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Electronic Supporting Information (ESI)

Controlled lignosulfonate depolymerization via solvothermal fragmentation coupled with catalytic hydrogenolysis/hydrogenation in continuous flow reactor

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S1. Materials

Industrial residues of Sodium lignosulfunate (LS) have been provided from Domsjö-Fabriker. D-(+) Glucose anhydrous (99.5%), 4-propyl-guaiacol (99%), and homovanyllyl alcohol (99%) were supplied by Sigma aldrich. Hydrochloric acid (0.1 M in water) was obtained from Merk. Urea and nickel nitrate hexahydrate (>99%) and 2-Methyltetrahydrofuran (MeTHF) were supplied by Roth. Guaiacol (99%) has been provided by Sigma. Homovanillyl alcohol (99%) and 4-propyl phenol (99%) were supplied from Aldrich. Dhydroconyferyl alcohol (97%) was supplied from AmBeed. Creosol (99%) was obtained from Acros Organics. $MgSO_3$ anhydrous has been purchased from J.T. Baker. Zinc oxide nanoparticles (average d = 20 nm) were ordered from Nanostructure and amorphous inc. Semolina (type durum wheat) was acquired from Divella. Forming gas (95/5) and H_2 bottles were purchased from Westfalia. All the chemicals were used as received without any further purification. The sodium poly-(styrene sulfonate) SEC standards (Mw of 29500 g mol^{-1}, 15800 g mol^{-1}, 13500 g mol^{-1}, 9740 g mol^{-1}, 3800 g mol^{-1}, 1670 g mol^{-1}, 891 g mol^{-1} and 246 g mol^{-1}) have been provided by Polymer Standard Service-USA inc. (PSS).

S2. Catalyst preparation

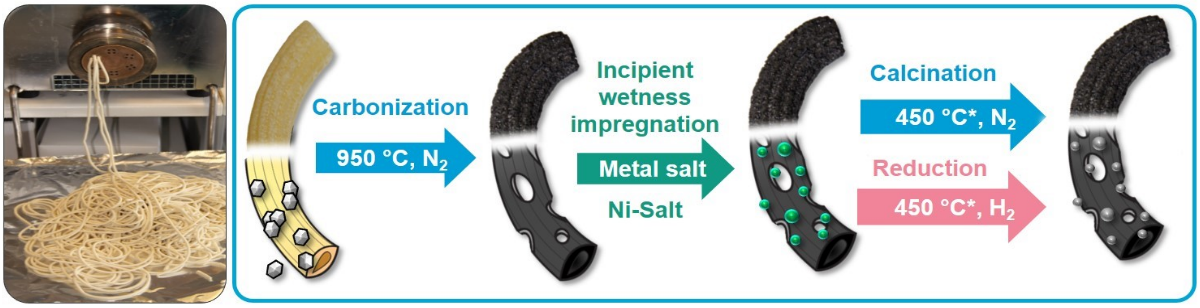

Figure S1 Schematic representation of the catalytic synthesis protocol starting from extrusion (left) followed by carbonization, incipient metal impregnation, calcination and reduction.[1]

The porous nitrogen-doped carbon (NDC) pellets were synthesized based on our group‘s prevision study.[1-4] 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 cm^3 water (20 wt..-% of the mixture) was added to the mixture as a plasticizer. Finally, the low-moisture mixture was extruded and cut in the 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°C min^{-1} and maintaining it for 2 h; (iii) elevating the temperature to 950°C with the heating rate of 3°C 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 have 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 cm^3) 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 air for 12 h. Afterwards, 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 N2 at room temperature for 30 min; ii) heating ramp to 450°C with 3°C min^{-1} rate and maintained for 2 h. Prior to 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°C min^{-1} and maintained for 5 h.

S3. Catalyst characterization

Combustion elemental analysis (EA)

Elemental analysis of C, H, O, and N from LS and 35Ni/NDC has been performed with a Vario-MICRO cube CHNOS elemental analyzer. Prior to the analysis, the sample has finely ground.

Inductively coupled plasma optical emission spectroscopy elemental analysis (ICP)

The measurements of Na, Ca Mg of LS and Ni of 35Ni/NDC were conducted via 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 ground and digested for 13 hours in 500 µL of *Aqua Regia* solution (3:1 molar ratio of HCl and HNO_3, respectively).

N_2 physisorption

The N_2 physisorption measurements of 35Ni/NDC were accomplished with N_2 at -196°C, after degassing the sample at 423 K for 20 h under vacuum, using a Quantachrome Quadrasorb SI porosimeter. The specific surface area was calculated by applying the Brunauer-Emmet-Teller (BET) model in the relative pressure region of (0-0.05) for the adsorption branch (A_{BET}).

Powder X-ray diffraction (XRD)

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

Thermogravimetric analysis (TGA)

The measurement for the LS has been performed using a Thermo Microbalance TG 209 F1 Libra (Netzsch, Selb, Germany). In a typical experiment, 0.01 g of sample were placed on a Pt crucible, dried at 423 K for 2 h, and then heat to 1273 K in a continuous flow of synthetic air (20 $cm^3\ min^{-1}$), with a heating rate of 10 K min^{-1}.

High-resolution scanning transmission electron microscopy (HR-STEM)

The HR-STEM images of 35Ni/NDC were acquired using a double-Cs-corrected JEOL RM200F, equipped with a cold field emission gun and an energy-dispersive X-ray (EDX) filter. The acceleration voltage was set to 80 kV for the investigation.

Energy-dispersive X-ray spectrometry (EDS)

The EDS investigation of LS and SHF-LS has been conducted on a Scanning electron microscope (SEM) – Gemini Leo 1550 equipped. Prior to the analysis, the detector has been calibrated with a standard Cu sample, the measure was conducted at 15 keV.

CO-chemisorption

CO-Chemisorption was performed using AMI-300 equipped with thermal conductivity detector (TCD) from Altamira Instrument. In each measurement, 0.05 g of catalyst was placed between two layer of quartz wool in the measurement cell (quartz U-tube). primarily, the sample was treated at 120°C in a flow He for 1 h. Afterwards, the sample was reduced by increasing the temperature to 450°C in the presence of a mixture of H_2 (20%) in He (80%) with a dwell of 4 h. Later, saturation of the catalyst with CO at 30°C was applied by flowing CO (20%) over the sample for 5 h. Then, the non-adsorbed CO was removed by flowing He (100%) over the sample for 30 min. To ensure a complete saturation of the samples, 20 pulses (509 µL each) of CO (20%) in He (80%) over the sample at 30°C. Finally, the CO desorption profile was recorded by increasing the temperature from 30°C to 550°C with 10°C min^{-1} with dwell of 30 min at 550°C.

Size exclusion gel permeation chromatography (SEC)

Size exclusion chromatography (SEC) of sodium lignosulfonate (LS) and depolymerized LS was conducted in a PSS Thermo Separation Products (TPS) equipped with a PSS SECurity^2 UV-1000\2000 detector and a two columns systems composed by: i) precolumn PSS-MCX 5 µm and ii) main column PSS-MCX-analytical 5 µm. The injection volume has been set to 100 µL, with an elution flow of 1.0 cm^3 min^{-1} using Na_2HPO_4 0.084 M aqueous buffer as eluent and column temperature of 25°C. Prior to the analysis the sample has been diluted 1:10 in the Na_2HPO_4 and the salt peak at 25°C has been used as internal standard. The molecular weight distributions quantification (M_w, M_n and Đ) has been performed using the PSS – WinGPC UniChrom software and sodium poly-(styrene sulfonate) standards. Accordingly, eight different standard have been used with a M_w of 29500 g mol^{-1} (RT 8.63 min), M_w of 15800 g mol^{-1} (RT 9.14 min), M_w of 13500 g mol^{-1} (RT 9.25 min), M_w of 9740 g mol^{-1} (RT 9.47 min), M_w of 3800 g mol^{-1} (RT 9.88 min), M_w of 1670 g mol^{-1} (RT 10.23 min), M_w of 891 g mol^{-1} (RT 10.44 min) and M_w of 246 g mol^{-1} (RT 10.9 min). The standards have been fit with a calibration curve applying a polynomial function of the seventh order (PSS –poly 7).

Two dimensional ^{1}H-^{13}C 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 sodium lignosulfonate (50 mg) was dissolved in 0.6 cm^3 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 (^{13}C dimension). The number of scans was 64 with an interscan delay of 1.5 s (D1).

Freeze-drying

The freeze-drying of the SHF-LS sample has been conducted using a Christ Alpha 1-4 LSC-basic device. Prior to the freeze-drying, the sample has been placed in a falcon tube and frozen at -10°C for 10 h. Afterwards, a further cooling step has been conducted in liquid nitrogen for 5 minutes. Then, the sample has been freeze-dried for 10 h at a pressure of around 4 kPa followed by 10 h at 0.5 kPa for complete drying.

pH-analysis

The pH of the reactant LS solution and the SHF-LS collected solution has been measured using a WTW Multilab 540 pH meter equipped with a KCL. Prior to the analysis, the pH meter has been calibrated using the Burkett standard buffer solution for pH of 4.0, 7.0 and 8.0. The pH has been measured while the sample has been kept under continuous stirring.

X-ray diffraction (XRD)

Powder XRD measurements for 35Ni/NDC were performed on a Bruker D8 diffractometer equipped with a CuKα source ($\lambda = 0.154$ nm) and a NaI scintillation counter-Scinti-Detector. The diffraction pattern was recorded in the 2θ range between 4-70° with steps of 0.05° and acquisition time of 2 sec per step.

Gas Chromatography equipped with mass spectrometer detector (GC-MS) and with flame ionization detector (GC-FID)

The qualitative and quantitative product analysis has been performed using a Gas chromatography (Agilent 8890 GC) equipped with a HP-5MS Ultra Inert column from Agilent (model: USR577054H), a split-splittles 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. The injection has been set in Split mode with a split ration 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 following: start at 50°C and maintaining for 1 min, then increasing to 300 °C with a heating rate of 10°C min^{-1} and maintaining 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 has been kept at 230°C and 150°C, respectively. The mass spectra of the compounds were analyzed integrating the peak area using the Agilent MassHunter Qualitative Analysisi 10.0 software from and comparing with the NIST 17 mass spectral database.

For the quantitative analysis GC-FID configuration has been used. The injection and the oven methods has been set identically to the GC-MS analysis above described. During the analysis the FID detector has been fed with H_2 flow of 30 cm^3 min^{-1} as fuel gas while the heater has been kept at 350°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.

