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Supporting Information

Catalytic lignocellulose biorefining in *n*-butanol/water: a one-pot approach toward phenolics, polyols, and cellulose

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I. Experimental procedures

Chemicals and materials

All commercial chemicals were analytic reagents and were used without further purification. 5 wt% Ru on carbon, 5 wt% Ru on alumina, 5 wt% Pd on carbon, 5 wt% Pd on alumina, 5 wt% Pt on carbon, 5 wt% Pt on alumina, guaiacol (2-methoxyphenol, 98%), 4-*n*-propylguaiacol (>99%), syringol (2,6-dimethoxyphenol, 99%), 4-methylsyringol (>97%), xylitol (≥99%), mannitol (>98%), xylose (≥99%), threitol (>99%), *myo*-inositol (99%), 2-isopropylphenol (>98%), pyridine (≥99%), *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (-), and tetrahydrofuran (>99%) were purchased from Sigma Aldrich. 4-Ethylguaiacol (98%), *n*-butanol (>99%), and hydroxylamine hydrochloride (97%) were purchased from Acros organics. Methanol (>99%), ethanol (>99%), dichloromethane (>99%), HCl (37% solution in water) and glucose (-) were purchased from Fischer Chemical Ltd. 4-*n*-Propanolguaiacol (3-(4-hydroxy-3-methoxyphenyl)-1-propanol, >98%) and meso-erythritol (>99%) were purchased from TCI chemicals. Galactitol (-), galactose (>99%), arabitol (-), and arabinose (>99%) were purchased from Fluka AG. Sorbitol (>99%) and mannose (>99%) were purchased from Janssen Chimica. 5 wt% Rh on carbon was purchased from Alfa Aesar.

Eucalyptus sawdust

Dry eucalyptus wood was milled and sieved to obtain a sawdust fraction with a size of 250-500 µm. Subsequently, a two-step extraction procedure was followed using a Soxtex 2055 Avanti apparatus to remove any extractives like fats, waxes, resins and terpenoids/steroids[1] which can interfer with analysis procedures (*e.g.* determination of the Klason lignin content). Porous thimbles were filled with 2-3 g sawdust, and were completely submersed for 15 minutes in 70 mL of a boiling solvent mixture comprising toluene and ethanol in a 2/1 (v/v) ratio. Next, a standard Soxhlet extraction step was executed in which the thimbles were kept above the boiling mixture for 3 h. After cooling, samples were washed with ethanol and dried overnight at 80 °C. Because completely dry sawdust is hygroscopic and difficult to handle, the sawdust was stored in an open recipient to equilibriate with air humidity for minimum 24h, resulting in a H_2O uptake of circa 4 wt%. This sawdust, hereinafter referred to as 'pre-extracted sawdust', was used for catalytic experiments.

Compositional analysis of the eucalyptus sawdust was performed by NREL according to NREL *Laboratory Analytical Procedures*.[2-5] The composition is summarised in Table S1.

Reductive catalytic fractionation reaction (100 mL scale)

The reductive catalytic fractionation (RCF) experiments were performed in a 100 mL stainless steel batch reactor (Parr Instruments & Co.). In a typical reaction, 2 g pre-extracted sawdust was loaded into the reactor together with the catalyst powder (0.2 g Ru/C or other) and a solvent mixture (40 mL) comprising *n*-butanol/water in equal volumetric ratio's. The reactor was sealed, flushed threefold with N_2, and pressurised with H_2 (30 bar at room temperature). Subsequently, the reaction mixture was stirred (750 rpm) and heated to 200 °C (~ 15 °C min^{-1}). When the reaction temperature was reached, the temperature was kept constant for 2 h after which the reactor was cooled and depressurised at room temperature. Afterwards, the reactor contents were quantitatively collected by washing the reactor with water and *n*-butanol.

Product separation

The obtained product mixture was filtered using a Por 4. fritted glass filter to separate the solid residue (pulp and catalyst) from the liquid products. The solid pulp was washed with additional water and *n*-butanol so that the resulting filtrate was composed of 120 mL water and 53 mL *n*-butanol. The two phases of the filtrate were separated from each other using a 250 mL separatory funnel, as depicted in Fig. 1 in the main article. Subsequently, the aqueous phase was washed two times with 33 mL *n*-butanol to fully extract the depolymerised lignin (see Fig. S1). In this way, the total *n*-butanol fraction measured ~ 120 mL, equal to the volume of the aqueous fraction.

The pulp was rinsed with ethanol to wash out residual *n*-butanol. The ethanol wash phase was not further used for analysis. The solids were dried overnight at 80 °C, followed by equilibration with air humidity (as in Section *Sawdust Preparation*).

Analysis of the *n*-butanol phase

The *n*-butanol was evaporated using a rotavap, thereby yielding a viscous orange-brown lignin oil. The lignin oil was dried overnight at 80 °C, after which the mass of the dry oil could be determined. To analyse the lignin monomers, a weighed amount of external standard (2-isopropylphenol, ~50 mg) was added to the lignin oil after which the content was completely resolubilised in 7 mL ethanol. A sample was then analysed on a GC (Agilent 6890 series) equipped with a HP5-column and a flame ionisation detector (FID). The following operating conditions were used: injection temperature of 300 °C, column temperature program: 50 °C (2 min), 15 °C min^{-1} to 150 °C, 10 °C min^{-1} to 220 °C and 20 °C min^{-1} to 290 °C (12 min), detection temperature of 300 °C. Sensitivity factors of most the monomer products were obtained by calibration with commercial standards (section Chemicals and materials). Sensitivity factors of a few remaining non-commercially available monomers (ethylsyringol, 4-*n*-propyl syringol and 4-*n*-propanol syringol) were deduced by interpolation based on (i) the sensitivity factors of analogues compounds and (ii) taking into account the basic principles of the 'effective carbon number method'.[6] The product yield is expressed in wt%, relative to the total lignin content (*i.e.* Klason + acid soluble lignin).

The dimers were analysed in the same way as the monomers, yet a derivatisation step was added to increase their volatility before GC analysis. Therefore, 0.2 mL of the resolubilised lignin oil with the internal standard 2-isopropylphenol, was dried under a continuous 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 80 °C for 20 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 250 °C, column temperature program: 60 °C (2 min), 10 °C min^{-1} to 280 °C (13 min), detection temperature of 290 °C.

To get more insight in the degree of lignin depolymerisation, 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 solubilised in THF (~ 2-5 mg mL^{-1}) and subsequently filtered with a 0.45 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 Waters 2988 Photodiode array detector.

NMR spectra were recorded on a Bruker Avanace 400 MHz spectrometer. 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).

Analysis of the aqueous phase

A weighed amount of external standard (*myo*-inositol, ~30 mg) was added to the aqueous phase. From the total solution, 3 mL was taken for GC analysis. The water was first evaporated under continuous nitrogen flow, and subsequently resolubilised in 0.5 mL pyridine containing 50 g hydroxylamine hydrochloride L^{-1}. The vial was sealed and put in an oven at 80 °C for 20 min. Hereafter, 0.5 mL *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide was added. The vial was again sealed and put in an oven at 80 °C for 20 min. The derivatised sample was analysed in the same way by GC as the lignin monomers and dimers (*vide supra*). Sensitivity factors for polyols and other low molecular weight products were obtained from calibration curves of commercial standards.

The (non-silylated) aqueous phase was also analysed by HPLC using an Agilent 1200 series HPLC equipped with a Varian Metacarb 67C column (300 x 6.5 mm) and a RI detecor. Samples were filtered using a 0.45 µm PES membrane prior to analysis, to remove any particulate matter.

Analysis of the pulp

The carbohydrate content and composition of the obtained carbohydrate pulps after hydrogenolysis were determined, using a standard total sugar determination procedure, adapted with hydrolysis conditions for cellulose-rich materials.[7-9] Samples of 10 mg were hydrolysed in a 13 M H_2SO_4-solution (1 mL) at RT for 2 h and subsequently hydrolysed in a diluted 2 M H_2SO_4-solution (6.5 mL) at 100 °C 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^{-1} β-D-allose solution of 1/1 benzoic acid/water) was added to 3 mL of the hydrolysed sample. NH_3 25% in water (1.5 mL) was added, as well as droplets of 2-octanol to avoid excessive foaming. Reduction was catalysed with $NaBH_4$ (0.2 mL of a 200 mg $NaBH_4$/mL 2 M NH_3 solution) for 30 min at 40 °C and the reaction was stopped by adding 0.4 mL acetic acid. At this point the procedure was 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 catalyse 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^{-1} 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 ionisation detector (FID). Separation was executed at 225 °C with injection and detection temperatures at 270 °C. Calibration samples, containing known amounts of the expected monosaccharides were included in each analysis. To calculate the carbohydrate content in the analysed samples, a correction factor was used to compensate for the addition of water during hydrolysis. Each substrate was analysed in threefold and the average values were used in the calculation of the carbohydrate retention.

