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Supporting Information

β-Zeolite-Assisted Lignin-First Fractionation in a Flow-Through Reactor**

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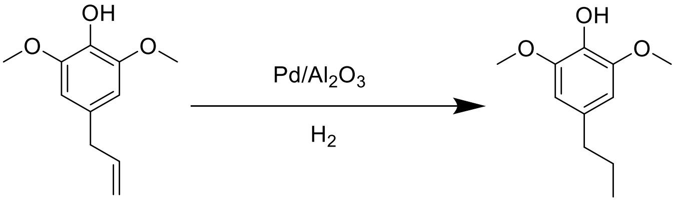
1. Table of contents

2. Materials

Monomer compounds were purchased from Sigma Aldrich all with purity ≥95% : 4-(propan-2-yl)phenol, 4-ethyl-2-methoxyphenol, 4-methyl-2-methoxyphenol 4-allyl-2-methoxyphenol, 4-hydroxy-3,5-dimethoxybenzaldehyde, 4-(3-hydroxypropyl)-2,6-dimethoxyphenol, 2-methoxy-4-[prop-2-enyl]phenol, 1-(4-hydroxy-3-methoxyphenyl)ethanone. Guaiacylglycerol-β-guaiacyl Ether ≥95% was purchased from TCI chemicals. Absolute HPLC grade ≥99% ethanol and ethyl acetate respectively were purchased from Biosolve. Hydrogen beta zeolite was purchased from Alfa Aesar with Si/Al = 320. Silicon carbide 300 mesh and Pd/Al_2O_3 5 wt.% was purchased from Sigma Aldrich. Birch (Betula) and Spruce (Picea) wood were locally grown in Eindhoven, Nederlands and harvested in 2018. Walnuts (Junglans regia) were purchased from www.allnuts.nl.

As schemed below, 2,6-Dimethoxy-4-propylphenol was synthesized from commercially available 2-methoxy-4-[prop-2-en-1-yl] phenol by hydrogenation with Pd/Al_2O_3 5 wt.% in a 200 mL stirred reactor with EtOH: H_2O 9:1 v/v. The initial concentration of reactant was 1g/L and 1 gram of catalyst was added. Room temperature hydrogen pressure was 10 bars. The reaction was carried out at 150°C for a total duration of 3 hours.



3. Experimental set-up

Solvent was supplied through a 500 mL ISCO pump (details). Liquid outlet is initially collected in a 5 mL volume vessel, which in case of overflow leads to a second larger 500 mL liquid collection vessel. The setup is pressurized with nitrogen through a backpressure regulator. Tubular reactors of 1 cm ID x 10 cm length are connected through a threaded middle joint piece and porous metal gaskets as shown in Figure S- 2

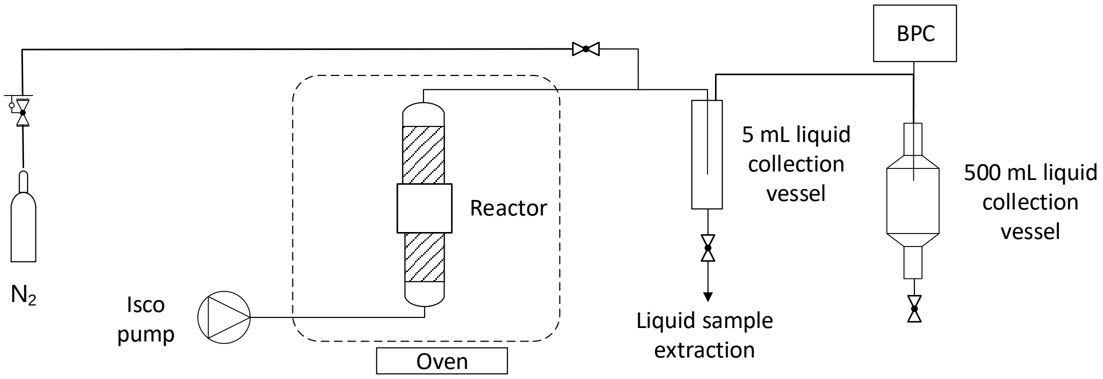


Figure S- 1: Experimental setup scheme

Figure S- 2: Dissassembled flow-through reactors and joint piece

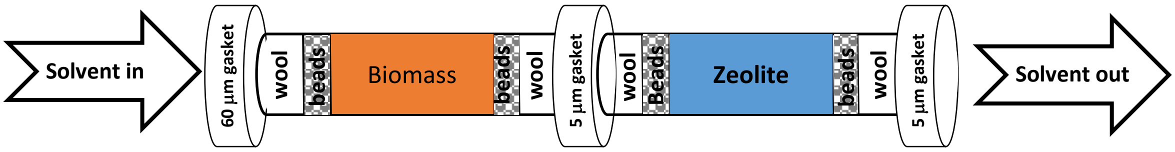


Figure S- 3: Scheme of reactor packing.

Each reactor was packed with 1 gram of quartz wool and 1 gram of 2 mm glass beads according to the confguration showed in Figure S- 3. Wool and beads ensure that the bed remains static during the experiment and allow for easy and circa loss-free recovery of used biomass and zeolite. The reactor has a total empty volume of 8.4 cm^3. The void volume for the packed reactor was measured by filling with water and ultrasound during 1 hour to ensure full liquid penetration in the wood/zeolite and subsequent weighing. For a loading of 1 g of biomass, the void volume is 4.6 cm^3 and for a loading of 2 g of zeolite, the void volume is 3.5 cm^3.

Figure S- 4: a) Assembled reactor in the oven. b) Sample taking section of the setup

4. Calculation of bubble point pressure

In order to keep the solvent in liquid phase during the operation, bubble point pressure for 9:1 v/v EtOH/H_2O mixture in 150 – 250°C is determined through simulations in Aspen plus software. As provided in Figure S- 5, ethanol and water are introduced to the system with flexible volume input in ambient conditions. The resulting mixture at 25°C – 1bar is fed to a heat exchanger, which is programmed to set its pressure to the corresponding bubble point pressure for given temperature.

Regarding the chemical properties, the base method is selected as non-random two liquid model combined with Redlich-Kwong equation of state (NRTL-RK).

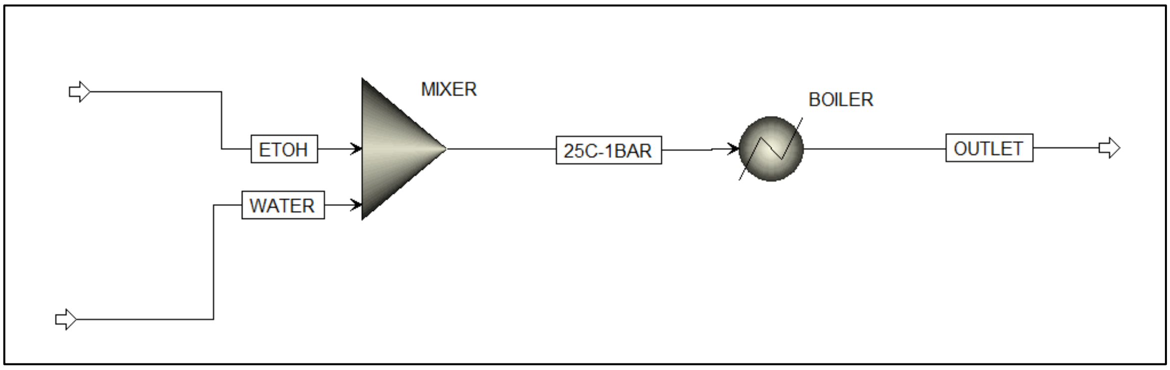


Figure S- 5: Aspen simulation diagram for bubble point pressure calculations

The resulting bubble point pressure in the temperature range of 150 – 250°C is given in Figure below. Since the current experimental setup is operable with a highest pressure of 51 bar, the maximum temperature throughout the experiments is set as 220°C.

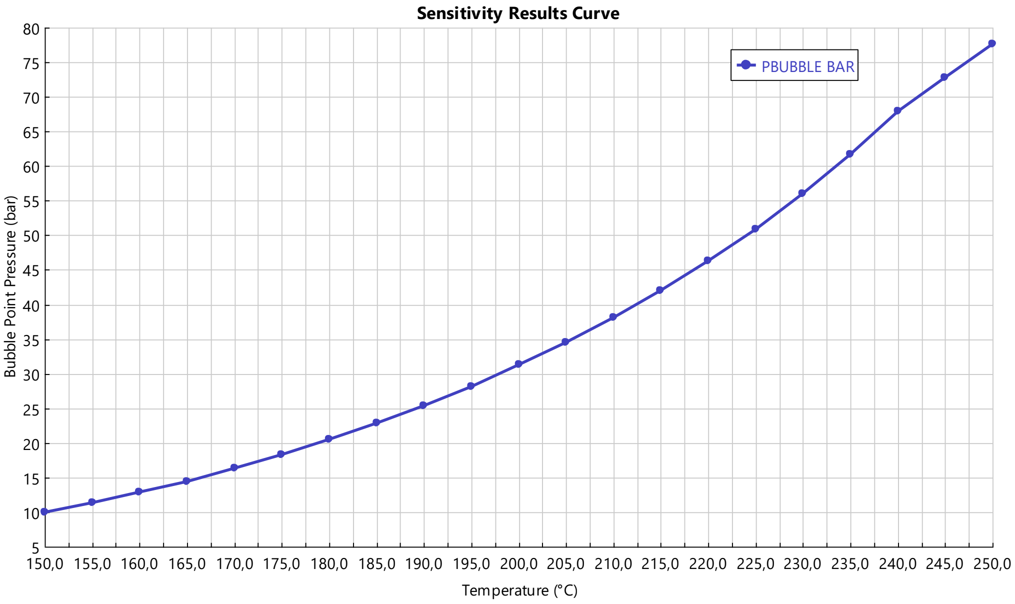


Figure S- 6: Bubble point pressure of 9:1 v/v EtOH/H2O solvent with respect to temperature

5. Experimental procedure

5.1. Preparation of biomass

Branches of lignocellusic biomass were drilled using a Bosch GSB 13 RE professional drill and a 16 mm wood drill bit, as show in Figure below. The resulting coarse sawdust was further milled using a planetary ball mill using 5-20 mm zirconia balls at 300 rpm during 10 minutes. The resulting fine sawdust was sieved to a particle size range of 50-150 µm, which has proved to be a particle size small enough to prevent diffusional mass transfer limitations[1] . Biomass sawdust was dried and pre-extracted using a Toluene/EtOH 2:1 v/v mixture in a Soxhlet for 6 hours. All experiments were carried out using dry and pre-extracted biomass.