S4. Reaction set up

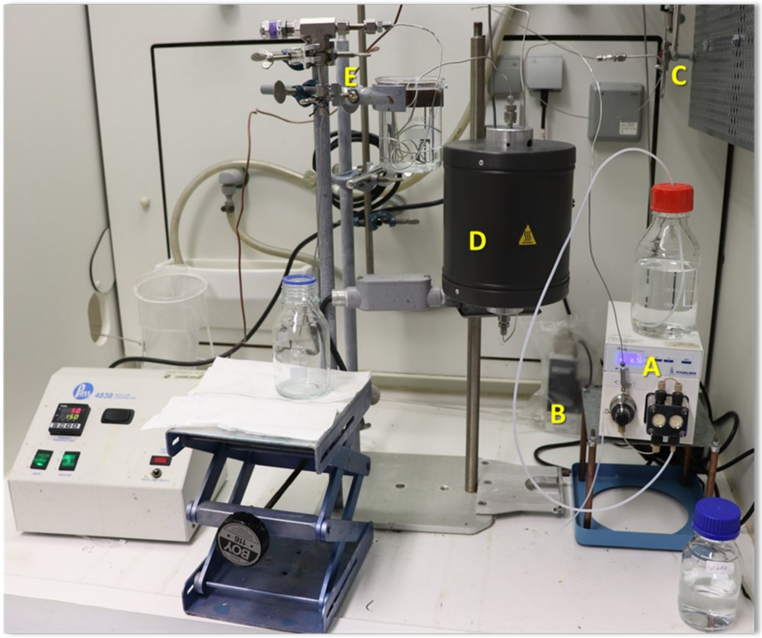

Figure S2. The setup for the continuous flow solvothermal fragmentation (SF) and Solvothermal combined with hydrogenolysis/hydrogenation LS fragmentation (SHF) consisting of of **A**) HPLC pump equipped with pressure control, **B**) T- piece for gas-liquid mixing **C**) Mass flow controller for H_2 **D**) heating unit (see the inner part of it at Figure S4) **E**) relief valve used for pressure controlling, connected with **s**ample collector.

Figure S3. Homemade aluminum heating block used to ensure efficient heating, consisting of three location bores: **1)** fixed bed reactor place **2)** thermocouple location for temperature control and **3)** pre-heating unit.

Figure S4. Stainless steel tubular reactor used as reactor (inner diameter 21 mm, outer diameter 24 cm, length 280 mm).

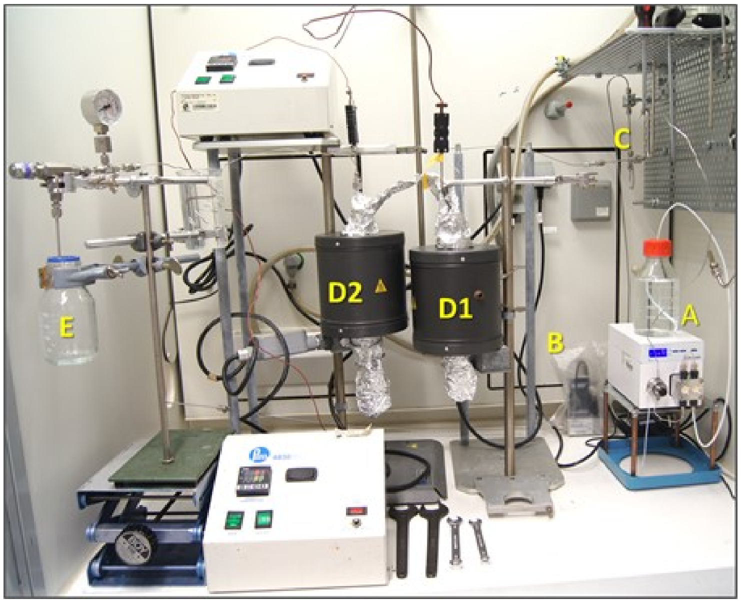

Figure S5. Coupled two reactor setup for solvothermal combined with catalytic hydrogenolysis/hydrogenation fragmentation (SHF) of LS, consisting of **A**) HPLC pump equipped with pressure control, **B**) Mass flow controller for controlling the flow of H_2, **C**) T-piece for gas-liquid mixing, **D1**) and **D2**) independents heating units and **E**) sampling unit equipped with proportional relief valve.

S5. Product analysis and quantification

An analytical procedure has been established to meets the requirement for each analytical techniques, *i.e.* solid specimen for EA, ICP, 2D HSQC NMR XRD, and FTIR) and liquid with minimized water content for GC analysis (GC-MS and GC-FID), see **Figure S6**. The used procedures for these methods are reported in detail in **Section S3** For every experiment, a sample of around 30 g has been collected. Initially, the alcohol solvent, *i.e.* MeOH and EtOH, have been removed with rotary evaporation. In the case of EtOH, where the water-EtOH azeotrope is formed, the rotary evaporation has been interrupted when the half of initial sample has been evaporated. When H_2O is used as solvent mixture, no preliminary rotary evaporation is conducted and the sample is directly extracted.

After the first step, the resulting liquid has been separated into two equals fractions of around 7.5 gram in order to be further treated for solid and liquid analysis separately.

In the case of solid analysis, the water solvent has been removed via freeze-drying. The resulting solid has been used for EA, ICP, 2D HSQC NMR and FTIR analysis.

The other portion has been treated in order to perform GC analysis. Accordingly, to separate the residual sulfonate fragments and to extract the monomer from the aqueous phase the sample has been extracted using MeTHF as extractive solvent. Thus, almost 5 g of water sample have been extracted with 50 cm^3 of MeTHF, with five iterative extractions of 10 cm^3 each. Afterwards, eventual water residuals in the solution have been dried adding almost 5g of $MgSO_3$ anhydrous. The $MgSO_3$ slurry has been removed via filtration. Finally, the MeTHF solution has been concentrated with rotary evaporation until an exact mass of almost 2.5 g has been reached.

The quantification has been conducted in comparison of calibration curve with standard compounds using GC-FID as detector. The single monomer yield and the cumulative monomers yield (Y_{CM}) expressed in mg g_{LS}^{-1} have been calculated as follow:

$$y_i = \left(C_i \cdot \frac{M_0}{M_f}\right) \cdot \frac{1}{c_{LS}} \cdot 1000$$

$$Y_{CM} = \sum_{n=1}^{N} (y_i)$$

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 analytical procedure, M_f represents the mass of the sample after the final step of the concentration and c_{LS} represent the LS concentration in the reactant solution.

The Space time cumulative monomer yield (STY_{CM}) and the weight hourly space velocity (WHSV) were calculated as follow and expressed in mg h^{-1} g_{Ni}^{-1} and g_{LS} h^{-1} g_{Ni}^{-1} .

$$WHSV = c_{LS} \cdot \dot{w} \cdot M_{Ni}^{-1}$$

$$STY_{CM} = Y_{CM} \cdot WHSV$$

Where c_{LS} indicates the weight concentration of LS in the feed solution, *i.e.* 1 or 2.5 wt.-%, $\dot{w}$ indicates the hourly mass feed flow rate, expressed in g h^{-1}, and M_{Ni} represents the mass of Nickel in g.

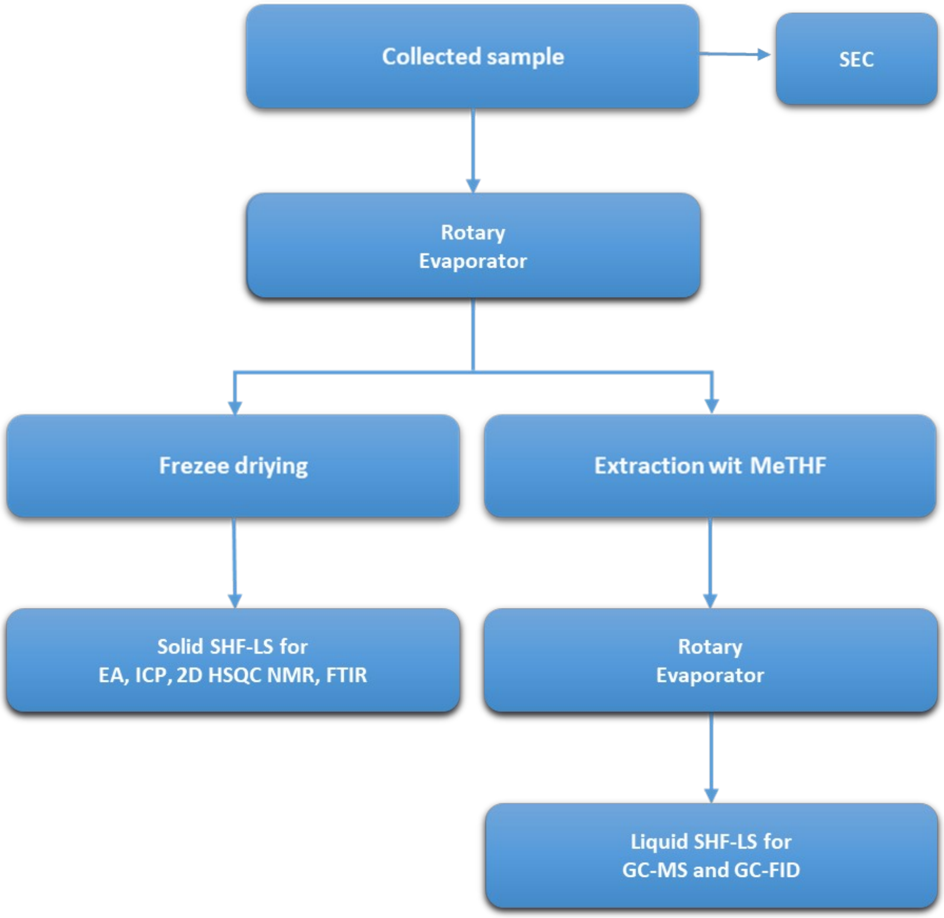

Figure S6 Analytical procedure scheme for solid SHF-LS and liquid SHF-LS analysis.

