Upgrading the Organic Fraction of Municipal Solid Waste by Low Temperature Hydrothermal Processes

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Abstract: In comparison to lignocellulosic biomass, which is suitable for thermo-chemical valorization, the organic fraction of municipal solid waste (OFMSW) is mainly treated via composting or anaerobic digestion (AD). An efficient utilization of OFMSW is difficult due to variations in its composition. Based on the characteristics of OFMSW, hydrothermal treatment (HTT) experiments at temperatures < 200 °C as an alternative OFMSW-processing were evaluated in this study. The raw OFMSW was characterized with a dry matter (DM)-based organic dry matter (oDM) content of 77.88 ± 1.37 %$_{DM}$ and a higher heating value (HHV) of $15{,}417 \pm 1258$ J/g$_{DM}$. Through HTT at 150, 170 and 185 °C, the oDM contents as well as H/C and O/C ratios were lowered while the HHV increased up to $16{,}716 \pm 257$ J/g$_{DM}$. HTT led to improved fuel properties concerning ash melting, corrosion stress and emission behavior. Negative consequences of the HTT process were higher contents of ash in the biochar as well as accumulated heavy metals. In the sense of a bioeconomy, it could be beneficial to first convert raw OFMSW into CH_4 through AD followed by HTT of the AD-digestate for the generation of solid fuels and liquid products. This could increase the overall utilization efficiency of OFMSW.

Keywords: biowaste; OFMSW; municipal waste; hydrothermal carbonization; waste treatment; biomass upgrading; biochar; biofuels; thermochemical valorization; anaerobic digestion

1. Introduction

In Germany, the Recycling Law [1] is the key element for the waste management industry and it implements EU-Directives into national law. The main research subject of this study is the separately collected organic fraction of municipal solid waste (OFMSW). Separately collected OFMSW (biowaste bin) is categorized as a municipal waste mainly originating from households. In waste statistics, OFMSW is usually assigned to the category of separately collected bio- and green waste and thus represents a partial amount of this category [2,3]. However, the residual waste bin often contains biogenic ingredients that could have been collected via biowaste bin. According to the Ordinance on the List of Waste [4], OFMSW is classified with the waste code 20 03 01 and the German Biowaste Ordinance [5] regulates source, treatment and utilization of residues of animal and plant-based origin. According to the legal definition, OFMSW as used in this study consists of organic residues such as food or green waste but also contains organic or inorganic

impurities. In comparison to lignocellulosic biomass, the composition of OFMSW is influenced by various parameters such as seasons or collection schemes. Composting has been the dominating method to treat OFMSW in Germany, but there is a growing trend towards utilization via anaerobic digestion (AD). Combining energy recovery by generating biogas together with the usage of the digestate is considered a more environmentally friendly approach [6,7]. Based on the material properties of OFMSW [8,9], hydrothermal treatment (HTT) processes could be an alternative to composting and AD.

Hydrothermal carbonization (HTC) was developed by Franz Bergius at the beginning of the 20th century to imitate the natural coalification process. Due to the growing utilization of lignite as a fuel and the expensive and complex extraction processes, he wanted to develop a more innovative way to produce coal [10]. A suspension of biomass and water is heated in a pressure-tight system for up to 8 h. Temperatures of up to 280 °C and autogenous pressures between 2000 and 10,000 kPa can be reached [11,12]. This thermochemical conversion process is mainly used for lignocellulosic biomass, which consists primarily of cellulose, hemicellulose, lignin and other extractives [13,14]. However, HTC processes are not exclusively suitable for pure lignocellulosic substrates [10]. In contrast to other conversion processes and especially in comparison to combustion processes, water is essential in HTC. Therefore, HTC processes are suitable for wet biomass. In general, substrates with high levels of lignification need higher temperatures to reach an appropriate level of carbonization [15]. Next to the solid products (biochars) in the form of biomass carbonates, process gases and liquids are produced. Among other acids, the latter contains aldehydes, phenols, and benzenes [16–19].

In contrast to HTC, HTT as applied in this study is defined by lower temperature- and pressure levels. This method resembles a gentle treatment with low carbonization rates. Previous studies with similar experimental setups regarding HTT temperatures have already shown that temperatures below 200 °C affect fuel properties [20,21]. Next to the most influential process parameters, such as temperature levels, a major challenge in HTC is the substrate composition. The proportion of inorganic and lignocellulosic components and the share of carbohydrates, lipids or proteins strongly impacts HTC and its products [16]. Lipids and proteins especially influence HTC negatively. Through higher N contents, more organic compounds accumulate in the process water, leading to a lower level of carbonization [22]. In general, biowaste is an energy-rich substrate and yet the processing is expensive [23]. Biowaste, with its heterogeneous and fluctuating composition as well as with its higher N contents [8], is difficult to treat in HTC. To understand HTC processes in detail, substrates with a high level of homogeneity serve best. From a practical perspective, complex materials such as OFMSW have a higher relevance. Untreated OFMSW, different green wastes and digestates, as well as the resulting HTC products were analyzed within another study [24]. While the raw OFMSW reached dry matter (DM) contents of $35.9 \pm 7.9\ \%_{\text{fresh mass (FM)}}$, an organic dry matter (oDM) content of $68.4\ \%_{\text{DM}}$ was measured after HTC starting from initial $76.4\ \%_{\text{DM}}$. The remaining DM (mass losses) was characterized by an increased C content ($44\ \%_{\text{DM}}$ compared to $41\ \%_{\text{DM}}$) and a declined O content ($18\ \%_{\text{DM}}$ compared to $29\ \%_{\text{DM}}$). The concentrations for H and N declined from 4.8 to $4.5\ \%_{\text{DM}}$ and from 1.8 to $1.6\ \%_{\text{DM}}$, respectively. The lower heating value (LHV) was increased by 0.7 MJ and reached $17.4\ \text{MJ/kg}_{\text{DM}}$. The experiments have shown that HTC can be suitable for OFMSW upgrading, leading to increased higher heating values (HHV). The utilization of OFMSW offers the potential for optimization, and further treatment approaches such as HTT, which has not been investigated in depth, are becoming attractive. Thus, the determination of the effects of different low-temperature HTT variants (below 200 °C) on the physico-chemical characteristics of OFMSW (especially with regard to the elemental composition) was the main objective of this study. Based on untreated OFMSW samples, the potential benefits of hydrothermally treated OFMSW materials and their behavior in combustion and AD processes are discussed. The chosen temperatures for HTT experiments were lower than the typical HTC temperatures, which is why it was called HTT. A secondary objective was to compare different HTT temperatures in order to determine optimum conditions with a balance between energy input and upgrading success.