Figure S- 7: Drilling lignocellulose branches to obtain coarse wood sawdust

5.2. Preparation of zeolite

Commercial β-zeolite is available as a fine powder which can't be used as such in the flow-through system due to loss of solids cause by the solvent flow. Therefore zeolite was pelletized at a pressure of 5 tons for a duration of 5 minutes. Pelletized zeolites were milled in a mortar and sieved to the desired particle size between 40 and 150 μm. Subsequently, the zeolite was thermally activated at 550ºC for 5 hours.

Figure S- 8: Pelletized beta zeolite

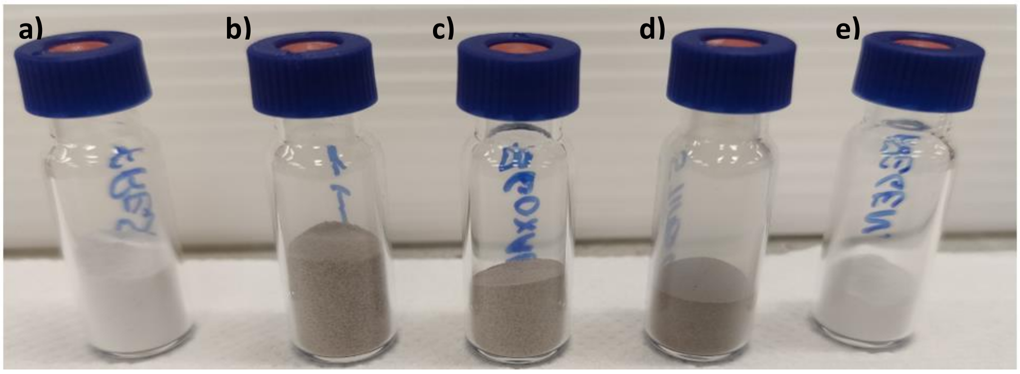


Figure S- 9: Pictures of zeolite samples otained at different conditions: a) Fresh zeolite after calcination. b) Used zeolite after one experiment at 220ºC without acid. c) Used zeolite after one experiment at 220ºC with 3g/L of oxalic acid. d) Used zeolite after five recycle experiments at 220ºC without acid. e) Thermally regenerated zeolite after five recycle experiments at 220ºC without acid

5.3. Flow-through reaction procredure

First, is important to degas the pump in order to ensure results consistency. The packed reactors are connected to the system and placed in the oven. The system is pressurized with nitrogen until 10 bars and vented three times in order to remove all oxygen.Subsequently, the system is heated until temperature setpoint, measured with an additional thermocouple inside the oven in order to ensure isothermal operation. Afterwards, the liquid flow rate is started. 5 mL liquid samples are collected at 10 minute intervals during the first hour of time on stream. During the final two hours of the experiment, liquid samples are collected every 20 minutes. Once the total time on stream of 180 minutes is reached, the oven is switched off and the liquid flowrate is stopped. The pressure drop across the system was monitored by comparing the pressure measurements of the pump and the back pressure controller. All experiments were carried out with a pressure drop of 0.7 bars. After reaction completion, the oven was switched off and the flowrate was stopped. The reactors were emptied and the contained biomass and zeolite are dried overnight at 110ºC.

5.4. Liquid sample work-up

Liquid samples were processed according to the scheme shown in Figure S- 10. For NMR, GPC and GC-MS analysis, samples were liquid-liquid extracted first in order to remove all sugar derived products. For this, samples were dried under 100 mbar and 40ºC in rotavap and were extracted with 10 mL of ethyl acetate and 10 mL of water three times. It was observed that after beta-zeolite assisted processing, the resulting ligning is more easily soluble in ethyl acetate and provides a better behavior during the extraction, being also less prone for undesirable emulsions.

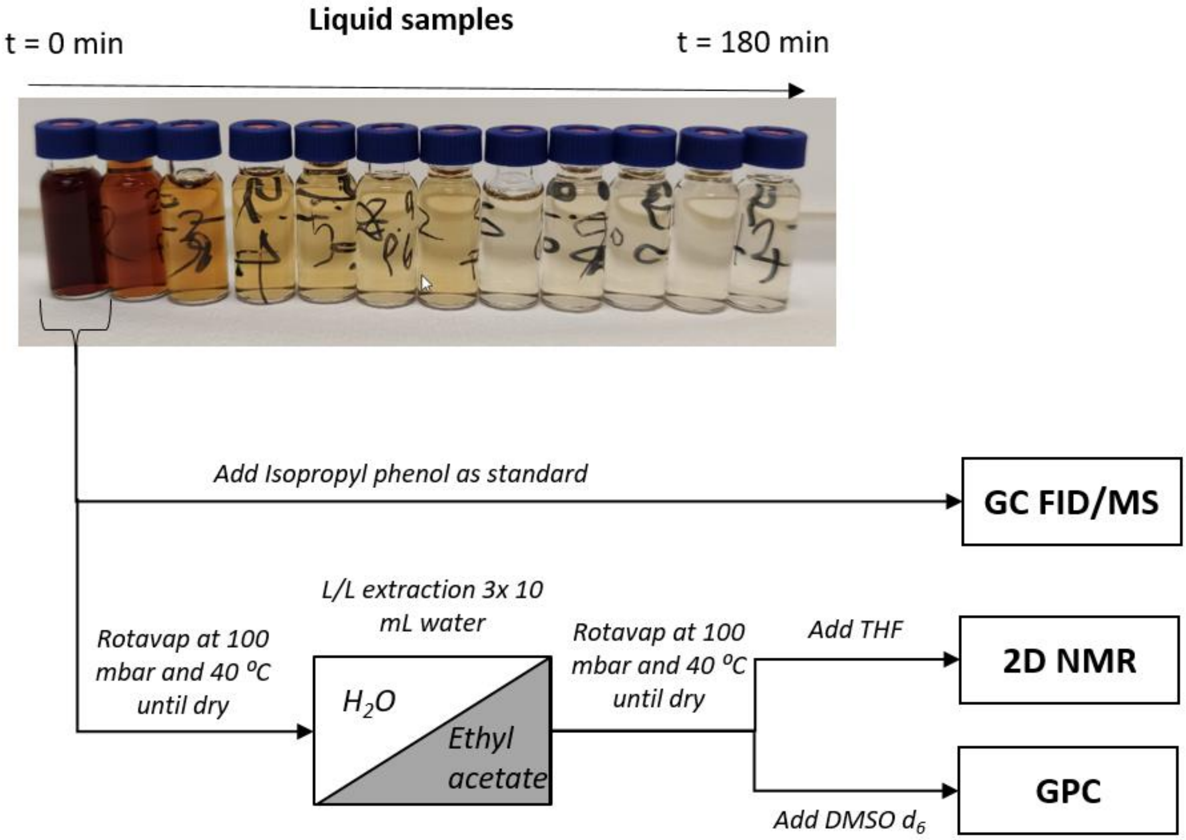


Figure S- 10: Scheme of liquid sample work-up

Figure S- 11: Liquid/liquid extraction of delignification liquor with (left) and without (right) beta-zeolite assisted fractionation

6. GC-MS

Sample preparation involves liquid-liquid extraction of the untreated sample with ethyl acetate and water, as shown in Figure S- 11. The organic phase was isolated and processed under 50 mbar and 40ºC until dryness. The resulting lignin oil was resolubilized in acetone and analyzed by GC-MS

A Shimadzu QP2020 GC-MS was used with a SH-Rxi-1ms capillary column. The analysis method consisted of an initial oven temperature of 50ºC kept for 1 minute. Temperature was increased at 15ºC/min until 300ºC where it was kept for a duration of 7.5 minutes, hence the total analysis duration was 25 minutes. Injection temperature was 250ºC and detector temperature was 200ºC. Peak characterization was carried out using the available compound library in the Shimadzu software and are well in line with prior work from literature [2].

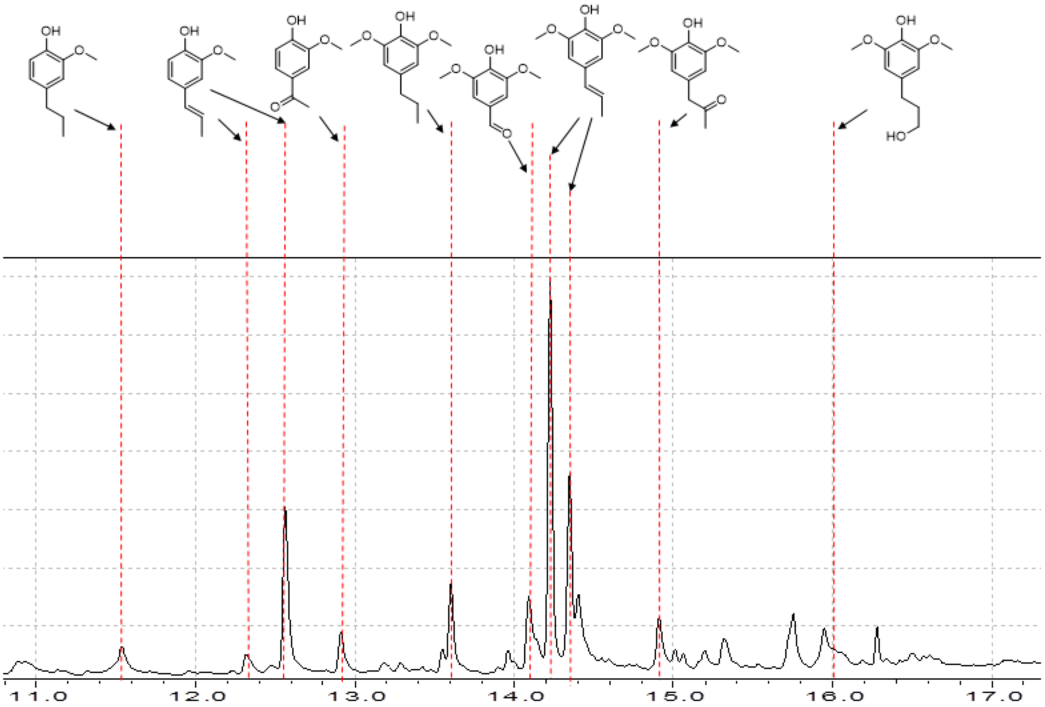
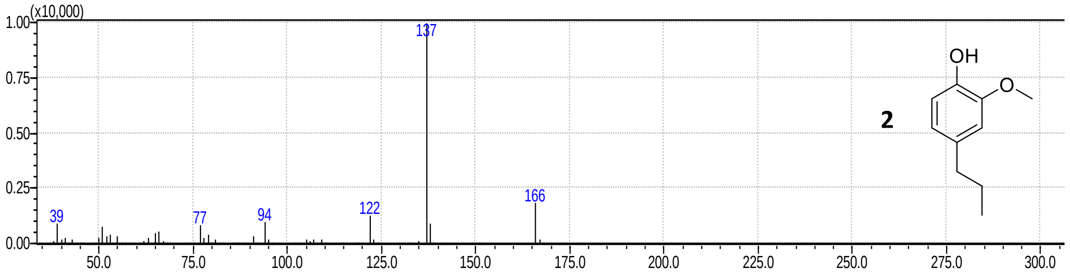