Analysis of the headspace

GC analysis of the gaseous products in the headspace was performed on an Interscience Trace GC equipped with HayeSep Q and RTX-1 columns and a FID and TCD detector. Commercial standards were used for identification and quantification.

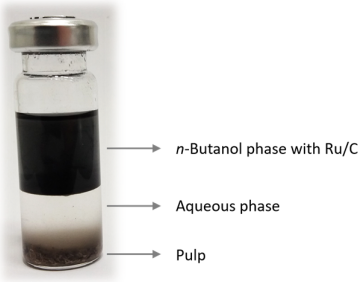
Reductive catalytic fractionation reaction (2 L scale)

The large scale reductive catalytic fractionation (RCF) experiment was performed in a 2 L stainless steel batch reactor (Parr Instruments & Co.). 80 g non-extracted eucalyptus sawdust was loaded into the reactor together with 8.0 g Ru/C and a solvent mixture (800 mL) comprising *n*-butanol/water in equal volumetric ratio's. The reactor was sealed, flushed threefold with N_2, and pressurised with H_2 (30 bar at room temperature). Subsequently, the reaction mixture was stirred (750 rpm) and heated to 200 °C (~ 30 min). When the reaction temperature was reached, the temperature was kept constant for 2 h after which the reactor was cooled and depressurised at room temperature. Afterwards, the reactor contents were quantitatively collected by washing the reactor with water and *n*-butanol.

Catalyst recuperation & reuse

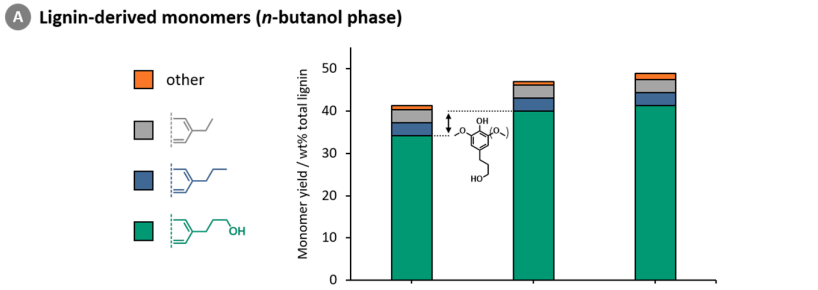
Catalyst recuperation is an important but challenging aspect given the fact that RCF involves a solid substrate and a solid redox catalyst. Different catalyst recuperation strategies have been disclosed, which have recently been reviewed by Barta and co-workers.[10, 11] Briefly, these include the use of ferromagnetic catalysts,[12-14] catalyst pellets,[15] a catalyst basket,[15, 16] a dual bed flow-through reactor,[17-19] or by performing liquid-liquid extraction.[20]

In this work, washing with *n*-butanol/water was applied to recover the spent catalyst from the pulp (Fig. S10). The carbon-supported catalyst is relatively apolar and primarily resides in the *n*-butanol phase. The pulp on the other hand is located at the bottom of the aqueous phase. After liquid-liquid extraction, the *n*-butanol phase containing part of the Ru/C was removed and fresh *n*-butanol was added. This was repeated until the *n*-butanol phase remained relatively clear.



The isolated catalyst was used to verify reusability under the standard reaction conditions (see Fig. 6 in the main article).

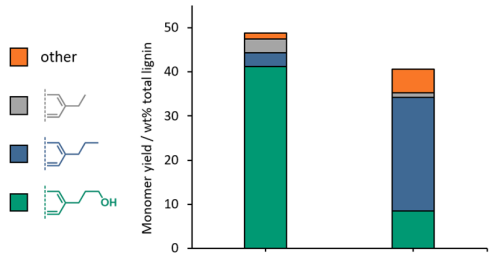
II. Figures



# extractions of aqueous phase[a]	1 step	2 steps	3 steps
Volume *n*-butanol (step 1)	70 mL	70 mL	53 mL
Volume *n*-butanol (step 2)	-	50 mL	33 mL
Volume *n*-butanol (step 3)	-	-	33 mL
Total volume *n*-butanol (step 1 + 2 + 3)	70 mL	120 mL	120 mL

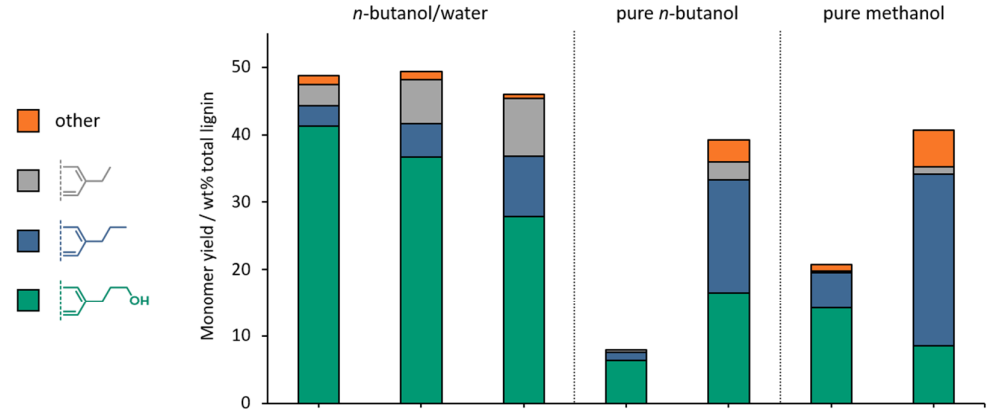
Fig. S1. (A) Influence of the extraction procedure on lignin monomer yields present in *n*-butanol phase. At least one additional extraction step of the aqueous phase is required to fully extract the more polar monomers (4-*n*-propanol guaiacol and 4-*n*-propanol syringol) in the *n*-butanol phase. To assure complete recovery of the lignin fraction in the *n*-butanol phase, a three-step extraction procedure (gray) was consistently used throughout this work. **(B)** A small amount of polyols was co-extracted from the aqueous phase by repeated washing with *n*-butanol, as also observed by HSQC-NMR (Fig. 2D of the main article). Reaction scheme: Fig. 1 in the main article. Reaction conditions: 20 mL *n*-butanol, 20 mL water, 2 g pre-extracted eucalyptus sawdust, 0.2 g Ru/C, 30 bar H_2 at room temperature, 200 °C, 2 h.

[a] Note: After RCF, washing, and isolation of the solids, a biphasic liquor was obtained comprising 120 mL water and 53 (or 70) mL *n*-butanol (see section *Product separation*). Separation of both streams is considered as the first extraction (step 1). In the standard procedure (gray), two additional extractions of the aqueous phase were performed (2 x 33 mL *n*-butanol).



Reaction conditions	This work	According to earlier work[21]
Temperature (°C)	**200**	250
Solvent(s) (mL)	***n*-butanol (20) water (20)**	methanol (40)
Catalyst (g)	Ru/C (0.2)	Ru/C (0.2)
Biomass (g)	Eucalyptus (2)	Eucalyptus (2)
H_2 pressure (bar)	30	30
Time (h)	2	2

Fig. S2. Lignin monomer yield and distribution obtained from Ru/C-catalysed RCF of eucalyptus (i) in *n*-butanol/water at 200 °C (Fig. 1 in the main article), and (ii) according to earlier work, using pure methanol at 250 °C.[21] For the reaction in methanol, the solvent was first evaporated, followed by the same work-up procedure as for the reaction in *n*-butanol/water (*vide supra*). Although the same catalyst was used in both reactions, the lignin product distribution is strikingly different, indicating that product selectivity is not only determined by the catalyst choice,[21] but also by the operating conditions (solvent and/or temperature, see Fig. S3).



Reaction conditions	This work						Earlier work[21]
Temperature (°C)	**200**	220	240	200	250	200	250
Solvent(s) (mL)	**BuOH (20) H_2O (20)**	BuOH (20) H_2O (20)	BuOH (20) H_2O (20)	BuOH (40)	BuOH (40)	MeOH (40)	MeOH (40)

Fig. S3. Lignin monomer yield and distribution obtained from Ru/C-catalysed RCF of eucalyptus using different combinations of temperature and solvent, in support of Fig. S2. Reaction conditions: 40 mL solvent, 2 h, 30 bar H_2 at room temperature, 2 g pre-extracted eucalyptus sawdust, 0.2 g Ru/C. For the reaction in pure methanol, the solvent was first evaporated, followed by the same work-up procedure as for the reaction in *n*-butanol/water (*vide supra*). Briefly, these experiments show that product selectivity is influenced by (i) the reaction temperature and (ii) the solvent composition. The selectivity towards propyl-substituted compounds generally increases with increasing temperature. This selectivity increase depends on the solvent, and is highest when processing in pure methanol, followed by pure *n*-butanol and *n*-butanol/water.