2. Materials and Methods

All analytic procedures were performed at the laboratory of the University of Applied Sciences Rottenburg following VDI 4630 [25] and corresponding standards.

2.1. OFMSW Sample, Dry Matter, Processing and Hydrothermal Treatment

As a raw material used for HTT, untreated OFMSW was chosen and collected at a full-scale thermophilic plug-flow bio-waste digestion plant in southern Germany. On-site, the untreated OFMSW (approximately 10 t_{FM}) was stored as a heap in a closed hall for no longer than 24 h. The collection was subdivided into 12 equal parts, providing the same amount of single samples with a minimum volume of 0.5 L. Afterwards, all single samples were merged to one bulk sample with a total FM of 10.5 kg and processed further within 2 h after collection. After processing (sorting and drying), the sample was stored in airtight buckets as DM until the experiments were carried out. For experiments and chemical characterization, representative amounts were taken from the bulk sample. All sampling procedures were carried out according to the German Biowaste Ordinance [5,26] and in accordance with VDI 4630 [25]. The FM of the untreated OFMSW bulk sample was manually sorted into different waste types to determine the DM content of each component, which was not relevant for this study. Afterwards, the remaining DM was re-combined and coarse impurities such as stones, metal, glass, plastics were removed. By using a cutting mill (Pulverisette 19, Fritsch, Idar-Oberstein, Germany), particle sizes of approximately 1 mm were obtained. The crushed DM of OFMSW was used as the final sample [25] for laboratory analyzes and HTT experiments. DM was determined according to the German Biowaste Ordinance [5] through drying for a minimum of 24 h at $103 \pm 2\,^\circ\mathrm{C}$ in a drying oven (UNP 700, Memmert, Schwabach, Germany) until a constant weight was reached [27].

To take into account the fact that OFMSW is inhomogeneous, the HTT was carried out in triplicate for each temperature level using a floor stand Parr reactor (Series 4530, Parr Instrument Company, Moline, IL, USA) with a 1000 W aluminum heater. In all test series, the 2000 mL reaction vessel was filled with DM of OFMSW and distilled water (DW) according to Table 1. The HTT experiments were conducted as batch processes. Thus, the reactor contained a mixture of solid (OFMSW), liquid (DW) and gaseous (ambient air) components. A twin-propeller stirrer was used for continuous mixing. The maximum pressure during HTT was between approximately 5000 hPa ($150\,^\circ\mathrm{C}$) and 12,000 hPa ($185\,^\circ\mathrm{C}$).

Before starting HTT experiments, the final sample of OFMSW was homogenized to compensate for the impact of storage. After HTT, the solid phase (biochar) was rinsed with DW, mechanically pressed in a filter sheet and prepared as DM [27]. The liquids (process water) were not analyzed. For all further analyzes of the HTT OFMSW products, representative amounts were taken. The temperature-dependent mass loss of the solids caused by HTT was determined by weighing educts and products.

2.2. Organic Dry Matter

For all solids, oDM was determined [28] at least in triplicate by using approximately 1 g_{DM} in a ceramic crucible by a muffle furnace (AAF 1100, Carbolite, Neuhausen, Germany). The method according to the German Biowaste Ordinance [5,29] differs from the procedure in this study [28] regarding temperature, heating rate and retention time. It was chosen due to the availability of a pre-programmed automatic furnace.

Table 1. Experimental setup for the hydrothermal treatment (HTT) of the organic fraction of municipal solid waste (OFMSW) based on dry matter (DM) together with distilled water (DW) including heating and cooling rates (Ramp).

HTT Variant	Feedstock	Heating Program	Output	Replicates
150 °C	OFMSW: 140 g_{DM} DW: 1.4 L	Ramp 40–150 °C: 2.7 °C/min Hold: 5 min Ramp 150–40 °C: −4.8 °C/min Mixing: 200 rpm	Solids	3
170 °C	OFMSW: 140 g_{DM} DW: 1.4 L	Ramp 40–170 °C: 3.8 °C/min Hold: 5 min Ramp 170–40 °C: −3.9 °C/min Mixing: 200 rpm	Solids	3
185 °C	OFMSW: 140 g_{DM} DW: 1.4 L	Ramp 40–185 °C: 3.8 °C/min Hold: 5 min Ramp 185–40 °C: −3.6 °C/min Mixing: 200 rpm	Solids	3

