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Supplementary Material

Supplementary Material: Enhancing Fuel Properties of Napier Grass via Carbonization: A Comparison of Vapothermal and Hydrothermal Carbonization Treatments

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Fiber analysis

A detergent fiber analysis was used to differentiate between the hemicellulose, cellulose and lignin parts of the Napier grass (FIBRETHERM Automated Fiber Analyzer; C. Gerhardt GmbH & Co. KG, Königswinter, Germany; VDLUFA, 2012: methods 6.5.1-3). Prior to the analysis, the feedstock was dried at 60°C and ground. Then 0.5g of the sample was placed into a filter bag and the analysis was performed in triplicate. Three detergents extractions were made to differentiate between highly digestible cell contents (sugars, carbohydrates, proteins, lipids; termed neutral detergent solubles, NDS) and nondigestible cell walls (hemicellulose, cellulose and lignin). The fiber fractions (neutral detergent fiber (NDF), acid detergent fiber (ADF), and acid detergent lignin (ADL)) are used to estimate the hemicellulose, cellulose and lignin composition. The following equations are used:

NDS = 100 - NDF -ash

NDF = lignin+ cellulose+ hemicellulose

lignin = ADL

cellulose = ADF-ADL

hemicellulose = NDF-ADF

The individual values estimated from each sample for lignin, hemicellulose and cellulose in the whole Napier grass, only leaves and only stem can be seen in Figure S1.

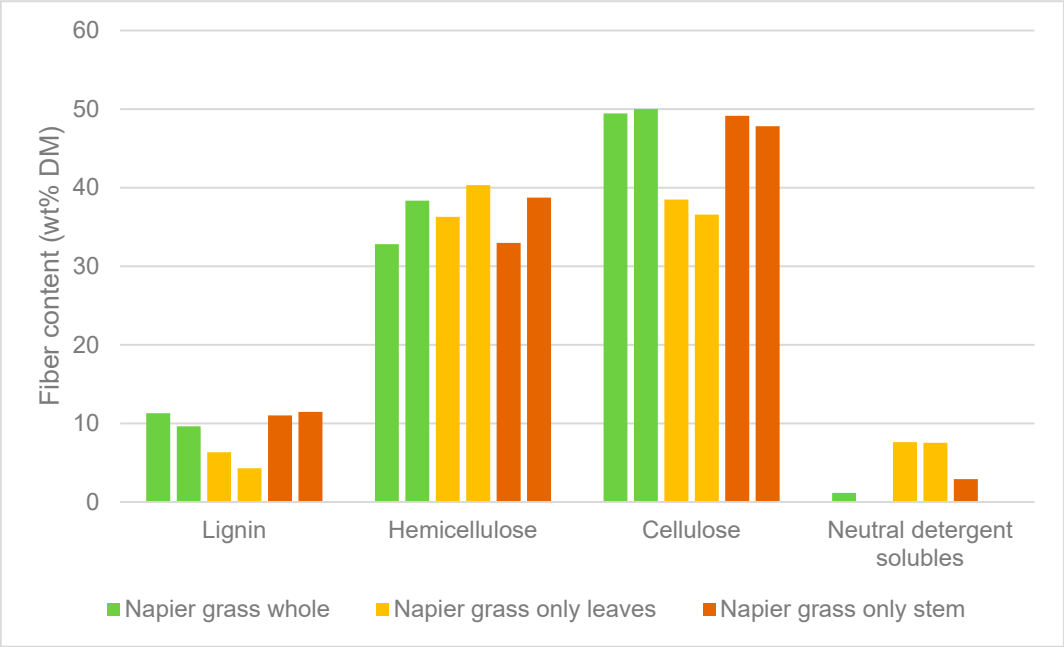

Figure S1. Fiber analysis values for each sample from Napier grass as whole plant (green) and only its leaves (yellow) or stems (brown).

Analytical methods

The analytical methods utilized for the determination of the various parameters in the Napier grass and their respective hydrochars and process water are detailed in Table S1, while the recommended analytical methods according to the EN ISO 17225 (for biomass and thermally treated biomass) are summarized in Table S2.