Figure S- 12: GC-MS chromatogram of birch wood lignin obtained at 220ºC with 1 gram of biomass and 2 g of β-zeolite



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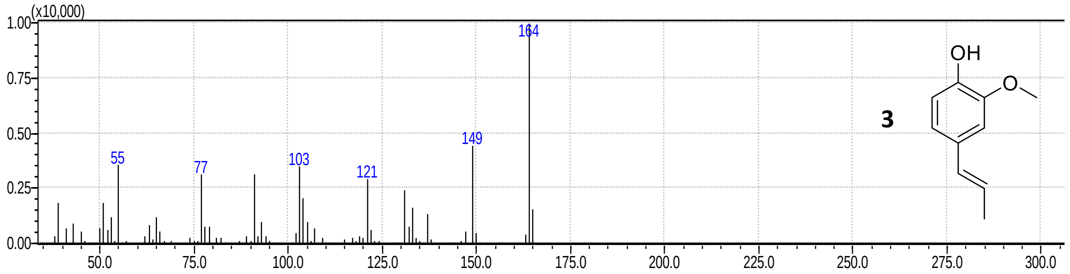

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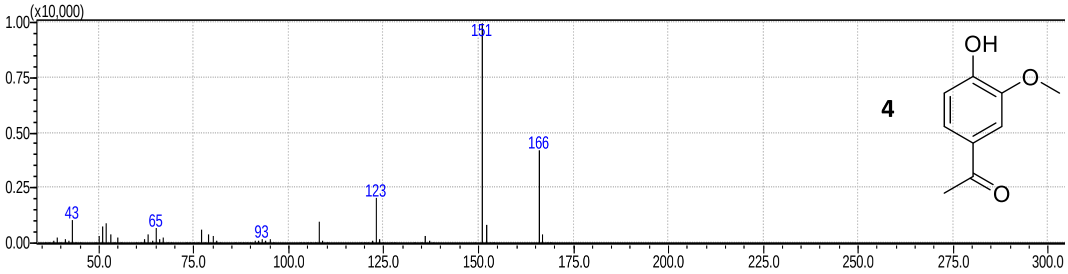

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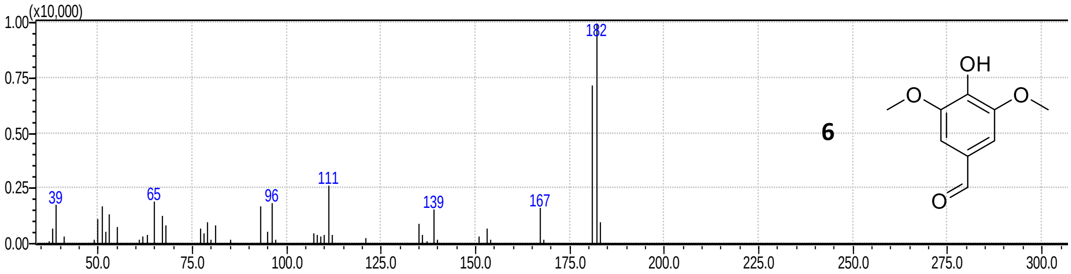

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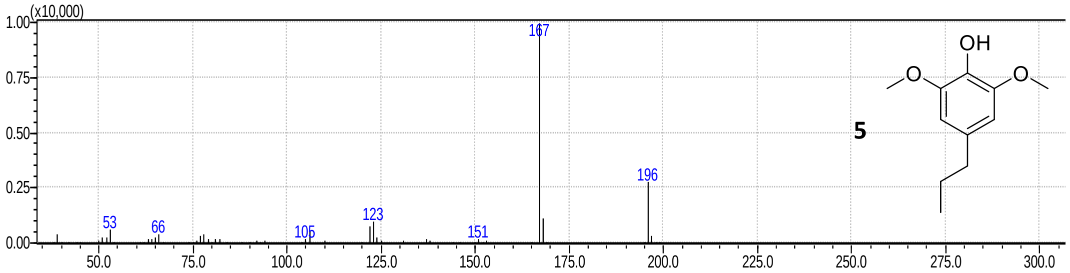

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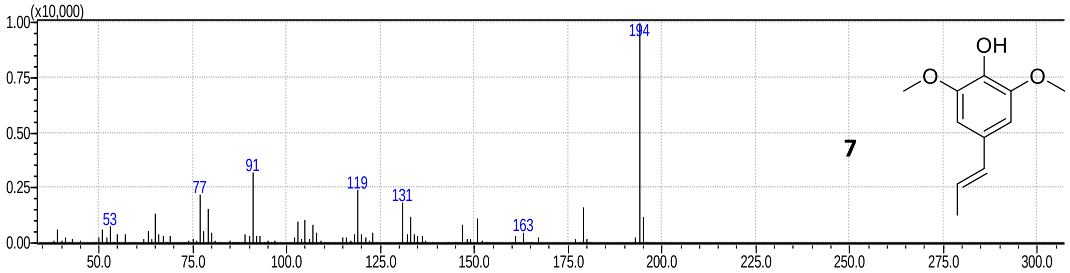

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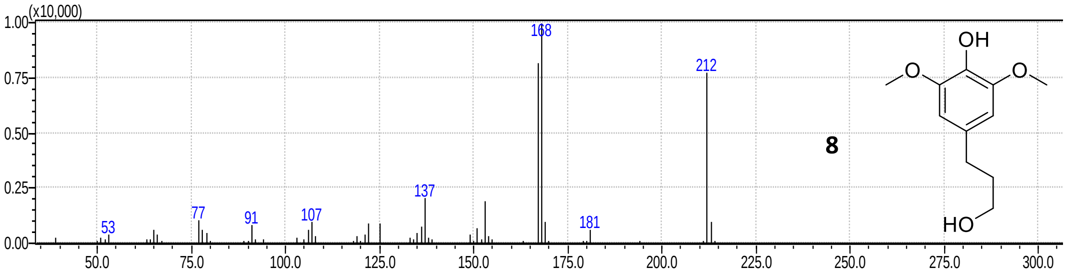

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7. GC-FID

2 mL aliquots of untreated liquid reaction samples were collected from the reactor. 1.5 mL of 5 g/L isopropyl phenol solution in EtOH: H_2O 9:1 v/v was added. The resulting mixture was filtered through an 0.45 μm teflon syringe filter.

Analysis was performed in a Varian CP-3800 gas chromatographer equiped with a CP-SIl-5 CB 30m capillary column and a flame ionization detector. The analysis method consisted of an initial oven temperature of 50ºC kept for 1 minute. Temperature was increased at 15ºC/min until 300ºC where it was kept for a duration of 12.33 minutes, hence the total analysis duration was 30 minutes. Injection temperature was 250ºC and detector temperature was 290ºC. Monomer yield was calculated for each sample according to effective carbon number principle in agreement with available protocols [3] and using the equations shown below. Main reaction products were identified by injection of available commercial standards. 2,6-Dimethoxy-4-propylphenol is one of the majoritary products and is not commercially available, hence the peak assignation was performed according to the GC-MS sequence, as shown in Figure S- 13.

$$n_{isopropyl\ phenol} = \frac{m_{isopropyl\ phenol\ in\ sample}}{MW_{isopropyl\ phenol}}$$

$$n_{monomer} = \frac{A_{monomer\ in\ sample}}{A_{decane\ in\ sample}} \times n_{isopropyl\ phenol} \times \frac{ECN_{isopropyl\ phenol}}{ECN_{monomer}}$$

$$m_{monomer} = n_{monomer} \times MW_{monomer}$$

$$Monomer\ yield\ (wt.\%) = \frac{m_{monomer}}{m_{initial\ lignin\ in\ biomass}} \times 100$$

