Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Reductive catalytic fractionation of black locust bark

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Table of contents

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% Pd on carbon, 5 wt% Ru on alumina, copper chromite, acetone-d_6 (99.9%), methyl stearate (>96%), 1-octadecanol (99%), 1-docosanol (98%), methyl 12-hydroxystearate (99%), guaiacol (98%), 4-*n*-propylguaiacol (>99%), syringol (99%), 4-methylsyringol (>97%), 2-isopropylphenol (>98%), tetrahydrofuran (>99%, stabilized with 250 ppm BHT) were purchased from Merck. 4-Ethylguaiacol (98%), chloroform (HPLC grade, stabilized with amylene), *n*-heptane (>99%), methyl palmitate (95%), methanol (99.9%) were purchased from Acros organics. 4-*n*-Propanolguaiacol (3-(4-hydroxy-3-methoxyphenyl)-1-propanol, >98%) was purchased from TCI Chemicals. Dichloromethane (>99%) was purchased from Fischer Chemical Ltd. Ni 5249P (Ni on silica, 64 wt%) was purchased from Strem Chemicals. Methyl behenate (99%) was purchased from MP Biomedicals. Nickel catalyst pellets (Ni 5256 E 3/64" RS, Ni on silica) were obtained from BASF catalysts.

Sawdust preparation

Black locust bark and wood were milled and sieved to obtain sawdust fractions with a size of <500 µm and 250-500 µm respectively. Both sawdust fractions were dried overnight at 80 °C and subsequently stored in an open recipient to equilibrate with air humidity for 24h. These substrates were used as such for catalytic experiments and are further simply refered to as 'black locust bark' and 'black locust wood'.

Determination of ash and moisture content

Moisture content was determined by drying the black locust bark and wood at 105 °C overnight, followed by cooling down in a dessicator for 1 hour. Moisture content was measured by weight difference and reported as fraction of the initial bark or wood sample. Ash content was determined by incinerating the bark or wood sample in a muffle oven at 525 °C. The samples were cooled down in a dessicator for 1 hour. Ashes were determined gravimetrically, and the ash content was reported as fraction of the initial bark or wood sample.

Determination of the extractives content

The extractives content of black locust bark and wood was determined using a Soxtex 2055 Avanti apparatus. This treatment removes extractives like fats, waxes, resins and terpenoids/steroids[1] which can interfere with analysis procedures (*e.g.* determination of the Klason lignin content and suberin 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 EtOH and dried overnight at 80 °C. Subsequently, the extracted sawdust was stored in an open recipient to equilibrate with air humidity for 24 h. This sawdust is hereinafter referred to as 'pre-extracted black locust bark'. The extractives content was determined gravimetrically.

Determination of the suberin content

Pre-extracted black locust bark was used for the determination of suberin content. The suberin was depolymerized *via* methanolysis, adapted from a procedure from Pereira.[2] 0.5 g of pre-extracted black locust bark (*vide supra*) was refluxed in a 100 mL solution of 3 wt% $NaOCH_3$ in methanol for 3 h. After cooling to room temperature, the mixture was filtered and the solid residue was refluxed again with 100 mL MeOH for 15 min. The combined filtrates were acidified with 2 M H_2SO_4 until a pH of 6-7 was reached. The solvent was evaporated using a rotary evaporator. The residue was suspended in 100 mL water and extracted with 25 mL DCM three times. The combined extracts were evaporated using a rotary evaporator, transferred into a 10 mL vial and subsequently dried overnight at 80 °C. These dried extracts were determined gravimetrically as suberin.

Determination of the total lignin content (Klason + acid soluble lignin)

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 black locust bark was based on a procedure from Lin & Dence.[3] Triplicate samples of pre-extracted, desuberinized black locust bark (1 g each) 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 being 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. 20 mL of this solution was kept aside for acid soluble lignin analysis. The precipitate was washed with hot water to remove any leftover acid and the obtained residue was dried at 80 °C overnight. The reported Klason lignin content was determined relative to the oven dried substrate by averaging the measured weight of the residues.

The acid soluble lignin (ASL) content was determined according to the procedure from NREL.[4] A wavelenght of 240 nm and an absorptivity at this wavelenght of 25 L g^{-1} cm^{-1} were used. Because the liquid solution is unstable, the measurement was performed within the first hour after completing the dilute acid hydrolysis step.

Determination of the carbohydrate content and composition

The carbohydrate content and composition in black locust bark as well as in the obtained pulps after catalytic fractionation were determined, using a standard total sugar determination procedure, adapted with hydrolysis conditions for cellulose-rich materials.[5-7] 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 in 50 % water, 50 % saturated benzoic acid solution) 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 overnight. 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 ionization 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 triplicate and the average values were used in the calculation of the carbohydrate retention.

