

Electronic Supporting Information (ESI)

Flow-through reductive catalytic fractionation of beech wood sawdust

Materials

Chemicals

D-(+) Glucose Anhydrous (>99.5%), sulfuric acid (95-97%), 4-Methyl-2,6-dimethoxyphenol, 4-Ethyl Guaiacol, Sodium borohydride (99%), 2-Octanol (>99%), and Methanol (>99.5%) were delivered from Sigma-Aldrich. β -D-allose (99%), L-arabinose (98%), D-xylose (99%) D-mannose (99%), D-galactose 99%), D-glucose (99%) were purchased by Sigma. Syringol was supplied by Aldrich. Urea and Nickel Nitrate hexahydrate (>99%) and 2-Methyltetrahydrofuran (MeTHF) were supplied from Carl Roth. Creosol, bromophenol blue (99%), and 1-methylimidazole (99%) were provided by Acros Organics. Dihydroconiferil alcohol was supplied by Ambeed. 4-Propyl Guaiacol was supplied by SAFC. Zinc oxide nanoparticles ($d = 20\text{nm}$) were ordered from Nanostructured and Amorphous inc. Semolina (type durum wheat) was purchased from the commercial brand Divella. The forming gas (5 wt.-% H_2 and 95 wt.-% N_2) bottles were purchased from Westfalia. Ammonia solution - NH_3 25% in water, Acetic acid (>99%), Acetic anhydride (99%), Anhydride sodium sulphate (99%), and KOH (99%), were acquired from VWR Benzoic acid (99.5-100%), and Ethyl acetate (99%), were supplied by Merck.

Wood feedstock

Beech wood sawdust (BWS) was purchased by GOLDSPAN® (product smoke B5/10). This commercial BWS is provided dried and cut, with the particle size in the range of 0.4 and 1.0 mm.¹ The beech wood sawdust (BWS) was stored closed in the received bag at room condition. No further pre-treatments were performed on the feedstock it was directly used as it was supplied.

Methods

Catalyst preparation



Figure S1 Schematic representation of the catalytic synthesis protocol starting from extrusion (left) followed by carbonization, incipient metal impregnation, calcination and reduction.²

The porous nitrogen-doped carbon (NDC) pellets were synthesized based on our group's previous study.²⁻⁶ Firstly, the glucose, urea, and water mixture with a molar ratio of 1: 3: 11 was prepared at

90°C for 2 h with continuous stirring. Then, a 2 kg mixture composed of semolina (48 wt.-%), the previously prepared glucose, urea, and water mixture (8 wt.-%), and ZnO nanoparticles $d = 20$ nm (24 wt.-%) were mixed using a commercial kitchen kneader (Bosch, professional home series, model MUMVH48BCN). To provide a consistency that allows for extrusion, 160 mL water (20 wt.-% of the mixture) was added to the mixture as a plasticizer. Finally, the low-moisture mixture was extruded and cut in pellet form with dimensions of 1 mm (diameter) and 1.5 mm (length) using a commercial noodle extruding machine (La Monferrina P3) equipped with a 1 mm PTFE die and automatic cutting knife, cf. **Figure S1**. The extruded pellets were dried at room temperature for 12 h. The dried pellets were carbonized at 950°C under N_2 atmosphere using a three-step program: (i) purging the oven atmosphere with N_2 at room temperature for 30 min; (ii) increasing the temperature to 120°C with the heating rate of $3^\circ C \text{ min}^{-1}$ and maintaining it for 2 h; (iii) elevating the temperature to 950°C with the heating rate of $3^\circ C \text{ min}^{-1}$ and maintaining it for 2 h, then cooling it down to room temperature. Finally, the carbonized pellets were washed using 0.1 M HCl solution under continuous stirring for 10 h to remove the residual Zn from the pellet. Afterward, the NDC pellets dried at 90°C for 12h. A loading of 35 wt.-% of Ni was incorporated on NDC via incipient wetness impregnation. Firstly, 170 g of $(Ni(NO_3)_4 \cdot 6H_2O)$ was dissolved in (110 mL) of millipore water, followed by dropwise addition with continuous stirring of the aqueous Ni solution on the NDC dried pellets until complete saturation of the support pores. Subsequently, the impregnated pellets were dried again at 60°C in the air for 12 h. Afterward, the catalyst was calcined under N_2 atmosphere at 450°C. The temperature program of the calcination process consists of two steps: i) purging with N_2 at room temperature for 30 min; ii) heating ramp to 450°C with $3^\circ C \text{ min}^{-1}$ heating rate and maintained for 2 h. Before the catalytic experiments, the catalyst was reduced in forming gas (5 wt.-% H_2 and 95 wt.-% N_2) using the following program: i) 30 min of purging at room temperature, ii) increasing the temperature to 450°C with a heating rate of $3^\circ C \text{ min}^{-1}$ and maintained for 5 h.

Characterization methods

Combustion Elemental Analysis (EA)

Elemental analysis of C, N, O and S was performed with a Vario-MICRO cube CHNOS Elemental Analyzer (Elementar Analysensysteme GmbH, Langenselbold) in the CHNS mode. Prior to the analysis, the samples were finely ground.

Inductive coupled plasma optical emission spectroscopy elemental analysis (ICP-OES)

The Ni content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an Optima 8000 ICP-OES from PerkinElmer. Prior to the analysis, the samples (0.1 mg) were finely grounded and digested for 13 hours in 500 μL of Aqua regia solution (3:1 molar ratio of HCl and HNO_3 , respectively).

X-ray diffraction (XRD)

Powder XRD measurements were performed on a Bruker D8 diffractometer equipped with a CuK_α source ($\lambda = 0.154$ nm) and a NaI scintillation counter-Scinti-Detector. The diffraction pattern was recorded in the 2θ range between $4-70^\circ$ with steps of 0.05° and an acquisition time of 2 sec per step.

N₂ physisorption

N₂ sorption measurements were accomplished with N₂ at -196°C, after degassing the sample at 150°C for 20 hours under vacuum, using a Quantachrome Quadrasorb SI porosimeter. The specific surface area was calculated by applying the Brunauer-Emmet-Teller model in the relative pressure region of (0-0.05) for the adsorption branch (A_{BET}). The pore volume was calculated using the program QuadraWin. The pore size distribution and the average pore size were also determined using the program QuadraWin with the quenched solid functional theory (QSDFT) for slit/cylindrical pores applied in the N₂ adsorption isotherm.

Thermogravimetric analysis (TGA)

TGA measurement has been performed using a Thermo Microbalance TG 209 F1 Libra (Netzsch, Selb, Germany). In a typical experiment, 0.01 g of sample was placed on a Pt crucible, dried at 150°C for 2 h, and then heat to 1000 °C with a heating rate of 10 °C min⁻¹. The heating has been performed under a synthetic air flow of 20 mL min⁻¹. Before the analysis, the samples have been dried for 6h at 89.85°C under a vacuum.

