



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

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Abstract: Napier grass is a herbaceous biomass that can be used as biofuel; however, its high ash, potassium, sulfur and chlorine content may cause problems when combusted. Napier grass was submitted to vapothermal carbonization (VTC) and hydrothermal carbonization (HTC) processes at 190 and 220 °C to compare their ability to enhance its fuel properties. The different water distribution between phases in the two processes was verified: up to 14.5% of the water vaporized to steam in the VTC ran at 220 °C, while over 99% of the water remained in the liquid state and in contact with the solids during all HTC runs. Both processes improved the calorific value of the Napier grass (up to 20.6% for VTC220 and up to 29.8% for HTC220) due to the higher C content in the chars. Both processes reduced the sulfur content, removing up to 15.3% of it with VTC190 and 28.5% of it with HTC190 compared to that of Napier grass. In contrast, the two processes had different effects on the ash and chlorine content. While HTC removed both ash and Cl from the Napier grass, VTC concentrated it in the chars (ash: 5.6%wt. Napier grass, 3.3%wt. HTC chars, 7.1%wt. VTC; chlorine: 1.08% wt. Napier grass, 0.19% wt. HTC chars, 1.24% wt. VTC). Only the HTC process leached high percentages of Cl (up to 80%), S (up to 70%), sodium (Na, up to 80%) and potassium (K, up to 90%) into the process water. This may prevent fouling and slagging problems when burning HTC char. The biofuel qualities of the raw Napier grass, VTC, and HTC chars were evaluated using two standards: the international standard for solid biofuels, EN ISO 17225, and the Korean regulation for biomass solid recovered fuels (Bio-SRF). Napier grass and VTC chars presented problems regarding Cl content thresholds for both EN ISO 17225 and Bio-SRF. Both VTC and HTC chars along with the Napier grass fulfilled the requirements for heavy metals (Pb, Ni, Cr, and Cd) except for copper. The choice of process in practical applications will depend on the goal; HTC improves fuel quality and VTC has higher high solid, carbon and energy yields.

Keywords: energy grass; vapothermal carbonization; hydrothermal carbonization; fuel; quality assessment; biofuel standard

1. Introduction

Herbaceous biomass such as grass offers numerous advantages as a solid biofuel: it can grow on diverse types of soils, and many varieties are water stress-resistant and require a low fertilizer amount to grow fast and achieve high yields (Napier grass up to 50 Mg/ha; Switch grass around 23 Mg/ha) [1]. Other advantages of planting herbaceous biomass are reduced soil erosion and nutrient run-off into water bodies [2]. Additionally, grass was compared with woody biomass, regarding its net energy yield (output energy—input energy), leading to the conclusion that it was up to 25% higher for herbaceous biomass than that for wood-based biomass [2]. Even though herbaceous biomass presents several



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). advantages, there are some drawbacks: compared with fossil fuels, its energy density is low, it has a high water content [3] and the amount of its inorganic constituents might be significant [4]. Herbaceous crops, on average, contain more nitrogen, sulfur and ashforming elements than do woody crops [5]. High nitrogen amounts can contribute to global warming, since nitrogen compounds produce nitrogen oxides (NOx) when combusted. In fact, it is estimated that 25% of the global NOx emissions come from biomass combustion [6]. The total ash content from herbaceous biomass can be up to 15%wt. [7]. Ash content in this range can form considerable amounts of particulate matter in the flue gas, which can deposit on the surface of the heat exchanger, causing a reduction in the boiler efficiency of a combustion plant [8]. Grasses can contain important amounts of Cl, S, K, Ca, and Si [5]. These compounds, together with other ash contents, can lead to operational problems in combustion systems such as corrosion, fouling, and slag formation, in addition to particle deposition [9–11].

Characteristics of herbaceous biomass are highly variable, both within and among plant species [12–15]. This variability has been reported to be higher for herbaceous biomass than that for woody biomass [15]. For instance, for switch grass, the ash content varied from 2.8 to 10.8%wt., and volatile matter varied from 68.6 to 81.2%wt. [15], while for poplar biomass, the ash content varied from 1.1 to 1.3%wt., and its volatile matter changed from 83.4 to 84.6%wt. [15]. This variability challenges the direct use of herbaceous biomass as an industrial fuel and hinders the change towards renewable energies [12–16]. Therefore, pre-treatment to homogenize herbaceous biomass is necessary to substitute fossil fuels.

There are different biological and thermochemical processes used to improve biomass characteristics for biofuel applications (for example, increasing the calorific value and carbon content, or reducing the water content) [17]. The most common thermochemical processes include pyrolysis, which produces charcoal and/or oil, gasification for mainly syngas, and hydrothermal carbonization (HTC), which mainly produces hydrochars, process water and a small amount of gas [3,17,18]. This last process, HTC, is a coalification process where biomass is submerged in liquid water under autogenic pressure and relatively low temperatures between 180 °C and 250 °C [3,17,19–21]. Carbonization can also take place with biomass submitted to high-pressure saturated vapor instead of liquid water [19,22]. This process is called vapothermal carbonization (VTC). VTC processes require a lower water-to-biomass ratio, which means energy consumption can be reduced [23].

Ro et al., in 2020, pointed out that the transition between HTC and VTC reported in the literature can be fuzzy since relatively small variations in the same reactor system can change the water distribution between the liquid and vapor phases [24]. In order to label the system VTC or HTC, the water phase distribution should be determined as well as the solid content parameter, %S(T), which describes the amount of liquid water in physical contact with feedstock at the reaction temperature.

Few studies have compared HTC and VTC chars for fuel properties [19,25,26]. Funke et al. [19] and Cao et al. [25] demonstrated that chars produced via VTC and HTC reach a higher carbon content than that of the feedstocks, and that HTC chars achieved a higher carbon content than did VTC chars. In terms of energy content, Yeoh et al. [26] obtained a higher calorific value by conducting VTC processes compared to that obtained via HTC processes, and Funke et al. [19] showed the same trend for digestate but the opposite one for wheat straw. Ash content was higher in VTC chars compared to that in the feedstocks in most cases [21,26]. Nevertheless, in the study conducted by Cao et al. [25], the ash content in HTC chars from sugar beet was higher than the ash content in VTC chars, but the trend was the opposite when carbonizing bark. Due to the low number of publications related to VTC, and the different feedstocks utilized in these studies, strong conclusions about these trends cannot be drawn. Moreover, important fuel properties such as Cl or heavy metal content have neither been evaluated nor compared yet.

Heavy metals and Cl contents are crucial properties to be analyzed when assessing the quality of biofuels. These, among other properties, will not only determine the design of the furnace and boiler, but also, that of flue gas cleaning and ash treatment, which will indirectly

determine both the operational and capital costs [13,14]. Quality standards for biofuels have been developed around the world. In the European Union, there are international standards (ISO) and European norms (EN). For instance, the EN ISO 17725, with nine parts, provides criteria that specific fuels (e.g., woody and non-woody pellets, briquettes or thermally treated biomass) must belong to a specific quality class [11]. The standard is divided into nine parts; parts 6 [5] and 7 [27] describe the classes for raw biomass while part 8 [28] classifies thermally treated biomass. In South Korea, there are standards for solid recovered fuels (Bio-SRF) produced from waste paper, waste wood, herbaceous or organic wastes (e.g., sewage sludge, manure, food waste and park waste including grass) [29]. At this time, HTC and VTC chars have not been classified in accordance with any standard.

