	6.4	0.5	2.9	22.2	0.1	1.3	1.0	**36.0**	82	62	78
11	1	750	1.1	0.4	7.6	0.4	2.9	21.0	0.1	0.8	0.8	**35.1**	85	60	70

[a] Reaction conditions: 2 g extracted birch sawdust, 40 mL MeOH, Ni-Al_2O_3 pellets (1.2x3 mm trilobe) in catalyst basket, 523 K and 3 MPa H_2 at RT. [b] 0.2 g Ni-Al_2O_3 pellets (1.2x3 mm trilobe) without catalyst basket [c] no catalyst and 0.1 MPa N_2 at RT.

Table S4 Detailed phenolic monomer yields of all reactions described in fig. 6c and 6d in the main article.[a]

Entry		Reaction time (h)	Catalyst size (mm)	H_2-pressure (MPa)	4-ethyl-G/S	4-propenyl-G/S	4-propyl-G/S	4-propanal/one-G/S	4-methoxypropyl-G/S	4-propanol-G/S (Poh-G/S)	4-methoxypropenyl-G/S	Coniferyl/sinapyl-alcohol	other	**Total monomers (C%)**	% S-monomers	Selectivity Poh-G/S (%)	Lignin oil yield (wt%)
1	no basket	3	< 0.25	3	1.1	1.1	6.0	1.1	2.0	29.3	0.0	1.9	1.5	**44.2**	81	66	87
2	no basket	3	0.25-0.5	3	1.4	1.2	5.9	0.7	2.6	27.8	0.2	2.0	1.0	**42.7**	81	65	88
3	no basket	3	0.5-1	3	1.4	1.3	6.4	0.7	2.8	27.4	0.2	1.8	1.0	**43.0**	81	64	89
4	no basket	3	1.2 x 3	3	1.2	1.2	6.2	0.9	3.1	22.8	0.1	1.5	1.3	**38.2**	83	60	91
5	basket	3	0.5-1	3	1.2	1.1	4.7	0.7	3.3	27.0	0.1	1.3	1.1	**40.5**	82	67	88
6	basket	3	1.2 x 3	3	1.3	1.2	5.2	0.9	3.6	21.1	0.2	1.7	1.2	**36.4**	82	58	84
7	no basket	0.5	< 0.25	3	0.3	1.1	1.2	0.9	1.1	20.3	0.1	4.6	0.7	**30.4**	80	67	68
8	no basket	0.5	0.25-0.5	3	0.4	1.1	1.6	0.8	1.4	19.4	0.1	3.8	0.7	**29.3**	80	66	66
9	no basket	0.5	0.5-1	3	0.4	1.3	1.7	0.6	1.5	19.3	0.2	4.4	0.6	**30.0**	80	64	68
10	no basket	0.5	1.2 x 3	3	0.4	1.5	1.7	0.9	1.7	14.5	0.4	4.7	0.8	**26.6**	80	55	67
11	basket	3	1.2 x 3	0.5	1.9	2.8	6.1	1.7	3.1	7.9	0.3	1.9	1.5	**27.1**	81	29	86
12	basket	3	1.2 x 3	1	1.7	1.5	6.2	0.9	3.6	17.8	0.2	1.9	1.1	**34.9**	80	51	86
13	basket	3	1.2 x 3	3	1.3	1.2	5.2	0.9	3.6	21.1	0.2	1.7	1.2	**36.4**	82	58	84
14	basket	3	1.2 x 3	5	1.3	0.9	2.5	0.4	3.6	26.1	0.2	1.1	1.0	**37.1**	81	70	85

[a] Reaction conditions: 2 g extracted birch sawdust, 40 mL MeOH, Ni-Al_2O_3 pellets (1.2x3 mm trilobe) in catalyst basket , 523 K and 3 MPa H_2 at RT.

Table S5 Physicochemical characterization of Ni-Al_2O_3 catalyst pellets through CO-chemisorption and N_2-physisorption.