Gas chromatography equipped with a mass spectrometer detector (CG—GC-MS) and with flame ionization detector (GC-FID)

The qualitative and quantitative product analysis has been performed using Gas chromatography (Agilent 8890 GC) equipped with an HP-5MS Ultra Inert column from Agilent (model: USR577054H), a split-splitless liner (Agilent 5190-2295) and coupled with both mass spectrometer detector, *i.e.* GC-MS configuration, (Agilent 5975 MSD) and flame ionization detector (Agilent), *i.e.* GC-FID configuration.

For qualitative analysis, the GC-MS configuration has been with used. The MS method has been set with a run time of 32 min, injection volumes of 1.0 µL, and He as carrier gas with a flow of 1 mL min⁻¹. The injection has been set in Split mode with a split ratio of 10 while the inlet has been kept at 280°C to evaporate the injection. The temperature program for the column oven has been set as follows: start at 50°C and maintain for 1 min, then increase to 300°C with a heating rate of 10°C min⁻¹ and maintain at 300°C for 6 min. The MS detector has been set to scan between 50 and 250 m/z with a gain factor of 1.1. The solvent delay has been set at 2.6 min, while the MS detector and the quadrupole have been kept at 230°C and 150°C, respectively. The mass spectra of the compounds were analyzed by integrating the peak area using the Agilent MassHunter Qualitative Analysis 10.0 software and comparing it with the NIST17 mass spectral database.

For the quantitative analysis, GC-FID configuration has been used. The injection and the oven methods have been set identically to the GC-MS analysis above described. During the analysis, the FID detector has been fed with H₂ flow of 30 mL min⁻¹ as fuel gas while the heater has been kept at 349.85°C to avoid product condensation at the GC/FID interface. The quantification of the peak has been conducted using the Agilent MassHunter Qualitative Analysis 10.0 using the ChemStation integrator.

Klason lignin quantification

The acid-insoluble lignin, called Klason Lignin (KL) of the beach wood sawdust (BWS) was determined based on the procedure reported by Nakano and Meshitsuka.⁷ Accordingly, 1g of BWS was transferred to 50 mL flask with 15 mL of H₂SO₄ solution (72 wt.-%). The mixture was left at room temperature for 2 h under continuous stirring. Afterward, the solution has been transferred to a round-bottom flask

containing 360 mL of water. Then, the solution was boiled for 4 h under reflux conditions. Afterward, the solution was directly filtrated without cooling. After filtration, brown sludge was retained. The precipitate was washed with hot water to remove any leftover acid and the obtained residue was dried at 120°C for 12 h. The mass of the KL has been determined gravimetrically from the weight of the dried residue. Therefore, the KL content has been quantified in wt.-% with respect to the initial BWS mass.

Determination of total monosaccharides

The carbohydrate content was measured by a standard sugar determination method, modified for hydrolysis of cellulose-rich materials (8). This procedure consists of 3 steps namely: i.) sugar hydrolysis; ii) reduction of hydrolysate sugars to sugar alcohols; iii) derivatization (acetylation) before GC analysis.

Typically, triplicate samples of 10 mg were hydrolyzed for 2 h in a concentrated H₂SO₄ solution (13 M, 1 mL) at room temperature, followed by hydrolysis at 100 °C for another 2 h in a diluted H₂SO₄ solution (2 M, 6.5 mL). The obtained sugars were reduced to sugar alcohols. In this step, 3 mL of hydrolysate, 1.5 mL of 25 wt.% aqua ammonia, 1 mL of a 1 mg mL⁻¹ β-D-allose solution of water, and (saturated) benzoic acid (V-to-V of 1) as internal standard, and droplets of 2-octanol to avoid excessive foaming, were mixed. The hydrolysate reduction has been conducted using NaBH₄ (0.2 mL of a 200 mg mL⁻¹ NaBH₄ solution containing 2 M NH₃) at 40°C for 0.5 h. Acetic acid (0.4 mL) was added to terminate the reaction. Then, 0.5 mL of 1-methylimidazole, 5 mL of acetic acid, and 1.0 mL of ethanol has been added to 0.5 mL of sugar solution to acetylate the alcohols. 10 mL of distilled Water have been added after 5 minutes and 0.5 mL of bromophenol blue solution (0.04%)w.v. The bromophenol blue will function as a dye to mark the phase separation. Twofold 5 mL of KOH 7M solutions are slowly added to the mixture while keeping it in an ice bath to prevent overheating (exothermic reaction). After 30 minutes the top oil phase is separated from the bottom water phase, dried with sodium sulphate anhydrous, and analyzed using GC.

The content of the reduced sugars, *i.e.*, arabinose, xylose, mannose, galactose, and glucose, has been determined based on the response factor (RF) to allose used as an internal standard. The response factor RF of the *i*th sugar is calculated as follows:

$$RF_i = \frac{M_i}{M_{IS}} \cdot \frac{A_{IS}}{A_i}$$

Where M and A are the known mass and measured integration area for the *i*th and IS, respectively.

The concentration of the *i*th sugar (C_i) in each sample is calculated using the RF as follows and expressed in wt%:

$$C_i [\text{wt}\%] = \frac{A_i}{A_{IS}} \cdot RF_i \cdot \frac{M_{IS}}{M_{BWS_dry}} \cdot 100\%$$

Finally, the mass content of cellulose and hemicellulose has been calculated as follows, respectively:

$$M_{Cellulose} [\text{wt}\%] = \frac{M_{glucan}}{M_{BWS_dry}} \cdot 100\%$$

$$M_{Hemicellulose} [\text{wt}\%] = \frac{M_{xylan} + M_{galactan} + M_{arabinan} + M_{mannan}}{M_{BWS_dry}} \cdot 100\%$$

Where M_i represents the *i*th mass of the measured sugars.

UV-Vis spectrometric analysis

UV-Vis measurement has been performed using a high-performance split beam T70+ UV-vis spectrophotometer. In a typical experiment, 100 μL of samples were diluted in 2.5 mL of solvent, *i.e.*,

MeOH, and MeTHF (according to the solvent used for the reaction), in a high-precision quartz cuvette, type 100-QS (10 mm size). The spectrophotometer is interfaced to a PC using the UV-Win software used for the determination of absorbance spectra, changing the wavelength from 1110 nm to 190 nm with 1nm steps.