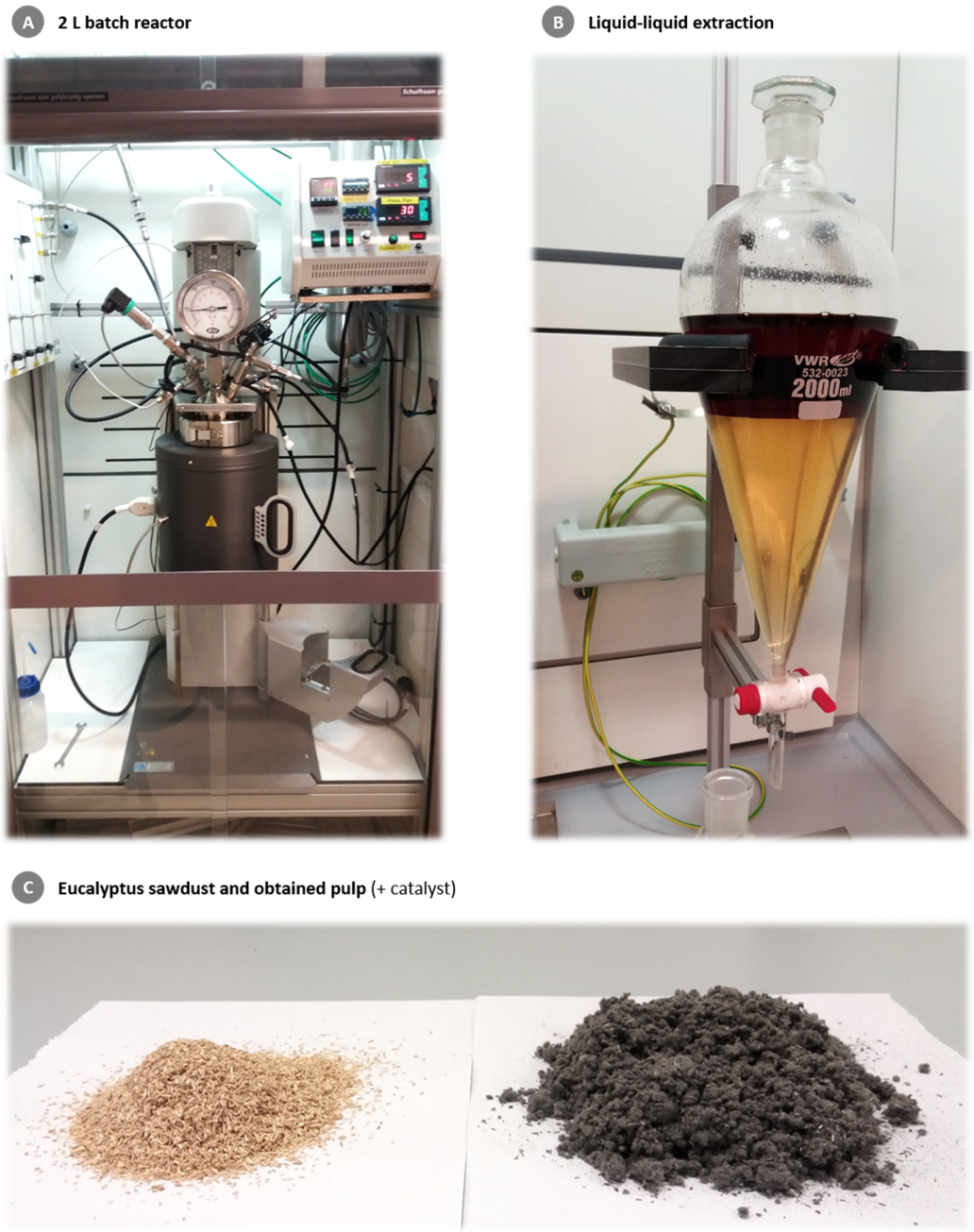
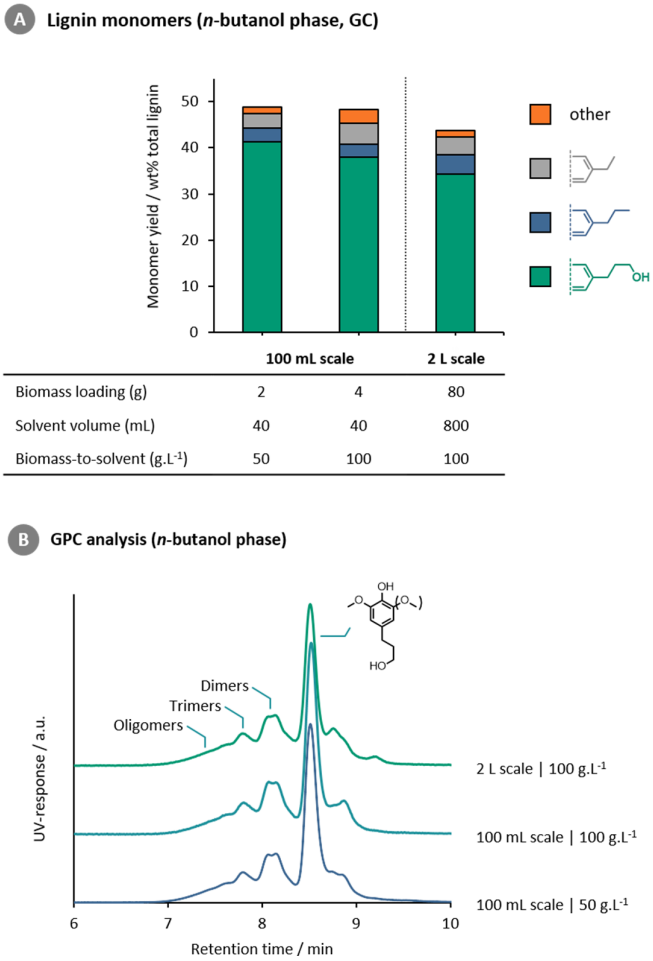


Fig. S4. Upscaling experiment. **(A)** 2 L Parr batch reactor. **(B)** Liquid-liquid extraction. *n*-Butanol phase containing depolymerised liquid is situated on top of the aqueous phase containing polyols. **(C)** Original eucalyptus sawdust (left) and obtained solid residue (pulp and spent catalyst). Note that the macrostructure of the wood particles undergoes substantial alterations upon processing. The individual fibres become less densely stacked, leading to a more open pulp.

Results of the upscaling experiment are presented in Fig. S5. Reaction conditions: 400 mL *n*-butanol, 400 mL water, 80 g non-extracted eucalyptus sawdust, 8 g Ru/C, 30 bar H_2 at room temperature, 200 °C, 2 h.



	100 mL scale		**2 L scale**
Biomass loading (g)	2	4	80
Solvent volume (mL)	40	40	800
Biomass-to-solvent ($g.L^{-1}$)	50	100	100

	100 mL scale		**2 L scale**
Biomass loading (g)	2	4	80
Solvent volume (mL)	40	40	800
Biomass-to-solvent ($g.L^{-1}$)	50	100	100

Fig. S5. RCF of eucalyptus sawdust in *n*-butanol/water using a 2 L reactor, demonstrating the scalability of the process. Results of 100 mL scale experiments are shown for comparison. Reaction conditions: 200 °C, 2 h, 30 bar H_2 at room temperature, Ru/C, 10 wt% catalyst relative to eucalyptus sawdust. **(A)** Lignin monomer yield and distribution. A high monomer yield of 43.7 wt% is obtained from the 2 L experiment (*vs.* 48.4 wt% at 100 mL scale). **(B)** GPC analysis of the *n*-butanol phase, confirming the high yield production of monomers on 2 L scale. The molecular weight distribution of the oils is similar on both scales, indicating extensive lignin depolymerisation. **(C)** Sugar monomer products present in the aqueous phase. Note that the biomass-to-solvent ratio affects the C5 polyol yield, as verified on 100 mL scale. We reason that a higher biomass-to-solvent ratio leads to a slightly lower pH due to deacetylation of hemicellulose, in line with a study by Rinaldi and co-workers.[22] A lower pH facilitates the conversion of hemicellulose to C5 and C6 polyols, as demonstrated in Fig. 8 of the main article.

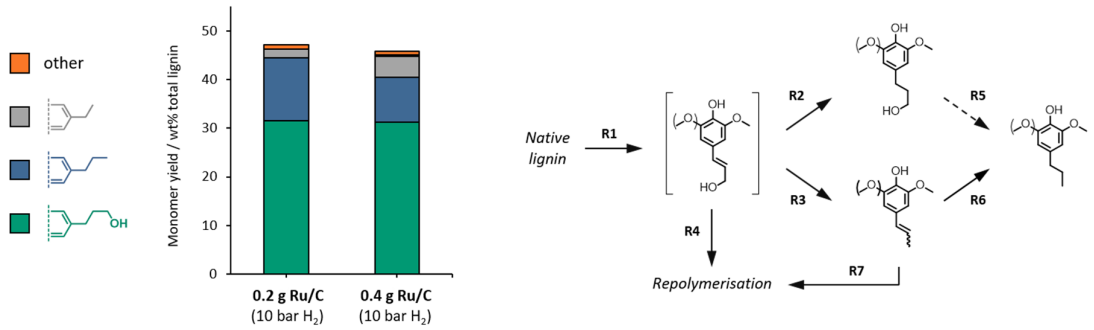


Fig. S6. Lignin monomer yield and distribution obtained from Ru/C-catalysed RCF of eucalyptus in *n*-butanol/water, with varying catalyst loading (*i.e.* varying contact time at constant biomass conversion). The yield of propyl-substituted compounds does not increase upon increasing contact time, indicating that propanol-G/S are not readily converted to propyl-G/S (dashed arrow). See discussion in the main article (section *Influence of pressurised hydrogen & reaction network*). Reaction conditions: 20 mL *n*-butanol, 20 mL water, 2 g pre-extracted eucalyptus sawdust, Ru/C, 10 bar H_2 at room temperature, 200 °C, 2 h.