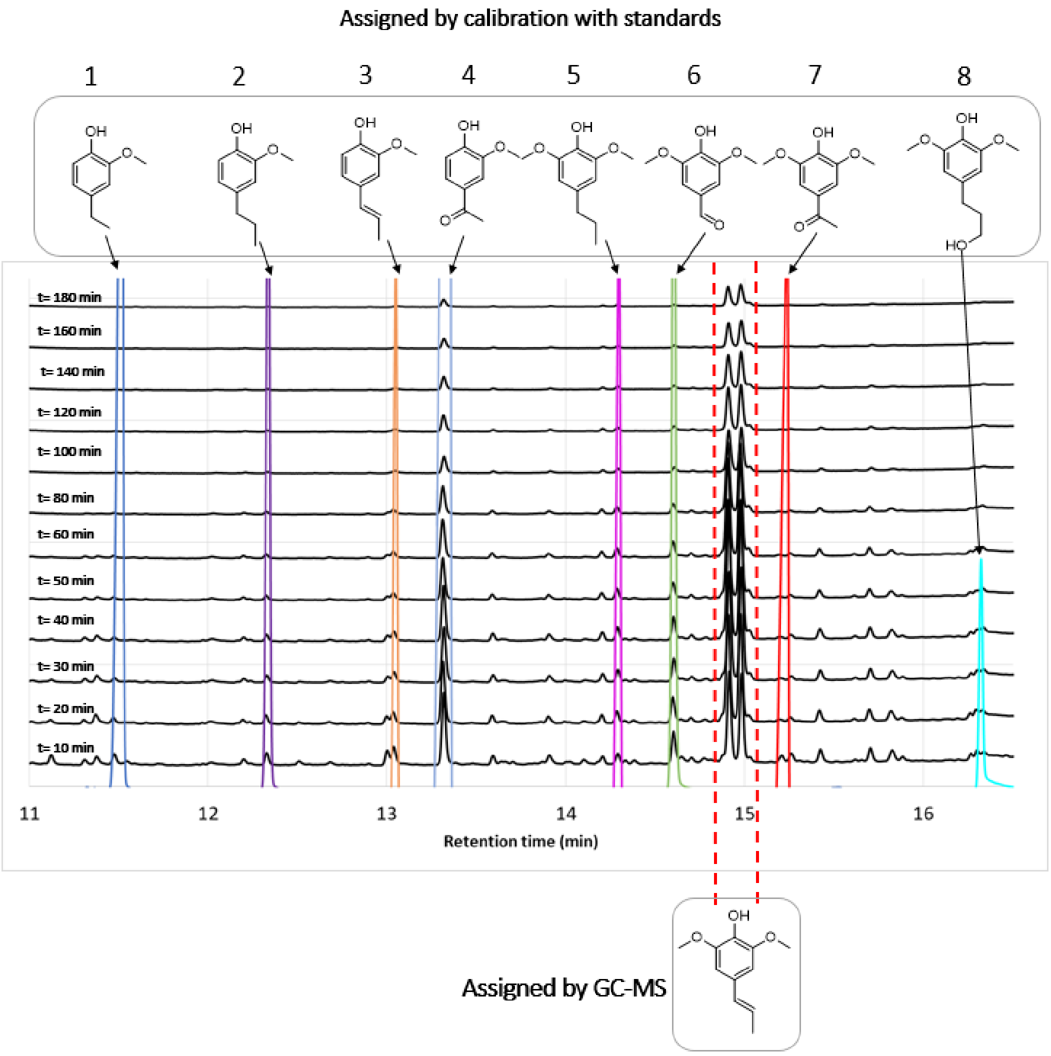

Figure S- 13: GC-FID of a complete set of 12 reaction samples. Overlaid are the chromatograms of pure aromatic monomer compounds.

8. 2D HSQC NMR

A solution of 45 mg of lignin in 0.6 mL of DMSO-d_6 were prepared and placed in the corresponding NMR tube. Samples were analyzed and in a Bruker 400 MHz spectrometer according to the standard program HSQC EDETGPSISP where a ^{1}H NMR sample of 32 scans with a relaxation delay of 2 seconds is coupled to a ^{13}C HSQC analysis of 16 scans and a relaxation delay of 2 seconds. The resulting spectra was analyzed using MestReNova. Assignment of peaks was carried out according to literature [4,5]

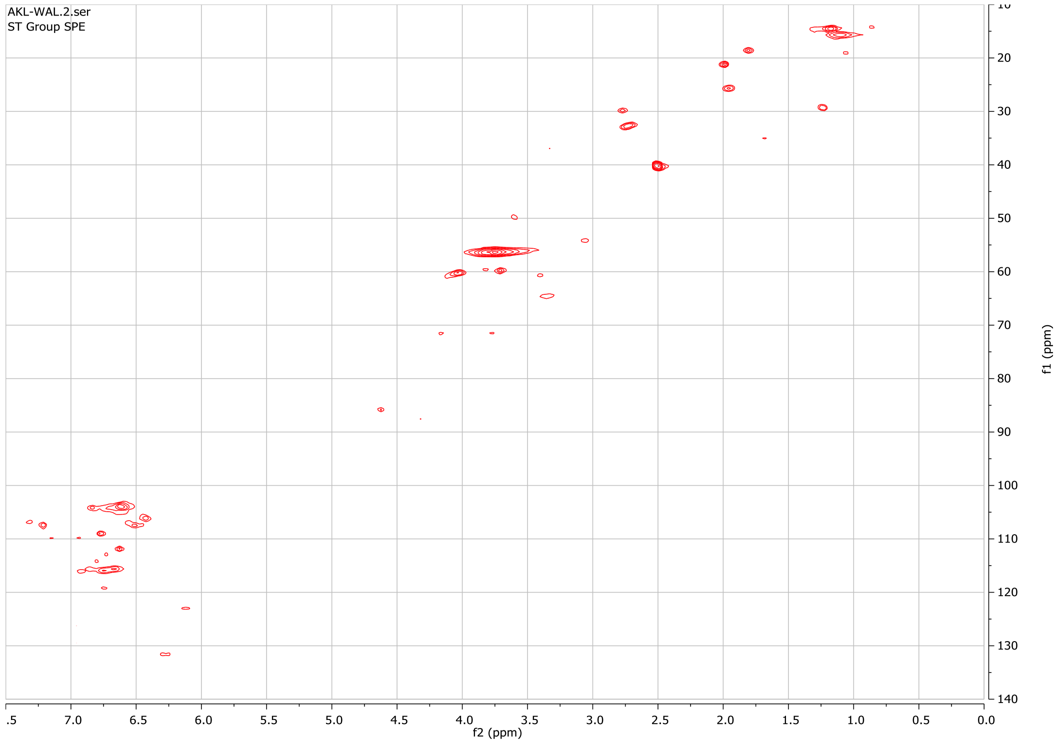

Figure S- 14: 2D HSQC NMR of walnut shell lignin

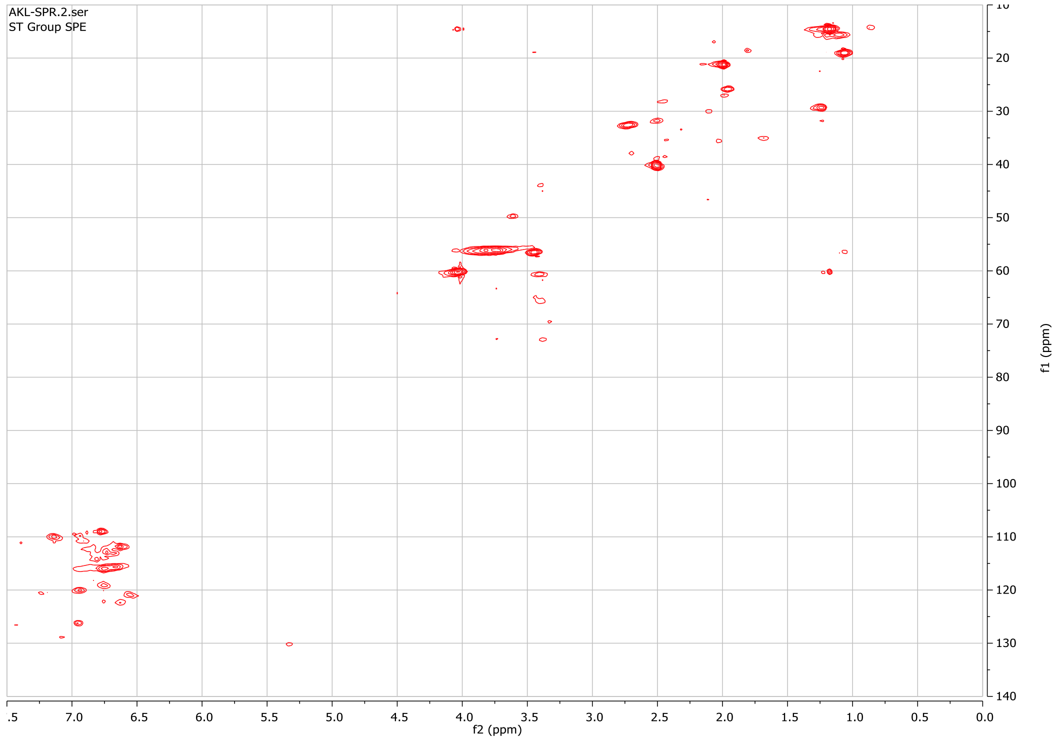

Figure S- 15: 2D HSQC NMR spectra of spruce lignin

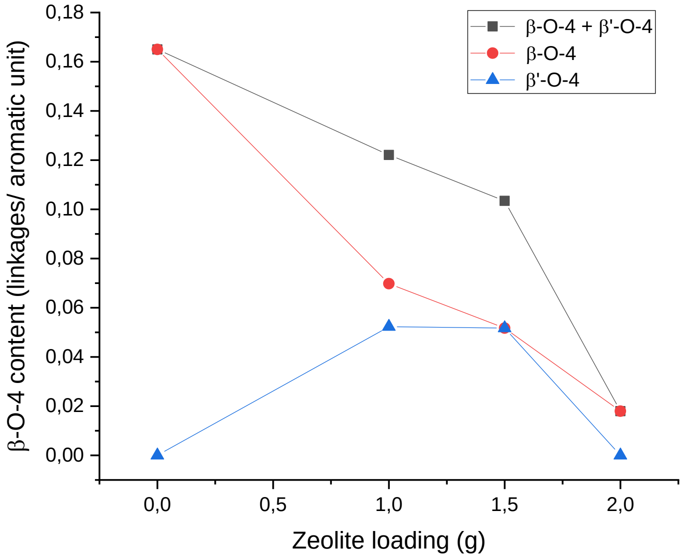

Figure S- 16: NMR-estimated amounts of ether bonds in lignins obtained at different zeolite loadings

9. Gel permeation chromatography (GPC)

The molecular weight of the isolated lignin was determined by gel permeation chromatography (GPC) analysis. The analysis was carried out on a Hewlett Packard 1100 series THF-GP. The lignin samples (10 mg) were dissolved in THF with toluene as a flow marker. Prior to analysis, the samples were filtered with a syringe filter (0.45 µm, PTFE). Analysis was performed with PSS WinGPC UniChrom.

Although the pressence of zeolite clearly leads to the production of low molar weight products, different acid concentration does not lead to a significantly different results.