The main goal of this study is to compare the fuel properties of VTC and HTC char to assess if the VTC and HTC processes can be used to improve the fuel quality of Napier grass. In the first step, the water phase distribution in the reactor system is assessed to assure that VTC or HTC conditions are achieved. Then, we compare important properties of the Napier grass and their respective HTC and VTC chars against the biofuel quality standards EN ISO 17725 and Bio-SRF to assess their potential to be used as biofuels. The parameters are discussed in this paper in the following groups: (1) general characteristics of fuels including calorific value, ash, and moisture content; (2) assessment of the toxicity of the fuel including all the heavy metals (As, Cd, Cr, Ni, Cu, Pb, Zn and Hg); and N, (3) estimation of the corrosion potential of the fuel, e.g., S and Cl.

2. Materials and Methods

2.1. Feedstock

The feedstock was the cuttings of a hybrid Napier grass (DAMO EnergyGrass(R)) received from India (ARAMEX INDIA PVT LTD., Coimbatore, India). This is an inter-specific hybrid between pearl millet (*Pennisetum americanum* L.) and a selection of a common Napier grass (*Pennisetum purpureum* Schum.) developed at Tamil Nadu Agricultural University in Coimbatore, India. The Napier grass was air-dried (at approximately 80% DM), cut into pieces (stems, ca. 3–4 cm; and leaves, ca. 10–15 cm) and shipped; it was stored at 4 °C upon arrival until the batch experimental runs were carried out in accordance with the experimental design.

The main fuel properties (elemental analysis, proximate analysis, calorific values, and K and Cl contents) of the Napier grass in this study (whole plant, leaves only and stems only) are shown in the last 3 columns of Table 1. They are compared with those of other Napier grass varieties reported in the literature. All properties measured in this study are similar to those already reported in the literature, with the contents of carbon (45.3%wt. DM), ash (5.6%wt. DM), K (1.0%wt. DM) and Cl (1.1%wt. DM) being in the ranges typical of herbaceous biomass [25].

Additionally, a detergent fiber analysis (FIBRETHERM Automated Fiber Analyzer; C. Gerhardt GmbH & Co. KG, Königswinter, Germany; VDLUFA, 2012: methods 6.5.1-3) was conducted for the whole Napier grass, as well as for leaves and stems. From the fiber fractions (neutral detergent fiber (NDF), acid detergent fiber (ADF), acid detergent lignin (ADL)), the mass fractions of lignin (ADL), cellulose (ADF-ADL) and hemicellulose (NDF-ADF) were determined, while the rest were determined after the ash was neutral detergent-soluble (see Supplementary Materials for more details and results; Figure S1).

Leaves contain less cellulose and lignin than do the stems and the whole plant (Figure 1). The hemicellulose contents were similar for all the samples. Since the stem is a major part of the plant (in weight), the results of only the stem and the whole plant are similar.

Property	Napier Grass (P. americanum)	Napier Grass (P. purpureum)	Napier Grass (Not Specified)	Hybrid Napier Grass (Not Specified)	Hybrid Napier Grass (P. americanum +	Hybrid Napier Grass (P. americanum + P. purpurum) (This Study)		
	(,	[30]	[31]	[32]	P. purpurum)	Whole	Leaves	Stems
Water content (%wt.)	12 * [33]	74.2	30.1	9.4 *	76.6–89.4 [34]	22.1 ± 0.1	7.9	6.2
C (%wt.)		45.1	45.1	42.4 *	44.4 [34] 44.8 [35]	45.3 ± 1.7	49.1	47.5
H (%wt.)		5.9	5.9	6.0 *	4.7 [35] 5.5 [34]	6.4 ± 0.3	8.1	8.2
N (%wt.)		1.5	0.5	1.7 *	0.4 [35] 1.2 [34]	0.7 ± 0.1	0.6	1.5
S (%wt.)		0.4	0.0	0.1 *	0.1 [34] 0.43 [35]	0.20 ± 0.0	0.3	0.3
O (%wt.)		47.2	48.5	45.3 *	44.3 [34] 49.8 [35]	41.9 ± 1.3	30.7	38.4
Ash (%wt.)	3.7 [33] 11.2 [36]	6.3	6.3	9.7	2.8 [35] 4.8–13.3 [34] 12.0–13.1 [37]	5.6 ± 1.1	11.3	4.0
K (%wt.)		3.8	1.4		0.4–1.3 [37]	1.0 ± 0.4	0.8	1.0
Cl (%wt.)		1.2	0.6	0.2 **		1.1 ± 0.0	-	-
Volatile Matter (%wt.)		85.2	85.5	72.6	73.5 [35] 70.7–77.2 [34]	-	-	-
Fixed Carbon (%wt.)		8.5	8.7	8.4 *	23.7 [35]	-	-	-
GCV (MJ/kg)	14.8 [31,34]	16.6	16.7		17.7 [35] 15.7–17.8 [34]	17.7 ± 0.3	16.2	17.7

Table 1. Characterization of the feedstock Napier grass used in this study (mean values \pm standard deviation, n = sample amount = 3) compared to the literature values.

All units are based on dry basis except water content. * air dried; ** organic Cl.



Figure 1. Fiber analysis of Napier grass as whole plant (green) and only its leaves (yellow) or stems (brown). Mean and spread of 2 values.

2.2. Experimental Design

The experimental design was a full factorial design of two (numeric continuous) factors and two levels. Each run was performed two times. The experiments were designed to assess the effects of the holding temperature, the carbonization processes (i.e., VTC or HTC) and the solid content (S_0) on the quality of the chars. For each VTC or HTC experiment, the two factors (i.e., T and solid content) were evaluated. The two levels for the temperature factor selected were as follows: 190 °C (-1) and 220 °C (+1). The levels regarding the S_0 were 7% (-1) and 33% (+1), where the first sets the HTC conditions in the reactor and the second sets the VTC conditions. All runs were batch experiments. Other operational parameters were fixed as follows for all the runs: a holding time of 3 h and heating rate of 2 K/min. The factors per run are shown in Table S1 in the Supplementary Materials.

2.3. Experimental Set-Up for the Hydrothermal Carbonization (HTC) and Vapothermal Carbonization (VTC) Batch Runs

In total, eight batch runs were carried out during this study, four runs under HTC process conditions, in which the biomass was fully submerged in liquid water, and four runs under VTC conditions, in which the feedstock made contact only with water vapor. Both types of batch tests were carried out in an 18.75 L pressure reactor (Model 4555, T 316 Stainless Steel, Parr Instrument, Moline, IL, USA) with a resistance heating system (6000 watts) and temperature controller (Model 4848BM) using SpecView 4848 data acquisition software version 2.5. The reactor was heated at a rate of 2 K/min. For the HTC runs, the desired amount of Napier grass (22.1%wt. water content) was added to the pressure reactor and deionized water was added to fully immerse the biomass, resulting in an initial solid content (%So) of 7%, including the water content of the Napier grass. For the four VTC runs, the Napier grass was added to a wire-mesh basket, which was suspended using the stirrer from the top of the reactor. The weight of the feedstock varied slightly between runs (approximately +15%) because of differences in the packing density of the coarsely cut Napier grass. Water was added to the bottom of the reactor below the basket to achieve a nominal %So of 33% for each run.

