Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Mechanocatalytic partial depolymerization of lignocellulosic feedstock towards oligomeric glycans

Gregor Meyer[a], Marius Wolf[b], Stefan Hanstein[b] and Marcus Rose[a]*

[a] Technical University of Darmstadt, Department of Chemistry, Chemical Technology II, Alarich-Weiss-Straße 8, 64287 Darmstadt, Germany

[b] Fraunhofer Research Institution IWKS, Bioeconomy Department, Brentanostraße 2a, 63755 Alzenau, Germany

E-mail: marcus.rose@tu-darmstadt.de (MR)

NREL-regulations

All described regulations were carried out at least in duplicate.

Determination of Total Solids in Biomass

Weighing dishes were pre-dried a 105 ± 3 °C drying oven for a minimum of four hours and cooled in a desiccator. Then 0.5 to 2 g of the sample to the nearest 0.1 mg were weighed in and recorded. The sample was placed in the oven at 105 ± 3 °C for a minimum of four hours. Afterwards the sample was weighed to the nearest 0.1 mg, placed back in the oven at 105 °C and was dried to constant weight. This was defined as ± 0.1 % change in the weight percent solids upon one hour of re-heating the sample.

Determination of Ash in Biomass

This method covers the determination of ash, expressed as the percentage of residue remaining after dry oxidation at 550 to 600 °C.

The porcelain crucibles were placed on the muffle furnace at 575 ± 25 °C for a minimum of four hours. Afterwards the crucibles were removed directly into a desiccator followed by 30 min cooling and the weight was recorded. Drying was continued until a constant weight was achieved. This was defined as less than ± 0.3 mg change in the weight upon one hour of re-heating. When constant weight was achieved 0.5 to 2 g were weighed into the tared crucible and the amount recorded. The sample was heated at 575 ± 25 °C for 24 ± 6 h and was removed into a desiccator for 30 min cooling. Drying was continued to a constant weight.

Determination of Extractives in Biomass

In parallel to the "Determination of Extractives in Biomass", the "Determination of Total Solids in Biomass" was performed to exclude errors due to changes in humidity.

Extraction was carried out with a Soxhlet apparatus. 2-10 g of the sample were placed in a tared extraction thimble. 190 mL HPLC grade water were added to a 250 mL receiving flask and refluxed for 24 h with 5-6 siphon cycles per hour. In the second step the reflux was run with 190 mL ethanol with 6-10 siphon cycles per hour for 16-24 hours. For both extractives the solvent was removed by rotary evaporation and further dried vacuum for 24 hours at 40 °C.

Determination of Structural Carbohydrates and Lignin in Biomass

This procedure was carried out after "Determination of Extractives". At the same time "Determination of Total Solids in Biomass" was carried out to avoid errors due to changes in humidity.

An appropriate number of filtering crucibles were placed in a muffle furnace at 575 °C for at least four hours. Afterwards the crucible was cooled down in a desiccator for 30 mins and was weighed.

For hydrolysis 300 mg of the sample were weighed into a tared pressure tube. 3.00 mL of 72 % sulfuric acid was added and stirred with a Teflon stir rod for one minute. After mixing, the pressure tube was placed in a 30 °C water bath for 60 min whereby it was stirred every 5-10 min without removal from the water bath. Afterwards, the acid was diluted to a 4 % concentration by adding 84 mL deionized water. The sample was mixed to eliminated separation between high and low concentration acid layers. The pressure tube was placed in an oil bath for one hour at 121 °C and cooled down to room temperature before removal of the cap.

Sample analysis for acid insoluble lignin:

The autoclaved hydrolysis solution was vacuum filtered through a previous tared filtering crucible and approximately 50 mL was transferred into a storage bottle (determination of soluble lignin and carbohydrates). Deionized water was used to quantitatively remove all remaining solids out of the pressure tube into the filtering crucible. Afterwards the crucible was dried at 105 °C for at least four hours. The weight was recorded after 30 min cooling in a desiccator. Lastly, the crucibles were placed in a muffle furnace at 575 °C for 24 h and weighed after dried for 30 min in a desiccator.