Entry		Nickel Dispersion[a] (%)	Pore volume[b] (cm^3/g)		
			Micro	Meso	Total
1	Fresh Ni-Al_2O_3	4.6	0.01	0.19	0.20
2[c]	Spent Ni-Al_2O_3	1.1	0.01	0.22	0.23
3[d]	Spent Ni-Al_2O_3 after H_2-treatment	5.8	< 0.01	0.23	0.23

[a] CO-chemisorption was used to assess the availability of the active Nickel species. Nickel dispersion is calculated, assuming the chemisorption of 1 CO molecule on 1 surface Nickel atom. [b] N_2-physiorption was used to determine the pore size volume. [c] Catalyst recovered after reaction entry 3, Table S1. [d] Catalyst from entry 2, Table S5 after regeneration at 773 K for 4h under a constant H_2-flow.

Table S6 Determination of nickel content in carbohydrate pulp through ICP-AES analysis.[a]

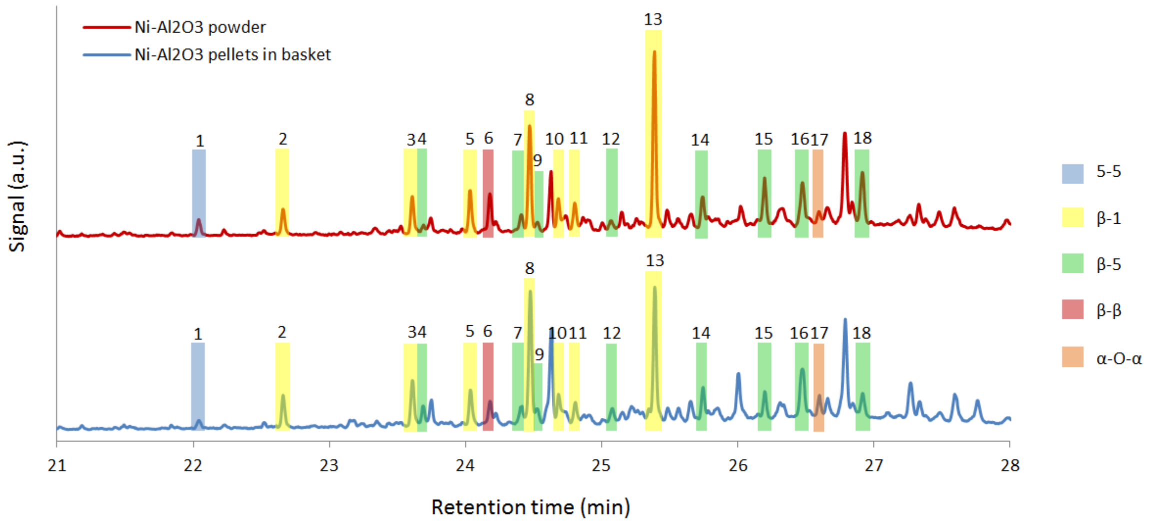
Entry		Ni-content in solution (ppm)	Ni-content in pulp (wt%)
1[b]	Blank	0.01	/
2[c]	Extracted birch sawdust	0.01	0.0001
3[d]	Pulp obtained from blank reaction	1.71	0.0171
4[e]	Pulp obtained from blank reaction + Ni-solution	5.07	0.0507
5[f]	Pulp obtained from blank reaction + Ni-Al_2O_3	6.23	0.0623
6[g]	Pulp obtained from catalytic reaction	1.11	0.0111

[a] An acid digestion method was used to solubilize the pulps (0.2 g) and Ni-Al_2O_3. After this procedure, a solution with a total volume of 20 mL was obtained (procedure in ESI, section A).[b] the digestion method was performed without biomass sample. [c] substrate in RCF reactions in the article. [d] pulp from entry 4, Table S1. [e] sample spiked with 100 µL of a 1000 ppm Ni-standard solution before acid digestion. [f] sample spiked with 0.50 mg Ni-Al_2O_3 powder (21% Ni-content) before acid digestion. [g] pulp from entry 3, Table S1.