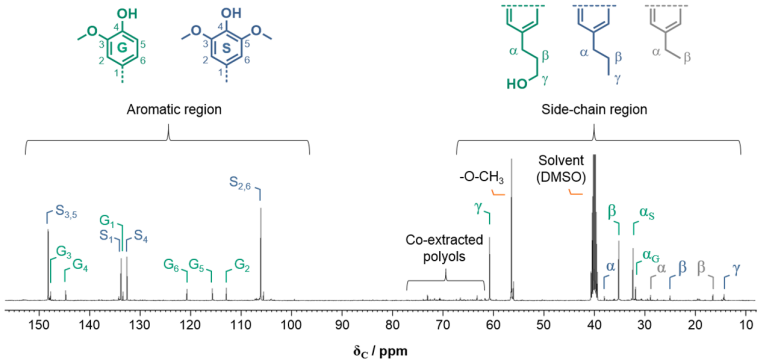


Fig. S7. ^{13}C NMR of lignin oil (*n*-butanol phase) from Ru/C-catalysed RCF, with assignment of signals. Reaction conditions: 20 mL *n*-butanol, 20 mL water, 2 g pre-extracted eucalyptus sawdust, 0.2 g Ru/C, 30 bar H_2 at room temperature, 200 °C, 2 h. Note that the obtained lignin oil is characterised by a high S content, with high selectivity for propanol side-chains.

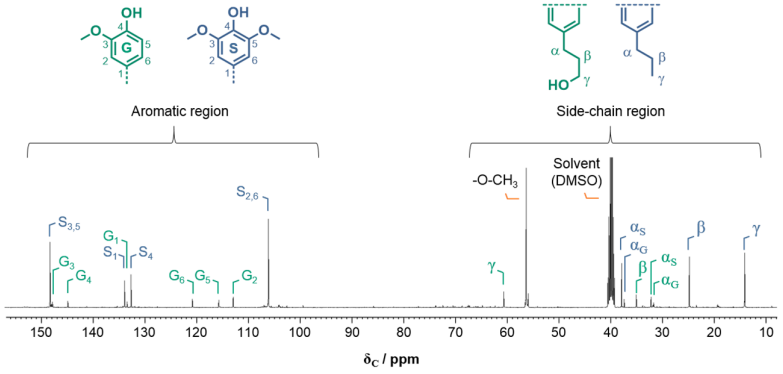


Fig. S8. ^{13}C NMR of lignin oil (*n*-butanol phase) from Rh/C-catalysed RCF, with assignment of signals. Reaction conditions: 20 mL *n*-butanol, 20 mL water, 2 g pre-extracted eucalyptus sawdust, 0.2 g Rh/C, 30 bar H_2 at room temperature, 200 °C, 2 h. Note that the obtained lignin oil is characterised by a high S content, with high selectivity for propyl side-chains.

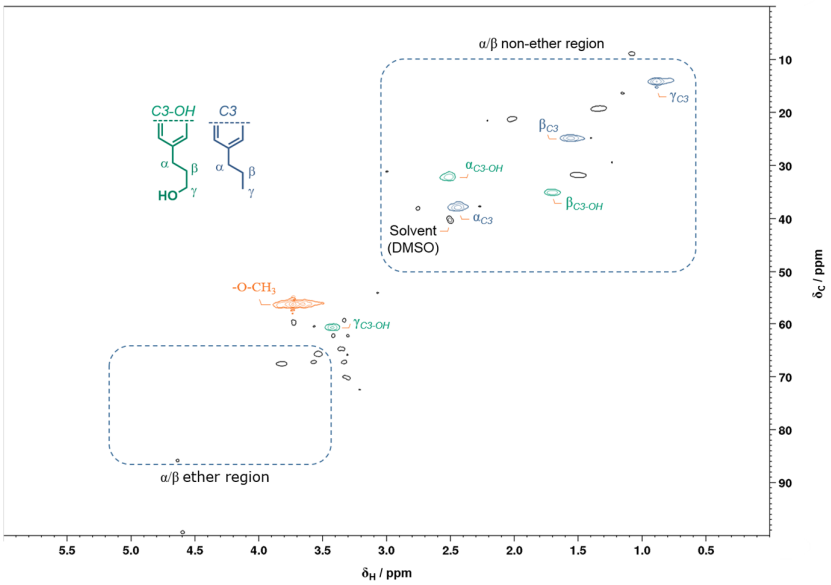


Fig. S9. HSQC NMR of the lignin oil (*n*-butanol phase) from Rh/C-catalysed RCF, with assignment of the main signals. Reaction conditions: 20 mL *n*-butanol, 20 mL water, 2 g pre-extracted eucalyptus sawdust, 0.2 g Rh/C, 30 bar H_2 at room temperature, 200 °C, 2 h.

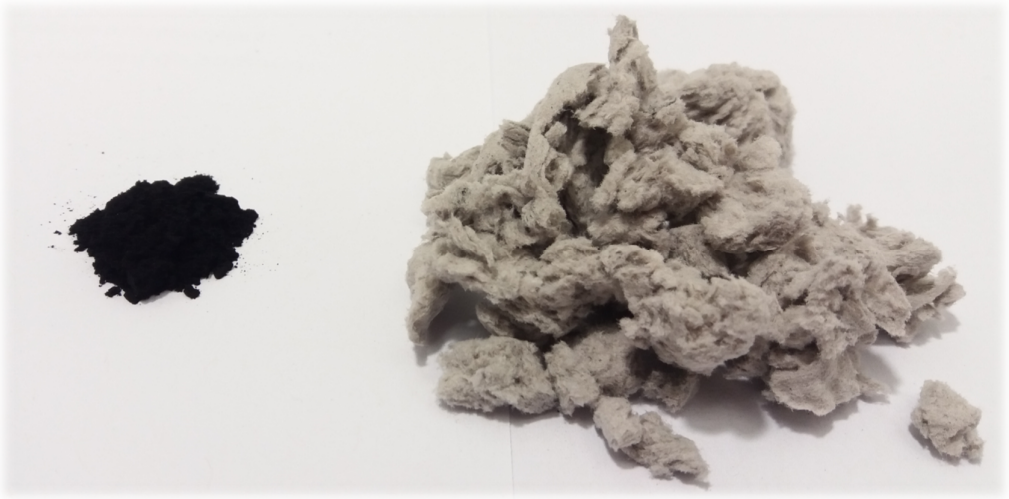


Fig. S10. Result of separating the catalyst (left) from the pulp (right) by washing the residual solids after reaction with *n*-butanol and water. The isolated black powder (*circa* 0.2 g) equals 98.1 wt% of the initial catalyst. The isolated pulp (*circa* 1 g) equals 96.4 wt% of the pulp mass.

Separation methodology: see page S4.