Sample analysis for acid soluble lignin:

Within six hours the sample was measured with a UV-Vis spectrophotometer. Deionized water was used as a blank. The samples were diluted to achieve absorbance values of 0.7-1.0. The calculation was carried out in accordance to the literature (https://www.nrel.gov/docs/gen/fy13/42618.pdf).

Sample analysis for structural carbohydrates:

Firstly, calibration calibration curves were measured for D-cellobiose, D(+)glucose, D(+)xylose, D(+)galactose, L(+)arabinose and D(+)mannose in a concentration range of 0.1-4.0 $mg \cdot ml^{-1}$.

20 mL aliquots of each liquor were transferred to 50 mL Erlenmeyer flasks and neutralized with calcium carbonate to pH 5-6. After settling the supernatant was decanted. The resulting liquid was analysed by HPLC and the concentrations were calculated in accordance to the calibration curves. A cellobiose concentration greater than 3 $mg \cdot ml^{-1}$ is an indicator for incomplete hydrolysis. In this case the analysis was performed again.

Table S1: Composition of used wheat straw, cocoa shells, beet pulp and apple pomace based on the NREL-regulations.

Component	Wheat straw	Cocoa shells	Beet pulp	Apple pomace
Extracttives / %	14.3	47.0	47.5	39.7
Water content / %	7.5	2.1	7.5	7.8
Ash / %	4.2	6.5	5.4	4.4
Lignin / %	19.1	32.2	11.9	17.3
Hemicellulose / %	20.1	2.9	3.1	9.0
Cellulose / %	29.8	12.4	11.1	13.7
Undetected / %	5.0	-	13.5	8.1

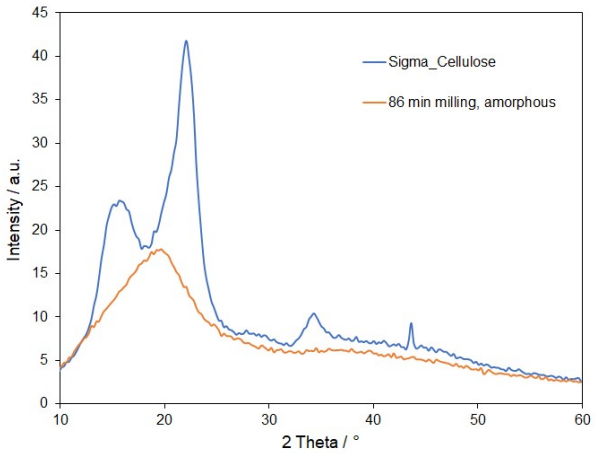

Figure S1: Comparison of the XRD-pattern of cellulose before and after ball milling for 86 min.