2.3. C, H, N, S, O and Stoichiometric CH_4 Potentials

C, H and N were determined by an elemental analyzer (vario MACRO cube, elementar, Langenselbold, Germany) in four replicates per sample based on DM [30]. S was not measured simultaneously due to the measurement accuracy of C, H, and N. Instead, inductively coupled plasma-optical emission spectroscopy (ICP-OES) results for S were used. O was calculated as a difference between 100°% and the contents of C, H, N, S and ash. Each sample was pressed into a zinc foil coated tablet. For raw OFMSW, 40 mg_{DM} per sample were analyzed without combustion additives. All HTT OFMSW variants (20 mg_{DM} per sample) were incinerated with WO_3 at a mixing ratio of 1:1 to ensure a sufficient O gradient for complete combustion. Based on the elemental composition, stoichiometric CH_4 yields were calculated according to Equation (1) [31,32].

$$C_nH_aO_bN_cS_d + \left(n - \frac{a}{4} - \frac{b}{2} + \frac{3}{4}c + \frac{d}{2}\right)H_2O$$
$$\rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3}{8}c - \frac{d}{4}\right)CO_2 + \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3}{8}c - \frac{d}{4}\right)CH_4 + cNH_3 + dH_2S \tag{1}$$
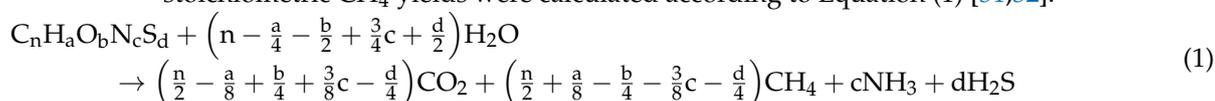
To display the process of HTT in the van Krevelen diagram, H/C and O/C ratios were converted to mmol/g using molar amounts for C (12 g/mol), H (1 g/mol) and O (16 g/mol).

2.4. Calorific Analysis, Cl and Ash Melting Behavior

The HHV was determined with approximately 1 g_{DM} per sample at a constant volume in at least quadruplicate for each variant with an automated isoperibol calorimeter (C6000, IKA-Werke, Stauffen, Germany). The LHV was calculated at a constant volume with the H content of the elemental analysis, according to Equation (2) [33].

$$LHV_{DM} = HHV_{DM} - (206.0 \times H_{DM}) \tag{2}$$

where LHV_{DM} (J/g) is the lower heating value, HHV_{DM} (J/g) is the higher heating value and H_{DM} (%) is the H content of the sample.

Before the experiment, 5 mL of water were added to the calorimeter bomb for subsequent chloride determination with the same repetition number as the HHV experiments. The residual solution of the HHV determination was analyzed with an ion chromatograph (833 Basic IC plus, Methrom, Filderstadt, Germany) equipped with a separation column (Metrosep A Supp—250/4.0, Methrom, Filderstadt, Germany). Based on the results for chloride, Cl contents were calculated according to Equation (3) and subsequently converted to mg/kg_{DM} [34].

$$Cl_{DM} = \frac{(c_{chloride} - c_{chloride\ blank}) \times V}{m_{sample}} \times 100 \tag{3}$$

where Cl_{DM} (%) is the Cl content, $c_{chloride}$ (mg/L) is the chloride concentration, $c_{chloride\ blank}$ (mg/L) is the chloride concentration of the blank, V is the volume (L) and m_{sample} (mg) is the mass of the corresponding sample.

The ash melting behavior was measured for untreated OFMSW in duplicate [35]. Therefore, ash of OFMSW was prepared [28] and combined with C_2H_5OH (96%). The mixture was milled in a mortar and pressed into a cylinder for measurement with a hot stage microscope (EM201/Ofen 1600/80, Hesse Instruments, Osterode am Harz, Germany). The influence of HTT (adjusting element ratios) on the ash melting behavior was discussed based on the results of ICP-OES measurements and based on literature references on elements relevant for the formation of ash and its behavior.

To cross-check the measured values, the ash melting behavior of untreated and HTT OFMSW was additionally calculated [36] based on the results of the ICP-OES analyzes for K, Ca and Mg according to Equation (4) (deformation temperature (DT)) and Equation (5) (flow temperature (FT)). Both equations are typically used for lignocellulose. However, literature references on the impact of specific single trace elements (TE) or TE ratios to the ash melting behavior are inconsistent. Therefore, all calculations were necessary to identify and discuss the general applicability of Equations (4) and (5) for OFMSW.

$$DT = 1172 - 53.9\,K + 252.7\,Ca - 788.4\,Mg \tag{4}$$

$$FT = 1369 - 43.4\,K + 192.7\,Ca - 698\,Mg \tag{5}$$

where DT is the deformation temperature (°C) and FT is the flow temperature (°C). Both DT and FT were calculated based on the concentrations for K, Ca and Mg ($\%_{DM}$).

2.5. Trace Elements

TE were measured four times for untreated OFMSW (one sample with four repetitions) and six times for each HTT OFMSW sample at 150, 170 and 185 °C via ICP-OES [37] after digestion in aqua regia [38–40]. For each sample, approximately 300 mg_{DM} were transferred into 50 mL Teflon vessels and combined with 1 mL H_2O_2. After a reaction time of approximately 5 min, 1.5 mL HNO_3 supra quality (69%) (Merck, Darmstadt, Germany) was added, followed by another 1.5 mL HNO_3 and 1.5 mL HCL supra quality (35%) (Roth, Karlsruhe, Germany) 60 min later. After 12 h of reaction time in closed vessels, 7.5 mL HCL was added before microwave digestion at 190 °C for 20 min with a heat ramping of 12.6 °C/min (Multi-wave GO 3000 Anton Paar, Graz, Austria). The digested residues were aliquoted to 50 mL with double-distilled water and measured with the ICP-OES system (Spectro Blue ASX-260 auto sampler, SPECTRO Analytical Instruments, Kleve, Germany).