S6. Results and discussion

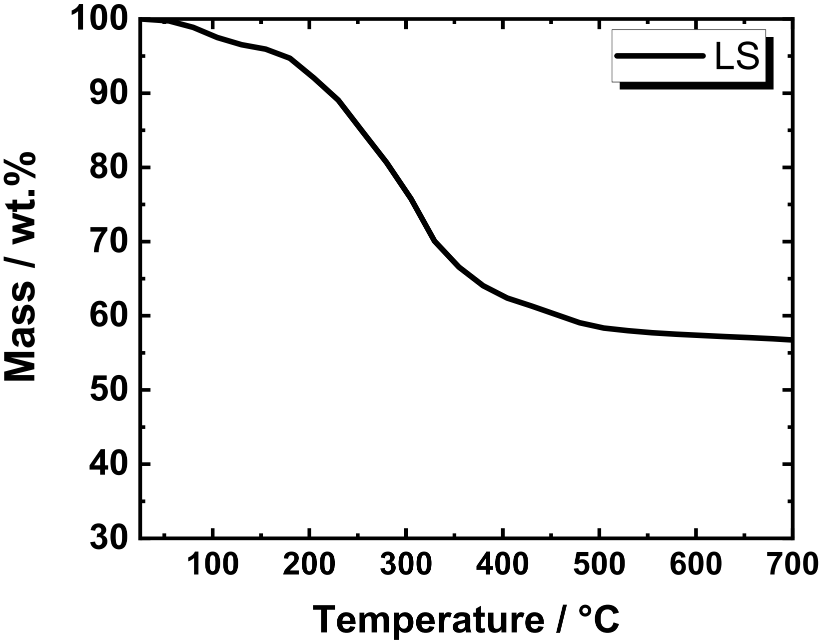

Figure S7. TGA of sodium lignosulfonate (LS) in synthetic air.

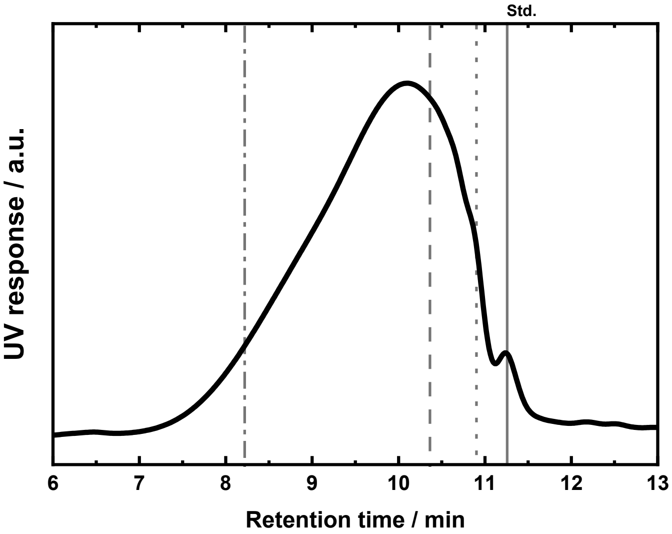

Figure S8. SEC chromatograms of LS. The straight line indicates the eluents buffer reference peak ($NaHPO_3$), dotted and dashed lines show the analytical standard peaks, i.e., sodium poly-(styrene sulfonate), with M_w of 246 g mol^{-1} (RT = 10.9 min) and with M_w of 891 g mol^{-1} (RT= 10.4 min), respectively.

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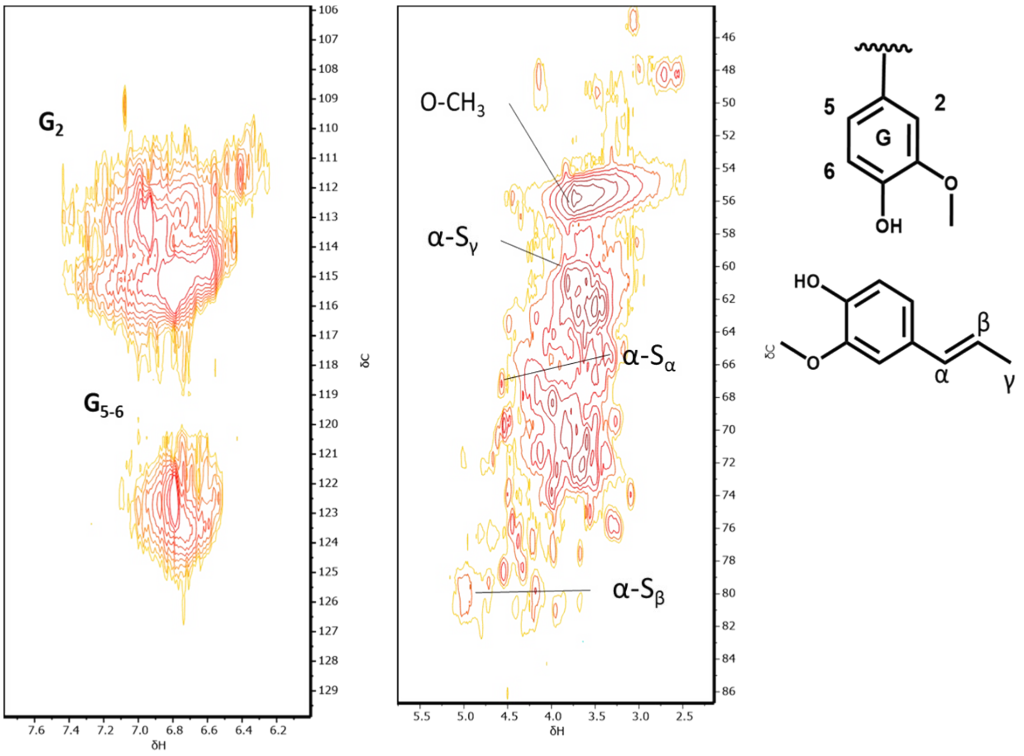


Figure S9. 2D HSQC NMR of LS. Selected structural motif are highlighted: Guaiacyl units ($G_{2,5,6}$) and sulfo-groups (α-$S_{\alpha,\beta,\gamma}$).

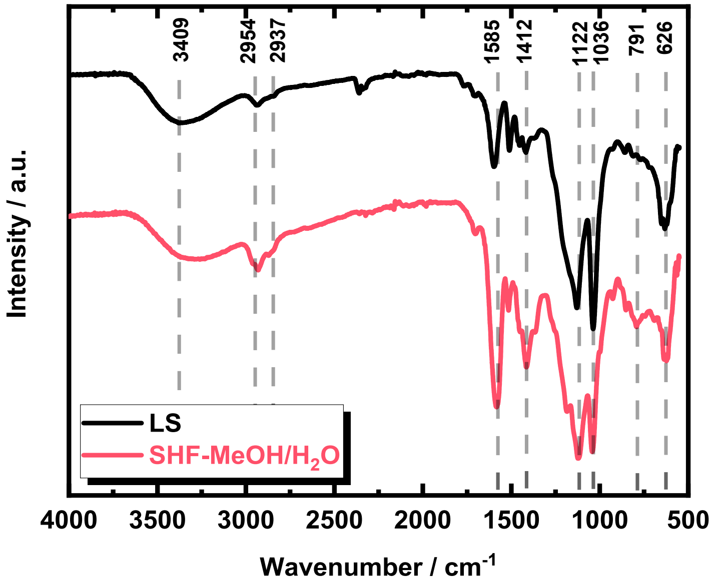


Figure S10. FTIR of sodium lignosulfonate (LS) and of the **SHF-LS** after **MeOH/H_2O** experiment. The highlighted peaks e assigned in **Table S1**.

Table S1 Main FTIR peak assignment from **Figure S10,** according to literature.

Wave number / cm^{-1}	**functional group**	**reference**
3450-3300	O-H stretching vibration	[5 6 7]
2934	C-H stretching CH_3 (and O-CH_3)	[5 6]
2854	C-H stretching CH_2	[5 6]
1713	C=O stretching vibration	[5]
1585	C=C stretching (aromatic) and C=O stretching	[6]
1390-1487	Aromatic ring breathing	[5 6]
1150-1200	O=S=O symmetric stretching	[6 7 8]
1122	C-O alkoxy group vibration	[9]
1036	S=O stretching	[7 9]
791	Aromatic C-H out of plane	[5 6]
626	C=O ketone vibration breathing	[5]

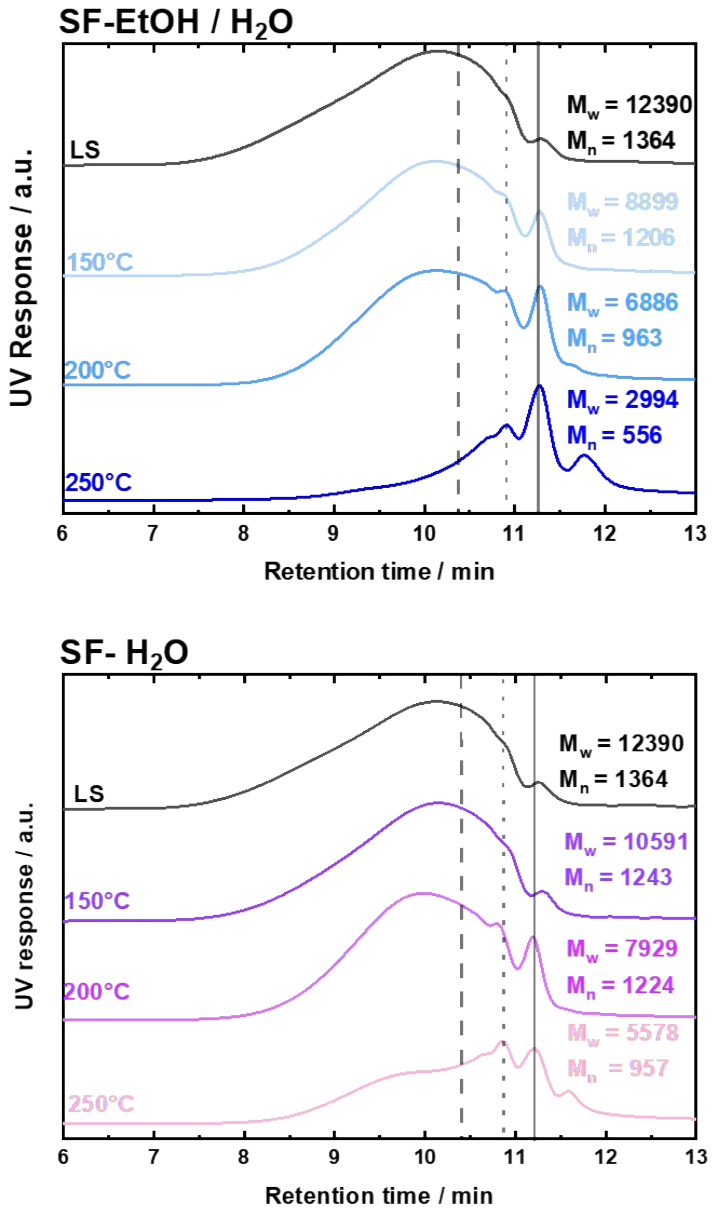


Figure S11. SEC chromatograms of the solvothermal fragmentation (SF) of LS in EtOH/H_2O. Reaction conditions: c_{LS} = 1.0 wt.-%, T = 150°C, 200°C and 250° C, p = 7.0 MPa, Q_{educt} = 1.0 cm^3 min^{-1},Q_{H_2} = 20 cm^3 $min^{-1}$and $t_{residence}$ = 50 min. The straight line indicates the eluents buffer reference peak ($NaHPO_3$), dotted and dashed lines show the analytical standard peaks, i.e., sodium poly-(styrene sulfonate), with M_w of 246 g mol^{-1} (RT = 10.9 min) and with M_w of 891 g mol^{-1} (RT= 10.4 min), respectively.