The process conditions (temperature, %So and mass of input per run) are given in Table 2. The runs were carried out at two different temperatures, 190 °C and 220 °C. The holding time remained constant at 3 h. Two runs were carried out at each temperature.

Proc	ess Operat	ion Param	ieters	In	put Mass	
Process	T (°C)	t (h)	%So (%)	Solid In (g DM)	Water (g)	Total (g)
HTC	190	3	7.1	779.4	10,221.2	11,000.6
HTC	190	3	7.1	779.3	10,222.4	11,001.7
HTC	220	3	7.1	779.3	10,221.2	11,000.6
HTC	220	3	7.1	779.3	10,220.6	10,999.9
VTC	190	3	33.1	566.7	1143.9	1710.5
VTC	190	3	32.8	700.8	1435.1	2135.9
VTC	220	3	33.2	776.1	1559.7	2335.8
VTC	220	3	34.9	670.5	1250.9	1921.4

Table 2. Specification of the process operational parameters and the mass input to the reactor for each hydrothermal carbonization and vapothermal carbonization run.

2.4. Verification of Water Phase Conditions for VTC and HTC

In order to assure that the desired water phase conditions were achieved for the processes operated, HTC and VTC, the mass and volume fractions of water in the liquid and in vapor phases were calculated as described in Ro et al., 2020 [24].

For the calculation of the mass fraction of vapor water, x_v , the following equation was used:

$$x_v = \frac{v_R - v_L}{v_v - v_L} \tag{1}$$

where

 v_R is the overall specific volume of the reactor, the reactor volume divided by the mass of water $\left(\frac{m^3}{kg}\right)$;

 v_L is the specific volume of saturated liquid water $\left(\frac{m^3}{kg}\right)$;

 v_v is the specific volume of saturated vapor water $\left(\frac{m^3}{kg}\right)$.

The fraction of the reactor that is filled up by water in the liquid state at temperature T, VF_w , is then calculated using the mass fraction of the vapor water, x_v , as follows:

$$VF_w = \frac{V_w}{V_R} = \frac{(1 - x_v)v_L}{v_R}$$
 (2)

where

 V_w is the volume of water in a liquid state in the reactor at temperature T (m³); V_R is the total volume of the reactor (m³); VF_w is the volume fraction of liquid water in the reactor at temperature T (–).

2.5. Analytical Methods

Napier grass, HTC chars, VTC chars and process water samples for each run and process were analyzed. The number of samples taken for Napier grass was three; for the chars and the process water, two samples were taken per run.

For Napier grass and the chars, an elemental analysis was carried out with Elemental Analyzer Vario El (Elementar Analysensysteme, Hanau, Germany) to estimate the amount of total carbon, total nitrogen, total sulfur and total hydrogen; the oxygen was estimated via difference. The water and ash content were determined via gravimetry at 105 and 550 °C, respectively. The gross calorific values (GCV) were determined using a calorimetric bomb (IKA Calorimeter C 200-System, Staufen, Germany) based on ISO 18125 [38]. Since the limit values for the calorific value in both EN ISO 17725 and Bio-SRF are based on the net calorific value (NCV) and not on the gross calorific value (GCV), the NCV was calculated from the measured GCV based on DIN EN 14918 [39]. Trace elements such as copper and zinc were determined through nitric acid digestion followed by an ICP-OES determination (ICAP6300 Duo, Thermo Fischer Scientific Inc., San Diego, CA, USA). Total Cl content was determined via an AOX method (instrument Behr CL10, Stuttgart, Germany). For the samples of process water in addition to the trace elements with ICP-OES, ammonium, nitrate, nitrate and chlorine were measured via ion chromatography (Dionex ICS 1000, Thermo Fischer Scientific, USA). The nitrogen in the water was measured as total Kjeldahl nitrogen in accordance with DIN EN 25663 [40]. Digestion was realized at 400 °C under sulfuric acid; afterwards, the solution was distilled with vapor (Vapodest30, Gerhatdt, Königswinter, Germany), and finally nitrogen was determined via titrimetric methods. More information about the analytical methods is available in Table S1 in the Supplementary Materials.

All instruments were properly calibrated before the measurement of the samples, and blank samples were also measured to prove there was no contamination between the steps. Additionally, reference materials were also used as quality assurance for the measurements.

Since the mass fractions and values from this study were compared to the different EN ISO 17225 standards and the Bio-SRF regulation, the analytical methods from the standards

were taken into account. For Bio-SRF regulations, the analytical methods were not found. The methods suggested in EN ISO 17225 are shown in Table S2 in the Supplementary Material.

Instead of the standard deviation, whenever only two values were available, the spread of duplicate results was calculated as follows:

$$sp = \frac{(max - min)}{2} \tag{3}$$

where

max = maximum value; min = minimum value; sp = spread of 2 values.

2.6. Alkali Index

The alkali index (AI) for the Napier grass and the VTC and HTC chars was calculated based on the Na₂O and K₂O content as explained by Jenkins et al., 1998 [41]. The AI was utilized to predict the fouling probability (AI > 0.17 kg/GJ) and the fouling occurrence (AI > 0.34 kg/GJ) of the Napier grass and the chars [41,42]. Since neither the Na nor the K were measured in the ashes, the following assumptions were realized. For the Napier grass, it was assumed that 75% of the K and 2% of the Na from the total amount of biomass were reactive and important to consider for the alkali index, as previous studies with Miscanthus grass concluded [43]. Internal experiments showed that 90% of the total K and Na stayed in the ashes after the combustion of HTC chars. This assumption was taken for both HTC and VTC chars. Similar HTC results were obtained by Hansen et al. in which the alkali metals and Cl content of various biomass, including lawn cuttings and wheat straw, were reduced after HTC at 180 °C and 210 °C and 2 h [44].

2.7. Assessment of Biofuel Quality for Napier Grass, VTC and HTC Chars

Two standards that set quality requirements for biomass as fuels were used to evaluate the properties of Napier grass and the chars: an international standard, ISO17225, "Solid biofuels. Fuel specifications and classes", and the South Korean biomass solid recovered fuel standard (Bio-SRF). Three parts of the ISO 17225 apply for this study, Part 6 "graded non woody pellets" and Part 7 "graded non-woody briquettes" for herbaceous biomass without any thermal pre-treatment, and Part 8 "thermally treated and densified biomass fuels" for biomass submitted to "[...] steam treatment, hydrothermal carbonization and charring, [...] which represent different exposure to, oxygen, steam or water" [28]. The thermal treatments used in this study are defined as mild (temperatures between 200 °C and 300 °C or more for a short holding time) [39,41–43]. The South Korean standard (Bio-SRF) applies to solid recovered fuels produced from waste paper, waste wood and herbaceous or organic wastes (e.g., sewage sludge, manure, and food waste or even grass), and differentiates between pellets and non-pellets [11,29,45]. Other solid recovered fuel or refuse-derived fuel standards were not considered, since they are produced mainly from plastics and other solid waste streams very different to biomass, which are not comparable with herbaceous biomass or thermally treated biomass. The parameters, with their values, from the different standards are summarized in Table 3.