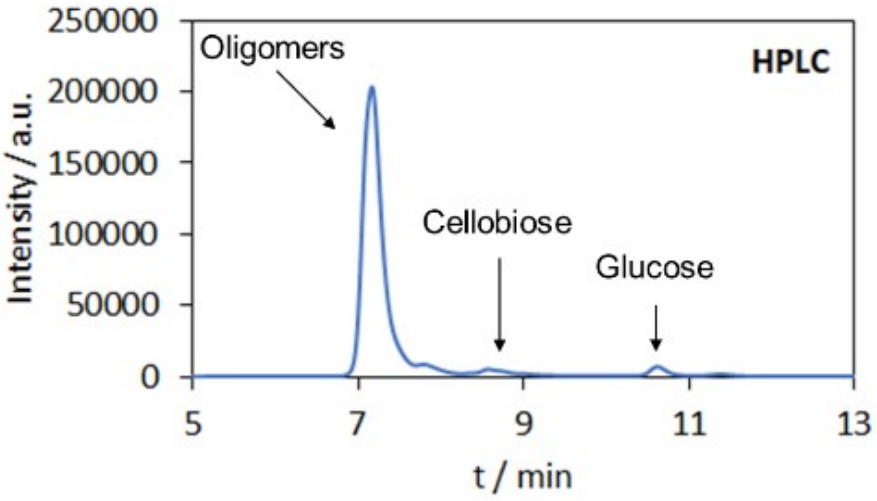

Figure S2: Exemplary HPLC-chromatogram of the soluble product mixture after partial depolymerization of cellulose.

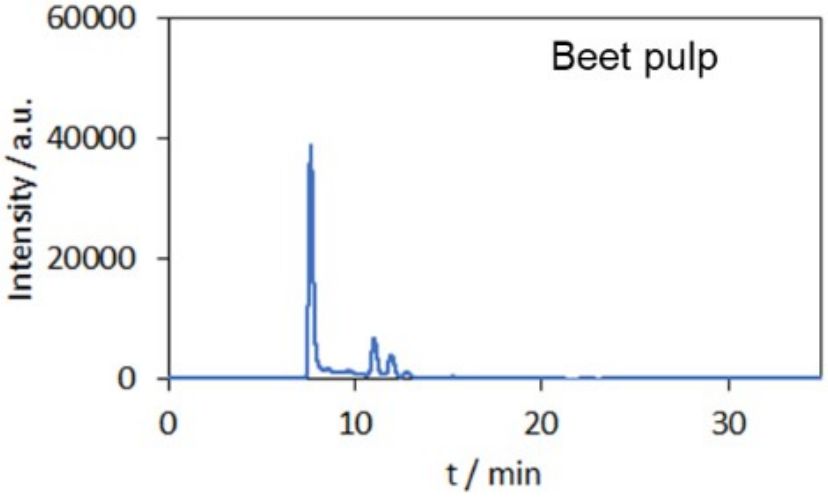

Figure S3: HPLC-chromatogram of the soluble product mixture after partial depolymerization of beet pulp after mechanocatalysis with 500 rpm and 6 % acid content after 170 min.

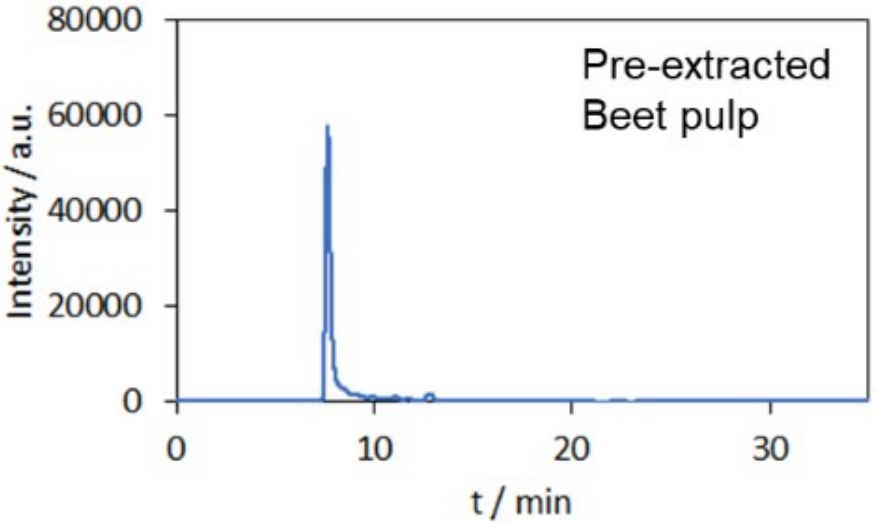

Figure S4: HPLC-chromatogram of the soluble product mixture after partial depolymerization of pre-extracted beet pulp after mechanocatalysis with 500 rpm and 6 % acid content after 170 min.