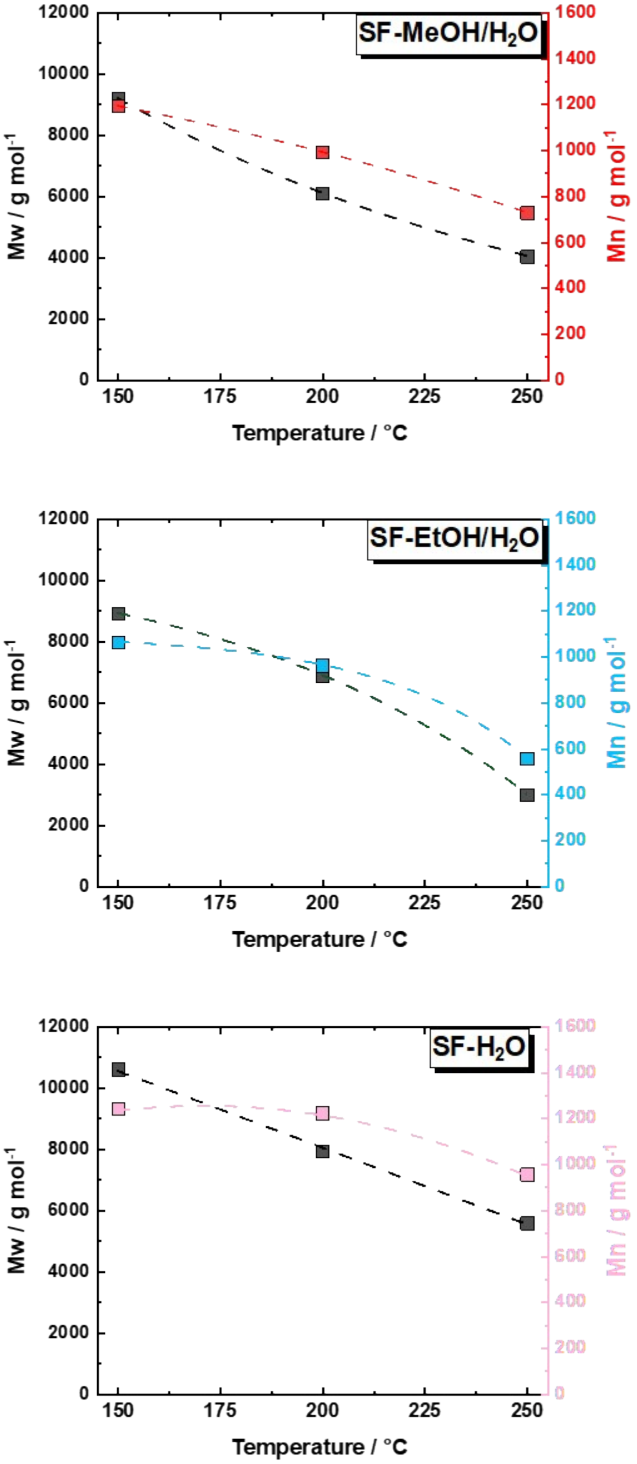


Figure S12. Mass-average (M_w) and number-average (M_n) molar mass for LS thermal fractionation (SF) with MeOH/H_2O (up), EtOH/H_2O (middle), and H_2O (down) as a function of reaction temperature. Reaction conditions: c_{LS} = 1.0 wt.-%, T = 150°C, 200°C and 250° C, p = 7.0 MPa, Q_{educt} = 1.0 cm^3 min^{-1},Q_{H_2} = 20 cm^3 $min^{-1}$and $t_{residence}$ = 50 min.

Table S2. Molecular weight (M_w) and number averaged molecular weight (M_n) distribution and dispertity (Đ) values calculated from SEC in function of different solvents in SF and SHF experiments.

Sample	**Entry**	**T / °C**	**M_w / g mol^{-1}**	**M_n / g mol^{-1}**	**Đ**
LS	1	n.a.	12390	1364	9.1
SF-MeOH/H_2O	2	150	9132	1192	7.7
	3	200	6093	991	6.1
	4	250	3856	586	6.5
SF-EtOH/H_2O	5	150	8899	1206	7.4
	6	200	6886	963	7.1
	7	250	2994	556	5.3
SF- H_2O	8	150	10591	1243	8.5
	9	200	7929	1224	6.5
	10	250	5578	957	5.8
SHF-MeOH/H_2O	11	150	10104	993	10
	12	200	3106	589	5.3
	13	250	433	360	1.2
SHF-EtOH/H_2O	14	150	8457	968	8.7
	15	200	1556	583	2.7
	16	250	502	485	1.1
SHF- H_2O	17	150	9555	1715	5.5
	18	200	8375	680	12
	19	250	1393	363	3.8

n.a.: not applicable

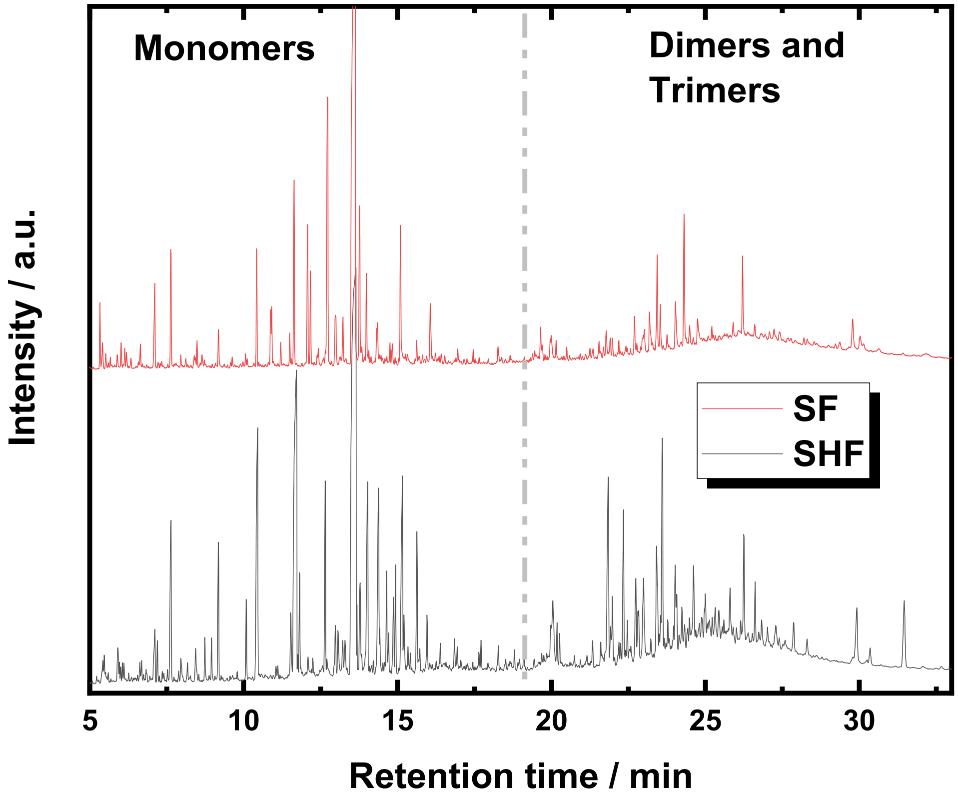
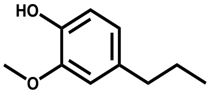
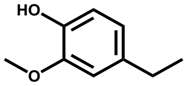
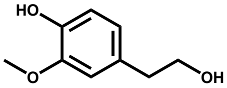
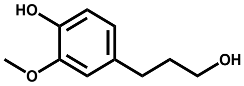
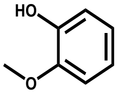
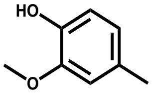
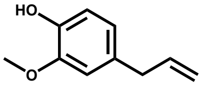
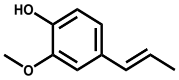
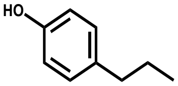
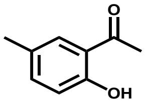
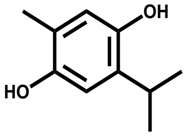
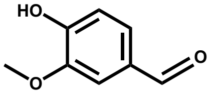
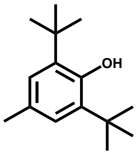
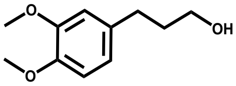
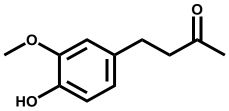
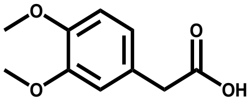


Figure S13. GC-MS-Chromatograms of solvothermal fragmentation (SF) of LS and solvothermal combined with catalytic hydrogenolysis/hydrogenation (SHF) with MeOH/H_2O solvent mixture. Reaction conditions: c_{LS} = 1.0 wt.-%, T = 250° C, p = 7.0 MPa, Q_{educt} = 1.0 cm^3 min^{-1},Q_{H_2} = 20 cm^3 min^{-1}, $m_{35Ni/NDC}$ = 10 g, $t_{residence}$ = 50 min, and weight hour space velocity (WHSV) = 0.17 g_{LS} h^{-1} mg_{Ni}^{-1}.

Table S3. Identified and quantified compounds via GC-MS and GC-FID of the solvothermal fragmentation (SF) experiment with MeOH/H_2O and EtOH/H_2O.