Reductive catalytic fractionation reaction

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 raw black locust bark (<500 µm) or wood (250-500 µm) was loaded into the reactor together with the catalyst powder (0.2 g Ru/C or other) or pellets (Ni 5256, crushed to 0.5-1 mm) and methanol (40 mL). The reactor was sealed, flushed threefold with N_2, and pressurized with H_2 (10-40 bar at room temperature). Subsequently, the reaction mixture was stirred (600 rpm) and heated to 200-250 °C during 40 min. When the reaction temperature was reached, the temperature was kept constant for 1-6 h after which the reactor was cooled and depressurized at room temperature. Afterwards, the reactor contents were quantitatively collected by washing the reactor with ethanol.

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 ethanol and dried overnight at 80 °C, followed by equilibration with air humidity (as in Section Sawdust Preparation).

The methanol (from reaction) and ethanol (from washing) were evaporated using a rotavap, yielding a viscous, brown oil. This oil was transferred quantitatively to a 10 mL vial using small amounts of ethanol. The ethanol was then again evaporated using a N_2 flow. Distilled water (5 mL) was added to the 10 mL vial with the oil and this mixture was extracted threefold with chloroform (2 mL) to separate the apolar products (mainly lignin- and suberin-derived products) from the polar products (e.g. glycerol and carbohydrate-derived products). The combined chloroform extracts were dried using an N_2 flow to evaporate most of the $CHCl_3$, followed by drying overnight at 80 °C. The resulting oily residue is further referred to as 'bark oil' (or 'lignin oil' in case of wood) and its mass was used to calculate the 'bark oil yield' (and 'lignin oil yield' in case of wood). Figure S2 presents an image of a typical bark oil.

Heptane extraction

As a proof-of-concept, further downstream separation of the bark oil was performed via heptane extraction. Approximately 0.3 g bark oil was extracted twice with 4 mL heptane at 70 °C under continuous stirring during 1 h. The combined extracts are referred to as 'heptane extract', the remaining oil is referred to as 'residue'.

Product analysis

To analyse the phenolic and aliphatic monomers after RCF, a weighed amount of external standard (2-isopropylphenol) was added to the bark oil after which the content was completely resolubilized in 7 mL chloroform. A sample was then analysed 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 300 °C, column temperature program: 50 °C (hold 2 min), 15 °C min^{-1} to 150 °C, 10 °C min^{-1} to 300 °C (hold 10 min), detection temperature of 310 °C. Response factors of most phenolic monomers and some aliphatic monomers were obtained by calibration with commercial standards (section chemicals and materials). Respnse factors of the remaining non-commercially available monomers were deduced by interpolation based on (i) the response factors of analogue compounds and (ii) taking into account the principles of the 'effective carbon number method'.[8] The product yield is expressed in wt% of the biomass.

Identification of the monomer signals was performed with GC-MS using an Agilent 6890 series GC equipped with a HP5-MS capillary column and an Agilent 5973 series Mass Spectroscopy detector. The following operating conditions were used: injection temperature of 300 °C, column temperature program: 50 °C (hold 2 min), 15 °C min^{-1} to 200 °C, 10 °C min^{-1} to 305 °C (hold 8 min), transfer line to detector at 310 °C.

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 bark oil (or lignin oil) was solubilized in THF (~ 2-5 mg mL^{-1}) 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^{-1}) and a UV detection at 280 nm with a Waters 2988 photodiode array detector.

NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. A sample of the bark or lignin oil (100 mg) was dissolved in 0.7 mL of acetone-d_6.

HSQC experiments had the following parameters: standard Bruker pulse sequence 'hsqcedetgp', spectral width of 8.6 ppm in F2 (^{1}H dimension) by using 1024 data points for an acquisition time (AQ) of 148 ms, spectral width of 165.6 ppm in F1 (^{13}C dimension) by using 256 data points for an acquisition time of 7.7 ms and an increment of delay of 60 µs. The number of scans was 24 with an interscan delay of 1.5 s (D1). Spectra were processed with fourier transform in 1024 data points in both F1 and F2 dimension.

^{13}C experiments had the following parameters: standard Bruker pulse sequence 'zgpg30', spectral width of 238.9 ppm using 65536 data points for an acquisition time (AQ) of 1.363 s. The number of scans was 3072 with an interscan delay of 1.5 s (D1).

II. Figures

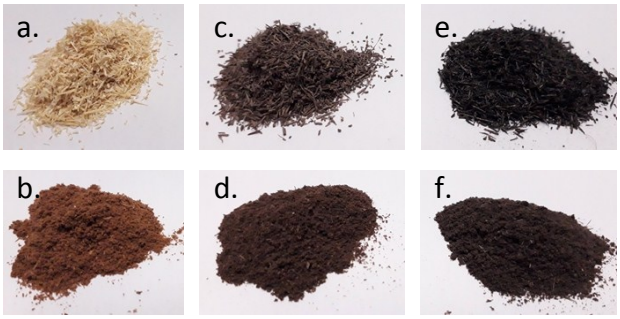

Figure S1: (a, b) Raw black locust wood (250-500 µm) and bark (<500µm). (c, d) Black locust wood and bark pulp obtained after RCF processing in methanol at 235 °C with nickel catalyst pellets (Ni on silica, 0.5-1 mm). (e, f) Black locust wood and bark pulp obtained after RCF processing in methanol at 235 °C with Ru/C, the black color is due to the presence of the Ru/C catalyst.