In the scope of this study, the Napier grass was considered to be in the form of pellets and compared to the parts of the standards, EN ISO 17725-6 for herbaceous biomass as pellets, and Bio-SRF for pellets, since the non-pellet part only evaluates 2 parameters: net calorific value and water content [5]. The VTC and HTC chars were compared to the part for thermally treated biomass in EN ISO 17725-8, and with Bio-SRF for pellets [28]. In the results and discussion section, the parameters are grouped together according to (1) the general characteristics of fuels including calorific value, and ash and moisture content, (2) an assessment of the toxicity of the fuel including all the heavy metals (As, Cd, Cr, Ni, Cu, Pb, Zn and Hg) and nitrogen (N) due to the NO_x potential production, and (3) an estimation of the corrosion potential of the fuel, e.g., S and Cl.

		EN ISO17225-6 Non Woody Pellets (2021)			EN ISO17225-7 Non Woody Briquettes (2021)			ISO17225-8 Thermally Treated and Densified Biomass Fuels (2022) ****		South Korean Biomass Solid Recovered Fuels (Bio-SRF)	
Parameter	Unit	Pe	llets	Briquettes		Pellets & Herbaceo	Briquettes us Biomass	Pellet	Non Pellet		
		Class A	Class B	Class A1	Class A2	Class B	Class TA1	Class TA2			
Quality classifications in this study *		High class	Low class	High class	Medium class	Low class	High class	Medium class	When f "complie otherwi complie	ulfilled d″ class, se "not d″ class	
Net calorific value	MJ/kg			≥14.5 **			≥1	≥17	≥12.5	≥12.5	
Ash content	%wt.	≤ 6	≤ 10	≤3	≤ 6	≤ 10	≤ 6	≤12	≤15		
Water content	%wt.**	≤12	≤15	≤12	≤12	≤15	ہ -	≤8	≤10	≤25	
Cl	%wt.	≤ 0.10	≤0.30	<0.10	<0.20	< 0.30	≤ 0.1	≤ 0.2	≤ 0.5		
S	%wt.	≤ 0.2	≤ 0.3	\leq	0.2	≤ 0.3	≤ 0.1	≤ 0.3	≤ 0.6		
N	%wt.	≤1.5	≤2.0	≤	1.5	≤2.0	≤1.5	≤2.5			
As ***	mg/kg	≤ 1	≤1.5	<	<u>≤</u> 1	≤ 1.5	≤2	≤ 4	≤ 0.6		
Hg ***	mg/kg			≤ 0.1							
Cd	mg/kg			≤ 0.5			≤ 0.5	≤ 1	<5		
Cr	mg/kg	<u></u>				≤ 30	≤ 50	≤ 70			
Ni	mg/kg				≤ 10						
Cu	mg/kg			≤ 20			≤ 30	≤ 50			
Pb	mg/kg	<u>≤</u> 10					\leq 30	≤ 100			
Zn	mg/kg	≤100						≤200			

Table 3. Quality classes for herbaceous biomass and thermally treated biomass according to the EN ISO 17225 and Bio-SRF standards.

All units are based on dry matter (DM). * There is another category called "no class" when the characteristics of the biofuel do not correspond with those of any class. ** As received, here, units of dry samples were used, in order to compare the calorific value between Napier grass and chars. *** Not measured in this study due to a lack of analytical instruments in our facilities to measure them. **** The limit values of the mass basis from Annex B, ISO 17225-8 [28], to allow comparisons between feedstock, chars and the Bio-SRF standard.

2.8. Mass Balances, Yields and Element Distribution

The distribution of each element (*n*) between the char and the process water was calculated for the VTC and HTC processes based on the total mass of the element in the products. $X_{n,char}$ (%wt.) is defined through the following equation:

$$X_{n,char} = \frac{m_{n,char}}{(m_{n,char} + m_{n,PW})} \cdot 100$$
(4)

where

 $X_{n,char}$ = mass share of element *n* in the HTC or VTC char (%wt); $m_{n,char}$ = mean mass of element *n* in the HTC or VTC char (mg); $m_{n,PW}$ = mean mass of element *n* in the process water (mg).

The distribution of the elements in the chars were then plotted using JMP 15 from SAS. Additionally, the solid yield (SY), carbon yield (CY) and energy yield (EY) were calculated as follows:

$$SY = \frac{m_{char}}{m_{feedstock}} \tag{5}$$

$$CY = \frac{m_{C,char}}{m_{C,feedstock}} \tag{6}$$

$$EY = \left(\frac{GCV_{char}}{GCV_{feedstock}}\right) \cdot SY \tag{7}$$

where

SY = solid yield (%wt); $m_{char} = \text{mass of char (g)};$ $m_{feedstock} = \text{mass of feedstock (g)};$ CY = carbon yield (%wt); $m_{C,char} = \text{mass of carbon in the char (g)};$ $m_{C,feedstock} = \text{mass of carbon in the feedstock (g)};$ EY = energy yield (%); $GCV_{char} = \text{gross calorific value of char (J/g)};$ $GCV_{feedstok} = \text{gross calorific value of feedstock (J/g)}.$

The difference between VTC and HTC values for GCV, EY and SY (Δ GCV, Δ EY and Δ SY) were calculated relative to the HTC value. Δ GCV was calculated as follows:

$$\Delta GCV = \left(\frac{GCV_{VTC,char} - GCV_{HTC,char}}{GCV_{HTC,char}}\right)$$
(8)

where

 $GCV_{VTC,char}$ = gross calorific value of the VTC char (J/g); $GCV_{HTC,char}$ = gross calorific value of the HTC char (J/g).

 Δ EY and Δ SY were calculated using the same equation, Equation (8), but replacing the GCV with EY or SY, respectively.

3. Results

3.1. Verification of VTC and HTC Reactor Conditions

In order for hydrothermal carbonization reactions to take place in VTC/HTC systems, the feedstock must be exposed to subcritical liquid water, either through submersion in liquid water (HTC), or through water contained within its cells or as a film on its surface (VTC) [24]. To verify that during the HTC process the Napier grass was in physical contact with liquid water and that during the VTC runs the Napier grass was only in contact with water vapor for the two reaction temperatures, we calculated the following for each run: the mass fraction of water in the vapor state (x_v), the solid content (%S_T) in the reactor at the reaction temperature and the changes in the volume fraction of liquid water from the initial (VF_0) to final (VF_w) values as suggested by Ro et al., 2020 [24]. The amount of water in contact with the feedstock is determined according to the physical dimensions of the reactor system as well as the expansion of the liquid water in the system (VF_w/VF_0) and the water distribution between the liquid and vapor phase at the reaction temperature. Based on the results in Table 4, we confirmed that, under the HTC process conditions, the feedstock was always submerged in the liquid water, while the feedstock in the VTC remained suspended above the liquid water for the reactor system used. Over 99% of the water remained in the liquid state during all HTC runs, causing almost no change in S_{T} from the initial value (7.1%), while in the VTC runs at 220 °C, up to 14.5% of the water vaporized into steam, leading $\%S_T$ to increase by 11% (36.9 to 37.7%). According to a review of past HTC and VTC experiments, these are typical ranges found in batch systems [24]. For batch HTC, they found that between 93.1 and 99.5% of the water remained liquid, with %S_T ranging from 1.0 to 19.9%. However, the authors reported that not all experiments labeled as VTC are similar. Both batch as well as semi-batch systems with continuous steam injection have been reported as VTC, resulting in VTC systems with widely varying amounts of water in

the vapor phase, from 1.4% to almost 61%, and $%S_T$ values ranging between 27.6% and 45.0% for VTC systems. The effects of these differences are discussed further in Section 4.1.