Size-exclusion gel permeation chromatography (SEC)

Viscosity measurements were performed with an automated micro viscometer AMVn (Anton Paar) applying the falling ball method. Depending on the sample viscosity, a glass capillary with a diameter of 1.6 or 1.8 mm and a ball with a diameter of 1.5 mm was used. Scanning force microscopy (SFM) measurements were performed on a Nanoscope Multimode IIIa microscope (Digital Instruments, Santa Barbara, CA) using silicon cantilevers with $k = 42$ N/m (Nanoworld, Switzerland). Surfaces were scanned at room temperature in tapping mode at a resonance frequency of 200–300 kHz. Samples were spin-coated at 2000 rpm onto UV/ozone-cleaned silicon wafers.

Size exclusion chromatography (SEC) of the extracted lignin sample was conducted in a PSS Thermo Separation Products (TPS) equipped with a PSS SECurity2 UV-1000\2000 detector and a two columns system composed 300 × 8 mm² MZ-SDplus (spherical polystyrene particles with an average diameter of 5 μm) columns with porosities of 10³ and 10⁵ Å. The injection volume has been set to 100 μL, with an elution flow of 1.0 mL min⁻¹ using Na₂HPO₄ 0.084 M aqueous buffer as eluent and column 111 temperature of 25°C. Calibration was done with poly(ethylene oxide) standards (Polymer Standards Service PSS, Mainz, Germany).

Two Dimensional ¹H-¹³C heteronuclear single quantum coherence nuclear magnetic resonance (2D HSQC- NMR)

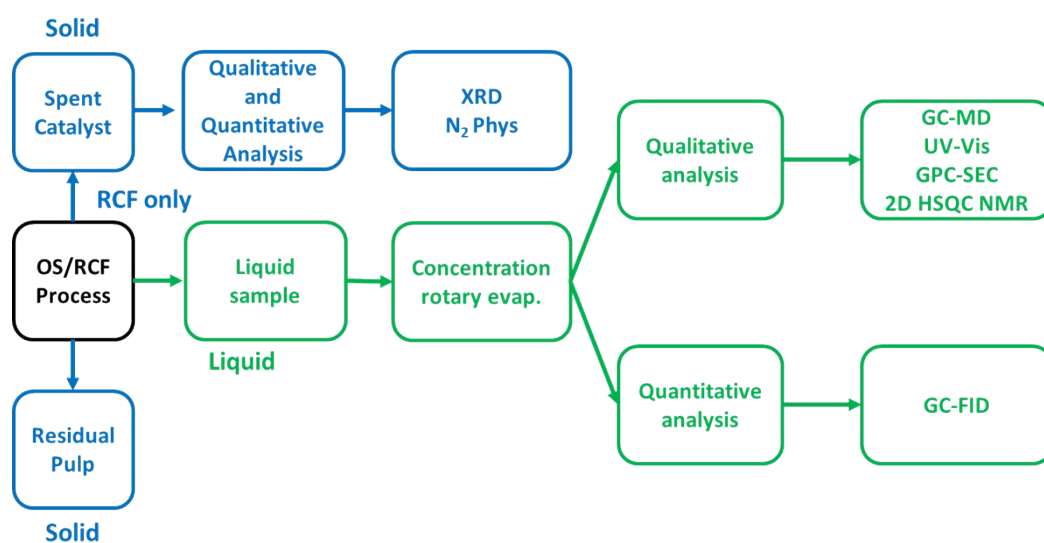
NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer. A sample of the extracted lignin was completely dried in an oven (70°C for 48h) and 10 mg were dissolved in 0.6 mL of DMSO-d₆. HSQC experiments had the following parameters: standard Bruker pulse sequence 'HSQC', spectral width of 8.6 ppm in F2 (1H dimension) by using 2048 data points for an acquisition time (AQ) of 159 ms, spectral width of 149 ppm in F1 (¹³C dimension). The number of scans was 64 with an interscan delay of 1.5 s (D1). The assignment of the HSQC peaks has been done by comparing the spectra with literature,⁹⁻¹¹ as well as using the "Predict 1H-NMR shift" and "Predict 13C-NMR" Tools from the Software ChemDraw Ultra.

Products analysis

The analysis of the BWS valorization products was conducted using GC-MS and GC-FID for qualitative and quantitative analysis, respectively. In order to obtain higher intensity signals, 5 g of the collected samples have been concentrated with a rotary evaporator until an exact mass of 1g was reached. Afterward, the concentrated samples have been injected in GC-FID. The quantification has been conducted in comparison of the calibration curve with standard compounds using GC-FID as the detector. The monomer yield was reported based on the Klason lignin (KL) content (mg g_{KL}⁻¹) and has been calculated as follows:

$$y_i = C_i \cdot \frac{M_i}{M_0} \cdot \frac{1}{M_{KL}} 1000$$

Where C_i indicates the measured concentration of the i^{th} compounds expressed in wt.-%, M_0 indicates the Mass of the collected sample before the rotary evaporation (generally 5.0 g), M_f represents the mass of the sample after the rotary evaporation (generally 1.0 g) and M_{KL} represents the Klason Lignin content. However, the sensitivity factor of the remaining non-commercially available monomers (4-ethyl syringol, propyl syringol, syringyl ethyl alcohol, dihydro sinapyl alcohol, allyl syringol, and isoallyl syringol) was deduced by applying the effective carbon number (ECN) principles on the sensitivity factor of analogous compounds.⁹



Scheme S1: Analytical process flowsheet after the FT-organosolv (OS) and reductive continuous fractionation (RCF). In blue is indicated the analysis of the solid fraction, while in green the analysis of the liquid products. Please note that the spent catalyst analysis is present only in the FT-RCF experiments.