A centrifuge separated solid residues (mainly Si) before the spectroscopy and their weight was deducted from the sample weight. In total, 33 elements were measured via ICP-OES. Ag, B, Be, Bi, Sb, Se, Tl, Ga and In were excluded from this study due to values below the detection limit or only limited amounts of consistent values. Within this study, 24 elements from ICP-OES were evaluated (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, Ti, V, Zn, Si, P and S). Values for Si only represented a partial amount of the total amount for Si (not completely digestible in aqua regia).

2.6. Statistics

The Mann-Whitney U test was used to identify significant differences between the results of raw OFMSW and HTT variants. Stars indicated the level of significance (*: $p < 0.05$; **: $p < 0.01$; ***: $p < 0.001$). Values > 0.05 were labeled as not significant (n.s.).

3. Results and Discussion

3.1. Characteristics of Raw and Hydrothermally Treated OFMSW

Based on the physico-chemical properties of OFMSW such as high WC and from a treatment perspective, hydrothermal processes seem suitable to upgrade raw OFMSW in order to generate materials with energetic application potentials such as solid fuels for

combustion or adjusted substrates for AD. The main disparity between this and other studies [23,41–43] was the operating temperature of the conducted experiments. The average treatment temperatures of HTC processes are usually between 180 to 300 °C, leading to several different chemical and physical reactions that influence the characteristics of the substrate. According to several studies [21,44,45], it is possible to change chemical properties such as increased C contents or heating values of the feedstock by HTT at lower temperatures between 150 and 190 °C. Basic material properties for raw OFMSW and the resulting biochars, as analyzed in this study, are shown in Table 2.

Table 2 also shows the different levels of significance for the comparison of raw OFMSW and HTT variants. The mass loss due to the HTT process is an important parameter and increased from 31% (at 150 °C) to 41% (at 185 °C), though it was not statistically significant. Mass loss processes also influence material properties. They are necessary for an overall assessment of HTT. In particular, the basis of comparison for generated solids, either in absolute or relative terms, is essential. In general, the basic material properties (Table 2) can be used to evaluate the potential effects of HTT on thermo-chemical (combustion) and bio-chemical (AD) conversion pathways. The HHV describes the inherent energy potential, which is relevant for both combustion and AD. The parameters DT and FT are only relevant for combustion processes describing the ash melting behavior while the oDM content is important for combustion and AD (ash content and energy potential). The contents of C, H, N, O and S can be used for the calculation of energy yields in both combustion (HHV and LHV) and AD (stoichiometric CH_4 yields). Additionally, the emission behavior (when using HTT OFMSW as solid fuel) or certain element ratios such as C/N (when using HTT OFMSW as substrate for AD) can be evaluated. The H/C as well as the O/C ratios can be used for the classification of the HTT experiments indicating the level of carbonization.

In accordance with findings of other studies [44,45], a statistically significant increase of the HHV was observed, although not as strong as typically observed for HTC processes. The maximum increase of the HHV was determined at a treatment temperature of 170 °C with 1.3 MJ/kg_{DM}. In line with these findings, the 170 °C HTT variant also achieved the highest contents for C with approximately 41.4 %$_{DM}$. However, relatively high standard deviations for C contents from the elemental analysis indicated the inhomogeneity of the raw OFMSW. While C was slightly heightened by the HTT, H, N, S and O were lowered, leading to H/C and C/O ratios, as presented in the van Krevelen diagram (Figure 1).

The inhomogeneity of OFMSW may also be a reason for the relatively large value spreads, as shown in Figure 1. However, the trend derived from all single measurements in the van Krevelen diagram is clear. The raw OFMSW was characterized by the highest O/C and H/C ratios. In particular, the O/C ratio decreased from a maximum of approximately 0.75 to 0.35 with increased treatment temperature. Similar results were observed for H/C ratios with values decreasing from approximately 1.60 to 1.35. Nevertheless, the value range of the scales was relatively small. Therefore, low-temperature HTT led to lower H/C and O/C ratios, but not as drastically as typically observed for standard HTC processes. The highest value spreads were observed at a treatment temperature of 150 °C, while the HTT variants at 170 °C delivered relatively similar values with the lowest O/C ratios explaining the highest HHV. For all HTT variants, an overlapping area at ratios of approximately 0.45 for O/C and between 1.45 and 1.50 for H/C was determined.

Table 2. Basic material properties (mean values ± standard deviation) including the level of significance for raw organic fractions of municipal solid waste (OFMSW) and hydrothermal-treated OFMSW (biochars) at 150, 170 and 180 °C. Deformation temperature (DT) and flow temperature (FT), dry matter (DM), higher heating value (HHV), organic dry matter (oDM), not significant (n.s.), * ($p < 0.05$), ** ($p < 0.01$), *** ($p < 0.001$).