Table S1. Analytical methods for the analysis of Napier grass, VTC and HTC chars and Process water for each run

Stream	Parameter	Method	Number of values obtained per sample	Reference
Napier grass and chars*	Total carbon, hydrogen, nitrogen, sulphur.	An Elemental Analyzer Vario ELIII (Elementar Analysensysteme, Hanau, Germany) was used to measure the elemental carbon, hydrogen, nitrogen, and sulfur (CHNS) by using the sulfonic acid as a reference	3	VDLUFA Mb Bd. 3 Chap 4.1.2
	Water content	Gravimetry 105 +2 °C until constant weight	2	ISO 18134

	Ash content	Gravimetry 550 + 10°C until constant mass	2	ISO 18122
	Gross calorific value	Bomb calorimeter method, utilizing an IKA Calorimeter C 200- System, Germany	3	ISO 18125
	Net calorific value	Calculation from the Gross calorific value	3	DIN EN 1418:2011
	Trace elements: cobalt, chromium, copper, potassium, sodium, nickel, phosphorus, sulphur, zinc	The solid samples were analyzed with an ICP-OES (ICAP6300 Duo, Thermo Fisher Scientific Inc., USA) equipped with an autosampler (ASX-520, CETAC Technologies, USA). A 0.1gDM sample of hydrochar was dissolved in 8ml HNO3 (65%v) for 30 minutes at 250°C in a microwave system UltraClave IV, then centrifuged for 10 minutes at 4500 rpm.	3	DIN EN 16173:2012
	Cl content	An AOX Analyzer with micro-colorimetric titration was used to determine total Cl content. The Instrument Behr CL 10 muffle oven with an AOX-module and a titration cell with an absorption column with sulphuric acid 96 % was used.	2	DIN 51408-2: 2009-06

Process water	Ammonium (NH_4+), nittrate (NO_3-), nitritte (NO_2-) chlorine (Cl-)	Anions and cathins were detected through ion chromatograph ICS 1000 from Dionex.	2	VDLUFA I, A.6.1.4.1, 4., ed. 2000
	N Kjeldahl (TKN)	Digestion and determination were realized with the Büchi machine.	2	Distillation: VDLUFA Bod.3 Chapter 4.1.1 Digestion and determination: DIN EN 25663
	Cobalt, chromium, copper, potassium, sodium, nickel, phosphorus, sulphur, zinc (trace elements)	The liquid samples were analyzed with an ICP-OES (ICAP6300 Duo, Thermo Fisher Scientific Inc., USA) equipped with an autosampler (ASX-520, CETAC Technologies, USA). 10 ml of process water was dissolved in 6ml HNO3 (65%v) for 30 minutes at 250°C in a microwave system UltraClave IV, then cool down to 60°C.	3	DIN EN 16173:2012

*chars include HTC and VTC chars

Table S2. Analytical methods according to the ISO 17225 for biomass and thermally treated biomass

Parameter	Pre-treatment	Method	Description	Reference
Total carbon, hydrogen, and nitrogen		**C, H, N: Elementar analyser** N alternative: Kjeldahl	Complete combustion of carbon into carbon dioxide, hydrogen to water and nitrogen to nitrogen gas (all NOx should be reduced to N2). The detection is done by the same machine.	ISO 16948

			Nitrogen can also be determined alternatively by the Kjeldahl method as in the DIN 51722-1 or ISO 333 1996.	
Water content		**Gravimetry**	105 +2 °C until constant mass (< 0.2 % mass difference in 1 hour) Minimum 100 grams material.	ISO 18134
Ash content	Determine water content	**Gravimetry**	550 + 10°C until constant mass	ISO 18122
Gross calorific value	Determine water content	**Combustion**	Bomb calorimeter method	ISO 18125
Trace elements: arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, molybdem, nickel, lead, anthymonium, selenium, tin, thalium, vanadium, zinc	**Microwave digestion***	1. For As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, V and Zn: 2. ICP-MS according to ISO 17294-2 3. **ICP-OES** according to ISO 11885 4. GF-AA 5. For As and Se: 6. HG-AAS according to ISO 17378-2 7. For Hg 8. CV-AAS according to the EN 12338	Digestion with H2O2 (30 %v), HNO3 (65%v), HF (40%v), this last can be substituted in some cases by H3BO3. The microwave digestion should reach 190°C in 15 min and hold 20 min at that temperature	ISO 16968
Sulphur and chlorine content	Combustion under O2-atmosphere and absorption solution as acids Digestion in closed containers according	For Cl and S: **1. AOX** or Elemental analyzer***** 2. Ion chromatography 3. ICP according to ISO 11885 4. For S also: 5. Turbidity method		ISO 16994

	to ISO 16967:2015	according to ASTM D516-07 6. For Cl also: 7. Coulometric determination according to DIN 51727 8. Potentiometric titration according to DIN 38405-1		

Bold methods are the ones applied in this study for the analytical determination for Napier grass and the char

*Microwave digestion was done only with HNO3 at 250°C for 30 minutes.

**For Cl

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