Table 4. Water vapor fractions (x_v) , solid content at the beginning (%S₀) and at the maximum temperature (%S_T), the ratio %S_T/%S₀, the volume fraction of the reactor filled by water in its liquid state at the beginning of the process (VF_0) and at the maximum temperature of the process (VF_w), and the ratio of these two factors (VF_w/VF_0) for the different experimental runs in this study (VTC 190, VTC 220, HTC 190 and HTC 220). The values show the mean + the spread.

Run	x_v	%S ₀ (%)	%S _T (%)	%S _T /%S ₀	VF ₀	VFw	VF _w /VF ₀
VTC 190	0.088 + 0.01	33.0 + 0.22	36.9 + 1.00	1.1 + 0.0	0.07 + 0.0	0.07 + 0.01	1.07 + 0.10
VTC 220	0.145 + 0.02	34.1 + 1.18	37.7 + 1.91	1.1 + 0.0	0.07 + 0.0	0.08 + 0.01	1.23 + 0.08
HTC 190	0.005 + 0.00	7.1 + 0.00	7.1 + 0.00	1.0 + 0.0	0.54 + 0.0	0.62 + 0.0	1.15 + 0.0
HTC 220	0.008 + 0.00	7.1 + 0.00	7.1 + 0.00	1.0 + 0.0	0.54 + 0.0	0.64 + 0.0	1.19 + 0.0

3.2. *Comparison of Napier Grass and VTC and HTC Chars to Biofuel Quality Standards* 3.2.1. Net Calorific Value

Comparing the mean net calorific value (NCV) of the Napier grass of 16.3 MJ/kg DM to the biofuel quality standards (Figure 2) shows that the biomass can be classified as a high-quality biofuel (EN ISO17225) and as an approved solid recovered fuel (Bio-SRF). After thermal processing, the NCV of every VTC and HTC char was higher than that of the Napier grass. The highest NCV was 21.5 MJ/kg DM, which was the NCV of HTC chars produced at 220 °C. In general, the NCV was more influenced by the operating temperature in the reactor than by the state of water in the reactor (vapor or liquid); the chars produced at 220 °C achieved higher NCVs than the ones produced at 190 °C did. The NCV after VTC processes increased on average by 11.3% and 18.8% (at 190 °C and 220 °C, respectively) and after HTC it increased on average by 14.7% and 24.25% (at 190 °C and 220 °C, respectively). All chars meet the calorific value limits for high-quality biofuels according to the EN ISO 17225-8 classification and comply with the lower requirements of Bio-SRF.



Figure 2. Comparison of the mean net calorific value of the Napier grass and the different chars produced via vapothermal carbonization (VTC) and hydrothermal carbonization processes (HTC) at 190 °C and 220 °C with the class requirements from EN ISO 17225 and the Bio-SRF minimum requirements. The standard deviation is also shown in the bars.

3.2.2. Ash Content, Sodium and Potassium Content

The ash content in biofuels is relevant to estimating slagging and fouling potential; however, ash composition also plays an important role, especially sodium (Na) and potassium content (K). The alkali index, based on the amount of oxidized forms of Na and K and the calorific value of the fuel, is often used to estimate the ash fouling potential of a fuel in a rapid way [8,41,46,47]. High contents of these elements lead to a decrease in ash melting temperature, which causes bed agglomeration both on the grate and the heat exchanger; it is a precursor for fouling, scaling and corrosion [42,43,47]. During combustion, reactive compounds evaporate, and sodium can form aerosols such as NaCl and Na₂SO₄, which then can condense on the surface of fly ashes, forming agglomerations and leading to slagging [43].

The mean ash content in Napier grass was 5.6%wt. DM, being already relatively high compared to that in woody biomass. In the VTC process, the ash content in the chars increased to 7.5%wt. DM at both temperatures. In contrast, the ash content was reduced via the HTC process (3.2%wt. DM HTC190) (Figure 3). Similar trends were found by Shafie et al. (2018) and by Yeoh et al. (2018) [26,48]. In both processes, there is a loss of solid mass due to its transfer to the liquid and gas phases. In the VTC process, almost all of the mass lost was organic material. In contrast, more than 98% of the ash remained in the solid at both temperatures, so the ash content almost reached the value predicted based on SY, 7.6%wt. In HTC, where the liquid water phase is in direct contact with the biomass, a much higher amount of inorganics leached into the process water; at 190 °C, 62% of the ash was removed, and 67% was removed at 220 °C. These trends were even stronger for the water-soluble compounds Na and K in HTC and correlated with temperature, with removals at 190 °C and 220 °C of 67, 87%wt. and 75, 91%wt., respectively.



Figure 3. Mean ash content (**above**), of sodium (**below left**) and potassium (**below right**), of the Napier grass, and the different chars produced via vapothermal carbonization (VTC) and hydrothermal carbonization processes (HTC) at 190 °C and 220 °C. Ash content is compared to the class requirements from EN ISO 17225 parts 6 and 8 and the limit values of the South Korean biomass solid recovered fuel standard (Bio-SRF). The standard deviation/spread is represented by the vertical lines in each bar.

A comparison of the ash content with the standard limits (Figure 3) shows that the original biomass attained a high-quality rating according to the EN ISO 17725-6 [5]. The HTC chars achieved a similar rating, while VTC chars only reached the low-quality rating. Despite the accumulation of ashes in the VTC chars, they were able to fulfill the requirements of the Bio-SRF, just as HTC chars and Napier grass were.

The fouling potential of fuel has been found to be correlated with the alkali index (AI) based on the mass of alkali metal oxides ($K_2O + Na_2O$) in the ash [8,41,45,46]. Based on estimates of the AI, HTC may reduce the fouling potential significantly since the leaching trends were even stronger for the water-soluble compounds Na and K in HTC than those for the ash and correlated with temperature, with removals at 190 °C and 220 °C of 67, 87%wt. and 75, 91%wt., respectively. A comparison of the values of the AI estimated for the Napier grass (0.48 kg/GJ), VTC chars (0.58–0.66 kg/GJ) and HTC chars (0.08–0.18 kg/GJ) from their Na and K content with common values for wheat straw (1.1 kg/GJ) and bituminous coal (0.07 kg/GJ) [42] show that HTC reduces the alkali index up to six times (0.08 kg/GJ vs. 0.48 kg/GJ). This reduction was also shown in Saha et al., 2023 [49]. These results conclude that HTC chars have a low fouling occurrence (AI < 0.34 kg/GJ) and in many cases a low fouling probability (AI < 0.17 kg/GJ).