Sample	Mass Loss (%DM)	HHV (J/gDM)	DT (°C)	FT (°C)	oDM (%DM)	C (%DM)	H (%DM)	N (%DM)	S (%DM)	O (%DM)	H/C (-)	O/C (-)
Raw	-	15,417 ± 1258	1162 M ± 7 / 1621 C	1263 M ± 21 / 1681 C	77.88 ± 1.37	39.49 ± 2.55	5.29 ± 0.35	2.13 ± 0.32	0.21 ± 0.01	30.76 ± 3.14	1.60	0.58
150 °C	31.16 ± 2.74	16,241 ± 345	1590 C	1670 C	73.75 ± 1.38	40.70 ± 2.61	5.20 ± 0.38	1.81 ± 0.24	0.10 ± <0.01	25.94 ± 3.25	1.52 ± 0.02	0.48 ± 0.03
170 °C	38.07 ± 0.57	16,716 ± 257	1562 C	1646 C	70.09 ± 1.43	41.44 ± 1.34	5.19 ± 0.19	1.62 ± 0.11	0.12 ± 0.03	21.72 ± 1.57	1.49 ± 0.01	0.39 ± <0.01
185 °C	40.79 ± 0.44	16,672 ± 325	1643 C	1703 C	68.96 ± 1.35	39.94 ± 1.61	4.80 ± 0.23	1.47 ± 0.08	0.10 ± <0.01	22.65 ± 1.48	1.43 ± 0.01	0.43 ± 0.02
p-values												
Raw vs. 150	-	n.s.	-	-	***	n.s.	n.s.	n.s.	***	n.s.	-	-
Raw vs. 170	-	*	-	-	***	n.s.	n.s.	**	***	***	-	-
Raw vs. 185	-	*	-	-	***	n.s.	n.s.	**	***	***	-	-
150 vs. 170	n.s.	**	-	-	***	n.s.	n.s.	**	***	***	-	-
150 vs. 185	n.s.	**	-	-	***	n.s.	*	***	n.s.	**	-	-
170 vs. 185	n.s.	n.s.	-	-	n.s.	*	***	***	***	n.s.	-	-

DT and FT were either calculated with mean values (indexed with C) or measured via hot stage microscope (indexed with M). In addition to the measured values for DT and FT of raw OFMSW, sintering point (1121 ± 4) and hemisphere temperature (1204 ± 8) were determined.
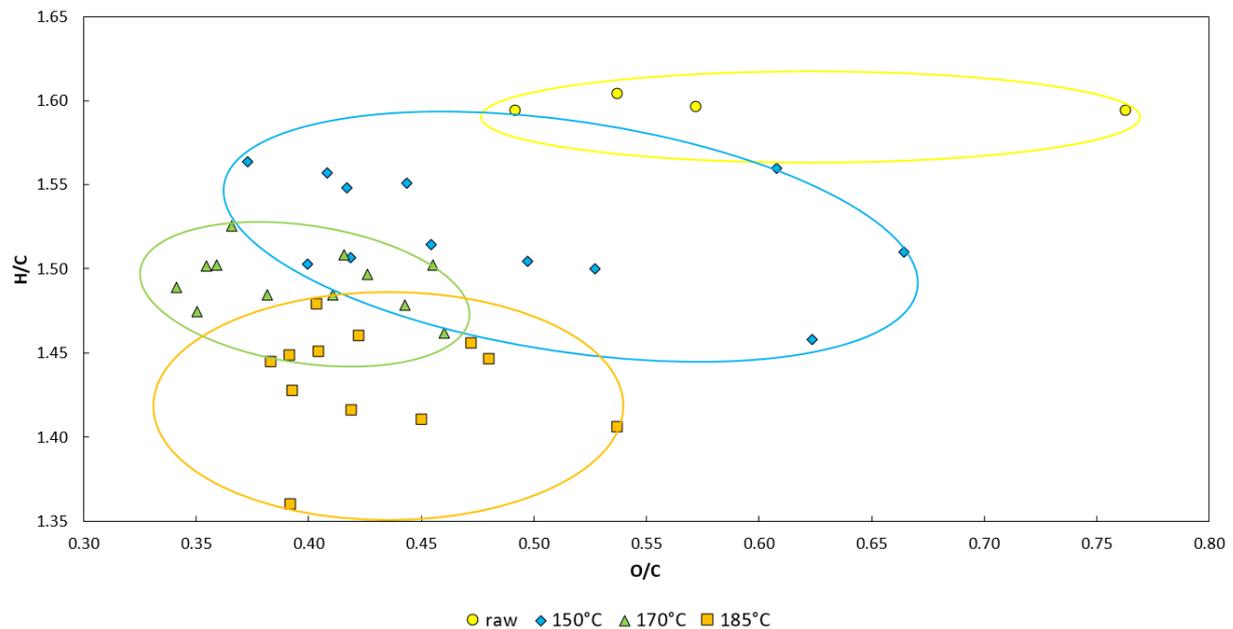
Figure 1. van Krevelen diagram with O/C and H/C ratios for all single measurements of raw organic fractions of municipal solid waste (OFMSW) and hydrothermally treated variants (biochars). The ellipses were estimated and inserted for illustrational purposes.

Figure 2 shows LHV values calculated with results for H contents from the elemental analysis for raw OFSMW and the biochars after HTT in comparison to legal limits for solid fuels according to prEN ISO 17225-8:2016 [46]. Raw OFMSW achieved an LHV of 14,327 $\pm$ 1258 J/g$_{DM}$, which is equal to 3.98 $\pm$ 0.35 kWh/kg$_{DM}$. The HTT variant with 150 °C delivered a LHV of 15,168 $\pm$ 350 J/g$_{DM}$ or 4.21 $\pm$ 0.10 kWh/kg$_{DM}$. While HTT at 170 °C reached the highest HHV, values for LHV at 170 °C (15,647 $\pm$ 256 J/g$_{DM}$ or 4.35 $\pm$ 0.07 kWh/kg$_{DM}$) were slightly lower than those of HTT at 185 °C (15,685 $\pm$ 305 J/g$_{DM}$ or 4.36 $\pm$ 0.08 kWh/kg$_{DM}$). A significant difference between HTT OFMSW at 170 °C and 185 °C was the lower H content (Table 2) of the 185 °C variant. The contents for H were relevant for converting HHV into LHV (higher H contents led to lower LHV). It can be ascertained that the spread of values decreases through HTT. This leads to a homogenization of the resulting solids, which is particularly important for materials with deviating properties such as OFSMW.

