Supplementary Material

Influence of the Carbonization Process on Activated Carbon Properties from Lignin and Lignin-Rich Biomasses

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	Beech wood ^{a)}	Pine bark ^{b)}	Oak bark ^{c)}
Lignin (ADL) %	14.7	44.9	19.6
Cellulose (ADF - ADL) %	57.8	25.4	30.0
Hemicellulose (NDF - ADF) %	19.4	14.7	20.5

Table S1 - Fiber analysis of the beech wood, pine bark and oak bark

a) measured and calculated based on the method proposed by van Soest et al. [1]

b) from [2]

c) from [3]

Table S2 - Maximal pressures after hydrothermal carbonization reactions

	Pressure	after reaction	time (bar)
	Repetition 1	Repetition 2	Repetition 3
Indulin	28	28	-
Kraft Lignin	28	28	27
Organosolv Lignin	40	43	-
Low Sulfonate Lignin	30	31	27
Pine wood bark	39	39	37
Oak wood bark	48	51	-
Beech wood	44	46	45

Table S3 – Organic com	position of the HTC	process waters mea	asured with GC-FID.
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	Content (mg/g _{Dry Matter})*							
Precursor	Phenol	Guaiacol	Catechol	4-Methyl- guaiacol	4-Ethyl- guaiacol	Syringol	Vanillin	Furfural
Beech wood	N.D.	<0.2	<1.3	N.D.	N.D.	0.53	<0.25	0.82
Oak bark	N.D.	0.50	<1.3	0.51	N.D.	0.27	N.D.	N.D.
Pine bark	N.D.	<0.2	<1.3	N.D.	N.D.	N.D.	N.D.	N.D.
Low sulfonate lignin	N.D.	1.96	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Alkali kraft lignin	<0.2	2.97	<1.3	0.23	0.33	<0.25	0.44	N.D.
Indulin AT lignin	<0.2	2.27	<1.3	<0.2	0.25	<0.25	0.54	N.D.

*Calculated from measured concentrations. N.D.: not detected.

The process water from Organosolv lignin was not analyzed since the extraction process of the organic components was not possible. This was attributed to an unclear boundary between the organic and the aqueous phase after the separation process. For this reason, a quantitative measurement could not be done. Instead, a qualitative analysis was conducted using a different column and it was possible to determine that the ratio of phenol to guaiacol was 1:1.

Table S4 – Minerals found in the HTC process water measured with ICP-OES.

Produceor	Content (mg/g _{Dry Matter})								
Frecuisor	Ca	Κ	Mg	Mn	Na	Р	S	Si	Zn
Beech wood	1.23	1.18	1.52	0.14	0.09	0.081	0.07	0.05	0.002
Oak bark	8.65	1.39	2.55	0.07	0.23	<0.02	0.35	0.44	0.003
Pine bark	1.55	0.49	0.69	0.01	0.15	0.067	0.14	0.17	0.009
Low sulfonate lignin	0.02	0.67	0.29	0.005	30.9	<0.02	18.4	0.06	0.001
Alkali Kraft lignin	0.06	0.86	0.25	0.003	5.68	<0.02	5.84	0.16	0.000
Indulin AT lignin	0.10	0.71	0.33	0.007	5.59	<0.02	5.21	0.13	0.001
Organosolv lignin	0.09	0.30	0.08	0.001	2.57	0.087	0.51	0.26	0.001

*Calculated from measured concentrations

Fig. S1 - N₂ Isotherms









Fig. S2 - FTIR Spectra - Beech Wood



Y-axis scaling and units are arbitrary

Fig. S3 - FTIR Spectra - Oak Bark



Y-axis scaling and units are arbitrary





Y-axis scaling and units are arbitrary





Y-axis scaling and units are arbitrary

Fig. S6 - FTIR Spectra - Alkali Kraft Lignin



Y-axis scaling and units are arbitrary

Fig. S7 - FTIR Spectra - Indulin AT Lignin



Y-axis scaling and units are arbitrary





Y-axis scaling and units are arbitrary



Fig. S9 - Methylene blue adsorption vs. total acidic groups



1. Fig. S10 - GC-FID Spectrum - Beech Wood HTC Process Waters



Fig. S11 - GC-FID Spectrum - Oak Bark HTC Process Waters

S14



Fig. S12 - GC-FID Spectrum - Pine Bark HTC Process Waters

S15



Fig. S13 - GC-FID Spectrum - Low Sulfonate Lignin HTC Process Waters5



Fig. S14 - GC-FID Spectrum - Alkali Kraft Lignin HTC Process Waters



Fig. S15 - GC-FID Spectrum - Indulin AT Lignin HTC Process Waters

References Supplementary Material

- P.J. Van Soest, J.B. Robertson, B.A. Lewis, Methods for Dietary Fiber, Neutral Detergent Fiber, and Nonstarch Polysaccharides in Relation to Animal Nutrition, J. Dairy Sci. 74 (1991) 3583–3597. doi:10.3168/jds.S0022-0302(91)78551-2.
- [2] L. Valentín, B. Kluczek-Turpeinen, S. Willför, J. Hemming, A. Hatakka, K. Steffen, et al., Scots pine (Pinus sylvestris) bark composition and degradation by fungi: Potential substrate for bioremediation, Bioresour. Technol. 101 (2010) 2203–2209. doi:10.1016/j.biortech.2009.11.052.
- W. Jin, K. Singh, J. Zondlo, Pyrolysis Kinetics of Physical Components of Wood and Wood-Polymers Using Isoconversion Method, Agriculture. 3 (2013) 12–32. doi:10.3390/agriculture3010012.