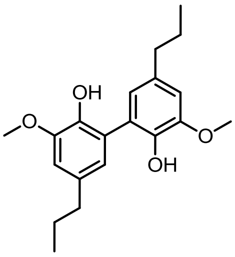
Discussion Table S5

The Ni-content in the pulp was examined with ICP-AES (after acid digestion of the pulp, procedure in ESI, section A) and the results are presented in Table S5. Interestingly, the pulp from a catalytic reaction (entry 3, Table 1) and a blank reaction (entry 4, Table 1) both had a comparable and low Ni-content of about 0.01 wt%. However, since no catalyst is used in blank reactions, the comparable Ni-content in both pulps cannot result from the Ni-Al_2O_3 pellets during reaction. Instead, the small amounts of Ni in the pulps likely originate from the T316 stainless steel alloy, from which the Parr reactor is made of and which contains 12% of Ni. The procedure was verified with two spiked pulps, to which either a soluble Ni-standard or a weight amount of Ni-Al_2O_3 powder was added before acid digestion. In both cases a Ni-content in the pulp of 0.05 wt% was prepared (corresponding to a hypothetical catalyst loss of about 2%), which was confirmed by ICP-AES. The results thus show that Ni-Al_2O_3 pellets are stable under the applied reaction conditions and can be used for the production of a catalyst-free carbohydrate pulp.

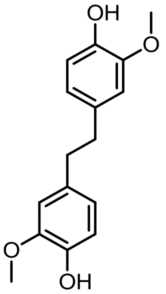
C. Figures



1: 5-5 (PG-PG)



2: β-1 (EG-G)



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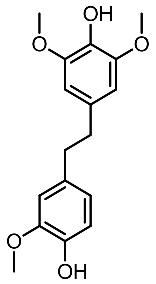

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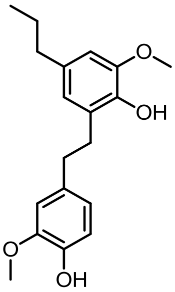
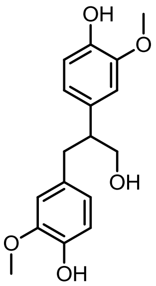
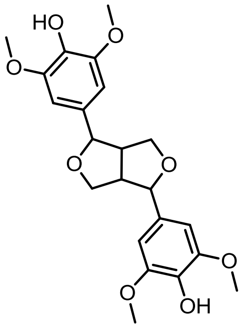


5: β-1 (PohG-G)



6: β-β (PS-PS,α-O-γ_2)



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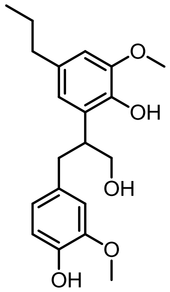

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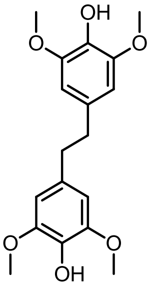

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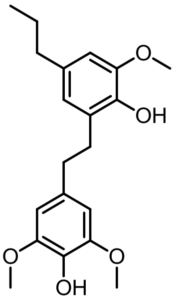

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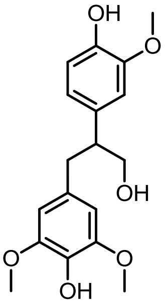

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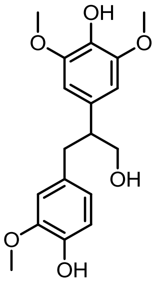

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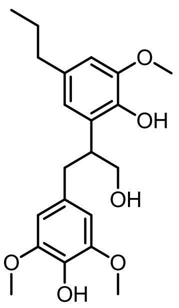
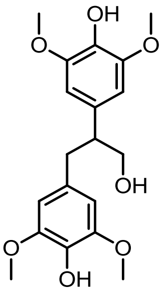
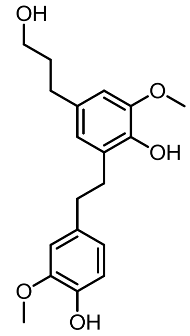


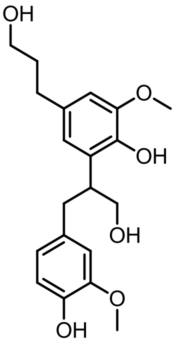
13: β-1 (PohS-S)



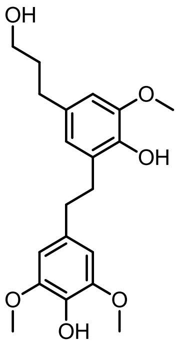
14: β-5 (EG-PohG)