3.2.3. Total Chlorine and Sulfur Content

Total chlorine and sulfur content are important for fuel quality since they are the main drivers of corrosion in combustion systems. The total mean Cl content in the Napier grass was 1.09%wt. DM, which is more than twice (Bio-SRF) to three times (EN ISO 17725-6) higher than all the limit values (Figure 4). In contrast, the value for sulfur averaged at 0.20%wt. DM, which is right at the limit of the high-quality range for herbaceous biomass as a biofuel (EN ISO 17225-6). Due to the heterogeneity of this herbaceous biomass, treatment may be necessary to consistently meet this limit.



Figure 4. Total chlorine (**left**) and total sulfur (**right**) content of the Napier grass, the different chars produced via vapothermal carbonization (VTC) and hydrothermal carbonization processes (HTC) at 190 °C and 220 °C, and their comparison with the requirements from EN ISO 17225 parts 6 and 8 and the South Korean biomass solid recovered fuel standard (Bio-SRF).

Thermal treatment produced highly contrasting results for Cl. In VTC chars, the Cl mass fraction was higher than that in Napier grass (1.31%wt. DM compared to 1.09%wt. DM), so it remained well above all standard limits (both EN ISO 17225-8 and Bio-SRF). The HTC chars, however, show the opposite pattern: a reduction of more than 80% in the Cl content, probably due to dissolution into the water. Nevertheless, the mass fractions remained high, putting the HTC chars into the low-quality class of thermally treated biofuel (EN ISO 17725-8). The Bio-SRF regulations were fulfilled by each HTC char. As regards to sulfur content, VTC and HTC chars all have lower mass fractions than the original biomass does; however, as thermally treated grass, they are classified as low-quality biofuels, due to the more stringent limit values. Bio-SRF requirements were fulfilled for Napier grass and VTC and HTC chars at both temperature conditions.

3.2.4. Total Nitrogen and Heavy Metals Content

Nitrogen and heavy metals content in biofuels can lead to pollutants that must be removed from the flue gas. Nonetheless, total nitrogen content is not regulated by the Bio-SRF standard despite its importance for estimating the NOx production from combustion. Comparison to the EN ISO 17225 limits in Figure 5 shows that Napier grass with a total N content of 0.67%wt. DM, as well as all VTC and HTC chars can be classified as high-quality biofuel materials, even though the chars had higher N contents than the Napier grass. Similar trends for N in HTC chars were seen in Hansen et al. 2022, where the N content increased after HTC of lawn cuttings at temperatures of: 180 °C, 210 °C, 240 °C and 270 °C. At higher temperatures, the N content in the chars increased [44].

Regulated heavy metals in the EN ISO 17225 include Hg, As, Cd, Cu, Cr, Ni, Pb and Zn, while the Bio-SRF pellet standard includes As, Cd, Cr, Pb. In this study Hg and As were not measured. Napier grass and all chars (VTC and HTC) did not have any problem achieving the high-quality requirements for the following heavy metals: Cd, Cr, Ni, and Pb. In contrast, the values for Cu content in the Napier grass and the chars showed a large variation in the individual values. For Napier grass, the values ranged from a minimum of 18.5 to a maximum of 44.5 mg/kg DM, resulting in a mean above the recommended class value of 20 mg/kg DM according to the EN ISO 17725-6. Due to the heterogeneity of the Napier grass, there is a high uncertainty on whether it can be classified as high-quality biofuel. The VTC 220 and HTC 190 chars did not reach the high-quality class requirements for Cu, however, they can be classified as low-quality thermally treated biofuels. The other chars produced (VTC 190 and HTC 220) were not able to be classified in any class. Copper values should be maintain low since Cu is considered a precursor for dioxins and furans formation [50,51]. As to Zn content, Napier grass and HTC chars can be classified as high-quality biofuels, while VTC chars values were up to 10 times higher than the limit values for low-quality thermally treated biofuels.

3.3. Summary of the Quality Classification

The Napier grass biofuel quality is low due to its high ash, Cl and Cu contents. The biofuel characteristics of the four chars produced by carbonizing the Napier grass using VTC and HTC processes at the two temperatures, 190 °C and 220 °C, are summarized in Figure 6. Based on the visual summary showing the compliance of the Napier grass and the four chars with the quality classes in EN ISO 17225 and the Bio-SRF, it can be concluded that 1. all five biofuels meet the requirements regarding the minimum heating value and that the NCV was improved after both carbonization processes; 2. VTC chars had problems complying with the ash limit values from EN ISO 17725, while for the other samples, ash did not present any problem, and the ash content decreased with HTC processes; 4. the chlorine content was higher than the limit values of both regulations for Napier grass and in VTC chars in that Cl content was reduced via HTC processes, but in VTC chars, Cl content increased, presenting even higher values than those in Napier grass; 5. sulfur content decreases in all chars but, nevertheless, limit values for thermally treated biomass

are stricter than those for raw biomass, so the quality class of chars was lower than that for Napier grass according to EN ISO 17725; 6. the N content increased in all VTC and HTC chars, but not at a high enough level to pose a problem in terms of limit values; 7. most heavy metals were under detection limit values in all streams, while Cu content was higher than the permissible value in all streams except VTC 220 and HTC 190, and Zn surpassed the allowance in the VTC chars.



Figure 5. Comparison of the mean total nitrogen content (%wt. DM) with heavy metal content (mg/kg DM) and their corresponding standard deviations for the Napier grass and the different chars produced via vapothermal carbonization (VTC) and hydrothermal carbonization processes (HTC) at 190 °C and 220 °C with the class requirements from the EN ISO 17225 parts 6 and 8 and the limit values from the South Korean biomass solid recovered fuel standard (Bio-SRF). * Notes: SRF-Bio limit value of Cd = 5 mg/kg DM and of Pb = 100 mg/kg DM; Ni was under the detection limit value for all biofuels analyzed.

	Net calorific value		Ash content		Cl content		S content	
	EN ISO 17725	Bio SRF	EN ISO 17725	Bio SRF	EN ISO 17725	Bio SRF	EN ISO 17725	Bio SRF
Napier Grass								
VTC 190								
VTC 220								
HTC 190								
HTC 220								
	Nitrogen content		Chromium, Nickel, Cadmium, Lead content		Copper content		Zinc content	
	EN ISO 17725	Bio SRF	EN ISO 17725	Bio SRF	EN ISO 17725	Bio SRF	EN ISO 17725	Bio SRF
Napier Grass								
VTC 190								
VTC 220								
HTC 190								
HTC								

Figure 6. Classification of Napier grass, vapothermal carbonization chars, VTC, and hydrothermal carbonization chars, HTC, at 190 °C and 220 °C as solid biofuel pellets according to EN ISO 17725 and as solid recovered fuels according to the South Korean biomass solid recovered fuel; standards. Green = high quality; orange = low quality; red = no compliance/no class; grey = no threshold or limit value.