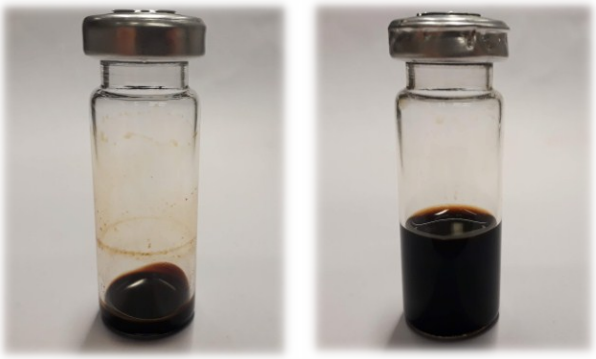

Figure S2: Dried (left) and solubilized in chloroform (right) bark oil obtained from RCF processing of black locust bark. Reaction conditions: 235 °C, 4h, 40 mL MeOH, 2 g black locust bark, 0.2 g Ru/C and 10 bar H_2 at room temperature.

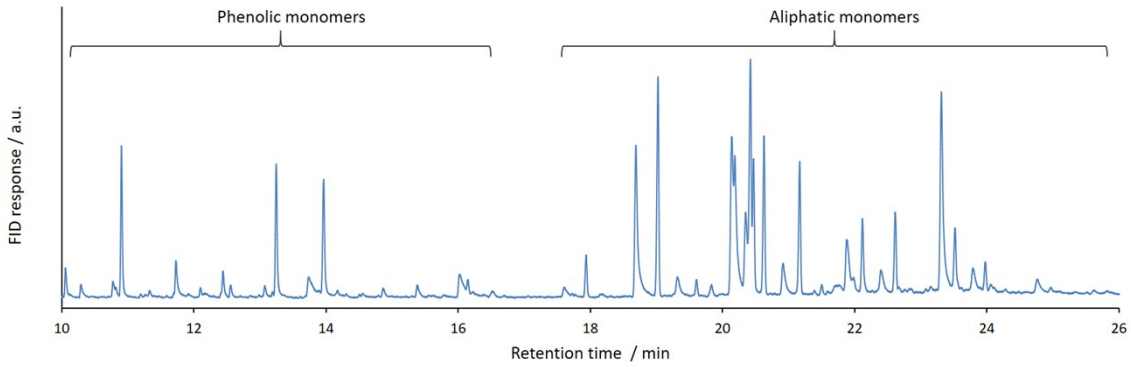

Figure S3: Typical GC-chromatogram of the obtained bark oil. Reaction conditions: 235 °C, 4 h, 40 mL MeOH, 2 g black locust bark, 0.2 g Ru/C and 40 bar H_2 at room temperature. The detailed composition of this bark oil can be found in table S1.

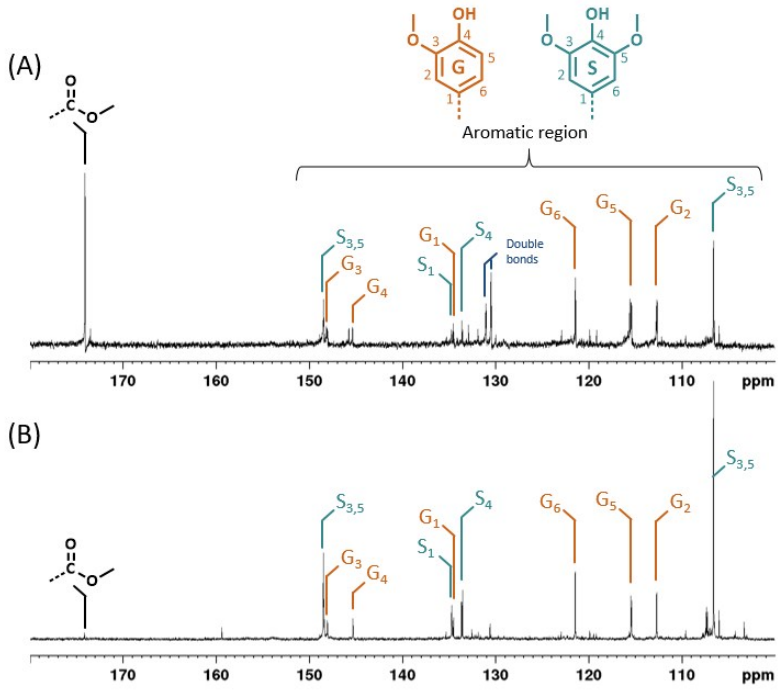

Figure S4: ^{13}C NMR of the aromatic region of the lignin oil and bark oil from RCF of (A) black locust bark and (B) black locust wood. Reaction conditions: 40 mL methanol, 235 °C, 4 h, 40 bar H_2 at room temperature, 2 g black locust wood, 0.2 g Ru/C. Signals were assigned based on literature and ChemDraw predictions.[9] Note that the lignin oil has a higher S content than the bark oil.