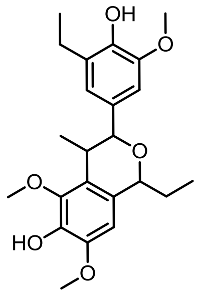
15: β-5 (PohG-PohG)



16: β-5 (ES-PohG)



17: Isochroman



18: β-5 (PohS-PohG)

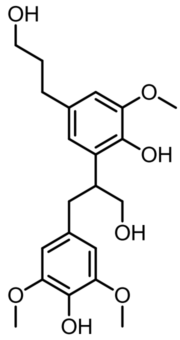


Fig. S1 GC-MS analyses to identify lignin dimer products after catalytic reductive fractionation of birch with a Ni-Al$_2$O$_3$ pellet and powder catalyst. Reaction conditions from entry 1 and 3 in table 1 in the main article. The corresponding mass spectrum for each peak can be found in our previous articles[13, 14] and is confirmed by literature.[15-19]

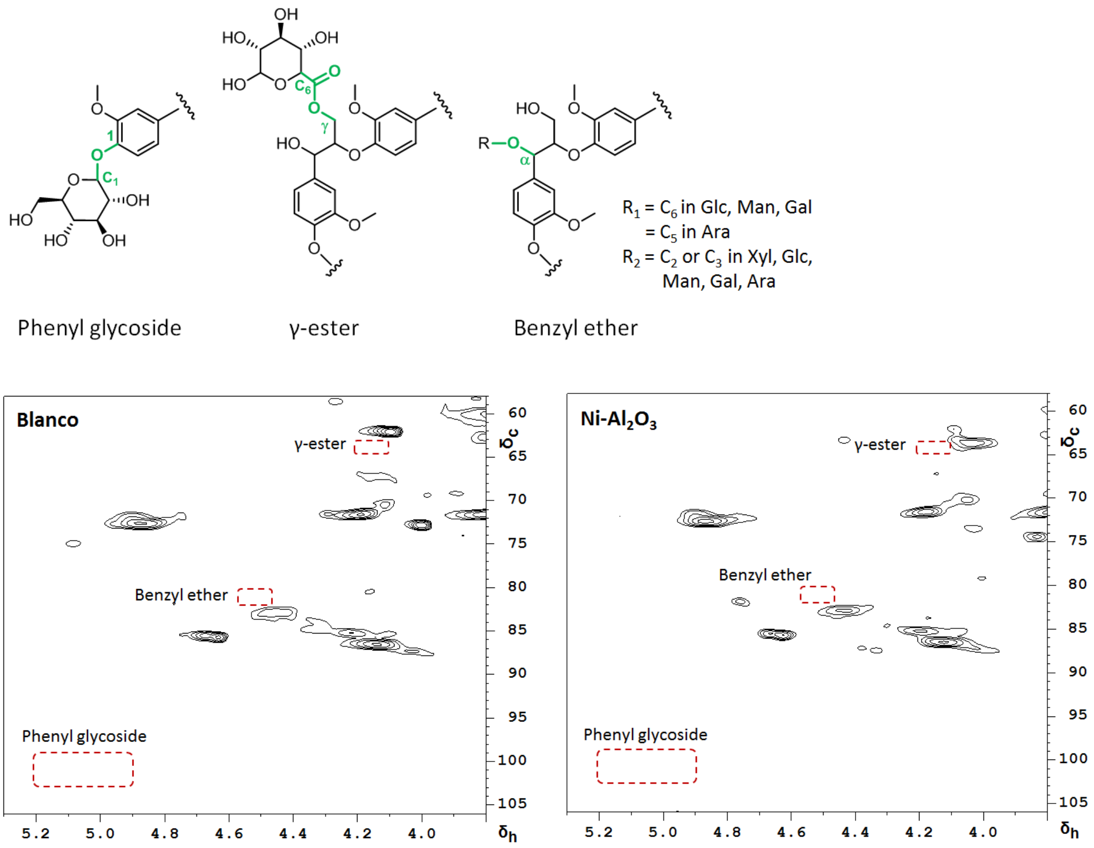


Fig. S2 2D HSQC NMR spectra illustrating the absence of three common lignin carbohydrate complexes (LCCs) in birch wood after heating to 523 K (0 h) with a catalyst (0.2 g Ni-Al_2O_3 powder, <0.25 mm) and without a catalyst (blank). Reaction conditions: 2 g extracted birch sawdust, 40 mL MeOH, 523 K and 3 MPa H_2 (0.1 MPa N_2 for blank) at RT, 750 rpm.