4. Discussion

4.1. Influence of Process Type and Process Conditions on Char Production

There are other important parameters that can be utilized to assess and compare the VTC and HTC processes and their chars, besides those that show compliance with regulated parameters in standards. Solid yield (SY), carbon yield (CY) and energy yield (EY) do not have any standard limit values or recommended values. However, they are important process parameters that can be used by decision-makers to choose between VTC and HTC processes, especially EY, which describes the percentage of the original energy in the feedstock that is available in the char. These values are interrelated but can show different trends. An overview of the results for whole Napier grass at the two temperatures and processes is shown in Figure 7. The variability between the replicate runs was probably due to the heterogeneity of the whole Napier grass feedstock, containing both leaf and stem. The difference in their composition was shown previously in Table 1.



Figure 7. Average solid yield (green), energy yield (yellow) and carbon yield (gray) from VTC and HTC runs under the two different temperature conditions. The bars represent the spread of the two different runs.

The results show that SY was higher for VTC than HTC at both temperatures. While the SYs for VTC 190 and VTC 220 were in a similar range, for HTC, the trend showed that at higher temperatures, the SY decreased. Past studies of HTC have shown the same dependency between SY and temperature [52–54].

Carbon yield was higher in VTC chars than in HTC chars, although carbon content in the HTC chars was higher than that in VTC chars, as reported in past studies [19,25]. This can be explained by the higher carbon losses to the process water in HTC processes than in those in VTC processes, due to the dissolution of organics rich in carbon [21]. Funke et al. found that in HTC processes, 30% of carbon was lost to the process water compared to 18% being lost in VTC processes for straw [19]. Temperature showed a positive correlation, with respect to CY for VTC; the opposite behavior was seen for HTC conditions.

Energy yield shows the same trend as carbon yield. This parameter depends on SY and GCV, which is dependent on carbon content. The higher the carbon content, the higher the GCV [53]. Although the GCVs of the HTC chars were higher than the ones of the VTC chars, the high mass loss reflected in the low SY was the determining factor for the low EY in HTC. For the VTC processes, since the SY was not so different among the two temperatures, the determining factor was the GCV, and indirectly their carbon content. The higher temperatures favor carbonization [19], and therefore at 220 °C, the carbon content was higher than that at 190 °C, resulting in a higher EY.

For a better comparison of these parameters, we classified them using five arbitrary criteria: (1) very high ($\uparrow\uparrow$ —when the yield is higher or equal than 85%); (2) high (\uparrow —when the yield is lower than 85% but higher or equal than 75%); (3) medium (\rightarrow —when the yield is lower than 75% but higher or equal than 65%); (4) low (\downarrow —when the yield lower than 65% but higher or equal than 65%); (4) low (\downarrow —when the yield lower than 65% but higher or equal than 65%); (4) low (\downarrow —when the yield lower than 65% but higher or equal than 55%); and very low ($\downarrow\downarrow$ —when the yield is lower than 55%). This is visualized in Figure 8. According to these criteria, VTC 220 achieved the best results: a high SY, very high CY and very high EY. HTC 220 had the lowest yields: a very low SY, a medium CY and a medium EY (despite its high NCV). Both HTC 190 and VTC 190 conditions produced high CYs and EYs. However, VTC190 achieved a higher SY than HTC190 did.

	Solid Yield	Carbon Yield	Energy yield
VTC 190	1	1	↑
VTC 220	1	\uparrow \uparrow	$\uparrow \uparrow$
HTC 190	\rightarrow	1	↑
HTC 220	\downarrow \downarrow	\rightarrow	\rightarrow

Figure 8. Classification of vapothermal carbonization (VTC) runs and hydrothermal carbonization (HTC) runs performed at 190 °C and 220 °C according to their solid yield, carbon yield and energy yield. Double arrow up = very high; arrow up = high; horizontal arrow = medium; arrow down = low; and double arrow down = very low.

Comparisons in the literature between chars from HTC and VTC for use as fuels have produced mixed trends in yields [19,26,48]. The trends in SY, GCV and EY from the literature and this study are visualized in Figure 9 as the difference between VTC and HTC values relative to HTC. The CY values could not be compared due to a lack of information from the literature. Funke et al. found trends for digestate and straw at 230 °C and 6 h that were similar to our results, with VTC producing a higher SY and EY than those produced via HTC for both feedstocks (see Label "VTC > HTC" in Figure 9). In contrast, Shafie et al. (2018) and Yeoh et al. (2018) reported mostly lower SYs from VTC than those from HTC (220 °C, 1 h) for the six feedstocks studied (HTC > VTC) [26,48]. However, for three feedstocks, Yeoh et al. (2018) found that this trend was reversed for the EY, with slightly higher values in VTC, similar to the results in this study [26]. A closer examination of the VTC/HTC conditions using the parameters calculated in Section 3.1 shows that the experiments carried out by Funke et al. (2013) were very similar to those in this study, i.e., batch VTC and batch HTC [19]. In contrast, the VTC process conditions for Shafie et al. (2018) were semi-batch using steam injection with a very high amount of water in the vapor phase (estimated at 25–61%) and with condensate separation, while no information was available to estimate the conditions in Yeoh et al. (2018) [26,48]. Therefore, we can conclude that for batch systems, VTC produced higher a SY and EY than those produced via HTC. In order to develop a larger basis for other types of VTC/HTC systems, further studies with better reporting of process conditions are still needed to draw stronger conclusions.

4.2. Distribution of Elements That Affect Fuel Quality between the Char and the Process Water

In this section, the distribution of elements that affect fuel quality between the char and the process water is discussed. These elements include those regulated in EN ISO17225 and in the Bio-SRF, i.e., Cl and S, due to their corrosion potential risk, N, to prevent NO_x emissions, and Cd, Cr, Ni, Pb, Zn and Cu, to avoid heavy metal and other pollutant emissions, as well as some non-regulated elements with important fuel properties: Na and K, with relevance for fouling and slagging potential, and P, which is considered a critical material with recovery potential. In order to evaluate the trends among the distribution for the process types, VTC/HTC, and temperatures, 190/220 °C, the distribution between the char and process water in the VTC and HTC processes was classified into five different groups based on the mass percentage retained in the char, $X_{n,char}$. These groups include the following: (1) All_CHAR (dark gray)—for $X_{n,char} \ge 90\%$, (2) Most_CHAR (light gray)—for $60\% \ge X_{n,char} < 90\%$, (3) 50_50 (green)—for $40\% \ge X_{n,char} < 60\%$, (4) Most_PW (blue)—for $10\% \ge X_{n,char} < 40\%$ and (5) All_PW (purple) for $X_{n,char} < 10\%$. The results are shown in Figure 10.



Figure 9. The difference between VTC and HTC values for GCV, EY and SY relative to HTC (Δ GCV, Δ EY and Δ SY) for eight feedstocks, and their respective HTC/VTC temperatures, from the literature and from the Napier grass in this study. Sources: 1. Yeoh et al., 2018 [26]; 2. Shafie et al., 2018 [48]; 3. Funke et al., 2013 [19].