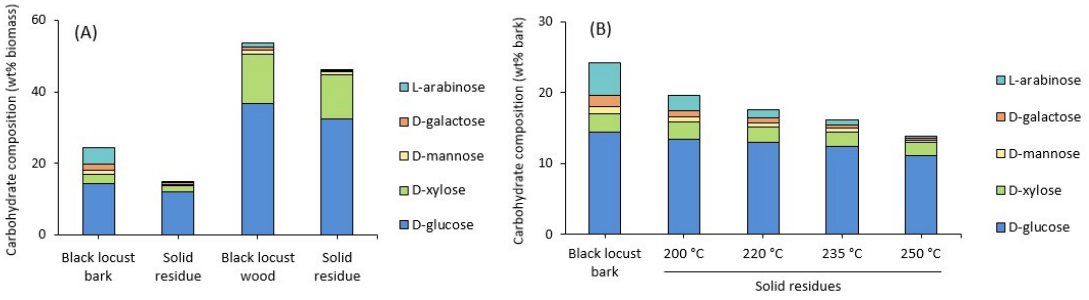

Figure S5: (A) Carbohydrate composition of the black locust bark and wood and their solid residue after RCF. Reaction conditions: 40 mL MeOH, 2 g black locust bark or wood, 0.2 g nickel catalyst pellets (Ni on silica, 0.5-1 mm), 40 bar H_2, 4 h, 235 °C. (B) Influence of reaction temperature on the carbohydrate composition of the solid residue after RCF. Reaction conditions: 40 mL MeOH, 2 g black locust bark, 0.2 g Ru/C, 20 bar H_2, 2 h, 200-250 °C.

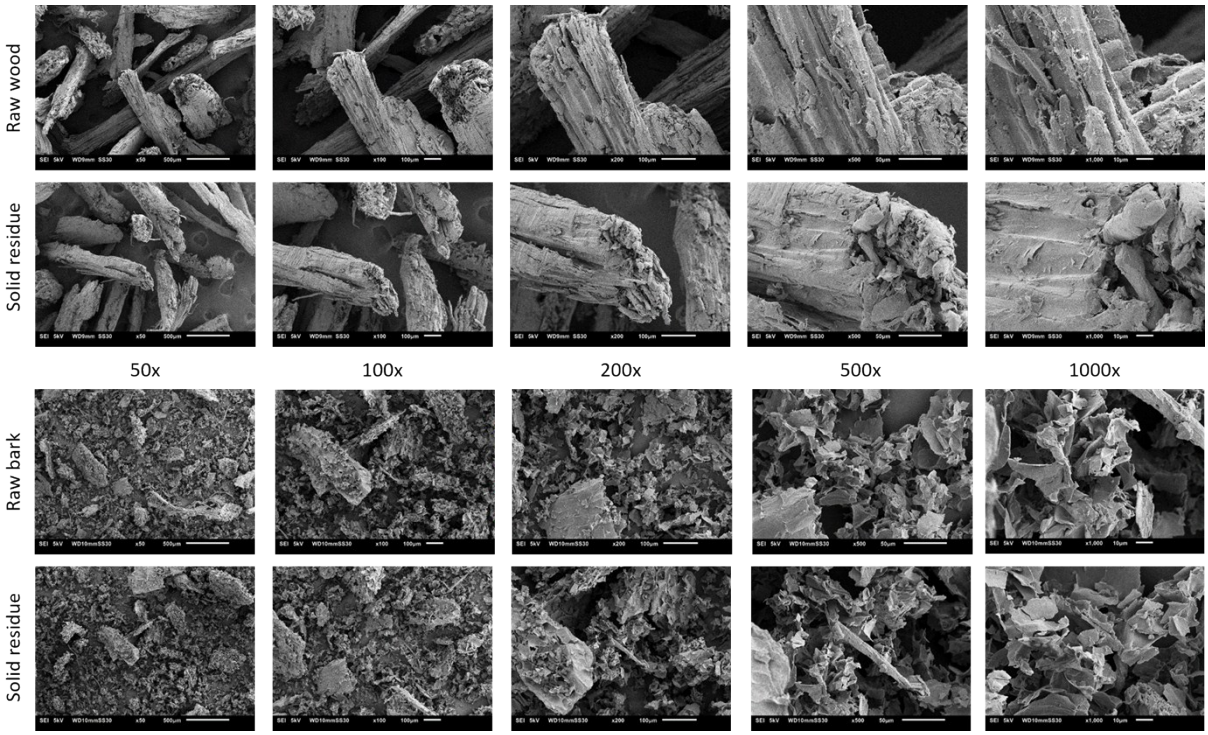

Figure S6: Scanning electron microscopy images of the raw black locust wood and bark, and their residual pulp after RCF, at various magnifications (50x - 1000x). RCF reaction conditions: 40 mL MeOH, 2 g black locust bark or wood, 0.2 g nickel catalyst pellets (Ni on silica, 0.5-1 mm), 40 bar H_2, 4 h, 235 °C. Notice the flaky nature of the bark powder (<500 µm) compared to the wood (250-500 µm). Both with bark and wood, the particle structure is well retained after RCF.