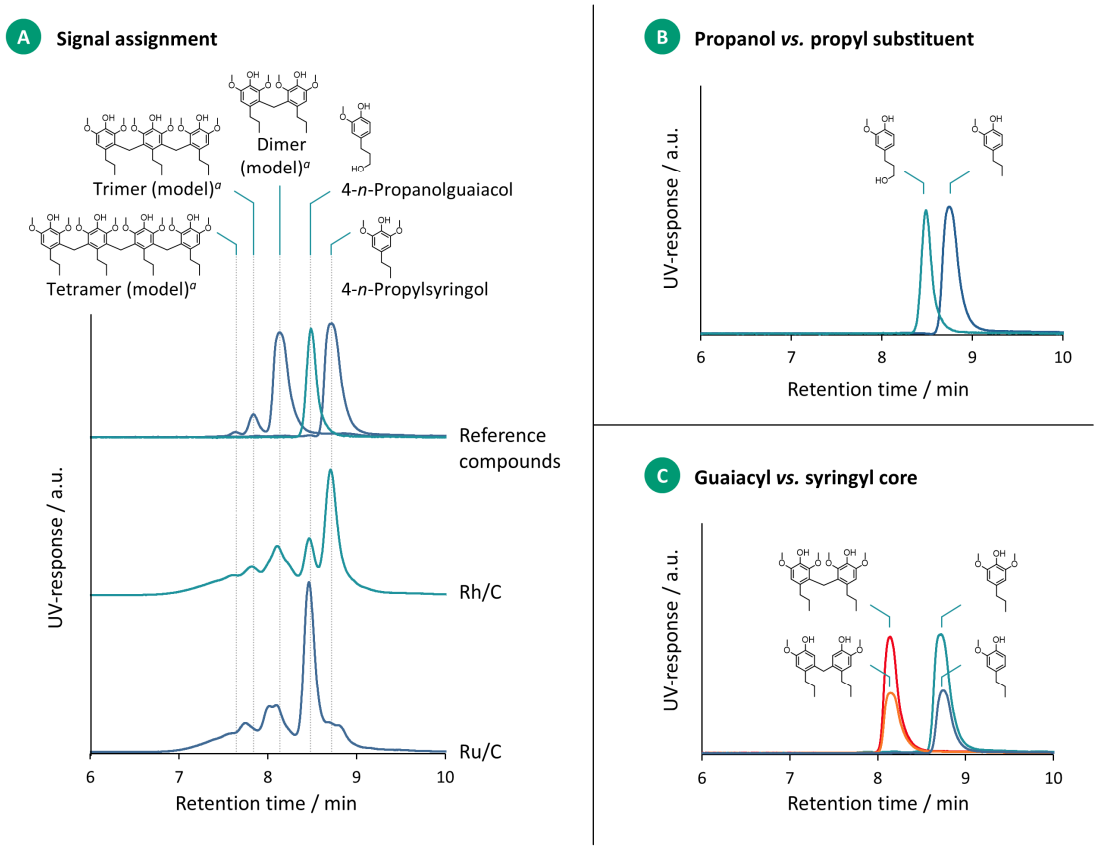


Fig. S11. (A) GPC of reference compounds supporting the assignment of monomer, dimer, and trimer signals. THF (1 mL min^{-1}) was used as eluent, UV-detection was performed at 280 nm. [a] Note that the reference dimer, trimer and tetramer merely serve as models to indicate the retention time of structurally related compounds obtained from RCF. **(B)** Propyl-substituted monomers elute later than propanol-substituted analogues. The reason for this is most probably interaction with the stationary phase. Note that dimers, trimers, and tetramers from Rh/C-catalysed RCF elute later than respective dimers, trimers, and tetramers from Ru/C-catalysed RCF (displayed in panel A), which is ascribed to the prevalence of propyl (Rh) or propanol (Ru) substituents. **(C)** Compounds that only differ in the amount of methoxy groups exhibit quasi-similar retention times.

Reference compounds: 4-*n*-Propylguaiacol and 4-*n*-propanolguaiacol (>98%) were obtained from Sigma Aldrich and TCI Chemicals respectively. 4-*n*-Propylsyringol (>99%) was self-prepared.[23] *m,m'*-Methylenebis(4-*n*-propylguaicol) and *m,m'*-methylenebis(4-*n*-propylsyringol) were synthesised as recently disclosed.[23, 24] The trimer and tetramer were obtained as by products from the synthesis of *m,m'*-methylenebis(4-*n*-propylsyringol).[23, 24]

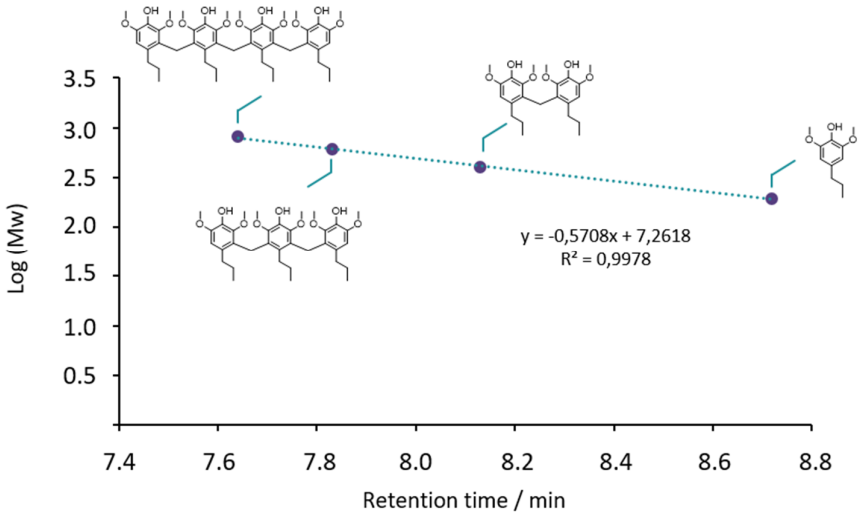


Fig. S12. GPC calibration curve based on self-prepared syringyl standards (see also Fig. S11).

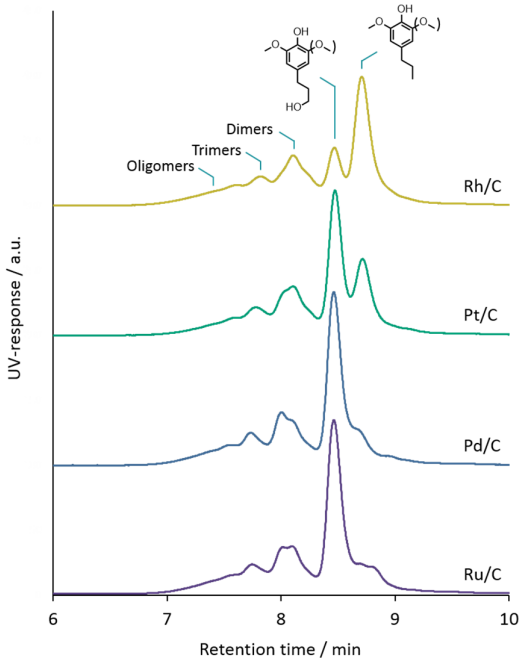


Fig. S13. GPC of the lignin product oil (*n*-butanol phase) for different carbon-supported catalysts. Reaction scheme: Fig. 1 in the main article. Reaction conditions: 20 mL *n*-butanol, 20 mL water, 2 g pre-extracted eucalyptus sawdust, 0.2 g catalyst, 30 bar H_2 at room temperature, 200 °C, 2 h. THF (1 mL min^{-1}) was used as eluent, UV-detection was performed at 280 nm. Note that dimers, trimers, and tetramers from Rh/C-catalysed RCF elute later than respective dimers, trimers, and tetramers from Ru/C- and Pd/C-catalysed RCF, which is ascribed to the prevalence of propyl (Rh) or propanol (Ru) substituents (see also Fig. S11).

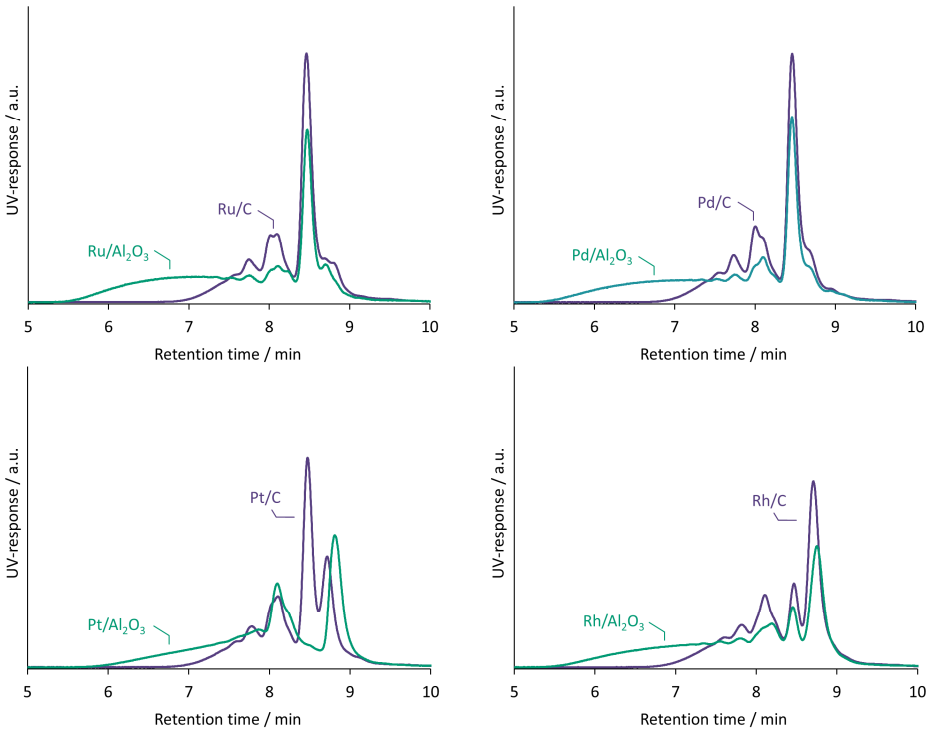


Fig. S14. GPC of lignin product oil (*n*-butanol phase), showing the influence of the catalyst support. Carbon-based catalysts result in more effective lignin depolymerisation. Reaction conditions: 20 mL *n*-butanol, 20 mL water, 2 g pre-extracted eucalyptus sawdust, 0.2 g catalyst, 30 bar H_2 at room temperature, 200 °C, 2 h. THF (1 mL min^{-1}) was used as eluent, UV-detection was performed at 280 nm.