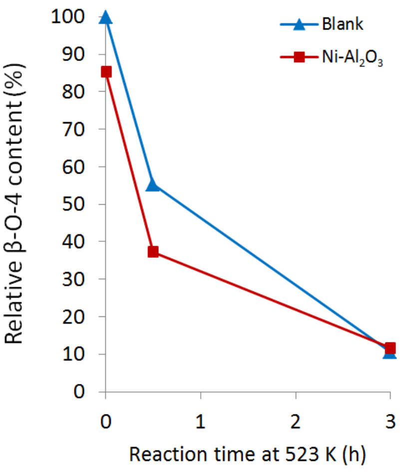


Fig. S3 Relative content of β-O-4 linkages after 0, 0.5 and 3 h of reactions with catalyst (0.2 g Ni-Al_2O_3 powder) and without catalyst (blank). Reaction conditions: 2 g extracted birch sawdust, 40 mL MeOH, 523 K and 3 MPa H_2 at RT (0.1 MPa N_2 for blank reactions). Calculations are based on the integrated volume of the β-O-4 α-carbon signal (δ_C 70-74, δ_H 4.7-5.0 ppm), using the aromatic $S_{2,6}$ signal (δ_C 102-108, δ_H 6.2-6.9 ppm) as internal reference.

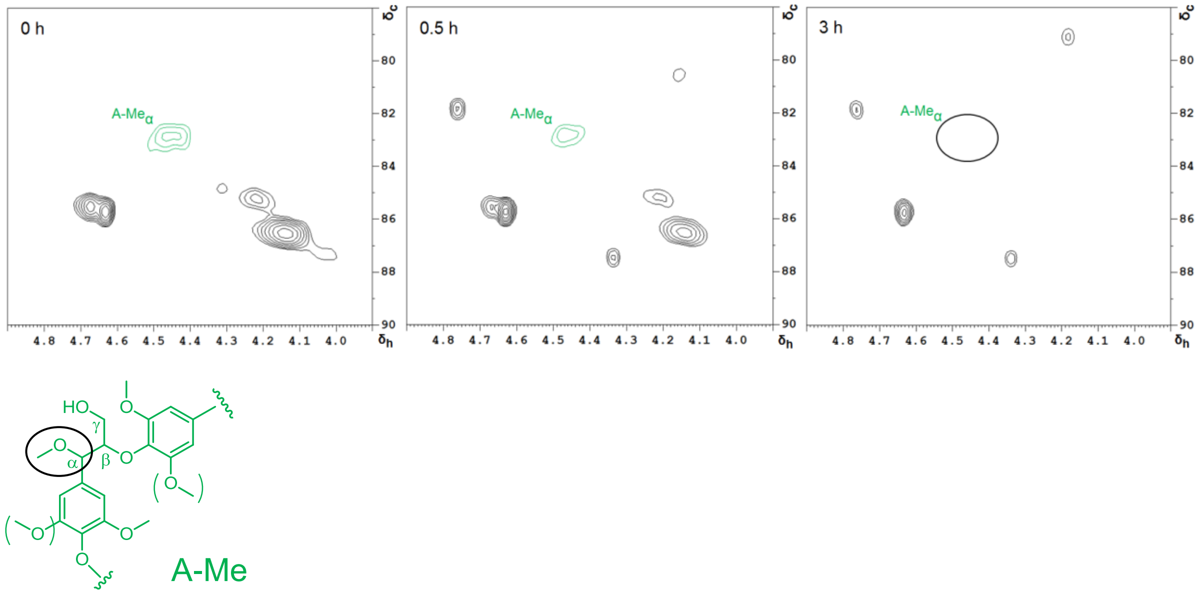


Fig. S4 2D HSQC NMR spectra illustrating the evolution of the α-methoxylated β-O-4 ether bond without catalyst or H_2 (blank).[20] Green signals represent the α-methylated β-O-4 linkage (A-Me). Reaction conditions: 2 g extracted birch sawdust, 40 mL MeOH, 523 K and 0.1 MPa N_2 at RT, 750 rpm