As presented in Figure 2, raw OFMSW and all HTT variants did not fulfill the minimum requirements for LHV according to prEN ISO 17,225 for classification as category 1 or category 2 fuel. Therefore, solid fuels based on OFMSW would have to be classified as category 3 fuel with no minimum requirements for LHV [46].

3.2. Potential Implications of Hydrothermal Treatment on Incineration and Anaerobic Digestion

In addition to the basic material properties, Figure 3 (TE > 1000 mg/kg$_{DM}$) and Figure 4 (TE < 1000 mg/kg$_{DM}$) show the behavior of TE depending on the HTT temperature level. Table 3 contains the levels of significance for the TE results as presented in Figure 3 or Figure 4. Existing legal limits for fuels according to prEN ISO 17,225 [46] and the German Biowaste Ordinance [5] are presented for TE such as Cl, S, As, Cd, Zn, Pb, Cu, Cr and Ni.
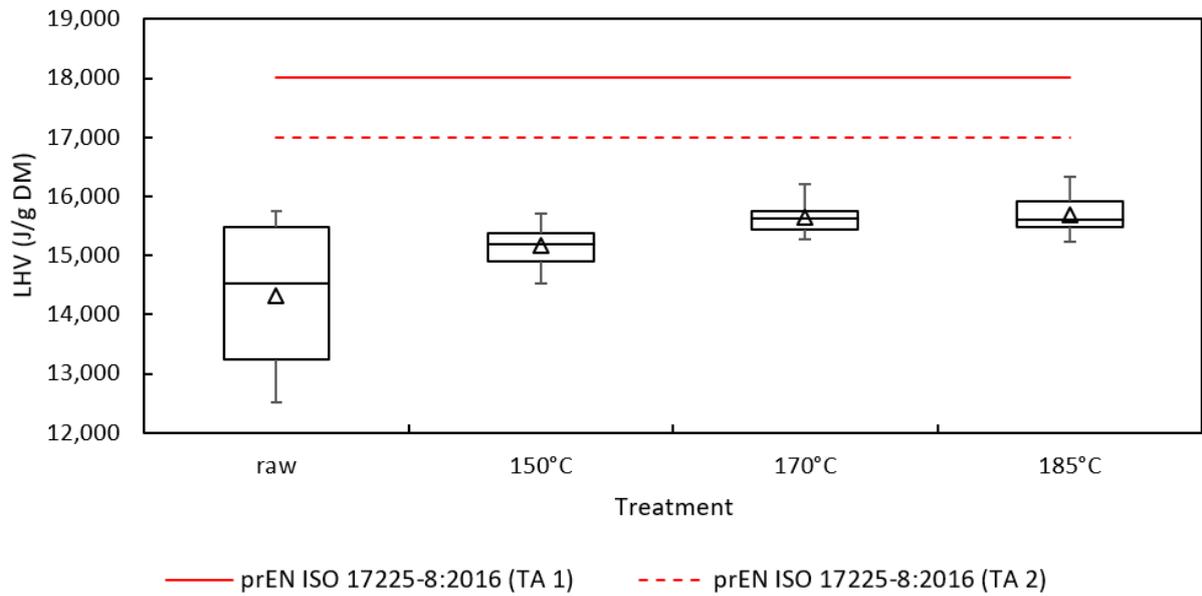
Figure 2. Lower heating values (LHV) based on dry matter (DM) for raw and hydrothermally treated (biochars) organic fraction of municipal solid waste (OFMSW) as boxplots including mean values (Δ). Minimum requirements for fuels according to prEN ISO 17225-8:2016 [46] category 1 and 2 are also presented.
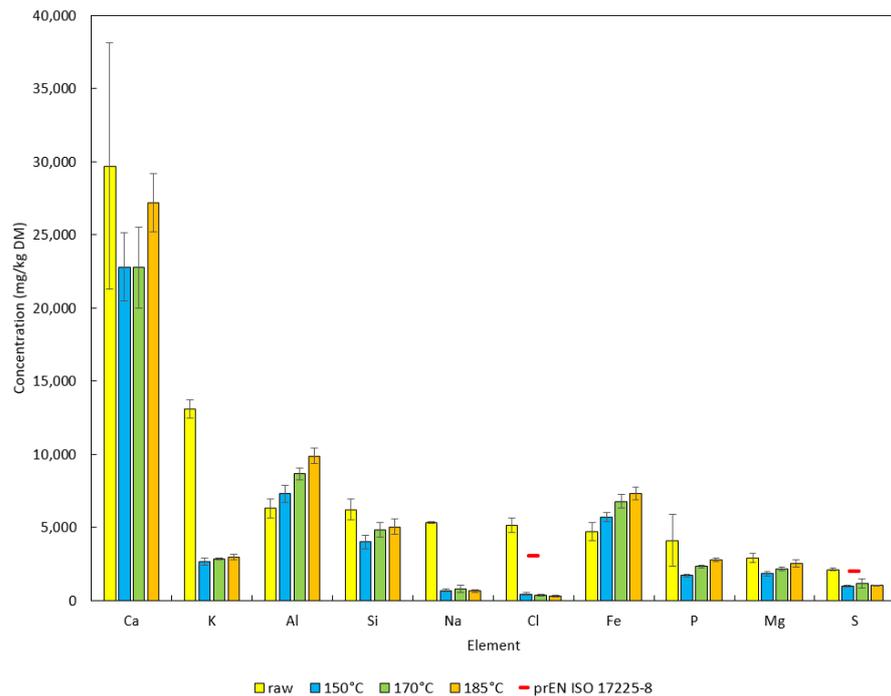
Figure 3. Mean values ± standard deviation of raw and treated (biochars) organic fraction of municipal solid waste (OFMSW) for elements with concentrations >1000 mg/kg$_{\text{dry matter (DM)}}$ and legal limits for fuels according to prEN ISO 17225-8:2016 [46].
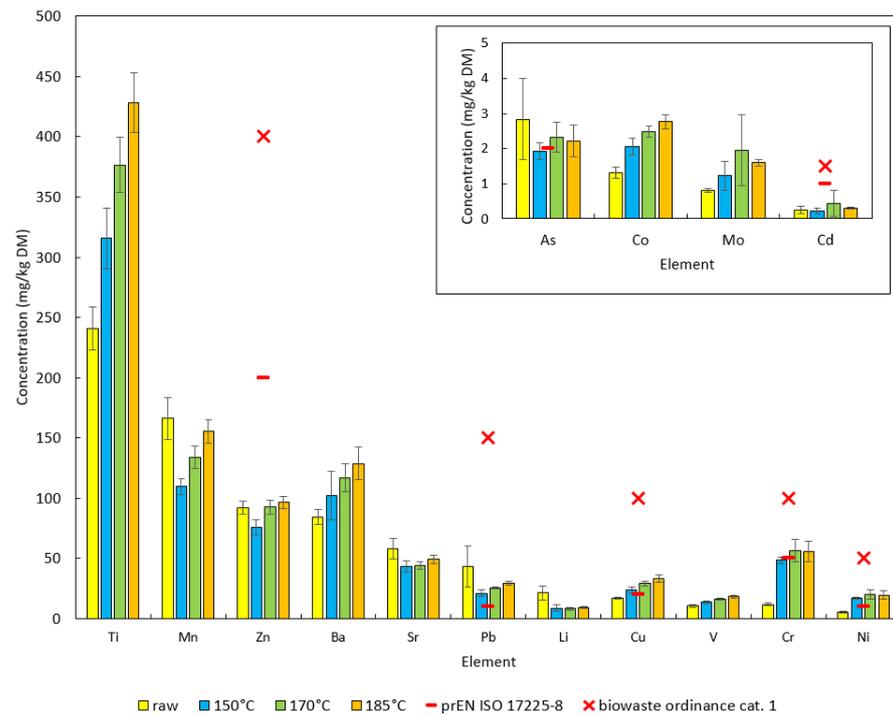
Figure 4. Mean values ± standard deviation of raw and treated (biochars) organic fraction of municipal solid waste (OFMSW) for elements with concentrations between 10 and 1000 mg/kg$_{\text{dry matter (DM)}}$ and with concentrations < 10 mg/kg$_{\text{DM}}$ (right upper diagram). Legal limits for fuels according to prEN ISO 17225-8:2016 [46] and the German Biowaste Ordinance [5] are included.