GC-MS RT/ Min	GC-FID RT/ Min	Structure	Name	Abbreviation	Quantified
11.653	14.70		4-Propyl guaiacol	**G1**	**Yes**
10.428	13.548		4-Ethyl guaiacol	**G2**	**Yes**
13.735	16.802		Homovanillyl alcohol	**G3**	**Yes**
15.098	18.137		Dihydroconiferyl alcohol	**G4**	**Yes**
7.632	10.810		Guaiacol	**G5**	**Yes**
9.158	12.330		Creosol	**G6**	**Yes**
12.730	15.961		Eugenol	**G7**	**Yes**
12.123	15.456		Isoeugenol	**G8**	**Yes**
10.058	13.134		4-Propyl phenol	**H1**	**No**
10.911	-		Ethanone,1-(2-hydroxy-5-ethylphenyl)-	**-**	**No**
11.542	-		*p*-Cymene-2,5-diol	**-**	**No**
12.079	-		Vanillin	**-**	**No**

13.645	-		BHT – MeTHF stabilizer	-	**No**
13.988	-		Benzene, 4 butyl alcohol-1,2-dimethoxy	-	**No**
14.753	-		Butanone,4-(4-hydroxy-3-methoxyphenyl)-	-	**No**
16.061	-		Benzeneacetic acid, 3,4 dimethoxy	-	**No**

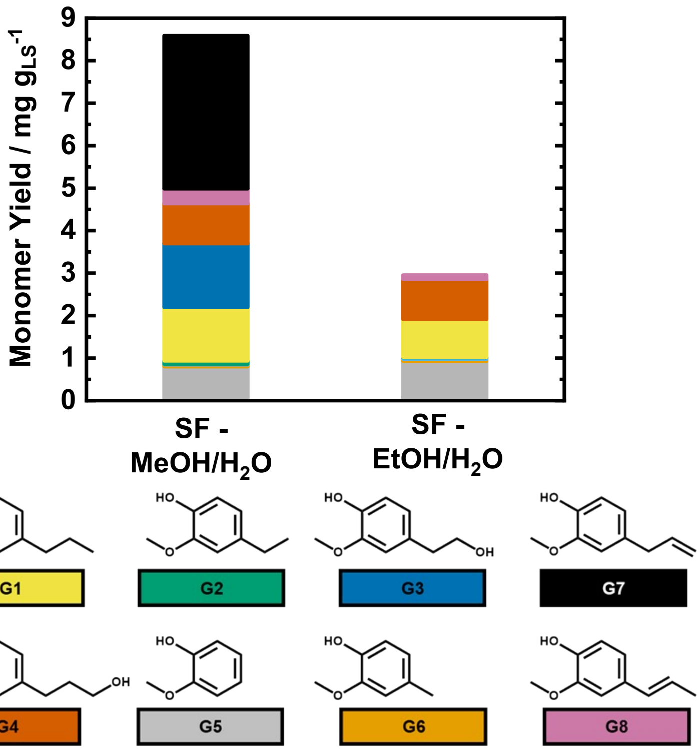


Figure S14. Monomer yield for the solvothermal fragmentation (SF) using MeOH/H_2O and EtOH/H_2O solvent systems (**top**) and identified monomers structure (**bottom**); Reaction conditions: c_{LS} = 1.0 wt.-%, T = 250° C, p = 7.0 MPa, Q_{educt} = 1.0 cm^3 min^{-1}, Q_{H_2} = 20 cm^3 min^{-1}, $m_{35Ni/NDC}$ = 10 g and $t_{residence}$ = 50 min.

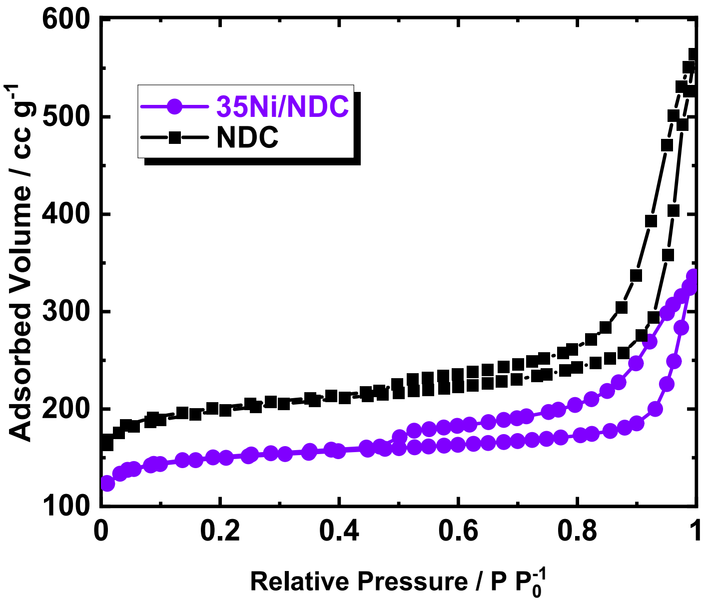


Figure S15.N_2-physisorption isotherms at 77 K of the NDC and 35 Ni/NDC.

Table S4. Textural properties and chemical composition of NDC and 35NiNDC obtained with N_2 physisorption and EA-ICP.

Catalyst	**C^{a} / wt.%**	**N^{a} / wt.%**	**C/N ratio**	**Ni^{b} / wt.%**	**A_{BET}^{c}/ m^2 g^{-1}**	**A_{Ni}^{d} / m^2 g^{-1}**
NDC	75	3.7	22	n.a.	755	-
35Ni/NDC	55	2.8	20	34.7	578	21

[a] measured with EA analysis, [b] measured with ICP analysis, [c] calculated from N_2 physisorption and [d] Measured via CO-TPD.

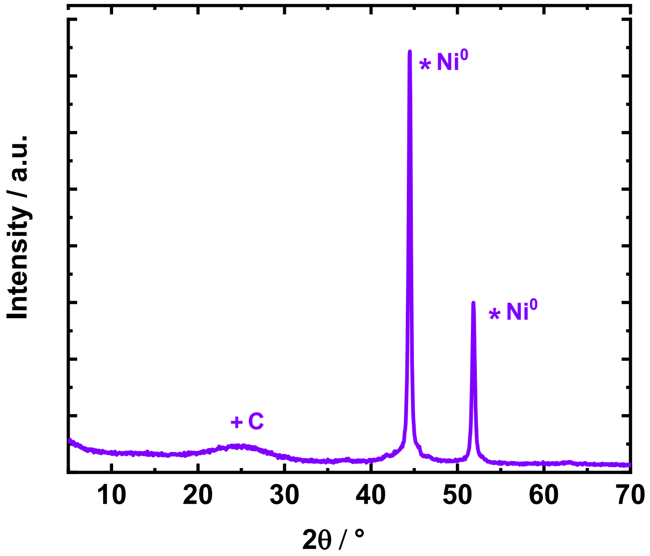


Figure S16. XRD pattern of 35Ni/NDC. The symbols indicate the typical reflection for Ni^0 and C already reported in literature.[1, 3]

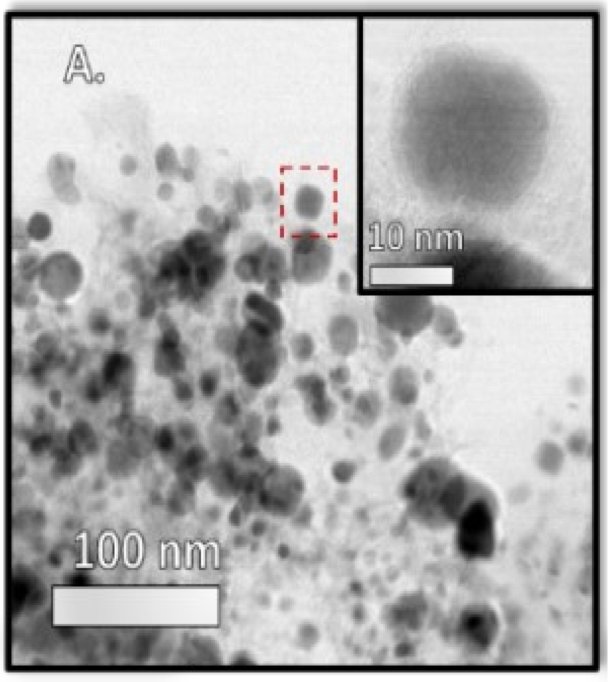


Figure S17. HR-TEM image for 35Ni/NDC.

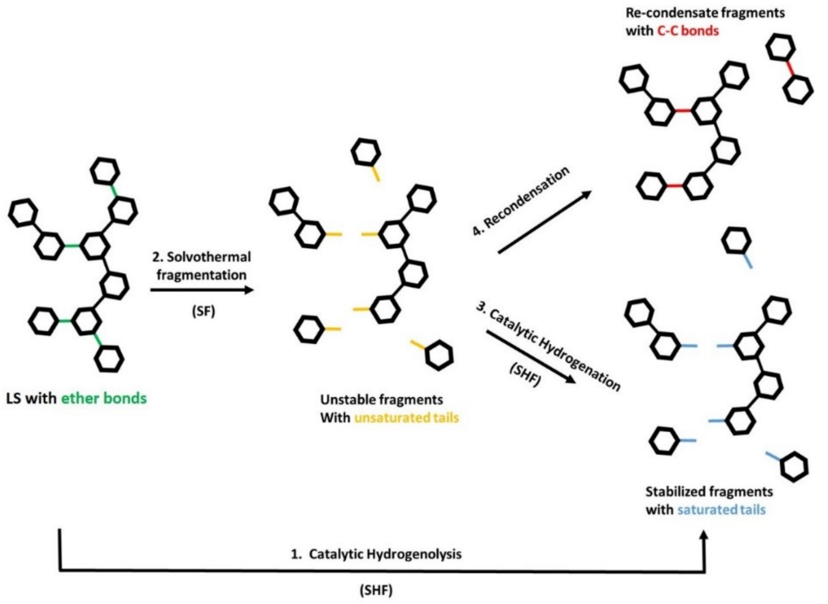


Figure S18. Proposed depolymerization scheme for the solvothermal assisted catalytic hydrogenation/hydrogenolysis of LS. The 35Ni/NDC catalyst accelerate the LS fragmentation through hydrolysis (**1**) as well as prevent eventual unstable fragments formed solvothermally (**2**) to recondensate via hydrogenation (**3**).