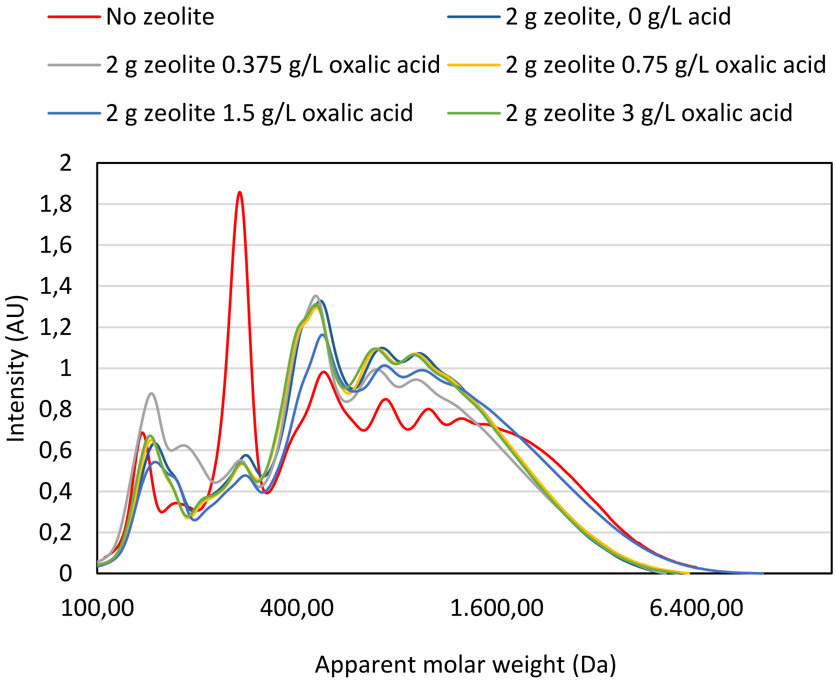

Figure S- 17: Lignin molar weight distributions obtained at different oxalic acid concentrations

10. Solid characterization

10.1. X ray diffraction (XRD)

X-Ray Diffraction is performed by a Rigaku MiniFlex 600. Using Cu Kα radiation, the detector angle 2θ is varied from 5° to 60°

10.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out in a Thermo Analysis TGA Q500. 10 mg of sample were heated from room temperature until a final temperature of 1000ºC at a rate of 10ºC/min. Weight loss at low temperatures significantly varies between the different analyzed samples, indicating different moisture contents. In order to provide conditions for a rigorous water-free comparison, the temperature program was changed. Samples were heated from room temperature until 110ºC at a rate of 10ºC/min and kept at constant temperature for one hour. Subsequently temperature was increased from 110ºC to 1000ºC at a rate of 10ºC/min.

10.3. N_2 physisorption

Approximately 100 mg of solid sample was weighed and prepared for analysis by heating at 150ºC under N_2 flow. N_2 physisorption was carried out in a Micromimetrics Tristar at 77K. BET area, pore volume and pore size distribution have been calculated with Micromimetrics software available at the device.

10.4. Ammonia temperature programmed desorption (NH_3-TPD)

Ammonia temperature programmed desorption was carried out in a Micromimetrics AutoChem II chemisorption analyzer. 100 mg of sample were heated to a temperature of 500ºC under a helium flow of 10 mL/min for one hour. Temperature was reduced to 100ºC under a helium flow of 10 mL/min for one hour. The sample was saturated under using a gas mixture of NH_3/He 5% under a flow of 10 mL/min for 2 hours. Temperature was increased until 700ºC at a rate of 20ºC/min. Amount of desorbed ammonia was determined by calibration with gas standards. Curve deconvolution was carried out in Origin 2019, as shown in Figure S- 18. A third peak with maxima at approximately 600ºC was observed. However, as reported previously [6], this peak is related to zeolite disproportionation and is not representative of the zeolite acidity.

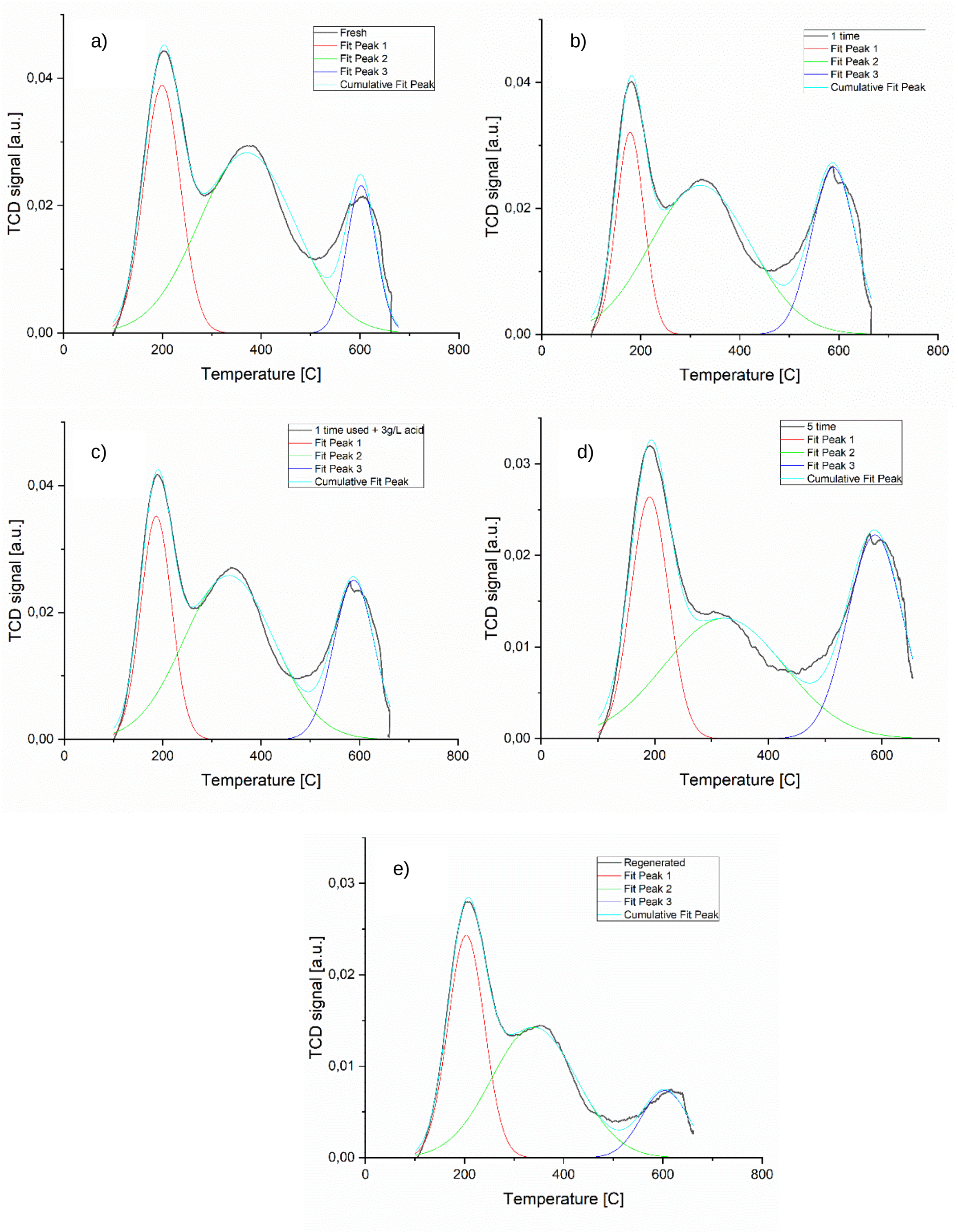

Figure S- 18: Deconvoluted NH3 TPD signals for each one of the samples a) Fresh zeolite after calcination. b) Used zeolite after one experiment at 220ºC without acid. c) Used zeolite after one experiment at 220ºC with 3g/L of oxalic acid. d) Used zeolite after five recycle experiments at 220ºC without acid. e) Thermally regenerated zeolite after five recycle experiments at 220ºC without acid

11. Reproducibility of the standard case and the effect of zeolite particle size

Experiments were carried out at standard conditions with 1 g of biomass loading in the first reactor and 2 g of zeolite in the second reactor at two different particle sizes. As shown in Figure S- 19, four experiments to check the reproducbility resulted in aromatic monomer yields in the range of 15.5 – 17.3 wt.%, resulting an average and standard deviation of 16.5 ± 0.9 wt.%. In addition to the consistency of overall yields, as also seen in Figure S- 19, distribution of aromatic products showed a consistent trend as well. Finally, as also provided in Figure S- 19, larger zeolite particle size resulted in a yield of 17.3 wt.% with similar product distribution, confirming the insignficance of mass transfer limitations in this range.

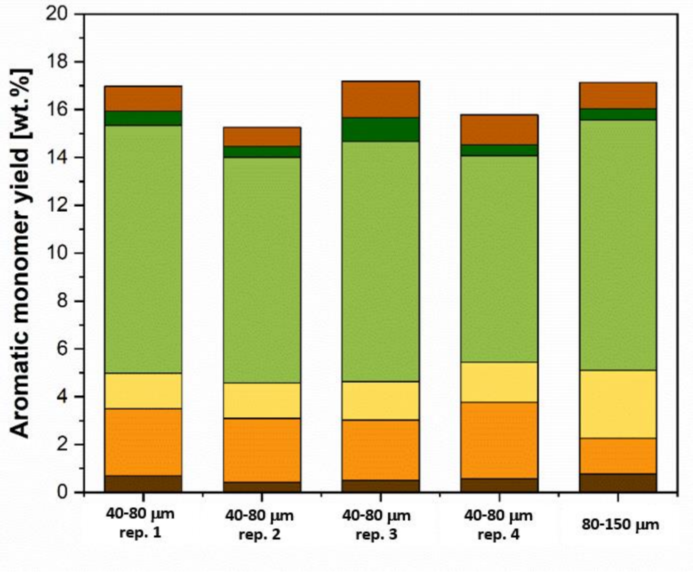

Figure S- 19: Monomer product distribution for reproducibility experiments carried out at differen zeolite particle size.