Setup

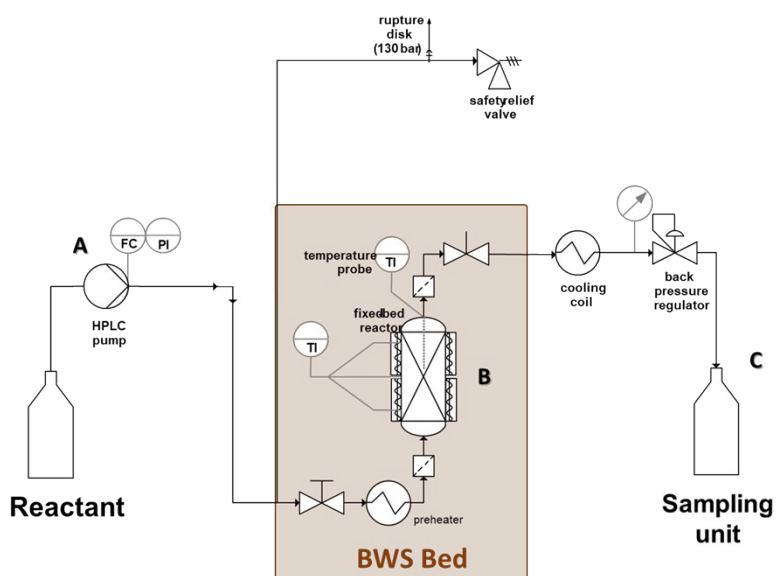
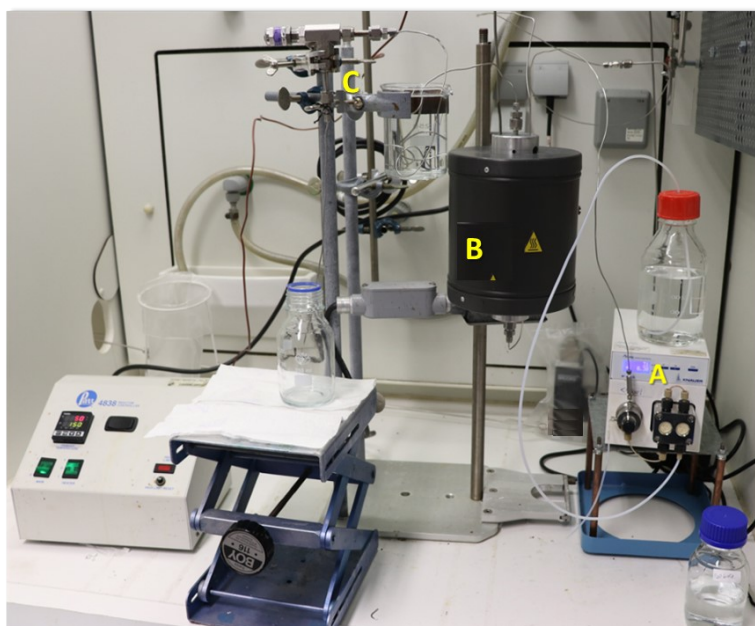


Figure S2. Flow-through (FT) setup for the reductive continuous fractionation (RCF) of beech wood sawdust (BWS). **Top:** Picture of the setup; **Bottom:** setup's flowchart. The setup consists of (A) an HPLC pump equipped with pressure control (Knauer Azura P 4.1S Series); (B) two-side opened independent heating units equipped with a heat controller (Model # 4848 from the Parr Instrument Company); (C) sampling unit equipped with proportional relief valves as a pressure regulator (Swagelok SS-RL4M8F8-EP).

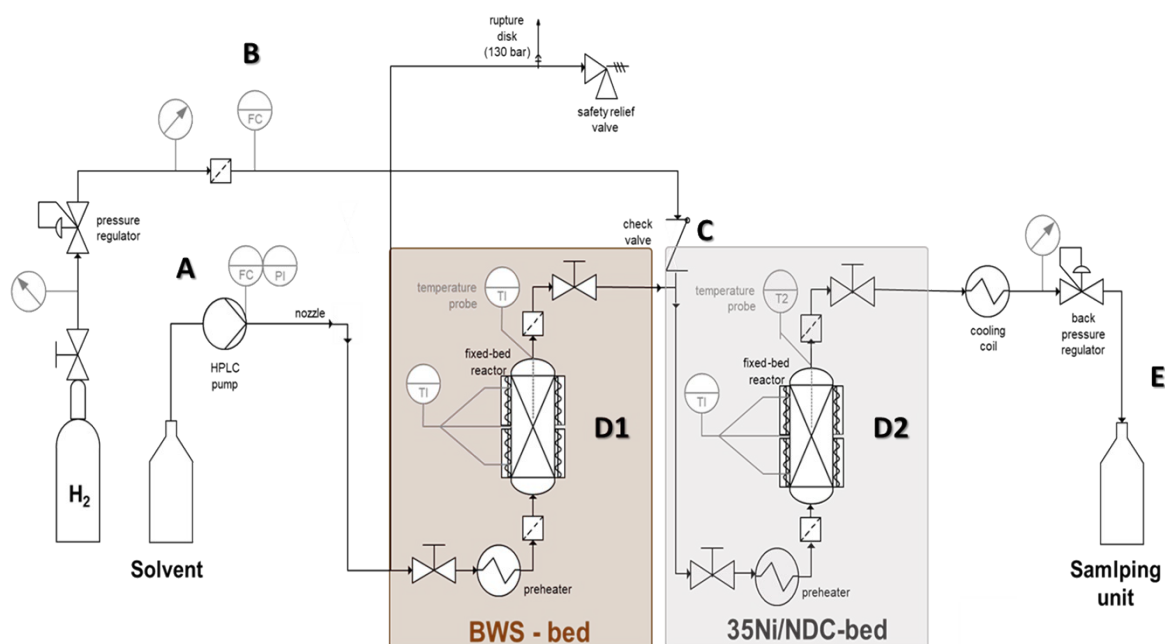
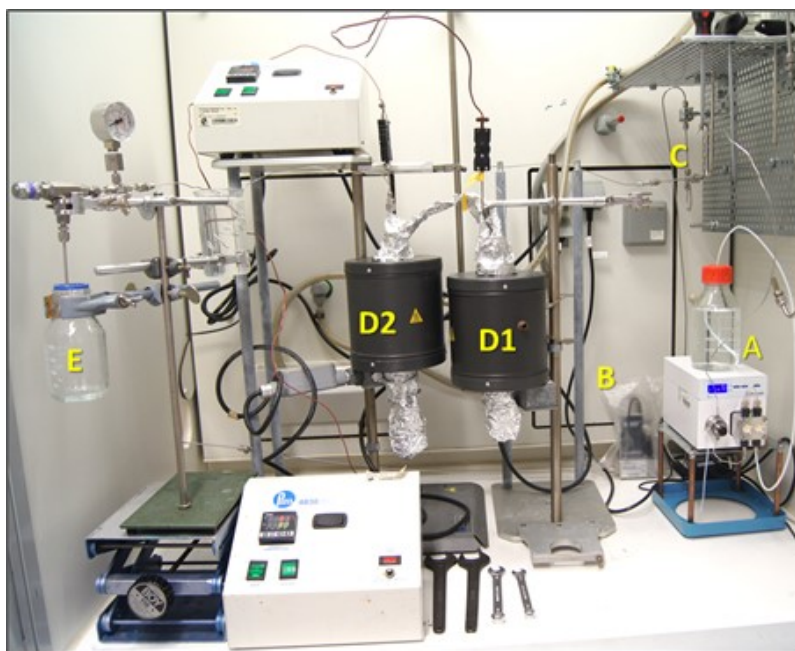


Figure S3. Flow-through setup for the reductive catalytic fractionation (FT-RCF) of beech wood sawdust (BWS). **Top:** Picture of the setup; **Bottom:** setup's flowchart. The setup consists of (A) an HPLC pump equipped with pressure control (Knauer Azura P 4.1S Series); (B) a Mass flow controller for controlling the flow of H₂ (Brooks Instruments, Model SLA5850SC1AF1B2A1); (C) "T" union for H₂-reactant mixing (Swagelok SS-400-30); (D1) and (D2) independent two-side opened independent heating units equipped with a heat controller (Model # 4848 from the Parr Instrument Company) to heat the BWS- and 35Ni/NDC-beds, respectively; (E) sampling unit equipped with proportional relief valves as a pressure regulator (Swagelok SS-RL4M8F8-EP).