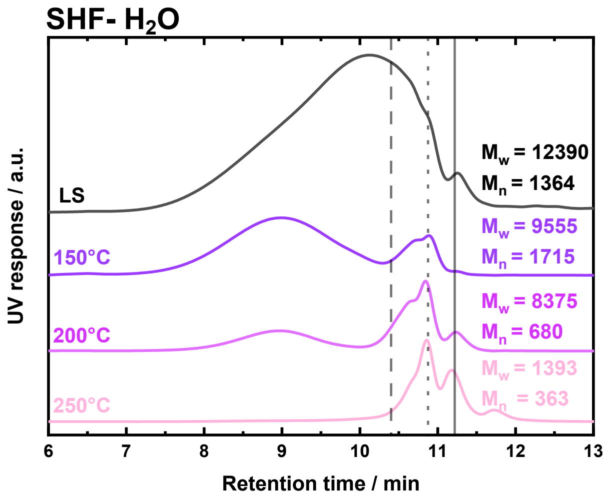


Figure S19. SEC elugram of SHF of LS using H_2O as a solvent. Reaction conditions: c_{LS} = 1.0 wt.-%, T =150°C, 200°C, and 250° C, p = 7.0 MPa, Q_{educt} = 1.0 $cm^3\ min^{-1}$, Q_{H_2} = 20 $cm^3\ min^{-1}$, $m_{35Ni/NDC}$ = 10 g , $t_{residence}$ = 50 min, and weight hour space velocity (WHSV) = 0.17 $g_{LS}\ h^{-1}\ g_{Ni}^{-1}$. The straight line indicates the eluents buffer reference peak ($NaHPO_3$), dotted and dashed lines show the analytical standard peaks, i.e., sodium polystyrene sulfonate, with M_w of 246 g mol^{-1} (RT = 10.9 min) and with M_w of 891 g mol^{-1} (RT= 10.4 min), respectively.

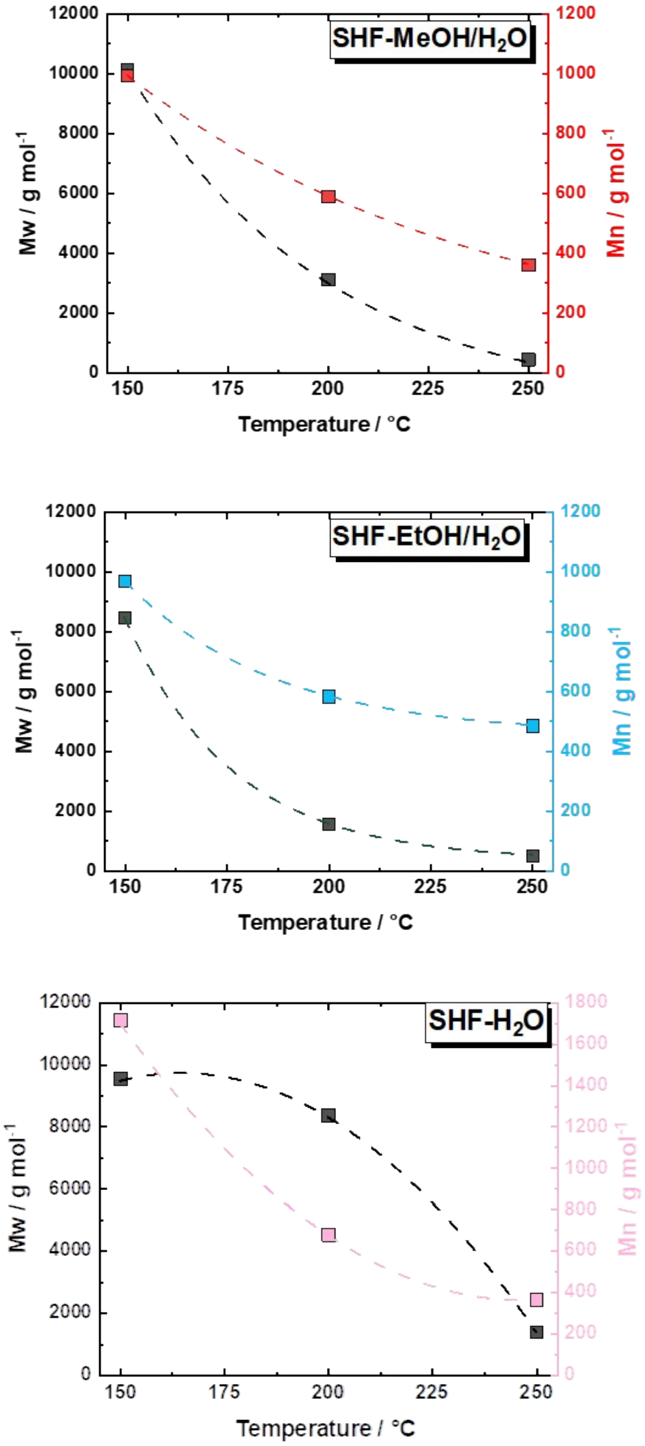


Figure S20. Mass-average (M_w) and number-average (M_n) molar mass for LS solvothermal assisted catalytic hydrogenolysis/hydrogenation (SHF) using MeOH/H_2O (up), EtOH/H_2O (center), and H_2O (down) as a solvent mixture, reported as a function of reaction temperature. Reaction conditions: c_{LS} = 1.0 wt.-%, T =150°C, 200°C, and 250° C, p = 7.0 MPa, Q_{educt} = 1.0 cm^3 min^{-1},Q_{H_2} = 20 cm^3 min^{-1}, $m_{35Ni/NDC}$ = 10 g, $t_{residence}$ = 50 min, and weight hour space velocity (WHSV) = 0.17 g_{LS} h^{-1} g_{Ni}^{-1}.

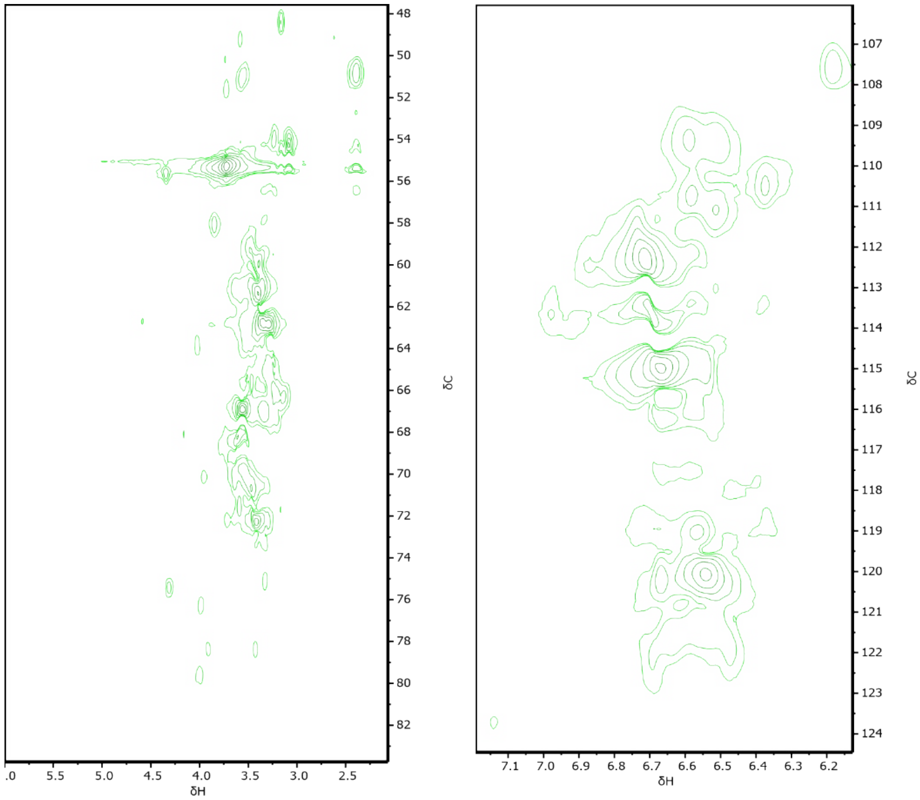


Figure S21. 2DHSQC NMR spectra of SHF-MeOH/H$_2$O. Reaction conditions: c_{LS} = 1.0 wt.-%, T = 250° C, p = 7.0 MPa, Q_{educt} = 1.0 cm^3 min^{-1},Q_{H_2} = 20 cm^3 min^{-1}, $m_{35Ni/NDC}$ = 10 g, $t_{residence}$ = 60 min, and weight hour space velocity (WHSV) = 0.17 g_{LS} h^{-1} $g_{Ni}$$^{-1}$.

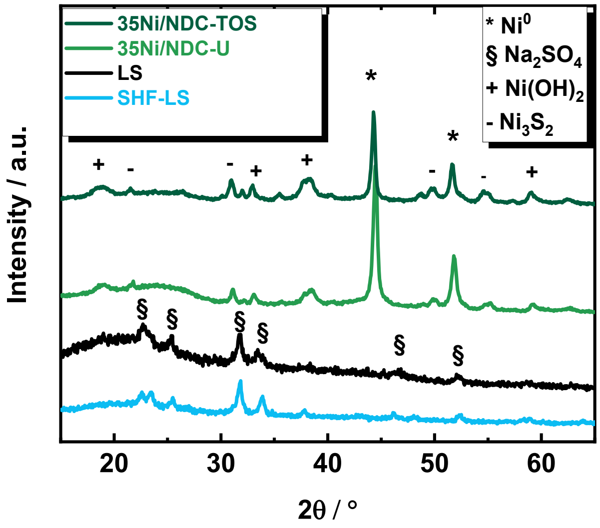
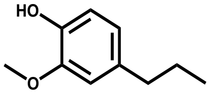
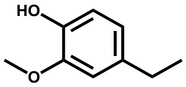
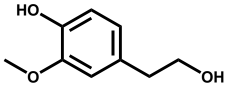
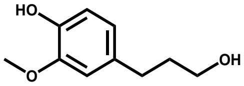
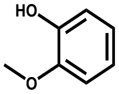
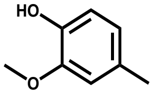
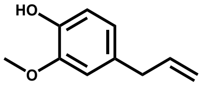
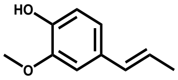
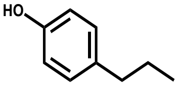
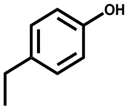
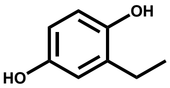
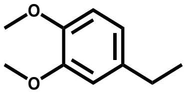
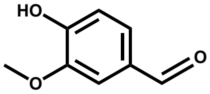
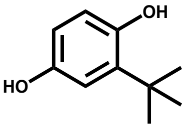
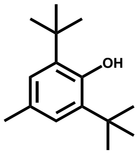
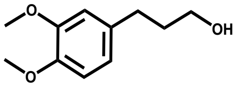
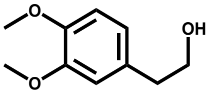
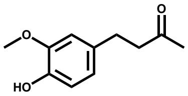
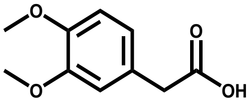


Figure S22. XRD reflection patterns of the spent catalyst after 1 h (35Ni/NDC-U), after 9 h of time on stream (35Ni/NDC-TOS), of the LS compared to the freeze-dried sample after SHF experiment (SHF-LS).

Table S5. Identified and quantified compounds via GC-FID and GC-MS of the SHF-LS fragmentation experiments.