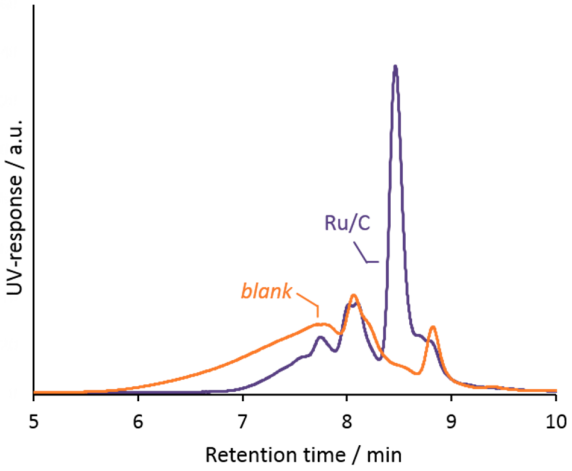


Fig. S15. GPC chromatograms of lignin oils obtained from RCF of eucalyptus in *n*-butanol/water (i) with 0.2 g Ru/C, and (ii) in absence of a redox catalyst (*blank*). THF (1 mL min^{-1}) was used as eluent, UV-detection was performed at 280 nm. Reaction conditions: 20 mL *n*-butanol, 20 mL water, 2 g pre-extracted eucalyptus sawdust, 30 bar H_2, 200 °C, 2 h. The blank run was performed without catalyst and under 30 bar N_2.

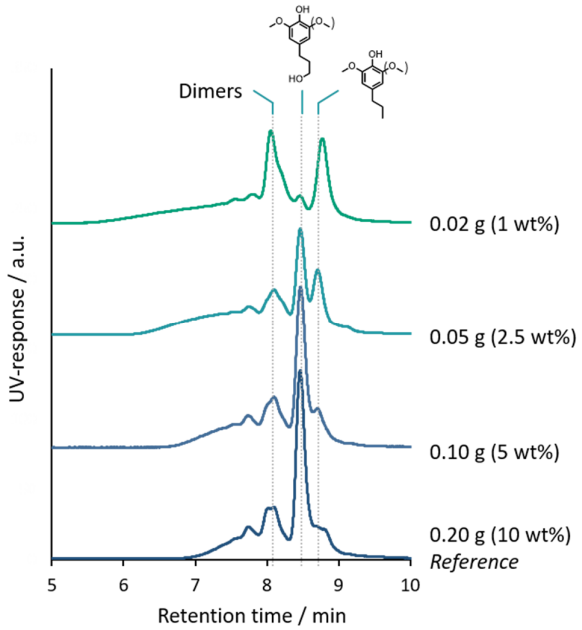


Fig. S16. GPC of the lignin product oil (*n*-butanol phase), showing the influence of the Ru/C loading. The mass of Ru/C relative to the mass of the eucalyptus sawdust is displayed between brackets. Reaction conditions: 20 mL *n*-butanol, 20 mL water, 2 g pre-extracted eucalyptus sawdust, Ru/C, 30 bar H_2, 200 °C, 2 h. THF (1 mL min^{-1}) was used as eluent, UV-detection was performed at 280 nm.

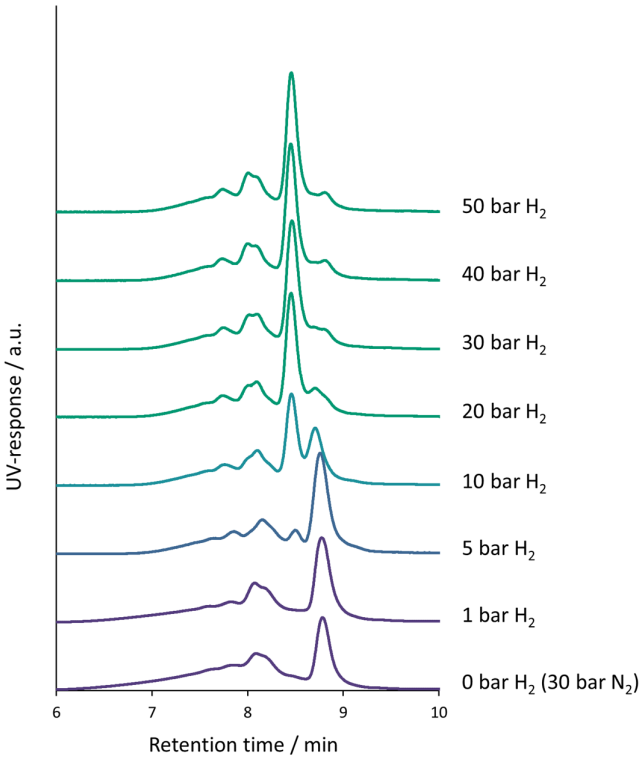


Fig. S17. GPC of the lignin product oil (*n*-butanol phase), showing the influence of initial H_2 pressure (at room temperature). Reaction conditions: 20 mL *n*-butanol, 20 mL water, 2 g pre-extracted eucalyptus sawdust, 0.2 g Ru/C, 30 bar H_2, 200 °C, 2 h. THF (1 mL min^{-1}) was used as eluent, UV-detection was performed at 280 nm.

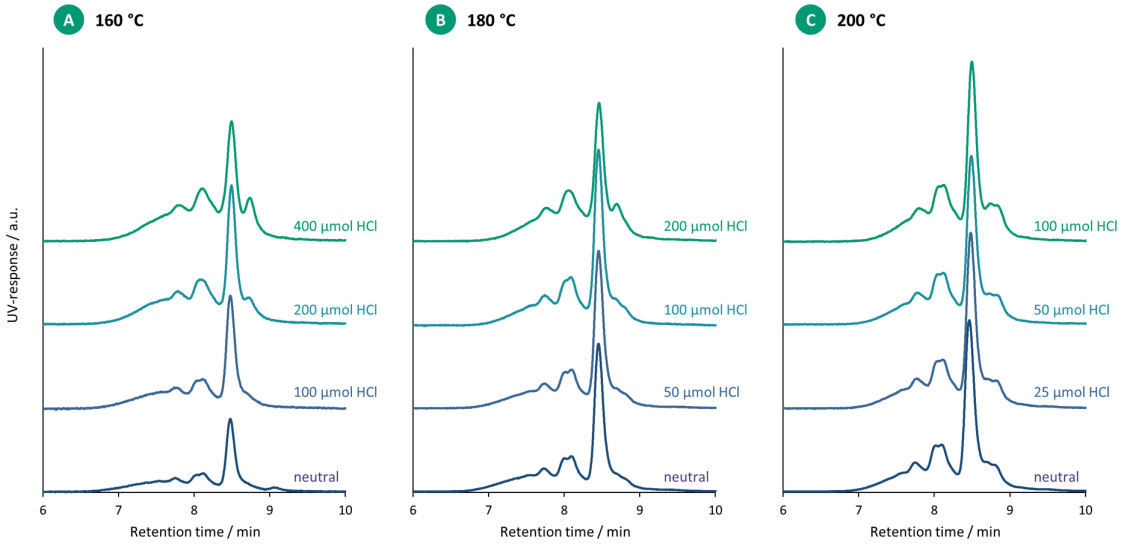


Fig. S18. GPC of the lignin product oil (*n*-butanol phase) obtained from RCF at (A) 160 °C, (B) 180°C and (C) 200°C, with different amounts of added HCl. The area under the curve is set proportional to the yield of the lignin oil. Reaction conditions: 20 mL *n*-butanol, 20 mL water, 2 g pre-extracted eucalyptus sawdust, 0.2 g Ru/C, 30 bar H_2, 2 h. THF (1 mL min^{-1}) was used as eluent, UV-detection was performed at 280 nm.