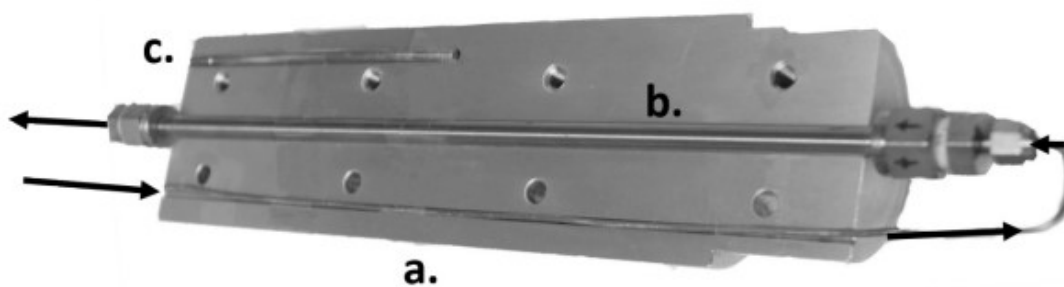


Figure S4. The customized aluminum cylinder is used to ensure efficient heat consisting of three holes, **A)** pre-heating unit, **B)** tubular reactor place, and **C)** thermocouple location for temperature control. In this case, the reactor has an outer diameter of 6.5 mm, a similar cylinder has been made for the bigger tubular reactor (outer diameter of 25 mm).



Figure S5: Stainless steel tubular reactor (inner diameter = 21 mm, outer diameter = 25 mm, length = 280 mm).

Results and Discussion

Table S1. Chemical composition obtained by elemental analysis of the K_L content in original beech wood sawdust (BWS).

	Moisture / wt.-%	K _L / wt.-%	Cellulose / wt.-%	Hemicellulose / wt.-%	Ashes / wt.-%	C / wt.-%	O / wt.-%	H / wt.-%
BWS	4.7	21	41.7	16.5	6.6	46	44	5.6

Table S2. Sugar
BWS.

composition of the

	Amount / - wt%
Arabinan	0.37
Xylan	16.12
Mannan	1.03
Galactan	0.63
Glucan	41.69

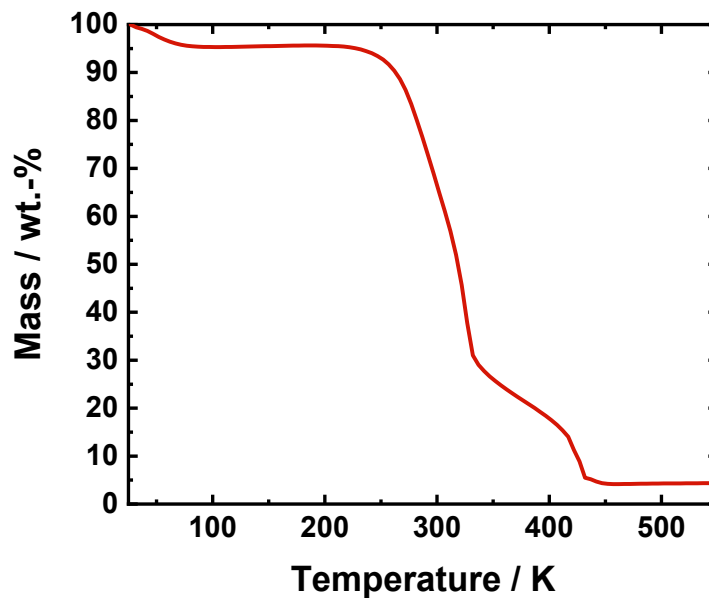


Figure S7. TGA in synthetic air of raw BWS feedstock.

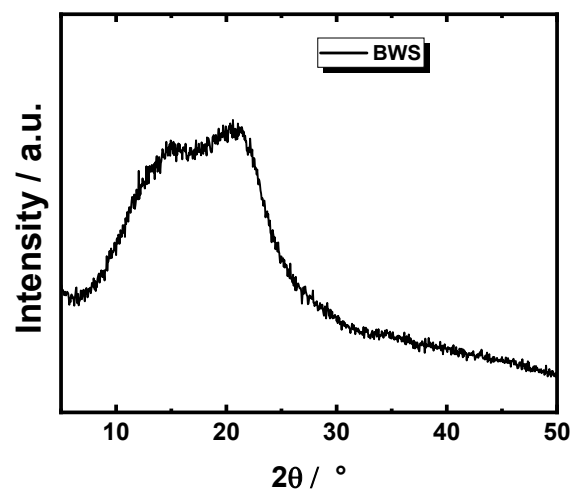


Figure S8. XRD pattern of the raw BWS feedstock.

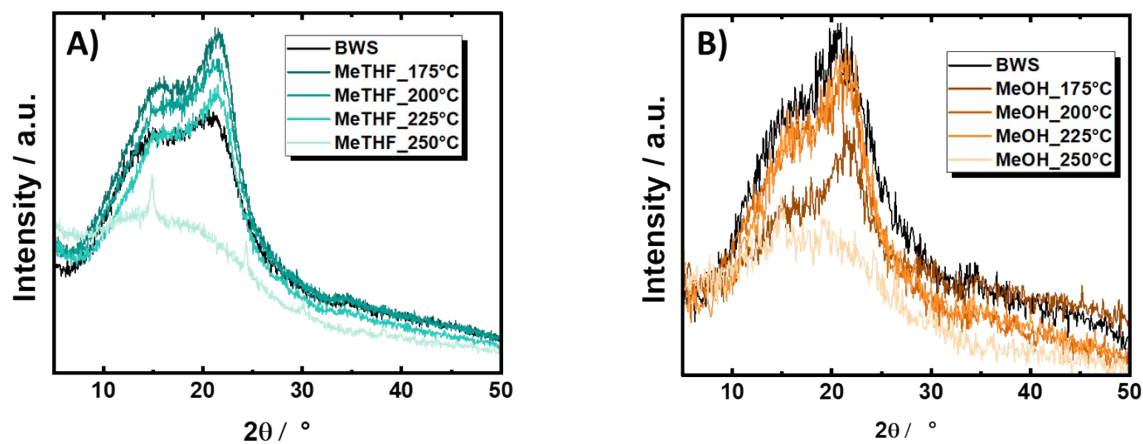


Figure S9. XRD reflection patterns for the initial BWS and the residual wood at different temperature using as a solvent: **A)** MeTHF, and **B)** MeOH. Reaction conditions: $m_{\text{BWS}} = 10 \text{ g}$, $T_{\text{extraction}} = 225 \text{ }^\circ\text{C}$, $p = 7.0 \text{ MPa}$, $Q_{\text{educt}} = 1.0 \text{ mL min}^{-1}$, $t_{\text{residence}} = 50 \text{ min}$. **Caution** the peaks in the 250 °C peaks at $2\theta \sim 14^\circ$ and $\sim 25^\circ$ are due to glass wool impurities in the sample.