12. Different feedstocks composition

Table S- 1: Monomeric product distribution for different lignocellulosic feedstocks

	Birch	**Spruce**	**Walnut Shell**
Initial biomass (mg)	1000	1000	1000
Lignin content of initial biomass (mg)	216	280	315
Holocellulose content (mg)	674	604	511
Furfural produced (mg)	20	4	20
Ethyl levulinate produced (mg)	7	9	3
Monomeric lignin-based products (mg)	36	27	30
Yield$_1$ (mass monomers/initial lignin weight)	16.5%	9.8%	9.4%
Yield$_2$ (mass monomers/initial biomass weight)	3.1%	2.7%	3.0%
Yield$_3$ (mass sugar derived products/ initial mass holocellulose)	3.9%	2.2%	4.5%

13. Lignin oligomers size considerations

Beta zeolite has a tridirectional pore structure with two large distinct pore systems. One of the pore systems consists of straight 12-membered ring channels with a free aperture of 6.6 x 6.7 Å along the [1 0 0] axis. The second pore system consists of zig zagged 12-membered ring channels with dimensions of 5.6 x 5.6 Å along the [0 01] axis. Lignin fragments with more than two aromatic rings (dimers) are too large to fit in these small pores, hence we hypothesize that depolymerization takes place on the external surface of the zeolite and not inside the pores

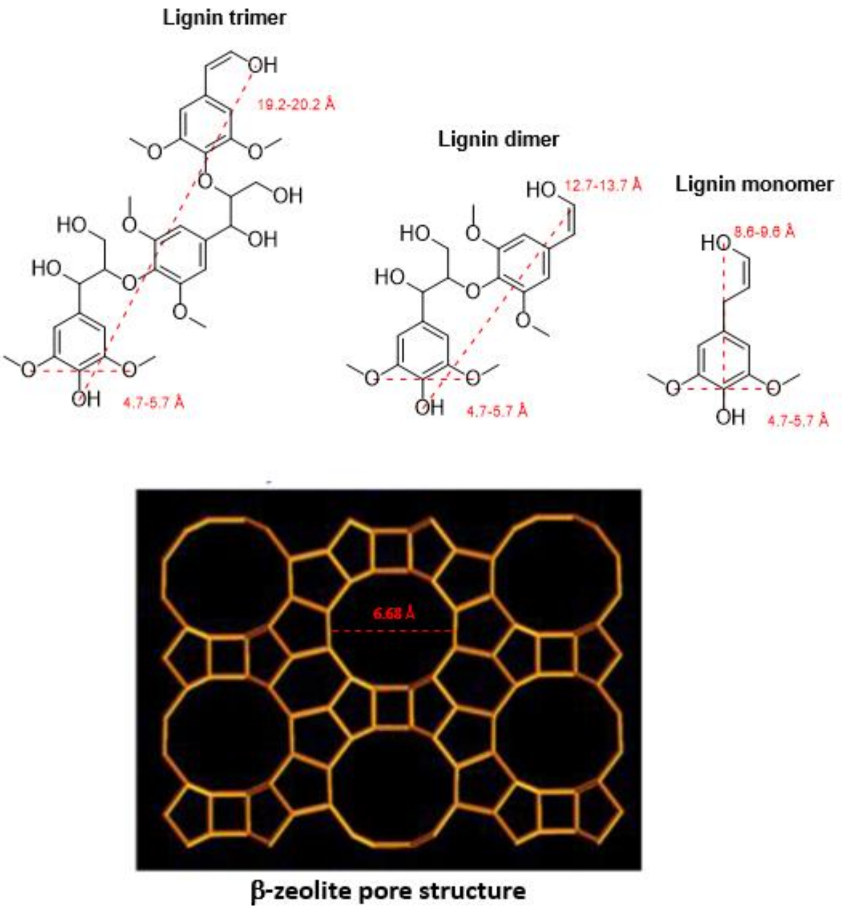

Figure S- 20: Estimation of characeristic dimensions of different lignin oligomers and comparison with β-zeolite pore size

14. Different reactor configurations

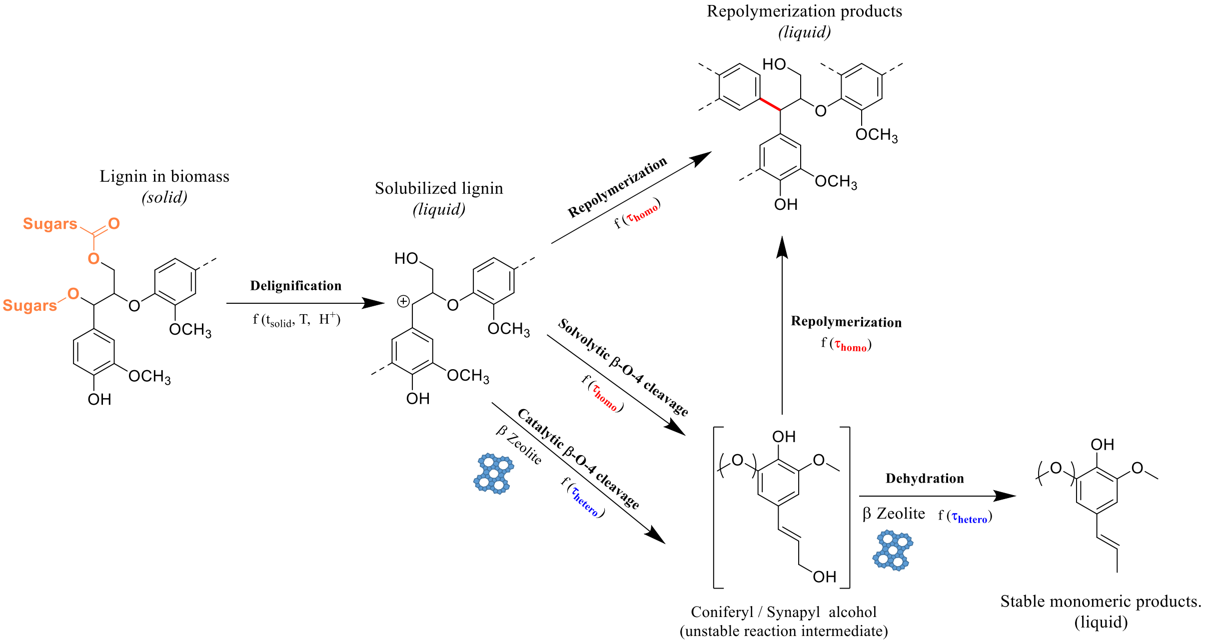

Figure S- 21: Simplified reaction mechanism with reactions described as a function of characteristic reaction times: t_{solid}, τ_{homo}, τ_{hetero}

Where:

$$\tau_{homo} = \frac{V_R \varepsilon_{void}}{Q_{v.l}}$$

$$\tau_{hetero} = \frac{W_{cat}}{Q_{v.l}}$$

Where:

τ_{homo} = Residence time for homogeneous reactions in liquid phase [min]

τ_{hetero} = Residence time for heterogeneous reactions catalyzed by zeolite [min]

W_{cat} = Weight of β–zeolite catalyst [g]

$Q_{v,l}$ = Volumetric flowrate of liquid in the reactor [mL/min]

ε_{void} = reactor voidage [m^3 void/ m^3 reactor]

15. Effect of acid addition without zeolite

In order to prove that β-zeolite has shape-selective properties and and not only acts as a source of acid sites, an experiment was carried out using exclusively an homogeneous acid in the absence of b-zeolite in the reaction medium. The concentration of acid sites in β-zeolite according to NH_3-TPD is approximately 200 mM/g. Zeolite equivalent acidity was calculated as the moles of acid sites divided by the void volume of the reactor. Hence an equivalent pH of 1.2 was calculated. Consequently an experiment using 1g of birch wood and a 0.1M Oxalic acid concentration in the solvent was performed in the flow-through reactor at 0.5 mL/min of liquid flowrate and a total duration of 3 hours at 220 °C.

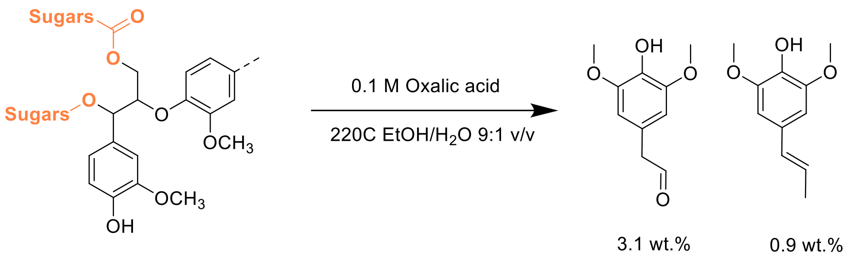

Figure S- 22: Reactants and products

16. Effect of solvent flowrate and biomass particle size on delignification rate

Effects of external and internal mass transfer for birch wood have been evaluated by performing delignification experiments with varying particle size and solvent flowrate. The delignification rate is expressed as $L_{Reactor}/L_0$, being L_0 the initial amount of lignin in the wood and $L_{Reactor}$ the amount of lignin remaining in the reactor, which is the sum of the lignin remaining in the wood and the lignin dissolved in the liquid inside the reactor at a a given reaction time ($L_{Reactor} = L_{wood}(t) + L_{liquid}(t)$). The experiments were carried out in the same flow-through reactor used in the present study at 200°C but with a different solvent mixture consisting of MeOH/H_2O 50/50% vol., which is known to be a more efficient solvent mixture in the delignification of lignocellulosic biomass than EtOH/H_2O 90/10% vol[7], hence providing a higher delignification rate. Consequently these findings regarding the effect of solvent flowrate and biomass particle size can be applied to the experiments carried out with EtOH/H_2O 90/10% vol.

As shown in Figure S23, an increase in solvent flowrate from 0.5 to 1 mL/min has no significant effect on delignification rate, indicating that there are no external mass transfer limitations for the studied liquid flowrate range. An increase in biomass particle size leads to a slower delignification for a particle size above 150 μm, which is in agreement with recent studies carried out in batch reactors[1]. Consequently, experiments carried out at F_L=0.5 mL/min and 150 μm>$dp_{,biomass}$>50 μm with EtOH/H_2O 90/10% vol. are free of internal and external mass transfer limitations, hence the system is operated within the kinetic delignification regime.