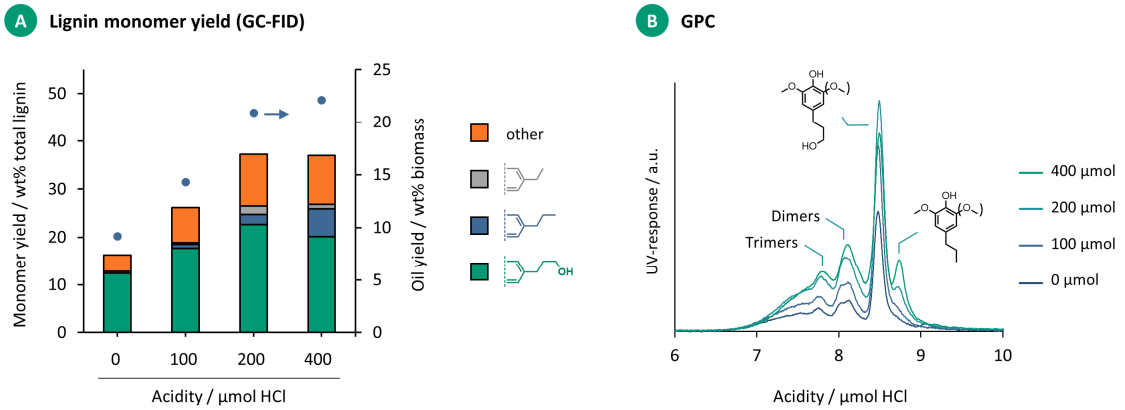


Fig. S19. (A) Lignin monomer yield as measured by GC-FID and **(B)** GPC chromatograms of the lignin product oil (*n*-butanol phase) obtained from RCF at 160 °C with different amounts of added HCl. The area under the curve is set proportional to the yield of the lignin oil. This alternative GPC representation shows that the relative intensity of the 4-*n*-propanol-G/S signal and 4-*n*-propyl-G/S signal in the GPC chromatogram (B) is quasi proportional to the yield as measured by GC-FID (A).

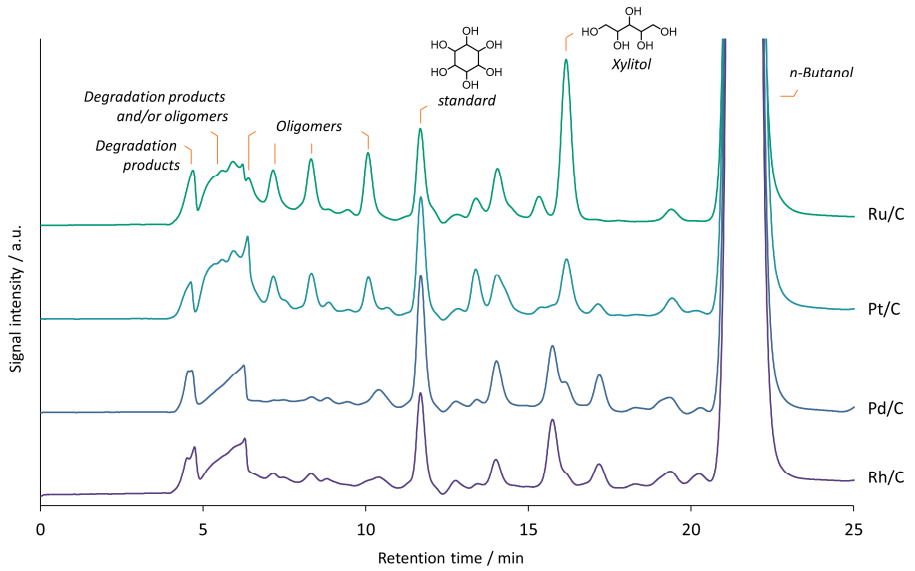


Fig. S20. HPLC analysis of the aqueous phase obtained from RCF with different carbon-supported catalysts, with assignment of the main signals. In the studied system, Ru/C is the most effective catalyst to yield polyols, as was also confirmed by GC analysis (Fig. 4B). Reaction conditions: 20 mL *n*-butanol, 20 mL water, 2 g pre-extracted eucalyptus sawdust, 0.2 g catalyst, 30 bar H_2, 200 °C, 2 h.

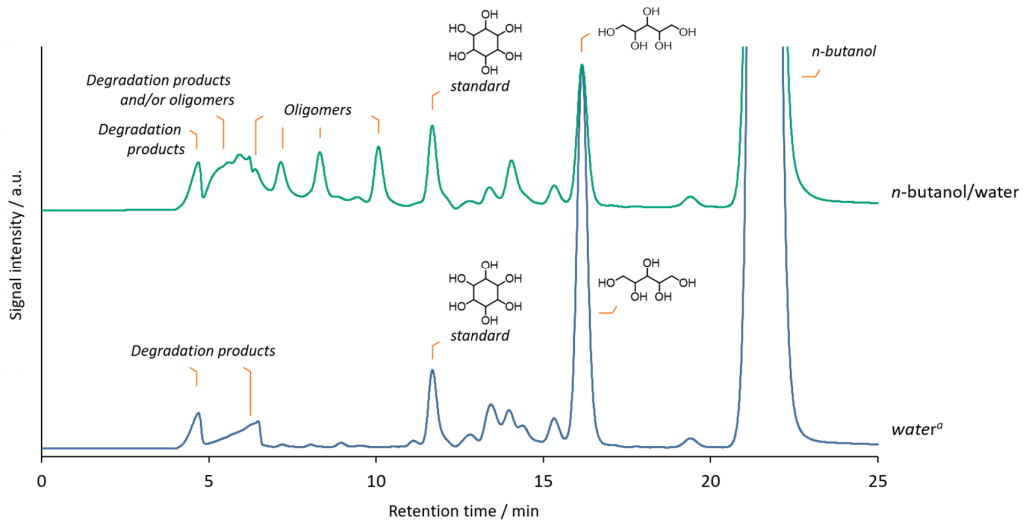


Fig. S21. HPLC analysis of the aqueous phase obtained from RCF in (i) *n*-butanol/water and (ii) pure water, in support of Fig. 8B. Pure water is more effective for hemicellulose hydrolysis than the mixed solvent system, resulting in higher C5 polyol yields (primarily xylitol) and lower amounts of oligomers. Reaction conditions: 40 mL solvent, 2 g pre-extracted eucalyptus sawdust, 0.2 g Ru/C, 30 bar H_2, 200 °C, 2 h.

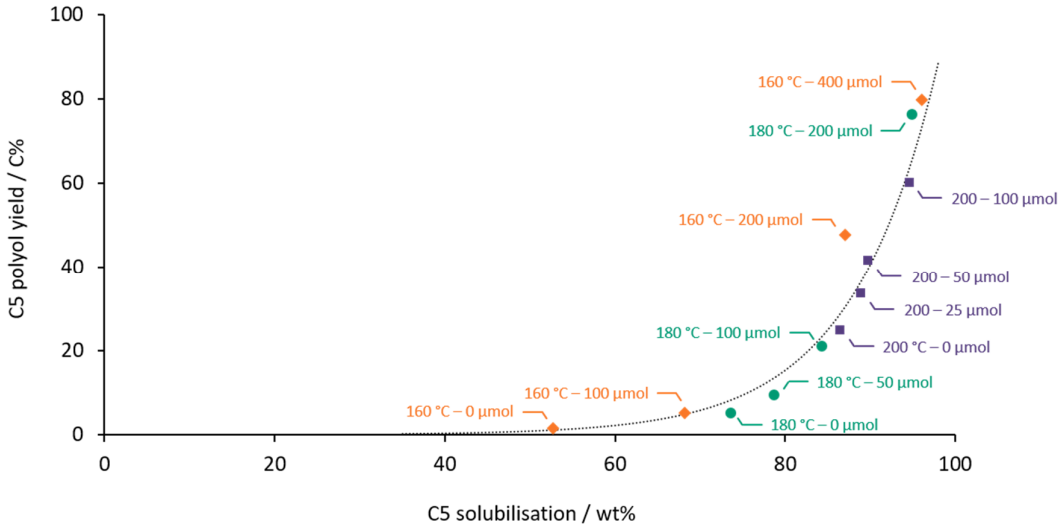


Fig. S22. C5 polyol yield in function of C5 solubilisation (*i.e.* xylan and arabinan) for different temperature-acidity (HCl) combinations. Other reaction conditions: 20 mL *n*-butanol, 20 mL water, 2 g pre-extracted eucalyptus sawdust, 0.2 g Ru/C, 30 bar H_2, 2 h.

III. Tables

Table S1. Composition of pre-extracted[a] eucalyptus sawdust.

Constituent	Content / wt%
Glucan (cellulose)	44.66
Hemicellulose	18.92
C5 carbohydrates	16.37
Xylan	15.98
Arabinan	0.39
C6 carbohydrates	2.56
Mannan	1.13
Galactan	1.43
Lignin	22.90
Acid insoluble	21.45
Acid soluble	1.45
Acetate	3.70
Water[b]	4.12
Total	94.30

[a] See section *Sawdust preparation* for extraction procedure.

[b] Measured gravimetrically by drying overnight at 120 °C.