GC-MS RT/ Min	**GC-FID RT/ Min**	**Structure**	**Name**	**Abbreviation**	**Quantified**
11.653	14.70		4-Propyl guaiacol	**G1**	**Yes**
10.428	13.548		4-Ethyl guaiacol	**G2**	**Yes**
13.735	16.802		Homovanillyl alcohol	**G3**	**Yes**
15.098	18.137		Dihydroconiferyl alcohol	**G4**	**Yes**
7.632	10.810		Guaiacol	**G5**	**Yes**
9.158	12.330		Creosol	**G6**	**Yes**
12.730	15.961		Eugenol	**G7**	**No**
12.123	15.456		Isoeugenol	**G8**	**No**
10.058	13.134		4-Propyl phenol	**H1**	**Yes**
8.742	-		Phenol 4-ethyl	-	**No**
8.961	-		Ethyl *p*-hydroxybenzoate	-	**No**
11.542	-		Benzene, 4-ethyl-1,2-diemthoxy	-	**No**
12.079	-		Vanillin	-	**No**

13.306	-		t-Butylhydroquinone	**-**	**No**
13.645	-		BHT – MeTHF stabilizer	**-**	**No**
13.988	-		Benzene, 4 butyl alcohol-1,2-dimethoxy	**-**	**No**
14.389	-		3,4-Dimethoxyphenyl alcohol	**-**	**No**
14.753	-		Butanone,4-(4-hydroxy-3-ethoxyphenyl)-	**-**	**No**
16.061	-		Benzeneacetic acid, 3,4 dimethoxy	**-**	**No**

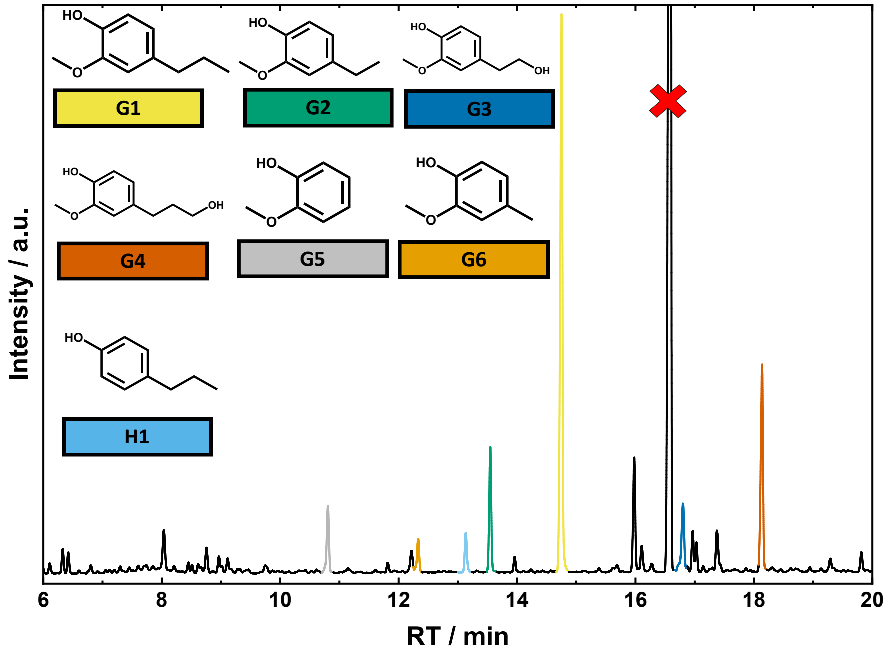


Figure S23. GC-FID Chromatogram of the MeTHF fraction extracted from the SHF-MeOH/H_2O. The red cross of the peak at 16.8 corresponds to the BHT stabilizer of MeTHF. Reaction conditions: c_{LS} = 1.0 wt.-%, T = 250° C, p = 7.0 MPa, Q_{educt} = 1.0 cm^3 min^{-1},Q_{H_2} = 20 cm^3 min^{-1}, $m_{35Ni/NDC}$ = 10 g and $t_{residence}$ = 50 min, weight hour space velocity (WHSV) = 0.17 g_{LS} h^{-1} g_{Ni}^{-1}.

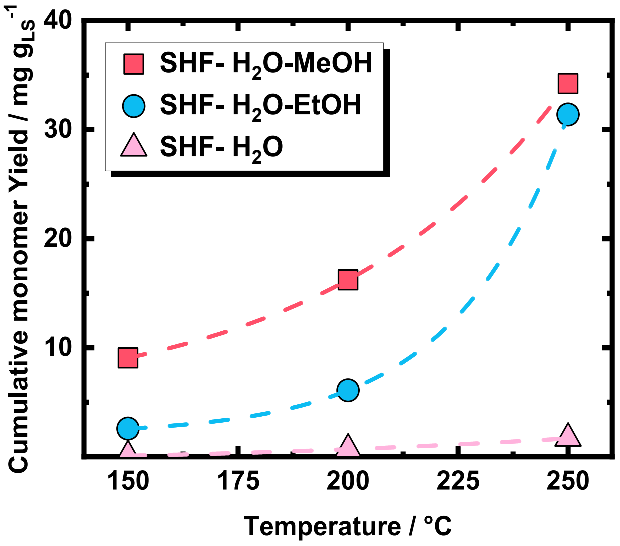


Figure S24. Cumulative monomer yield for the SHF-MeOH/H_2O, SHF-EtOH/H_2O, and SHF-H_2O as function of temperature. Reaction conditions: c_{LS} = 1.0 wt.-%, T = 150°C, 200°C and 250° C, p = 7.0 MPa, Q_{educt} = 1.0 cm^3 min^{-1},Q_{H_2} = 20 cm^3 min^{-1}, $m_{35Ni/NDC}$ = 10 g, $t_{residence}$ = 50 min, and weight hour space velocity (WHSV) = 0.17 g_{LS} h^{-1} g_{Ni}^{-1}.

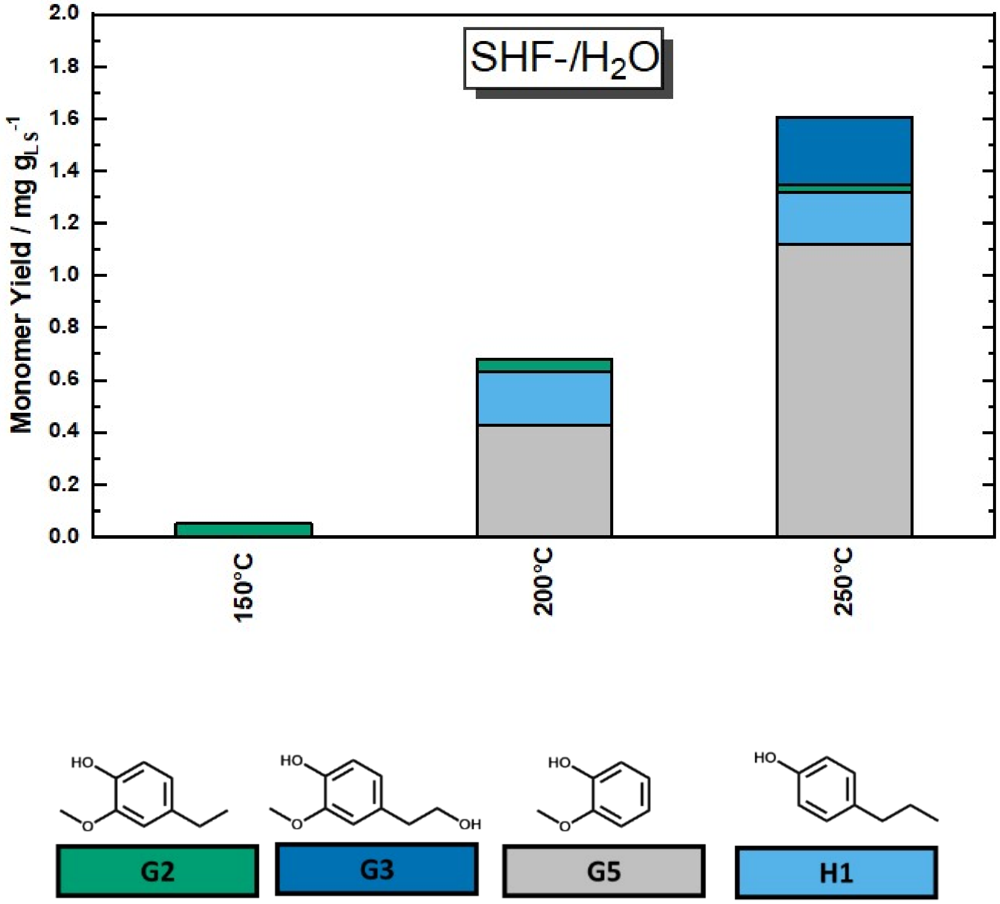


Figure S25. Monomers yield derived from the SHF-H_2O in continuous flow system as a function of reaction temperature; Reaction conditions: c_{LS} = 2.5 wt.-%, T = 150°C, 200°C, and 250° C, p = 7.0 MPa, Q_{educt} = 1.0 cm^3 min^{-1},Q_{H2} = 20 cm^3 min^{-1}, $m_{35Ni/NDC}$ = 10 g, $t_{residence}$ = 50 min, and weight hour space velocity (WHSV) = 0.17 g_{LS} h^{-1} g_{Ni}^{-1} .