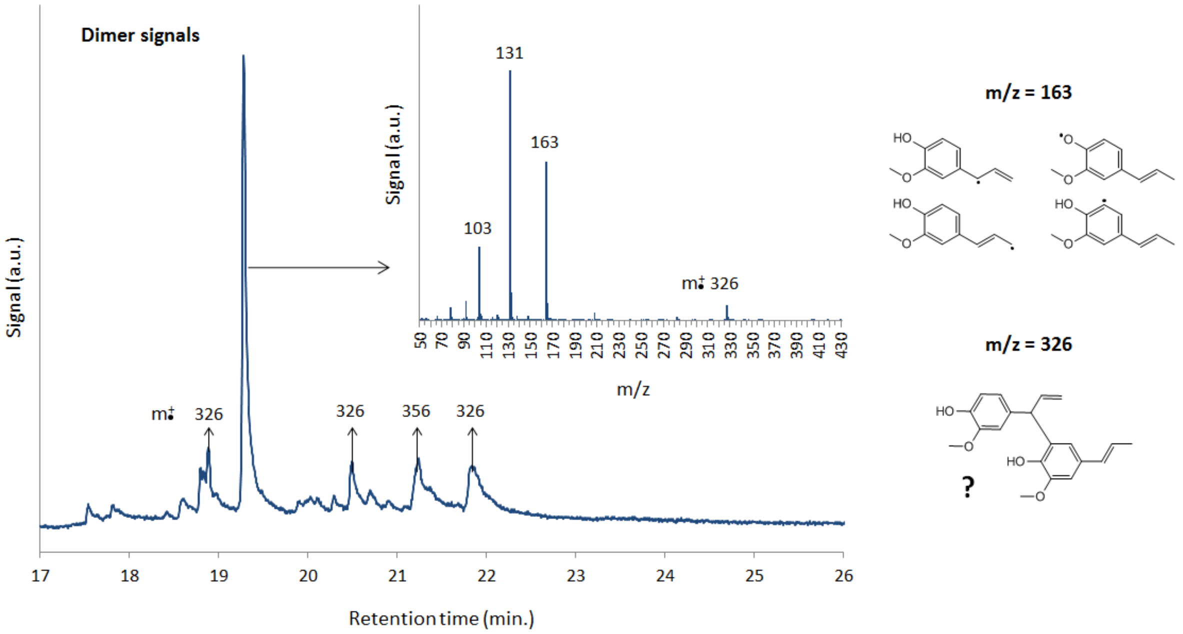


Fig. S5 GC-MS analysis on soluble repolymerization products (dimers) after a blank reaction on coniferyl alcohol. Reaction conditions: 0.05 g coniferyl alcohol, 20 mL MeOH, 523 K and 0.1 MPa N_2 at RT in 50 mL Parr batch reactor.

Fig. S6 Encrusted precipitate on the reactor surface after reaction on coniferyl alcohol without catalyst (blank). Reaction conditions: 0.05 g coniferyl alcohol, 20 mL MeOH, 15 minutes at 523 K, 0.1 MPa N_2 at RT, 750 rpm.