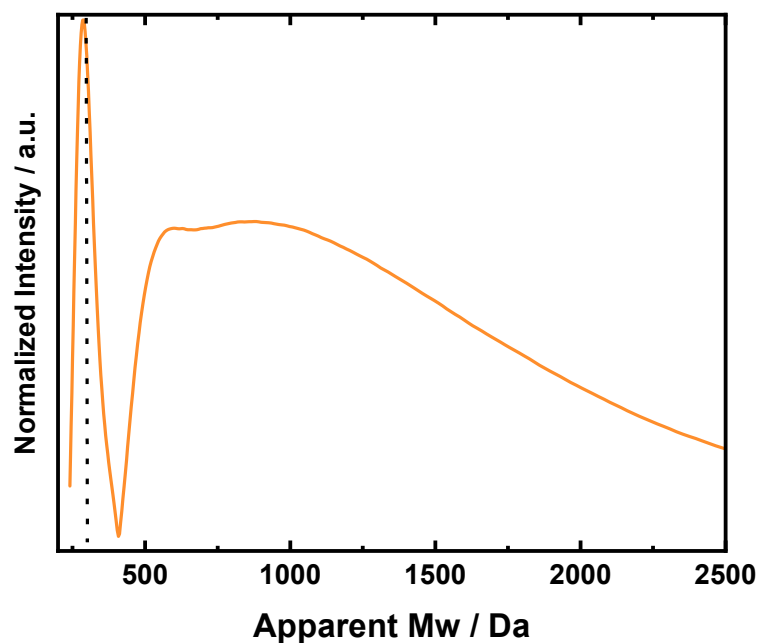


Figure S10. SEC molar mass distribution of the solvolytic experiment using MeOH as a solvent. The black dot line indicates the toluene peak, used as internal standard.

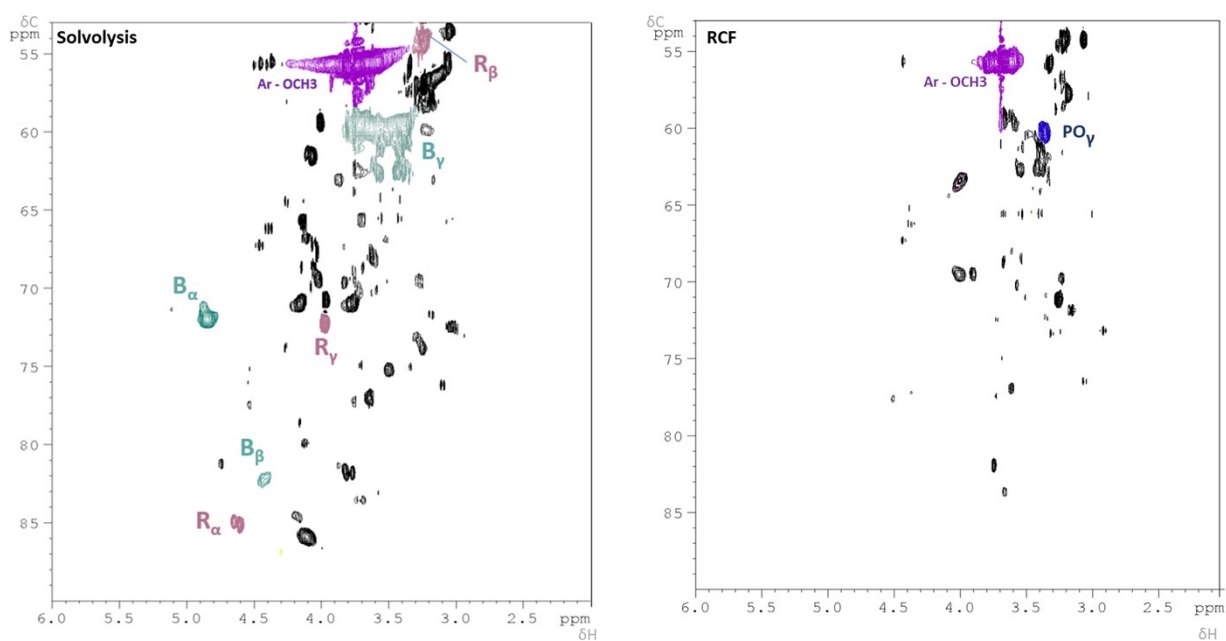


Figure S11. Detail of 2D-HSQC NMR spectra $\delta C/\delta H = 53\text{-}90/2\text{-}6$ ppm (left) FT-solvolytic and (right) FT-RCF (MeOH). The colors and names of assigned groups are similar to the ones in **Figure 2** in the main text of the manuscript.