Table 3. Level of significance for the influence of hydrothermal treatment on element contents in raw and treated organic fractions of municipal solid waste (OFMSW). Comparison of raw OFMSW with OFMSW treated at 150, 170 and 185 °C (biochars). Not significant (n.s.), * ($p < 0.05$), ** ($p < 0.01$), *** ($p < 0.001$).

Samples	Ca	K	Al	Si	Na	Cl	Fe	P	Mg	S	Ti	Mn	Zn
Raw vs. 150	n.s.	***	*	***	***	***	n.s.	***	***	***	***	***	***
Raw vs. 170	n.s.	***	***	***	***	***	***	***	***	***	***	**	n.s.
Raw vs. 185	n.s.	***	***	***	***	***	***	***	**	***	***	n.s.	n.s.
150 vs. 170	n.s.	*	***	***	n.s.	n.s.	***	***	***	***	***	***	***
150 vs. 185	***	***	***	***	n.s.	*	***	***	***	n.s.	***	***	***
170 vs. 185	***	*	***	n.s.	n.s.	**	**	***	***	***	***	***	n.s.

Samples	Ba	Sr	Pb	Li	Cu	V	Cr	Ni	As	Co	Mo	Cd
Raw vs. 150	n.s.	***	***	***	*	**	***	**	**	**	*	n.s.
Raw vs. 170	***	***	***	***	***	**	***	**	n.s.	**	**	n.s.
Raw vs. 185	***	**	***	***	**	**	***	***	n.s.	**	**	n.s.
150 vs. 170	***	n.s.	***	n.s.	***	***	*	*	***	***	**	***
150 vs. 185	***	***	***	*	***	***	*	*	*	***	*	***
170 vs. 185	*	***	***	**	***	***	n.s.	n.s.	n.s.	***	n.s.	n.s.

Raw OFMSW exceeded legal limits for Cl and S, while the HTT variants fulfilled legal requirements due to erosions through HTT. The Ca content decreased at all treatment temperatures; however, the highest decrease was observed at 150 °C and 170 °C, while the K content as a relevant component for the combustion behavior of solid fuels decreased significantly at all HTT temperatures [6,47,48]. Contrary to this, Al and Fe contents increased through HTT, which is typical for certain TE. Increasing contents were also observed for Ti, Ba, Cu, V, Cr, Ni, Co, Mo and partially Cd as well as for Zn.