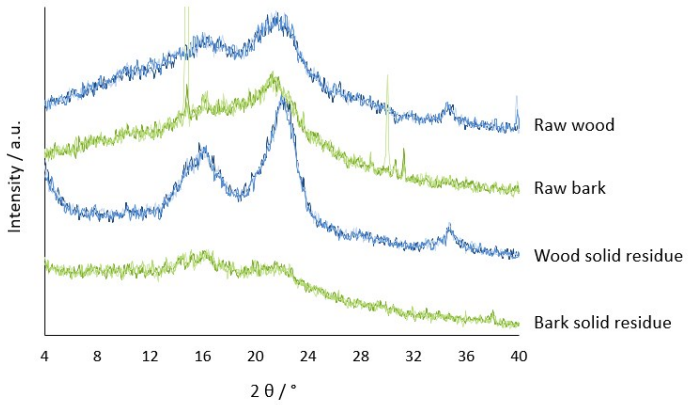

Figure S7: X-ray diffractograms, measured in threefold, of the raw black locust wood and bark, and their residual pulp after RCF. These diffractograms illustrate the crystalline nature of the cellulose present in wood, and especially upon of the residue upon RCF processing. The bark and bark residue are largely amorphous. RCF reaction conditions: 40 mL MeOH, 2 g black locust bark or wood, 0.2 g nickel catalyst pellets (Ni on silica, 0.5-1 mm), 40 bar H_2, 4 h, 235 °C.

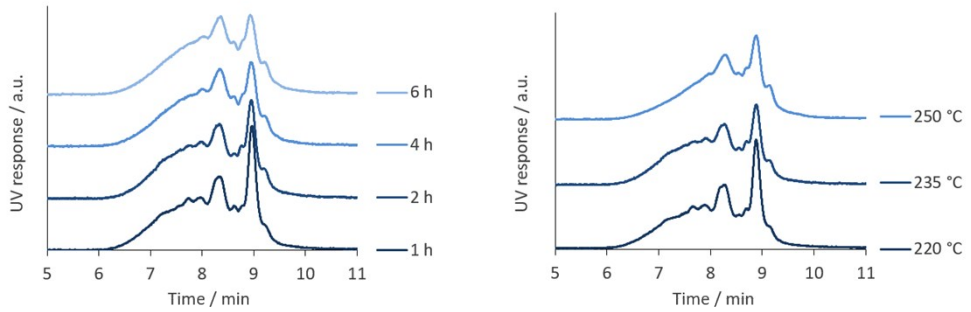

Figure S8: GPC of bark oils resulting from RCF at varying reaction time and temperature. The area under the curves is set to be equal, allowing the comparison of selectivity towards phenolic components. RCF Reaction conditions: 40 mL MeOH, 2 g black locust bark powder, 0.2 g Ru/C, 20 bar H_2. Reaction time variation (A) was done at 235°C. Temperature variation (B) was done with 2 h reaction time. Increasing process severity (temperature or time) decreases the phenolic oligomeric fraction.

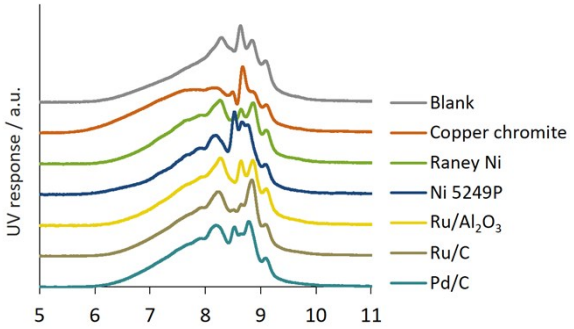

Figure S9: GPC of bark oils resulting from RCF with different hydrogenation catalysts. The area under the curves is set to be equal, allowing the comparison of selectivity towards phenolic components. RCF Reaction conditions: 40 mL MeOH, 2 g black locust bark powder, 0.2 g catalyst, 20 bar H_2, 250°C, 2h.