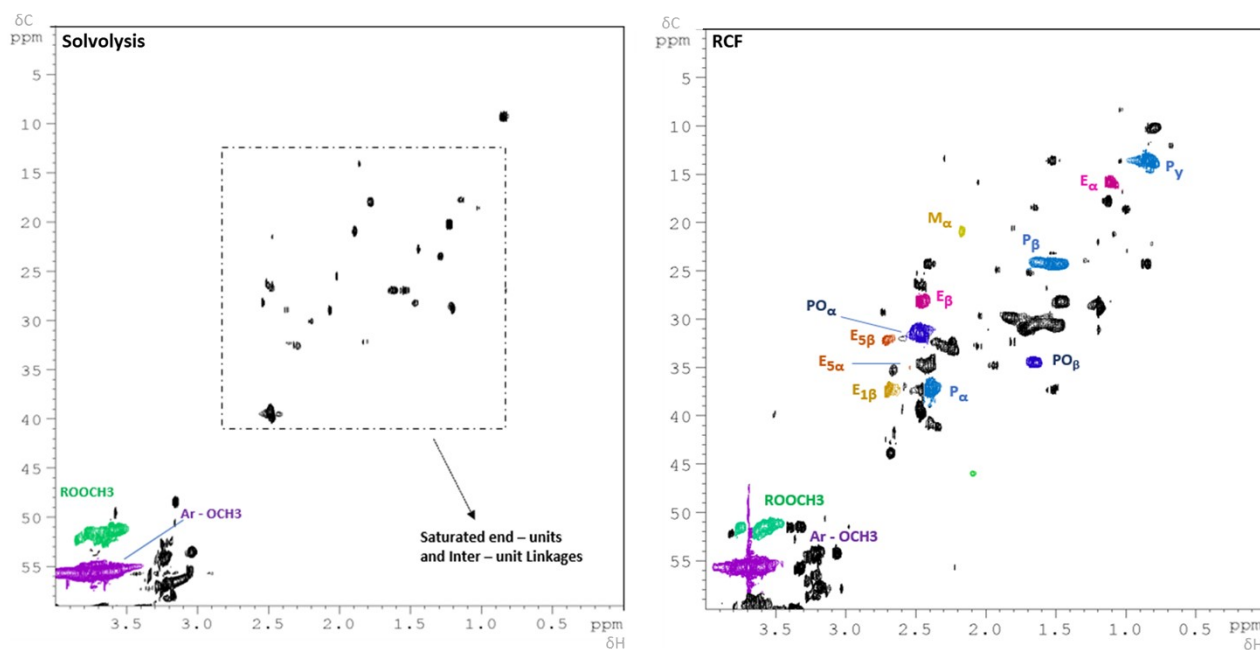


Figure S12. Detail of 2D-HSQC NMR spectra $\delta C/\delta H = 0-60/0-4$ ppm of FT-solvolytic (**left**) and FT-RCF (**right**) (MeOH). The colors and names of assigned groups are similar to the ones in **Figure 2** in the main text of the manuscript.

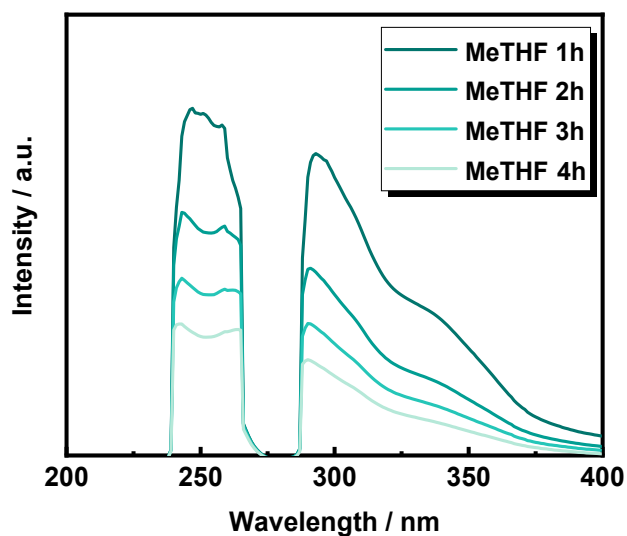


Figure S13. UV-Vis spectra of OS samples using Methf as a solvent at different time on stream. **Reaction conditions:** $m_{BWS} = 10$ g, $T_{\text{extraction}} = 225^{\circ}\text{C}$, $p = 7.0$ MPa, $Q_{\text{educt}} = 1.0$ mL min^{-1} , $t_{\text{residence1}} = 50$ min, Time on stream = 1h, 2h, 3h, 4h. **Caution:** the negative intensity peaks at around 280 nm and 220 nm are interferences due to the presence of butylated hydroxytoluene (BHT) – UV inhibitor- used as a stabilizer in the supplied MeTHF.

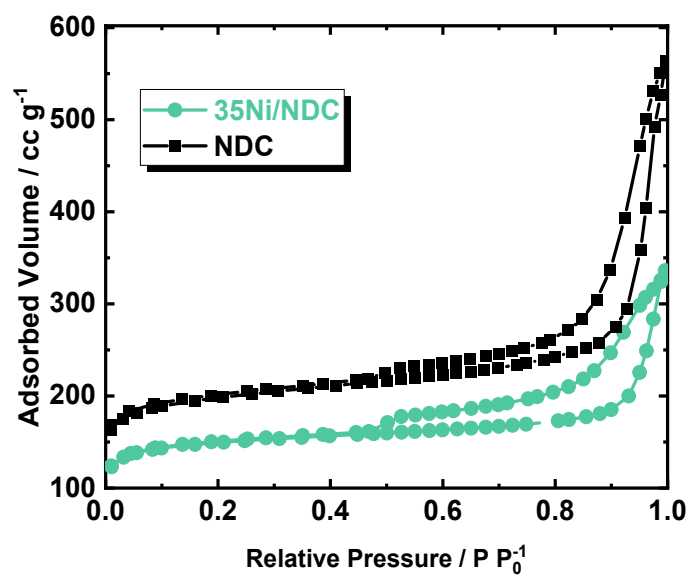


Figure S14. N_2 -physorption isotherms at 77 K of the NDC and 35 Ni/NDC.

Table S3. Textural properties and chemical composition of NDC and 35NiNDC obtained with N_2 physorption and EA-ICP.

Catalyst	C ^a / wt.%	N ^a / wt.%	Ni ^b / wt.-%	C/N ratio	A _{BET} ^c / m ² g ⁻¹
NDC	75	3.7	-	22	755
35Ni/NDC	55	2.8	35	20	578

^a measured with EA analysis, ^b measured with ICP analysis, ^c calculated from N_2 physorption.

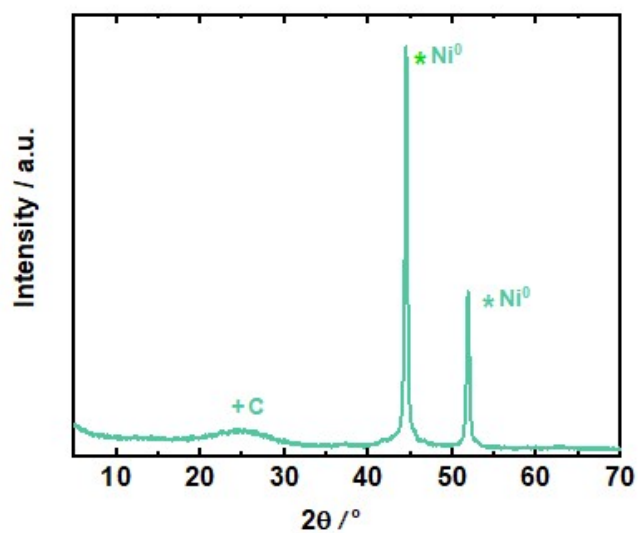


Figure S15. XRD pattern of 35Ni/NDC. The symbols indicate the typical reflection for Ni⁰ and C already reported in literature.²⁻⁴

Table S4. Identified and quantified compounds via GC-FID and GC-MS of the RCF experiments.