Table S2. Overview of the phenolic monomer yields (main products, wt%) of reactions with different C-supported and Al_2O_3-supported catalysts, partly illustrated in the article in Fig. 4A.[a]

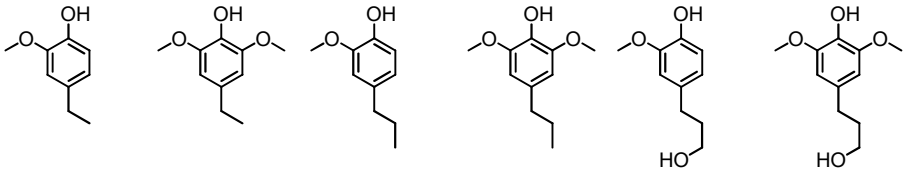
Catalyst	4-ethylguaiacol (**1**) [b]	4-ethylsyringol (**2**) [b]	4-*n*-propylguaiacol (**3**) [b]	4-*n*-propylsyringol (**4**) [b]	4-*n*-propanolguaiacol (**5**) [b]	4-*n*-propanolsyringol (**6**) [b]	Other [b]	Total monomers / wt% [b]	Biomass conversion / wt%	Oil yield / wt% of biomass [d]
Ru/C	0.5	2.7	0.6	2.5	6.1	35.1	1.4	**48.8**	49.6	22.2
Ru/Al_2O_3	0.2	0.8	0.4	2.8	3.3	21.6	1.8	**30.9**	50.1	22.5
Pd/C	0.5	0.2	0.7	2.4	7.6	37.7	1.1	**50.2**	50.3	24.4
Pd/Al_2O_3	0.2	0.1	<0.1	1.8	5.2	25.5	1.6	**34.5**	51.3	24.7
Pt/C	0.1	0.9	2.5	10.6	5.3	29.0	0.9	**49.3**	45.4	23.4
Pt/Al_2O_3	0.5	<0.1	0.4	2.8	0.5	0.4	14.0 [c]	**18.7**	55.7	30.5
Rh/C	0.1	0.5	4.9	28.4	2.3	9.6	1.0	**46.9**	52.2	24.3
Rh/Al_2O_3	<0.1	0.2	2.2	14.4	2.7	7.4	10.3	**37.3**	51.4	25.4

[a] The reaction conditions are as follows: 2 g pre-extracted eucalyptus sawdust (0.25-0.50 mm), 0.2 g catalyst, 20 mL *n*-butanol, 20 mL water, 200 °C, 2 h reaction time and 30 bar H_2 at RT.

[b] Expressed relative to the total lignin content (22.9 wt% of pre-extracted eucalyptus wood).

[c] Mainly propenyl-substituted G/S (12.9%).

[d] Note that the oil yield for catalysts other than Ru is higher than the lignin content of the pre-extracted sawdust (22.9 wt%). This may be due to the formation of hemicellulose degradation products that are relatively apolar. With catalysts other than Ru, hemicellulose sugars are not effectively stabilised (towards polyols) and therefore prone to degradation.



1 **2** **3** **4** **5** **6**

Table S3. Overview of the phenolic monomer yields (main products, wt%) of reactions with different hydrogen pressure, partly illustrated in the article in Fig. 7A.[a]

Hydrogen pressure / bar	4-ethylguaiacol (**1**) [b]	4-ethylsyringol (**2**) [b]	4-*n*-propylguaiacol (**3**) [b]	4-*n*-propylsyringol (**4**) [b]	4-*n*-propanolguaiacol (**5**) [b]	4-*n*-propanolsyringol (**6**) [b]	iso-eugenol [b]	iso-allylsyringol [b]	other [b]	Total monomers / wt% [b]
0 (30 bar N_2)	0.1	<0.1	0.4	0.4	0.7	<0.1	3.5	9.2	1.9	16.8
1	0.1	0.2	0.3	0.5	1.0	0.3	3.5	11.8	2.4	20.3
5	<0.1	0.2	6.2	28.2	0.9	4.4	<0.1	1.0	1.3	42.7
10	0.2	1.6	2.6	10.3	4.9	26.7	<0.1	<0.1	0.9	47.2
20	0.1	1.4	0.6	3.7	6.9	35.6	0.1	0.1	<0.1	48.3
30	0.5	2.7	0.6	2.5	6.1	35.1	0.4	0.2	0.8	48.8
40	0.4	3.0	0.3	2	4.6	31.6	1.1	<0.1	2.5	45.4
50	0.3	2.7	0.3	1.7	3.4	30.0	1.5	<0.1	3.6	43.5

[a] The reaction conditions are as follows: 2 g pre-extracted eucalyptus sawdust (0.25-0.50 mm), 0.2 g Ru/C, 20 mL *n*-butanol, 20 mL water, 200 °C, 2 h reaction time.

[b] Expressed relative to the total lignin content (22.9 wt% of pre-extracted eucalyptus wood)

IV. References

1. S. Burkhardt, L. Kumar, R. Chandra and J. Saddler, *Biotechnology for Biofuels*, 2013, **6**, 90.
2. *National Renewable Energy Laboratory, Biomass Compositional Analysis Laboratory Procedures,* https://www.nrel.gov/bioenergy/biomass-compositional-analysis.html, (accessed accessed March 2018).
3. A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton and D. Crocker, *Determination of Structural Carbohydrates and Lignin in Biomass*, Report NREL/TP-510-42618, National Renewable Energy Laboratory, Golden, CO, 2008 (revised 2012).
4. A. Sluiter, R. Ruiz, C. Scarlata, J. Sluiter and D. Templeton, *Determination of Extractives in Biomass*, Report NREL/TP-510-42619, National Renewable Energy Laboratory, Golden, CO, 2005.
5. J. Sluiter and A. Sluiter, *Summative Mass Closure*, Report NREL/TP-510-48087, National Renewable Energy Laboratory, Golden, CO, 2010 (revised 2011).
6. L. A. Colón and L. J. Baird, in *Modern Practice of Gas Chromatography*, eds. R. L. Grob and E. F. Barry, John Wiley & Sons, Inc., 2004, pp. 275-337.
7. C. M. Courtin, H. Van den Broeck and J. A. Delcour, *Journal of Chromatography A*, 2000, **866**, 97-104.
8. C. Gourson, R. Benhaddou, R. Granet, P. Krausz, B. Verneuil, P. Branland, G. Chauvelon, J. F. Thibault and L. Saulnier, *Journal of Applied Polymer Science*, 1999, **74**, 3040-3045.
9. J. Snelders, E. Dornez, B. Benjelloun-Mlayah, W. J. J. Huijgen, P. J. de Wild, R. J. A. Gosselink, J. Gerritsma and C. M. Courtin, *Bioresource Technology*, 2014, **156**, 275-282.
10. Z. Sun, B. Fridrich, A. de Santi, S. Elangovan and K. Barta, *Chemical Reviews*, 2018, **118**, 614–678.
11. Z. Sun and K. Barta, *Chemical Communications*, 2018, 10.1039/C8CC02937G.
12. Z. Cao, M. Dierks, M. T. Clough, I. B. Daltro de Castro and R. Rinaldi, *Joule*, 2018, **2**, 1118-1133.
13. C. Chesi, I. B. D. de Castro, M. T. Clough, P. Ferrini and R. Rinaldi, *Chemcatchem*, 2016, **8**, 2079-2088.
14. P. Ferrini, C. A. Rezende and R. Rinaldi, *ChemSusChem*, 2016, **9**, 3171-3180.
15. S. Van den Bosch, T. Renders, S. Kennis, S.-F. Koelewijn, G. Van den Bossche, T. Vangeel, A. Deneyer, D. Depuydt, C. M. Courtin, J. Thevelein, W. Schutyser and B. F. Sels, *Green Chemistry*, 2017, **19**, 3313-3326.
16. M. V. Galkin and J. S. M. Samec, *ChemSusChem*, 2014, **7**, 2154-2158.
17. E. M. Anderson, M. L. Stone, R. Katahira, M. Reed, G. T. Beckham and Y. Román-Leshkov, *Joule*, 2017, **1**, 613-622.
18. I. Kumaniaev, E. Subbotina, J. Savmarker, M. Larhed, M. V. Galkin and J. Samec, *Green Chemistry*, 2017, **19**, 5767-5771.
19. E. M. Anderson, M. L. Stone, M. J. Hülsey, G. T. Beckham and Y. Román-Leshkov, *ACS Sustainable Chemistry & Engineering*, 2018, **6**, 7951–7959.
20. S. Van den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S. F. Koelewijn, T. Renders, B. De Meester, W. J. J. Huijgen, W. Dehaen, C. M. Courtin, B. Lagrain, W. Boerjan and B. F. Sels, *Energy & Environmental Science*, 2015, **8**, 1748-1763.
21. S. Van den Bosch, W. Schutyser, S. F. Koelewijn, T. Renders, C. M. Courtin and B. F. Sels, *Chemical Communications*, 2015, **51**, 13158-13161.
22. P. Ferrini and R. Rinaldi, *Angewandte Chemie International Edition*, 2014, **53**, 8634-8639.
23. S.-F. Koelewijn, C. Cooreman, T. Renders, C. A. Saiz, S. Van den Bosch, W. Schutyser, W. De Leger, M. Smet, P. Van Puyvelde, H. Witters, B. Van der Bruggen and B. F. Sels, *Green Chemistry*, 2018, **20**, 1050-1058.
24. S.-F. Koelewijn, S. Van den Bosch, T. Renders, W. Schutyser, B. Lagrain, M. Smet, J. Thomas, W. Dehaen, P. Van Puyvelde, H. Witters and B. F. Sels, *Green Chemistry*, 2017, **19**, 2561-2570.