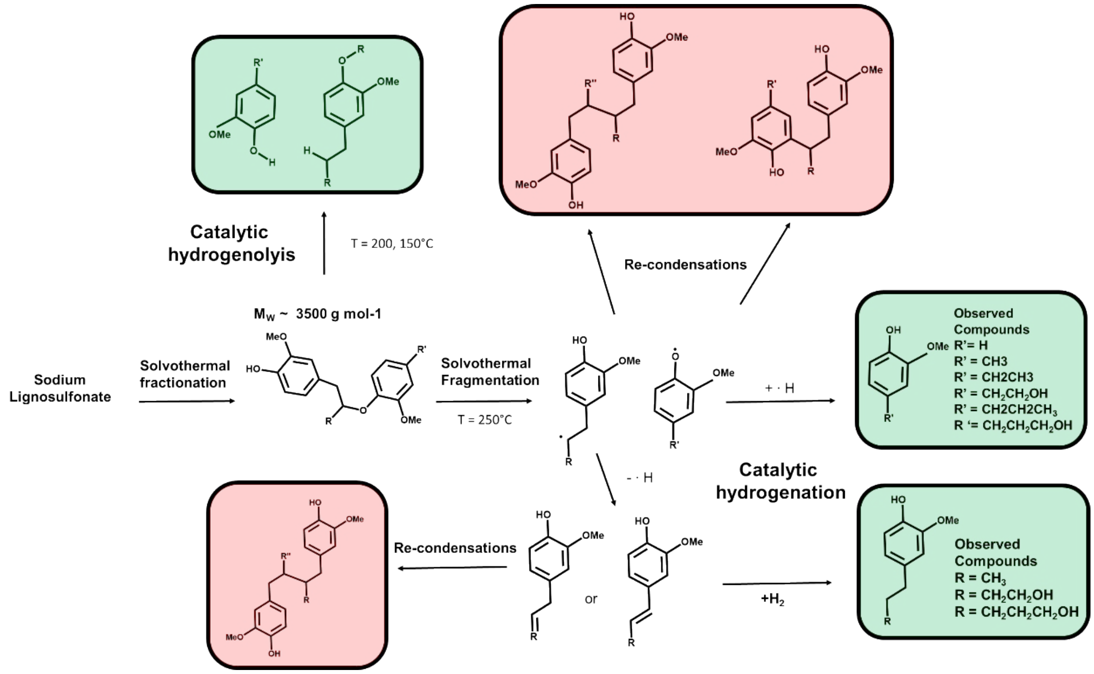


Figure S26. Proposed depolymerization pathway for the SHF experiments using 35Ni/NDC as catalyst. At lower temperature (150°C and 200°C) the fragmentation occurs mostly through hydrogenolysis, while at 250°C bonds are cleaved mostly solvothermal.

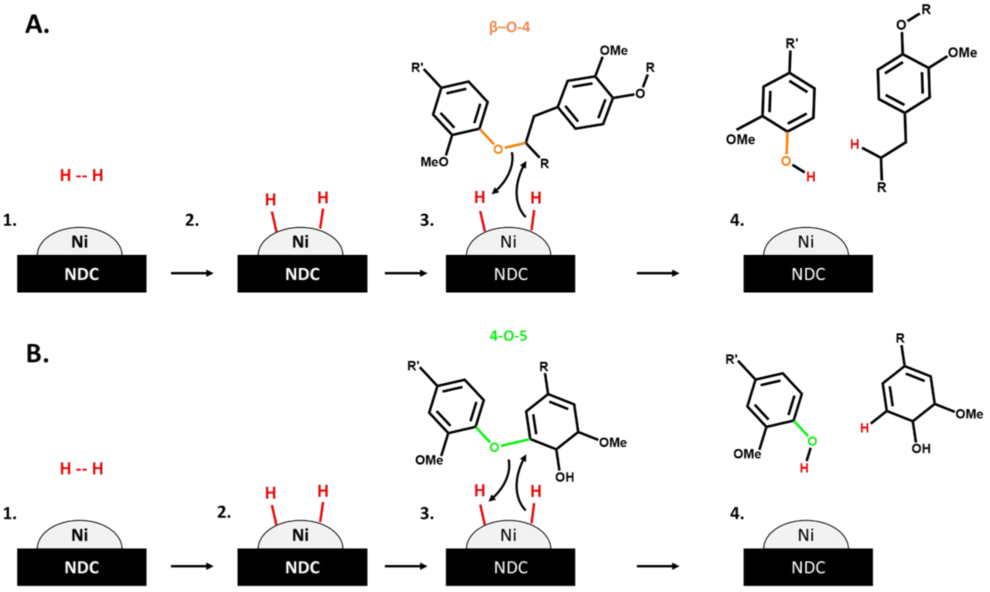


Figure S27. Proposed hydrogenolysis mechanism of **A)** β-O-4 and **B**) 4-O-5 ethers linkages over 35Ni/NDC. Mechanism: **1.** H_2 diffusion through the pores, **2.** H_2 dissociative adsorption on Ni surface, **3.** Molecules adsorption and protonation, **4.** Products desorption.

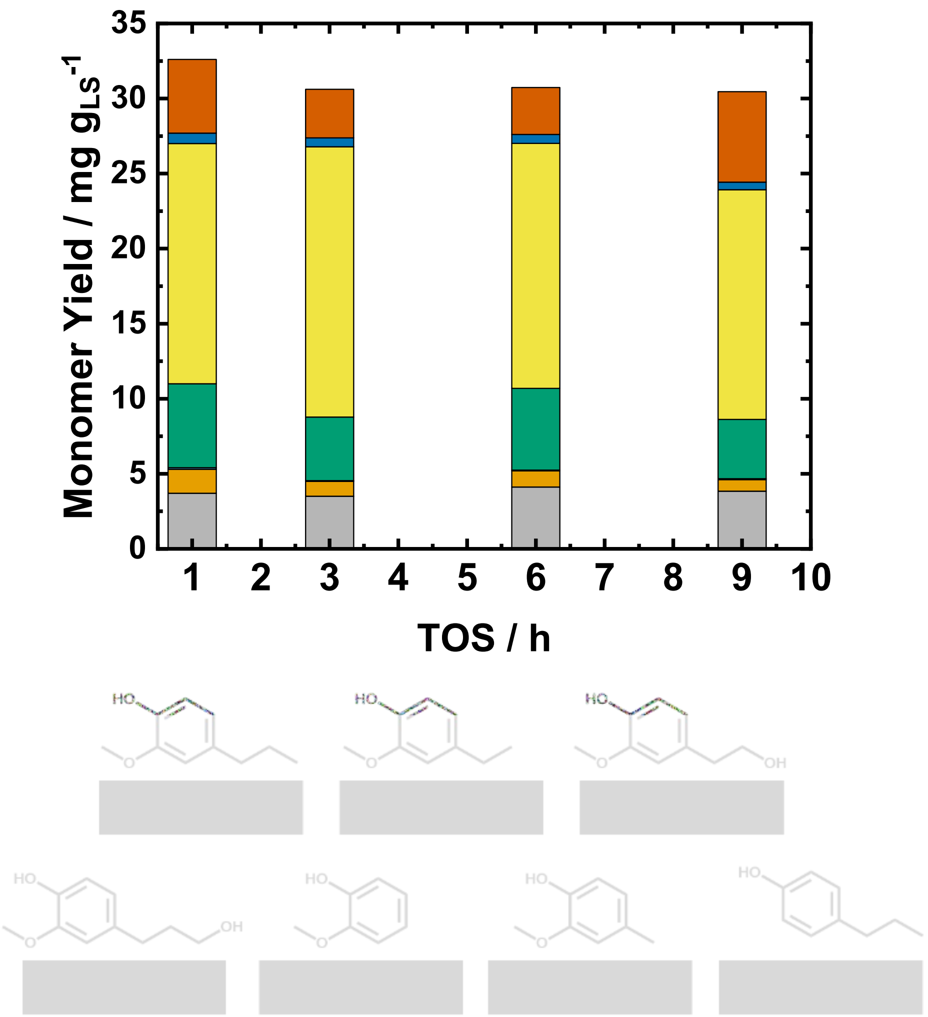


Figure S28. Monomers yield derived from the SHF-MeOH/H2O in continuous flow system as a function of time on stream (TOS); Reaction conditions: c_{LS} = 2.5 wt.-%, T = 250° C, p = 7.0 MPa, Q_{educt} = 1.0 cm^3 min^{-1},Q_{H2} = 20 cm^3 min^{-1}, $m_{35Ni/NDC}$ = 10 g, $t_{residence}$ = 50 min, and weight hour space velocity (WHSV) = 0.43 g_{LS} h^{-1} g_{Ni}^{-1} .

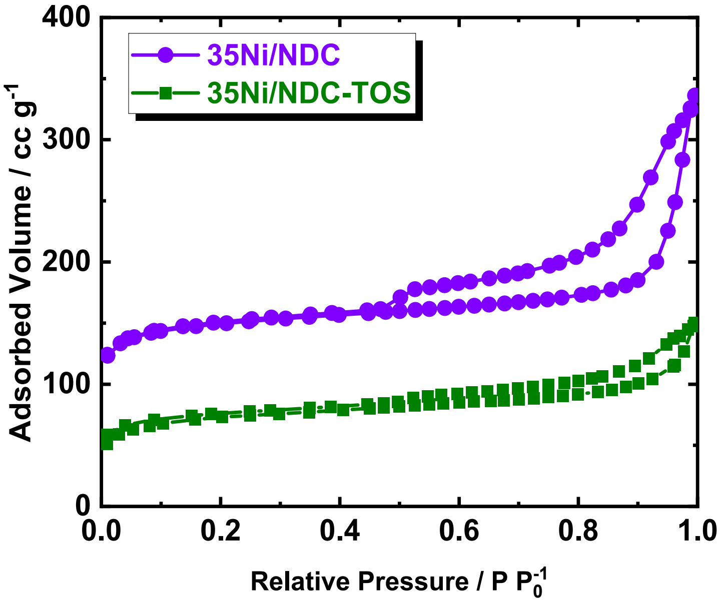


Figure S29. N_2 physisorption isotherms at 77 K of the fresh 35 Ni/NDC and after 9 h of time on stream (35Ni/NDC-TOS.)

S7. References

1. F. Brandi, M. Bäumel, V. Molinari, I. Shekova, I. Lauermann, T. Heil, M. Antonietti and M. Al-Naji, *Green Chem*, 2020, **22**, 2755-2766.
2. M. Al-Naji, J. A. Mendoza Mesa, F. Brandi, I. Shekova and M. Antonietti, *Green Chem*, 2020, DOI: 10.1039/d0gc01517b.
3. F. Brandi, M. Bäumel, I. Shekova, V. Molinari and M. Al-Naji, *Sustain. Chem.*, 2020, **1**, 106-115.
4. F. Brandi, I. Khalil, M. Antonietti and M. Al-Naji, *Acs Sustain. Chem. Eng.*, 2020, DOI: 10.1021/acssuschemeng.0c08167.
5. C. Mei, C. Hu, Q. Hu, C. Sun, L. Li, X. Liang, Y. Dong and X. Gu, *Catalysts*, 2020, **10**.
6. V. Hemmilä, R. Hosseinpourpia, S. Adamopoulos and A. Eceiza, *Waste and Biomass Valorization*, 2019, **11**, 5835-5845.
7. W. Chen, X.-w. Peng, L.-x. Zhong, Y. Li and R.-c. Sun, *Acs Sustain. Chem. Eng.*, 2015, **3**, 1366-1373.
8. P. Cui, H.-X. Fang, C. Qian and M.-H. Cheng, *Chromatographia*, 2019, **83**, 87-93.
9. R. Shu, Y. Xu, L. Ma, Q. Zhang, T. Wang, P. Chen and Q. Wu, *RSC Adv.*, 2016, **6**, 88788-88796.