GC-MS RT/ Min	GC-FID RT/ Min	Structure	Name	Abbreviation	Quantification method
11.653	14.70		4-Propyl guaiacol	G1	Calibration with standard
10.428	13.548		4-Ethyl guaiacol	G2	Calibration with standard
13.735	16.802		Homovanillyl alcohol	G3	Calibration with standard
15.098	18.137		Dihydroconiferyl alcohol	G4	Calibration with standard
7.632	10.795		Guaiacol	G5	Calibration with standard
9.158	12.156		Creosol	G6	Calibration with standard
12.123	15.456		Isoeugenol	G7	Calibration with standard
11.168	14.456		Syringol	S1	Calibration with standard
12.256	15.567		4-Methyl syringol	S2	Calibration with standard
13.423	16.534		4-Ethyl syringol	S3	ECN
15.324	17.545		4-Propyl syringol	S4	ECN
17.125	19.456		Syringyl ethyl alcohol	S5	ECN
17.421	20.514		Dihydro sinapyl alcohol	S6	ECN
15.248	18.385		Allyl syringol	S7	ECN
15.478	18.589		Isoallyl syringol	S8	ECN

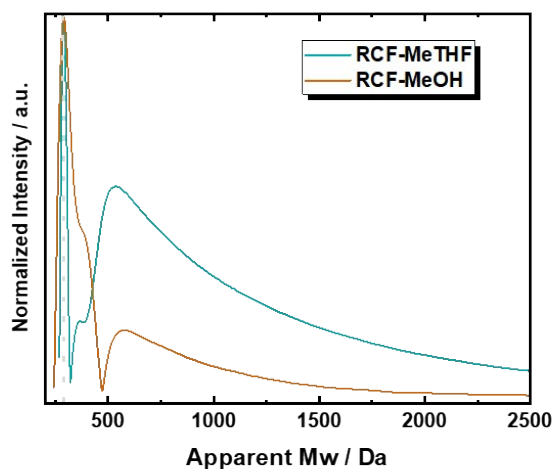


Figure S16. SEC molar mass distribution of the reductive catalytic fractionation (RCF) experiments using MeOH and MeTHF as a solvent (RCF-MeOH and RCF-MeTHF). The Gray dot line indicates the toluene peak, used as an internal standard.

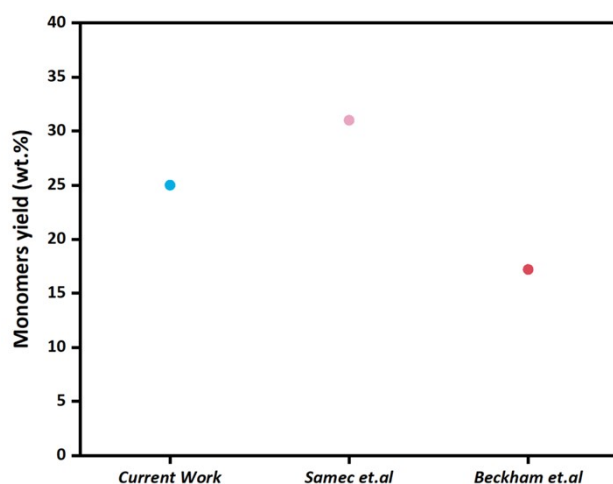


Figure S17. Cumulative monomer yield of FT-RCF comparison between the current work and literature. The current work is compared with work conducted by Samec¹³ and Beckham¹⁴ groups in terms of monomer yield expressed in wt.-% of klason lignin in the original feedstock. **Caution:** all these works have been conducted with different feedstocks and catalysts, beech wood sawdust and 35Ni/NDC in the current work, birch wood and Pd/C and H₃PO₄ for the work from Samec group, and poplar wood and pelletized 50-50 Ni/C – SiO₂ for Beckham group.

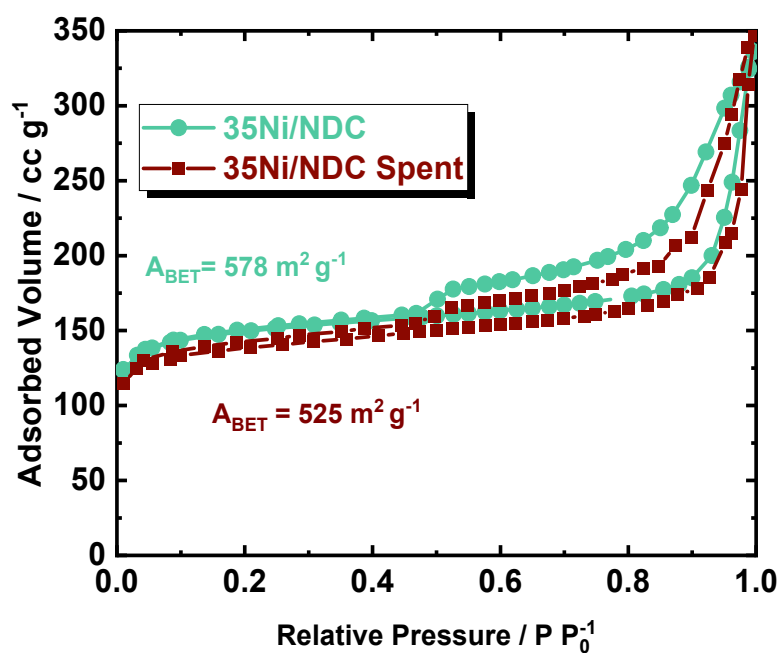


Figure S18. N₂-physorption isotherms at 77 K of the fresh 35Ni/NDC and spent 35Ni/NDC_spent.

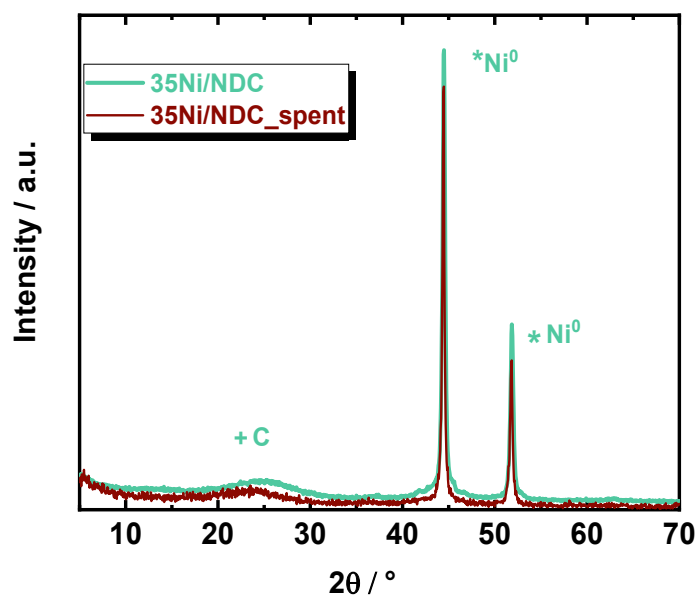


Figure S19. XRD pattern the fresh 35Ni/NDC and spent 35Ni/NDC_spent. The symbols indicate the typical reflection for Ni⁰ and C already reported in literature.²⁻⁴

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