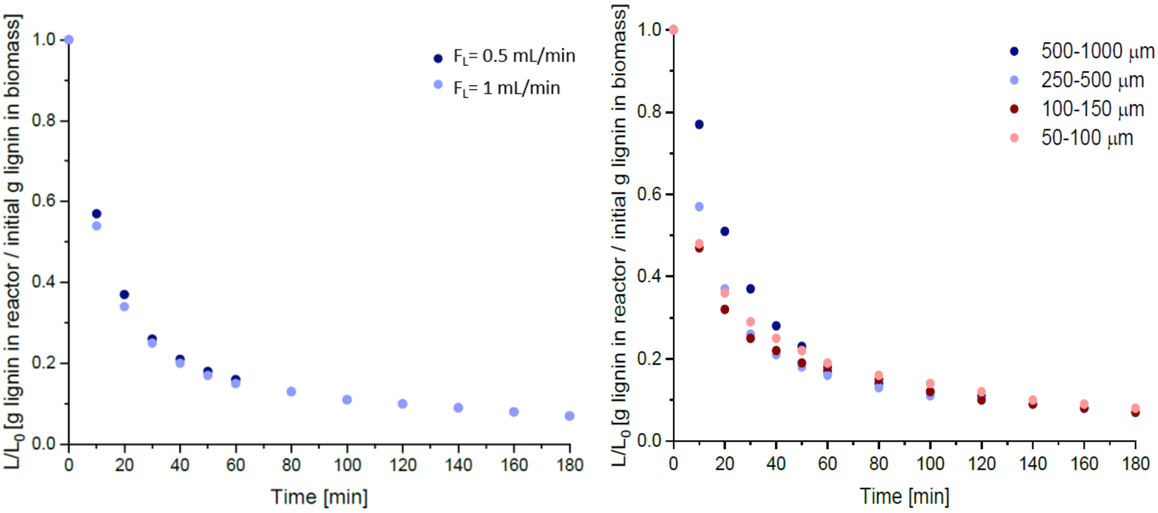

Figure S- 23: Left:Effect of liquid solvent flowrate on delignification rate of birch wood at d_p= 50-100μm. Right: Effect of particle size on delignification rate of birch wood at F_L=0.5 mL/min

17. Reaction experiment conditons

Table S- 2: Experimental conditions for the reported reaction experiments

Experiment No.	T (°C)	Flow Rate (ml/min)	Oxalic Acid (g/L)	Feedstock Type	Feedstock Mass (mg)	Zeolite Mass (mg)	Zeolite Size (μm)	Note
1	220	0.5	-	Birch	1000	0	-	
2	220	0.5	-	Birch	1000	2000	40-80	Reproducibility (1)
3	220	0.5	-	Birch	1000	2000	40-80	Reproducibility (2)
4	220	0.5	-	Birch	1000	2000	40-80	Reproducibility (3)
5	220	0.5	-	Birch	1000	2000	40-80	Reproducibility (4)
6	220	0.5	-	Birch	1000	2000	40-80	Recycled zeolite
7	220	0.5	-	Birch	1000	2000	40-80	Recycled zeolite
8	220	0.5	-	Birch	1000	2000	40-80	Recycled zeolite
9	220	0.5	-	Birch	1000	2000	40-80	Recycled zeolite
10	220	0.5	-	Birch	1000	1400	40-80	Re-calcined
11	220	0.5	-	Birch	1000	1400	40-80	
12	220	0.5	-	Birch	1000	1000	40-80	
13	220	0.5	-	Birch	1000	3000	40-80	
14	220	0.5	-	Birch	500	3000	40-80	
15	220	0.5	-	Birch	1000	2000	40-80	Configuration 2
16	220	0.25	-	Birch	500	1500	40-80	Configuration 4
17	220	0.25	-	Birch	500	1500	40-80	Configuration 3
18	220	0.5	-	Birch	1000	2000	80-150	
19	220	0.5	1.5	Birch	1000	2000	40-80	
20	220	0.5	0.75	Birch	1000	2000	40-80	
21	220	0.5	3	Birch	1000	2000	40-80	
22	220	0.5	0.375	Birch	1000	2000	40-80	
23	200	0.5	-	Birch	1000	2000	40-80	
24	190	0.5	-	Birch	1000	2000	40-80	
25	210	0.5	-	Birch	1000	2000	40-80	
26	210	0.5	-	Birch	1000	1000	40-80	
27	200	0.5	-	Birch	1000	1000	40-80	
28	190	0.5	-	Birch	1000	1000	40-80	
29	220	0.5	-	Spruce	1000	2000	40-80	
30	220	0.5	-	Walnut Shells	1000	2000	40-80	

18. Reaction experiment results

Table S- 3: Monomer yields for all reported experiments

Experiment No.	4-ethyl-2- methoxy phenol	4-allyl-2- methoxy phenol (Eugenol)	2-methoxy-4-(prop-1-en-1-yl)phenol (Isoeugenol)	1-(4-hydroxy-3-methoxyphenyl) ethanone	2,6-dimethoxy -4-propylphenol	4-hydroxy-3,5-dimethoxy benzaldehyde	2,6-dimethoxy-4-(prop-1-en-1-yl) phenol	4-(3-hydroxypropyl) -2,6-dimethoxy phenol	**Total Yield (wt.% lignin)**
1	0.0%	0.0%	0.1%	0.0%	0.1%	0.2%	1.4%	0.0%	**1.7%**
2	0.1%	0.1%	0.5%	3.2%	0.5%	1.7%	8.6%	1.2%	**15.9%**
3	0.2%	0.2%	0.5%	2.8%	0.6%	1.5%	10.4%	1.0%	**17.1%**
4	0.2%	0.0%	0.4%	2.7%	0.4%	1.5%	9.4%	0.8%	**15.4%**
5	0.1%	0.1%	0.4%	2.5%	1.0%	1.6%	10.0%	1.5%	**17.3%**
6	0.0%	0.3%	0.6%	2.9%	0.7%	1.6%	9.2%	1.1%	**16.3%**
7	0.0%	0.1%	0.6%	2.4%	0.2%	1.2%	9.0%	1.2%	**14.6%**
8	0.0%	0.0%	0.5%	2.6%	0.0%	1.3%	7.7%	1.0%	**13.2%**
9	0.0%	0.4%	0.5%	2.1%	0.1%	1.3%	6.6%	0.9%	**11.8%**
10	0.0%	0.2%	0.5%	2.3%	0.1%	1.1%	7.1%	1.0%	**12.3%**
11	0.0%	0.3%	0.6%	2.7%	0.2%	1.7%	8.6%	1.4%	**15.7%**
12	0.1%	0.1%	0.7%	2.9%	0.2%	0.9%	7.9%	0.1%	**12.9%**
13	0.2%	0.3%	0.5%	2.9%	1.0%	2.2%	11.2%	1.2%	**19.4%**
14	0.1%	0.1%	0.5%	2.9%	1.1%	1.8%	12.4%	1.3%	**20.5%**
15	0.1%	0.4%	0.5%	1.9%	0.2%	1.2%	4.2%	0.8%	**9.4%**
16	0.0%	0.1%	0.5%	2.3%	0.3%	2.0%	7.7%	1.2%	**14.1%**
17	0.0%	0.2%	0.4%	2.1%	0.5%	1.3%	9.7%	0.0%	**14.1%**
18	0.1%	0.2%	0.6%	2.8%	0.5%	1.5%	10.5%	1.1%	**17.3%**
19	0.1%	0.1%	0.8%	3.5%	1.6%	1.3%	10.6%	0.5%	**18.5%**
20	0.1%	0.2%	0.6%	3.0%	0.8%	2.0%	11.6%	1.8%	**20.1%**
21	0.1%	0.1%	0.5%	2.5%	0.8%	1.6%	10.0%	1.5%	**17.1%**
22	0.0%	0.1%	0.6%	2.6%	0.9%	2.0%	10.4%	1.7%	**18.3%**
23	0.0%	0.0%	0.4%	2.2%	0.0%	1.0%	7.0%	1.0%	**11.6%**
24	0.0%	0.0%	0.4%	1.8%	0.0%	1.2%	5.3%	1.2%	**9.8%**
25	0.0%	0.1%	0.6%	2.8%	0.5%	1.6%	10.4%	2.9%	**18.8%**
26	0.0%	0.1%	0.7%	1.9%	0.0%	1.6%	7.5%	0.5%	**12.4%**
27	0.0%	0.0%	0.5%	0.9%	0.0%	0.7%	2.7%	1.3%	**6.2%**
28	0.0%	0.0%	0.3%	0.7%	0.0%	0.1%	1.8%	0.4%	**3.4%**
29	0.8%	0.5%	1.3%	5.3%	0.3%	1.2%	0.5%	0.0%	**9.8%**
30	0.2%	0.0%	0.6%	2.6%	0.1%	1.1%	4.3%	0.4%	**9.4%**

19. Kinetic measurements

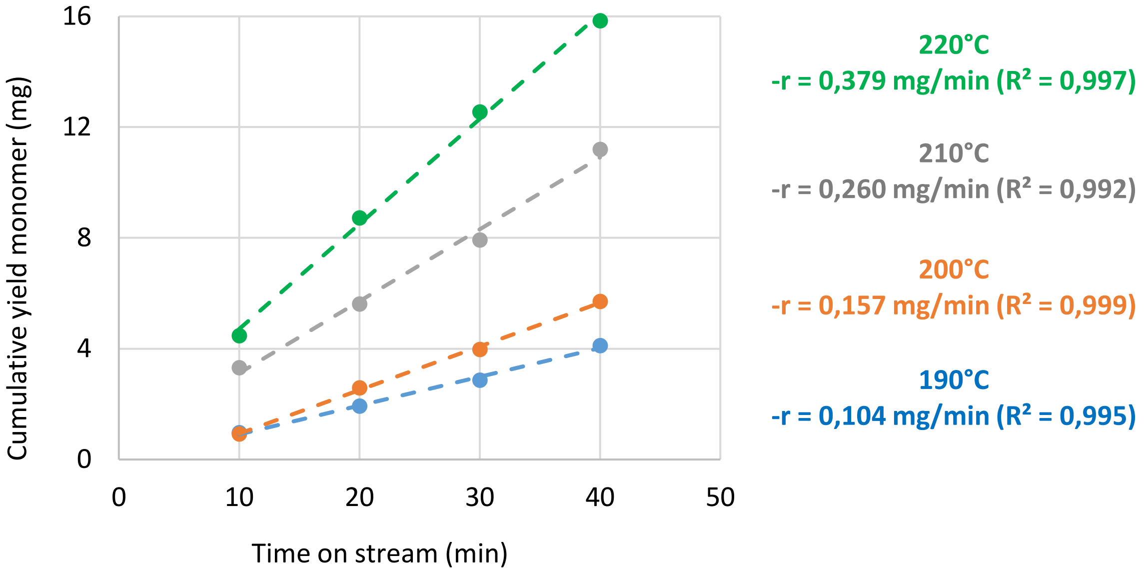

Figure S- 24: Period of constant monomer production rate for 2g β-zeolite loading