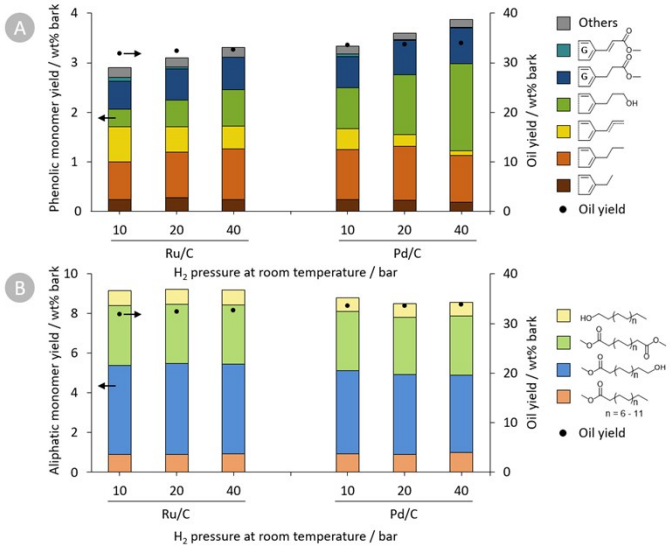

Figure S10: Influence of hydrogen pressure on the RCF of black locust bark using Ru/C or Pd/C catalysts. Effect on (A) phenolic monomers and (B) aliphatic monomers. Reaction conditions: 40 mL MeOH, 2 g black locust bark powder, 0.2 g Pd/C or Ru/C, 10-40 bar H_2, 235°C, 4 h. Increasing the H_2 pressure causes an increase in total phenolic monomer yield as well as a selectivity increase towards propanol-G/S and a decrease towards propenyl-G/S. The effect on the aliphatic monomers is minimal.

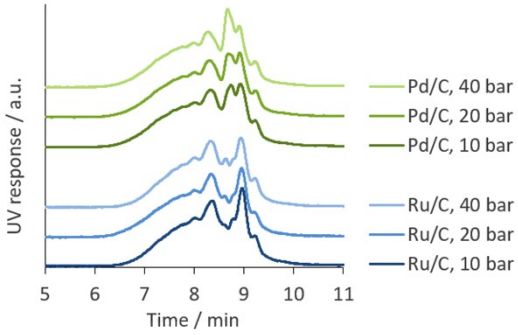

Figure S11: GPC of bark oils resulting from RCF with Pd/C and Ru/C at different H_2 pressures. The area under the curves is set to be equal, allowing the comparison of selectivity towards phenolic components. RCF Reaction conditions: 40 mL MeOH, 2 g black locust bark powder, 0.2 g catalyst, 10-40 bar H_2, 235°C, 4h. Increasing the H_2 pressure increases the selectivity towards propanol-G/S

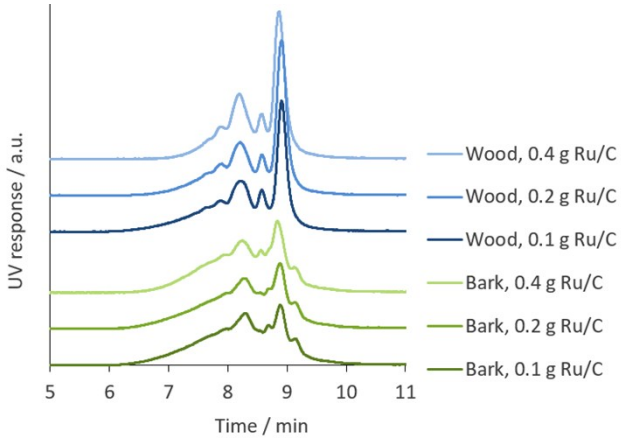

Figure S12: GPC of lignin and bark oils resulting from RCF of black locust wood and bark with varying Ru/C loadings. The area under the curves is set to be equal, allowing the comparison of selectivity towards phenolic components. Signals from wood were shifted in time with respect to signals from bark so that the propyl-G/S components elute at the same moment. RCF Reaction conditions: 40 mL MeOH, 2 g black locust bark or wood, 0.1-0.4 g Ru/C, 20 bar H_2, 250°C, 2h.

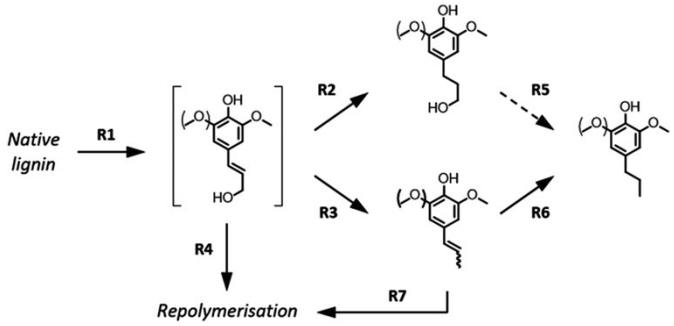

Figure S13: Reproduced with permission from Renders *et al.*[9] Proposed reaction network of lignin depolymerization to phenolic monomers. Direct hydrogenation (R2) and hydrogenolysis (R3) followed by hydrogenation (R6) are the catalytic pathways by which the solvolytically formed coniferyl and sinapyl alcohol are stabilized. Hydrogenolysis of propanol-G/S (R5) is not observed under the investigated reaction conditions.