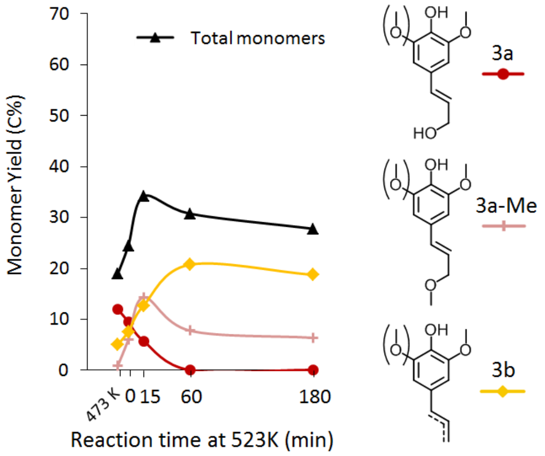


Fig. S7 Lignin monomer yields in function of time without catalyst (blank) on guaiacylglycerol-β-guaiacylether (β-O-4 dimer). Products: (3a) coniferyl alcohol, (3a-Me) 4-methoxy-*n*-propenyl-G and (3b) 4-*n*-propenyl-G. Reaction conditions: 0.05 g substrate, 20 mL MeOH, no catalyst, 523 K (also product analysis during the heating phase at 473 K) and 0.1 MPa N_2 at RT in 50 mL Parr batch reactor.

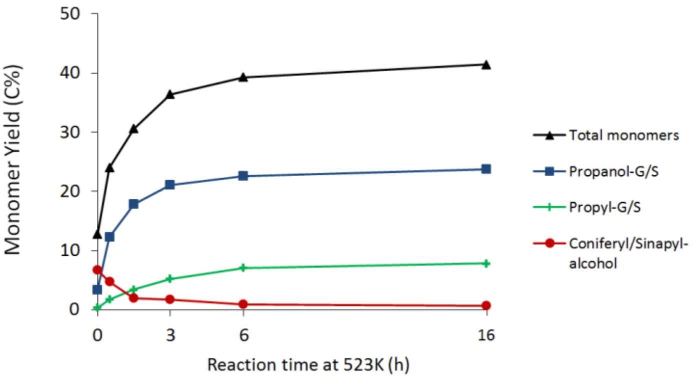


Fig. S8 Lignin monomer yields in function of time with 0.2 g Ni- Al_2O_3 catalyst pellets (1.2 x 3 mm trilobe). Maximum theoretical monomer yield for birch is 45-58%. Reaction conditions: 2 g extracted birch sawdust, 40 mL MeOH, 523 K and 3 MPa H_2 at RT, 750 rpm stirring speed.

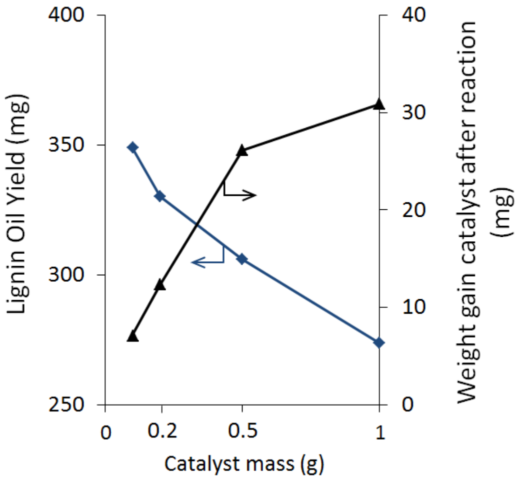


Fig. S9 Influence of the catalyst mass on the obtained lignin oil yield (wt%) and the catalyst weight gain (in mg) after reaction. Reaction conditions: 2 g extracted birch sawdust, 0.2 g Ni- Al_2O_3 pellets (1.2x3 mm trilobe), 40 mL MeOH, 523 K and 3 MPa H_2 at RT, 750 rpm stirring speed.

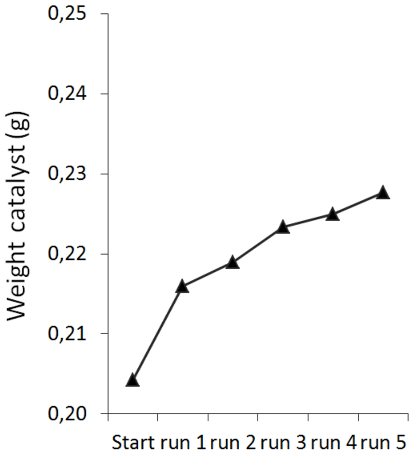


Fig. S10 Catalyst weight profile (in mg) after five consecutive reactions without H_2-treatment. Reaction conditions: 2 g extracted birch sawdust, ~0.2 g Ni- Al_2O_3 pellets (1.2x3 mm trilobe), 40 mL MeOH, 523 K and 3 MPa H_2 at RT, 750 rpm stirring speed.

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