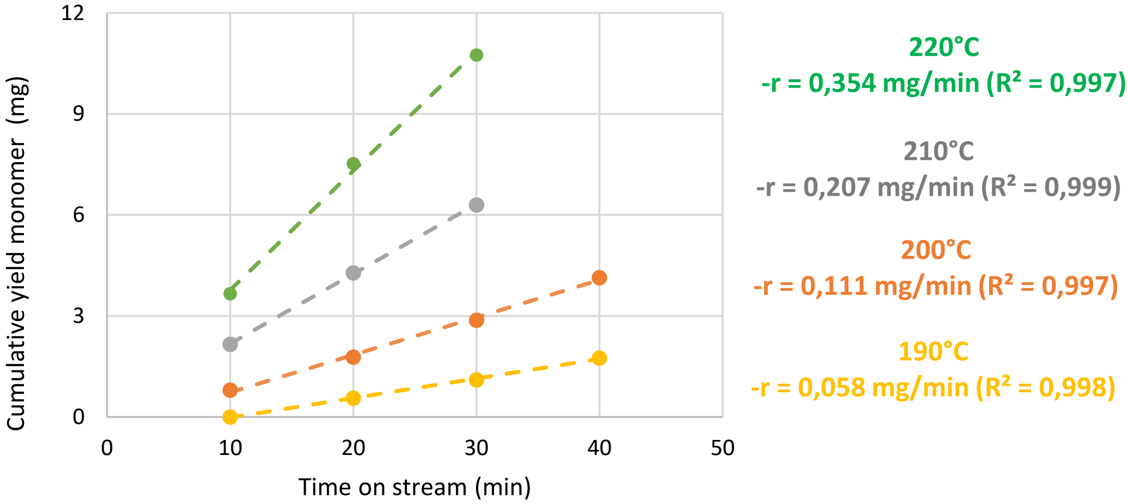

Figure S- 25: Period of constant monomer production rate for 1g β-zeolite loading

20. ICP-AES analysis of zeolites

Zeolite samples obtained after the stability study were collected and analyzed for aluminium content with inductively coupled plasma atomic emission (ICP-AES). 10 mg of sample were digested in 25 mL HNO_3 70% vol. at 80ºC for 48 hours, until the resulting solution was completely transparent and no solids where observed. The resulting solutions after digestion were analyzed in Agilent 4200 MP-AES and the results are shown in Figure S-26

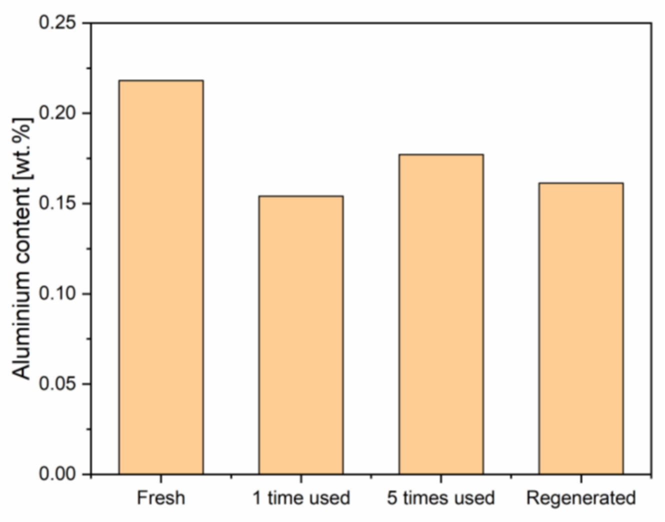

Figure S- 26: Aluminium content in fresh zeolite and the spent zeolites obtained after the stability study (corresponding to the samples whose properties are reported in Table 1)

21. Quantification of ethanol derived products

Two additional experiments were carried out to quantify the conversion of ethanol in the system under the used reaction conditions. In the first experiment the reactor was packed exclusively with 2 grams of β-zeolite, quartz wool and glass beads. In the second experiment, two sequential beds comprised of lignocellulosic biomass and β-zeolite respectively were used in segregated configuration. A 9:1 v/v EtOH:H_2O flowrate of 0.5 mL/min was used at 220°C and 50 bar for a total duration of 3 hours for both experiments. Since the employed reactor setup is not equipped with an in-line gas chromatographer, gas samples were collected at the reactor back pressure regulator outlet in a sealed bag and subsequently analysed in a separated gas chromatographer.

Gas samples were collected over a reaction time period of 35 minutes and injected into TRACE 1300 Gas Chromatograph equipped with a flame ionization detector (FID). An MXT QBond 30m 0.53mm column was used with a ramp of 6.5°C/min with temperatures ranging from 50 to 250°C, leading to a total analysis time of 30 minutes. Chromatograms for both experiments are shown in Figures S-27 and S-28.

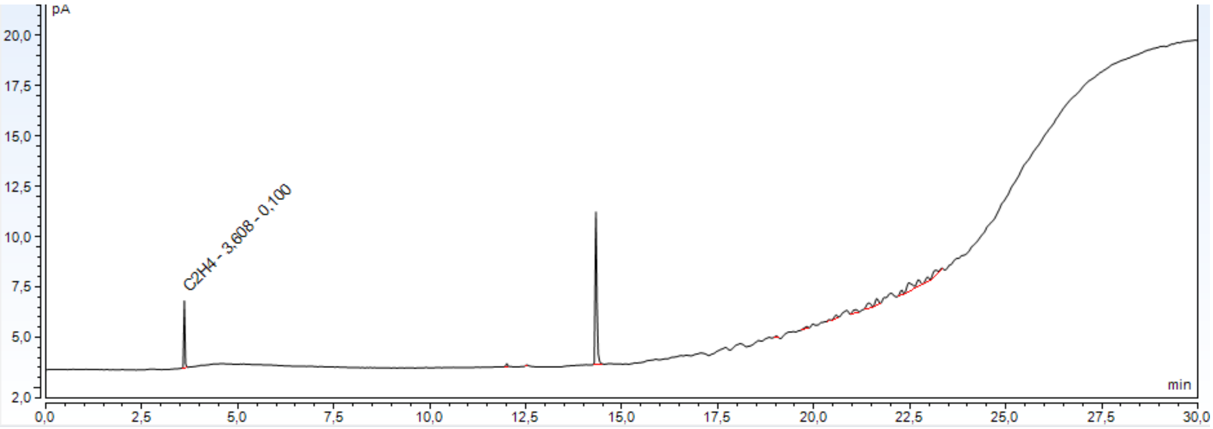

Figure S- 27: Gas chromatogram of gas sample from first reaction (no lignocellulose)

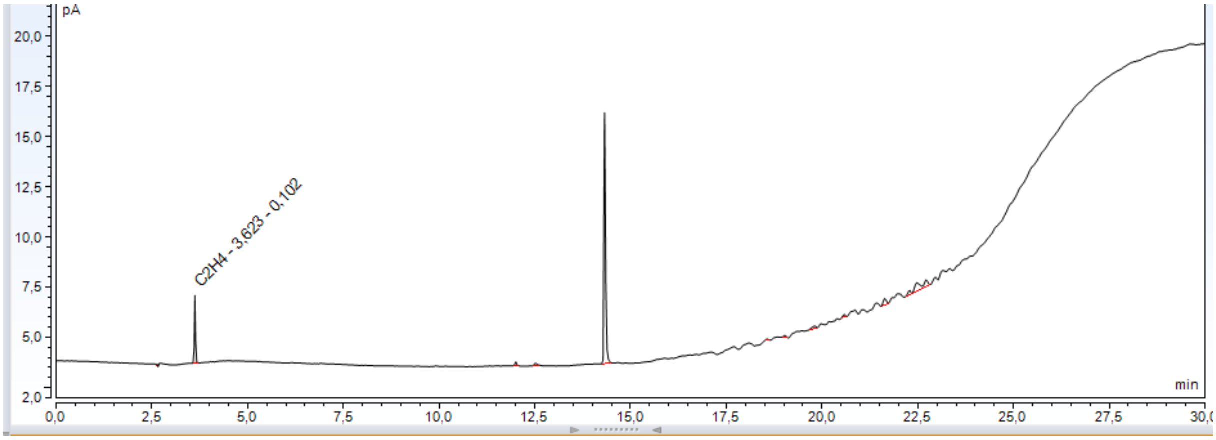

Figure S- 28: Gas chromatogram of gas sample from first reaction (with lignocellulose)

Ethylene as gas phase product is observed (RT=3.6 min), as well as ethanol (RT=14.8 min). Ethylene quantification was carried out using commercial gas standards. The concentration of ethyelene was 0.190 vol.% and 0.188 vol.% for first and second experiments respectively. Based on these results, ethanol conversion for each experiment was calculated to be $1.73 \cdot 10^{-2}$ % and $1.71 \cdot 10^{-2}$ % for each experiment respectively.

Additionally, liquid samples of the experiment without lignocellulose were analyzed in GC-MS and no additional products were found.

22. Effect of oxalic acid addition on polysacharide retention

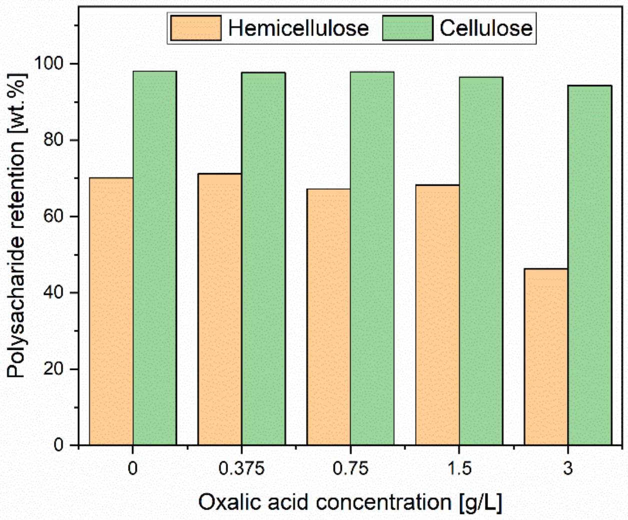

Figure S- 29: Cellulose and hemicellulose retention in the remaining pulp after the reactions carried out with different oxalic acid concentrations

23. References

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