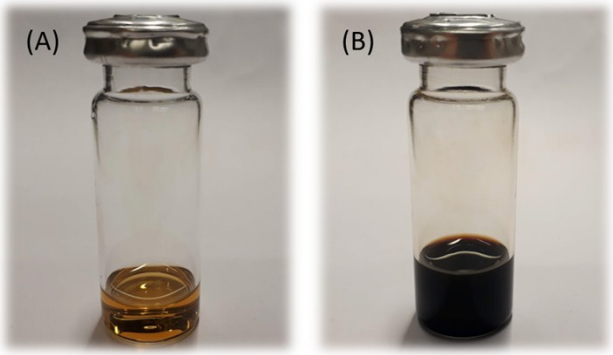

Figure S14: (A) Heptane extract and (B) heptane residue, both solubilized in chloroform. Reaction conditions: 235 °C, 4h, 40 mL MeOH, 2 g black locust bark, 0.2 g Ni 5249P and 40 bar H_2 at room temperature. For heptane extraction conditions, see section product separation.

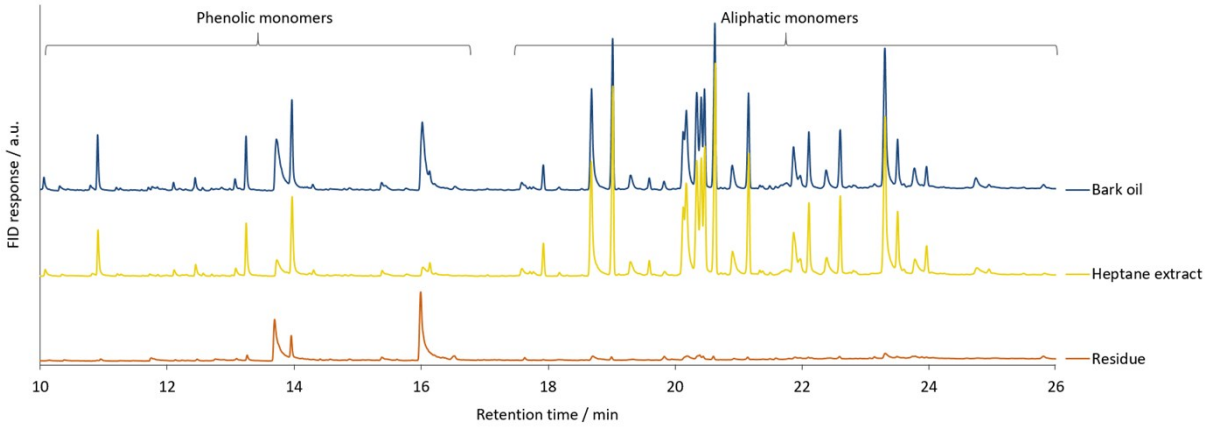

Figure S15: Gas chromatogram of bark oil, heptane extract and residue. RCF reaction conditions: 40 mL MeOH, 2 g black locust bark powder, 0.2 g Ni 5249P, 40 bar H2, 235°C, 4 h. For heptane extraction conditions, see section product separation. From these chromatograms, it is clear that almost all aliphatic monomers are extracted into the heptane phase, while the phenolic monomers are split amongst both fractions.

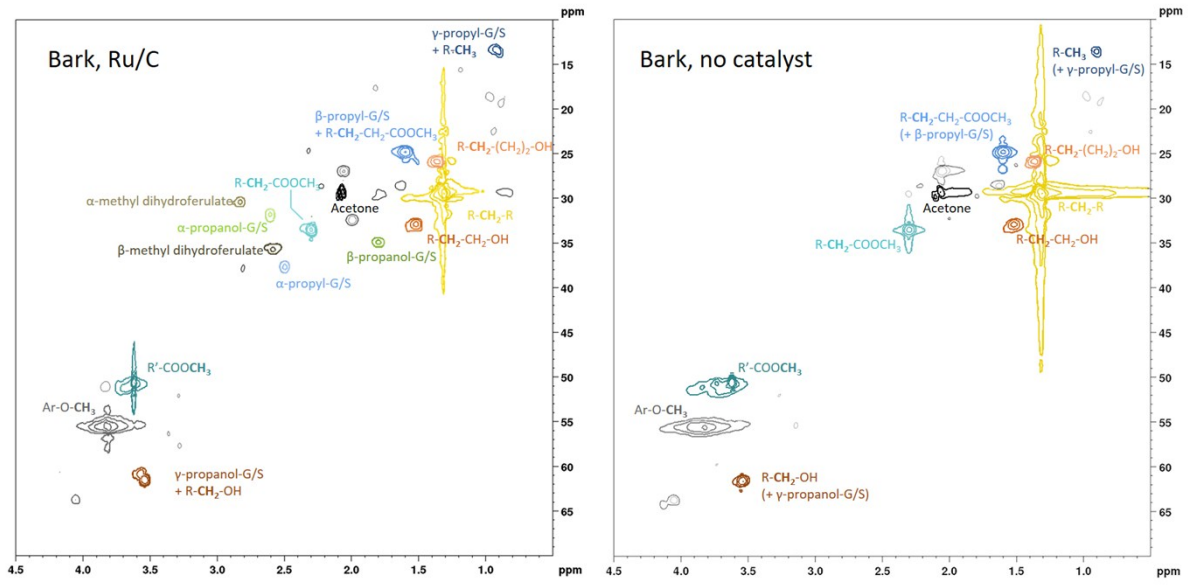

Figure S16: ^{1}H-^{13}C HSQC NMR spectrum of the oil resulting from RCF of bark with Ru/C and without catalyst. These spectra show the absence of the propyl- and propanol-side chain signals in the uncatalyzed reaction, highlighting the effect of hydrogenation catalysis on the RCF of black locust bark. RCF reaction conditions: 40 mL MeOH, 2 g black locust bark, 0.2 g Ru/C (or no catalyst), 40 bar H_2 with Ru/C (6 bar N_2 without catalyst), 235°C, 4 h.