Figure 10. Distribution of main elements used to characterize the quality of chars as a fuel. Squares represent HTC chars, circles represent VTC chars, the blue color represents chars produced at 190 °C and black represents chars at 220 °C. PW = process water. The shaded areas represent the different classifications: dark grey = All_CHAR; light grey = Most_CHAR; green = 50_50; blue = Most_PW; purple = All_PW. The mass fractions of Ni were under detection limit values for all. The Cr values existed only for HTC 220 and therefore a comparison was not possible, perhaps due to the leaching of the reactor.

The element precursors of corrosion Cl and S tend to accumulate in the solid products of VTC processes. Cl and S are found in the classes All_CHAR or Most_Char for both

temperatures. In contrast, the trend goes in the opposite direction for HTC; S and Cl are found more in the process water. Reza et al. (2013) reported the same tendency for S in HTC processes with various feedstocks including miscanthus and switch grass [55]. Temperature had a clear trend for Cl in both VTC and HTC processes; the higher the temperature was, the more Cl was leached into the PW. While this trend was true for the S behavior in VTC chars, the reverse was seen in HTC. Overall, in order to remove elements with corrosion potential, the HTC process is to be preferred above the VTC process.

The elements that are regulated due to their production of emissions include the heavy metals Cd, Cr, Cu, Ni, Pb and Zn, and, due to the NOx formation during combustion, N. The heavy metals accumulate (mostly or all) in the char for both VTC and HTC processes, except for Zn, which classifies as 50_50. The Cd, Cu and Pb distribution in the HTC process was not influenced by temperature. A similar pattern was published by Reza et al. (2013), where Pb mass distribution remained constant, regardless of the HTC temperature conditions for the different feedstocks, miscanthus, switch grass and rice hull [56]. Contrary to HTC trends, temperature had an effect on Cd and Pb for VTC chars [56]. The temperature influence was similar in both processes for Cu and Zn, and no effect was seen on Cu distribution, while Zn was affected by temperature in both chars. At the lower temperature, the metals tended to accumulate in the VTC chars. This accumulation with temperature in HTC chars was seen for Zn in the study of Liu et al. (2018) [55]. No conclusions can be drawn for Ni and Cr. The values for Ni were under the detection limit for all samples (Napier grass; all chars and all of the process water). The mass fractions of Cr were also below the detection limit for the feedstock and all runs except HTC 220. This was perhaps due to leaching from the stainless-steel reactor.

Nitrogen was mostly found in the VTC chars and was reduced to almost half when HTC processes were run. These values for HTC are similar to those found in the study of Wang et al. (2019); when sewage sludge was submitted to HTC, only 30% of the nitrogen was left in the char [57]. Alhnidi et al. (2020) discovered nitrogen recovery in HTC chars of between 23 and 47% for different glucose nutrient solutions, while Idowu et al. (2017), when carbonizing food waste, found that between 45 and 82% of N was distributed in the HTC char at 225 °C [58,59]. This means that, depending on the temperature and feedstock (or more exactly, the nitrogen speciation), nitrogen can be distributed from Most_PW to Most_Char for HTC processes. In this study, the HTC process produced chars with less N mass than that produced by VTC chars; therefore, the combustion of HTC chars would emit less NO_x emissions than the combustion of VTC chars would. Further investigations with different feedstocks and nitrogen speciation analysis are needed to find better trends for a better VTC/HTC comparison.

The trends for elements relevant for the determination of fouling and slagging potential (Na and K) were similar to those from Cl. VTC processes accumulated these elements in their chars, while in HTC processes, K and Na were located in the PW (grouped as Most_PW and as All_PW). Similar trends for K were found in Funke et al. (2015) while studying the fate of nutrients from straw and corn digestate submitted to HTC at 220 °C and by Reza et al. (2013), where only around 20% of K was left in the char after HTC at 200, 230 and 260 °C in the four different feedstocks [56,60]. The trends followed by K and Na in the study of Idowu et al. (2017), where food waste was submitted to HTC in order to recover nutrients at 225, 250 and 275 °C, were similar to those in this study [59]. Idowu et al. (2017) found that between 0% and 30% of Na stayed in the HTC char and that K followed with similar behavior, with a 32% to 1% mass of K found in the char. In this matter, the HTC process is also to be preferred above the VTC process to avoid fouling and slagging (Na and K tend to leach into the process water) [59]. Temperature also plays a role in Na and K distribution. In both processes, the higher the temperature, the more the elements are leached out of the char. The same was concluded for HTC processes by Reza et al., 2013, and by Wang et al., 2019 [56,57].

Phosphorus, defined as a critical material, was mainly distributed in the solid phase during the VTC process; however, most of the P was found in the process water (PW) for

HTC. Up to 40% of the phosphorus in the PW of HTC was phosphate (PO4⁻³). Similar results were reported in Reza et al. (2013), where only 20% of the initial P was found in the HTC char of switch grass after HTC was performed at 230 °C [56].

In general, VTC trends could not be compared to those in the literature since the few available studies did not report enough information about element distribution or data with which to calculate the distribution.

5. Conclusions

Napier grass is a fast-growing crop that can be used as a biofuel because it has a good net calorific value of around 16.3 MJ/kg DM. Nevertheless, since it is a herbaceous biomass, it often has a high ash content (mean value of 5.6%wt.), and can have a high mass fraction of chlorine (1.09% wt. DM), which can lead to fouling, slagging and high-temperature corrosion problems when combusting. With the set of experiments performed in this study, it could be shown that both vapothermal carbonization (VTC) and hydrothermal carbonization (HTC) processes brought advantages in improving the Napier grass biofuel characteristics. Both VTC and HTC increased the calorific values. Furthermore, HTC decreased ash, potassium, chlorine, sulfur and sodium contents, reducing the risk of corrosion, fouling and slagging. The HTC chars can be used as solid recovered fuels according to the South Korean standard (Bio-SRF). According to EN ISO 17225 for biofuels, HTC chars can be classified as a high-quality fuel based on the net calorific value, ash, N, Cr, Cd, Ni, Pb, and Zn contents, but as a low-quality biofuel based on Cl and S contents despite its lower mass fraction compared to that from Napier grass. Problems in complying with limit values of Cu content were found in all samples, except for HTC190 and VTC220 chars. Although HTC produces chars with higher fuel quality, VTC offers higher solid, energy and carbon yields. Comparing process conditions for just HTC, it was seen that HTC runs at low temperatures had higher yields (solid, carbon and energy) than at higher temperatures, and, quality-wise, these chars were similar to the high-temperature HTC chars. For mono-combustion, HTC 190 processes are recommended. For co-combustion with other high-quality fuels, the low fuel quality of VTC char may not be relevant and the VTC process may be preferred due to its higher yields. Further studies on co-combustion and economics are recommended to advance the science of these processes and for actual field applications in the future.

Supplementary Materials: The following supporting information can be downloaded at https://www. mdpi.com/article/10.3390/agronomy13122881/s1. Figure S1: Fiber analysis values for each sample from Napier grass as a whole plant (green) and only its leaves (yellow) or stems (brown). Table S1: Analytical methods for the analysis of Napier grass, VTC and HTC chars, and process water for each run. Table S2: Analytical methods according to ISO 17225 for biomass and thermally treated biomass.

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