III. Tables

Product	wt% bark
Guaiacol	0,10
ethylguaiacol	0,13
eugenol	0,09
isoeugenol (cis+trans)	0,20
propylguaiacol	0,46
pronanolguaiacol	0,33
Sum guaiacol monomers	**1,32**
syringol	0,04
methylsyringol	0,05
ethylsyringol	0,11
allylsyringol	0,02
isoallyl syringol (cis+trans)	0,14
propylsyringol	0,56
propanolsyringol	0,41
Sum syringol monomers	**1,34**
S/G ratio	**1,01**
Methyl dihydroferulate	0,65
Sum phenolic monomers	**3,31**

Product	wt% bark
C16 OH	0,05
C18 OH	0,07
C20 OH	0,13
C22 OH	0,18
C24 OH	0,16
C26 OH	0,17
Sum alkanols	**0,76**
C16 ω-OH FAME	0,84
C18 ω-OH 9-ene FAME (cis+trans)	1,48
C18 ω-OH FAME	0,53
C20 ω-OH FAME	0,40
C22 ω-OH FAME	1,17
C24 ω-OH FAME	0,12
Sum ω-OH FAMEs	**4,54**
Sum aliphatic monomers	**9,20**

Product	wt% bark
C16 FAME	0,04
C18 FAME	0,12
C20 FAME	0,05
C22 FAME	0,37
C24 FAME	0,24
C26 FAME	0,11
Sum FAMEs	**0,91**
C16 dimethyl ester	0,73
C18 9-ene dimethyl ester (cis+trans)	1,19
C18 dimethyl ester	0,51
C20 dimethyl ester	0,29
C22 dimethyl ester	0,27
Sum α,ω-dimethyl esters	**2,98**

Table S1: Phenolic and aliphatic monomer yields for the proof-of-concept reaction. RCF reaction conditions: 40 mL MeOH, 2 g black locust bark, 0.2 g Ru/C, 40 bar H_2, 4 h, 235 °C.

IV. References

1. Burkhardt, S.; Kumar, L.; Chandra, R.; Saddler, J., How effective are traditional methods of compositional analysis in providing an accurate material balance for a range of softwood derived residues? *Biotechnol. Biofuels* **2013,** *6* (1), 90.
2. Pereira, H., Chemical composition and variability of cork from Quercus suber L. *Wood Science and Technology* **1988,** *22* (3), 211-218.
3. Dence, C. W., The Determination of Lignin. In *Methods in Lignin Chemistry*, Lin, S.; Dence, C., Eds. Springer Berlin Heidelberg: 1992; pp 33-61.
4. Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D., Determination of structural carbohydrates and lignin in biomass. *Laboratory analytical procedure* **2010,** (TP-510-42618).
5. Courtin, C. M.; Van den Broeck, H.; Delcour, J. A., Determination of reducing end sugar residues in oligo- and polysaccharides by gas-liquid chromatography. *J. Chromatogr. A* **2000,** *866* (1), 97-104.
6. Gourson, C.; Benhaddou, R.; Granet, R.; Krausz, P.; Verneuil, B.; Branland, P.; Chauvelon, G.; Thibault, J. F.; Saulnier, L., Valorization of maize bran to obtain biodegradable plastic films. *J. Appl. Polym. Sci.* **1999,** *74* (13), 3040-3045.
7. Snelders, J.; Dornez, E.; Benjelloun-Mlayah, B.; Huijgen, W. J. J.; de Wild, P. J.; Gosselink, R. J. A.; Gerritsma, J.; Courtin, C. M., Biorefining of wheat straw using an acetic and formic acid based organosolv fractionation process. *Bioresour. Technol.* **2014,** *156* (0), 275-282.
8. Colón, L. A.; Baird, L. J., Detectors in Modern Gas Chromatography. In *Modern Practice of Gas Chromatography*, Grob, R. L.; Barry, E. F., Eds. John Wiley & Sons, Inc.: 2004; pp 275-337.
9. Renders, T.; Cooreman, E.; Van den Bosch, S.; Schutyser, W.; Koelewijn, S.-F.; Vangeel, T.; Deneyer, A.; Van den Bossche, G.; Courtin, C.; Sels, B., Catalytic lignocellulose biorefining in n-butanol/water: a one-pot approach toward phenolics, polyols, and cellulose. *Green Chemistry* **2018**.