A more or less significant reduction for elements of the first main group (the alkaline metals of the periodic table) was determined through HTT. For the elements of the subgroups, either an accumulation or a reduction in proportion to the treatment temperature was observed. Accumulation processes as a negative aspect from the perspective of legal limits tended to be the lowest at a treatment temperature of 150 °C. Reduction processes as a beneficial aspect from a fuel property perspective tended to reach the optima at 150 °C. Elements close to or above legal limits were As, Pb, Cu, Cr, Ni while Zn and Cd were found below the legal limits. Values for Ni, Cu and Cr were below legal limits for raw OFMSW only.

From a combustion perspective, the sum of K, Na, Pb and Zn can serve as an indicator for aerosol formation. Raw OFMSW can be estimated as fuel with high aerosol formation potential ($>10,000$ mg/kg$_{DM}$). The molar ratios for Si/(Ca + Mg) and (Si + P + K)/(Ca + Mg) can be used to estimate ash melting tendencies [6], while the latter ratio accounts for fuels with high contents of P. In addition, the ash melting temperatures can be calculated according to Equations (4) and (5). As presented in Table 2, the calculated DT ranged between 1562 and 1643 °C. These values were significantly higher than the values measured for different wood species or anthracite with approximately 1300 °C [6]. Calculations for raw OFMSW according to both molar ratios led to index values <1. This means OFMSW can be characterized as fuel with a low tendency for slagging. This should be questioned. In order to cross-check and validate these results, raw OFMSW was measured under a hot stage microscope. The measured DT of 1162 °C was considerably lower than estimated, which led to the assumption that Equations (4) and (5) may not be suitable for OFMSW. Equations (4) and (5) are usually used in a lignocellulose context. This could be investigated in further research.

However, raw OFMSW as used in this study was characterized by a high WC of approximately 67 %$_{FM}$. Therefore, direct combustion without pre-treatment is disadvantageous. The LHV of raw OFMSW decreases from approximately 14,300 J/g$_{DM}$ to approximately 3200 J/g$_{FM}$ or 0.9 kWh/kg$_{FM}$ while the WC of raw OFMSW is not problematic for AD and HTT processes. From an energy content view, the combustion of fully or partly dried raw and HTT OFMSW is possible. Additionally, a combination of AD and HTT technologies may create synergies since the digestate produced in AD still contains high contents of oDM. The influence of low-temperature HTT on the characteristics and the potential areas of application of the digestates (e.g., solid fuel, fertilizer) could be a field of further research. However, it could be expected that basic material properties and TE concentrations of hydrothermally treated digestates will be influenced with similar tendencies as observed in this study for raw OFMSW. In order to create beneficial and holistic treatment approaches, digestate-based HTT solids and liquids both have to be considered equally.

The practical use of biogenic solid fuels is influenced by their physico-chemical composition and combustion properties. Raw and HTT OFMSW are not classified as a standard fuel according to the first Federal Emission Control Act [49], which is why they are currently not usable in small-scale furnaces [24]. Based on the chemical analyzes within this study, it can be expected that only an adjusted firing technology, such as in the thermal utilization of straw, can utilize raw or treated OFMSW via combustion. An effective ash removal due to high ash contents with efficient measures against possible ash melting (slagging within the combustion chamber), as well as flue gas cleaning and corrosion protection seem necessary. According to Kaltschmitt et al. [6] N is the most relevant parameter for NO$_x$ formation. Untreated OFMSW is indicated with N contents (>2 %$_{DM}$) several times larger than in lignocellulosic biomass. Although low-temperature HTT led to statistically significant lowered N contents in the biochars (Table 2), the NO$_x$ formation seems to remain problematic (contents of N between 1.5 and 1.8 %$_{DM}$) for solid fuels based on HTT OFMSW. K has negative impacts on corrosion processes, fine dust emissions and ash melting behavior. Ca and Mg heighten the ash melting point and Ca reduces SO$_2$ emissions additionally. Si lowers the ash melting point but can lower aerosol formation. S and Cl negatively affect emissions, aerosol formation and corrosion

processes. Furthermore, Na, Pb and Zn are also relevant for aerosol formation [6]. Based on ICP-OES analyzes in this study of HTT OFMSW, the concentrations of K, Si, Cl, S, Pb, Na, N and partially Zn as negative TE were lowered. Ca and Mg as positive TE were also lowered, but not drastically. Therefore, it can be assumed that the ash melting behavior, the potential fine dust emissions and the tendency of corrosion processes of raw OFMSW are influenced positively by HTT. Other TE and especially heavy metals seemed to accumulate. The results are similar to findings within other studies [24]. Further experiments such as combustion tests could validate the assumptions.

In addition to HTT and incineration, AD including composting should be considered for the evaluation of energy potentials from OFMSW. The stoichiometric CH_4 yield of raw OFMSW amounted to approximately 510 L/kg_{oDM} (990 L_{Biogas}/kg_{oDM}) for standard conditions while HTT variants reached 573 (150 °C), 635 (170 °C) and 606 L/kg_{oDM} (185 °C) due to changing elemental compositions. These yields are several times larger than usual for OFMSW-based AD plants in practice. Depending on the reactor design, typical OFMSW biogas yields in Germany vary between 0.08 and 0.12 m^3/kg_{FM} [2]. Besides the fact that stoichiometric calculations assume a complete digestion of oDM, retention times in full-scale plants tend to be relatively short due to throughput-oriented operating modes. Therefore, OFMSW could deliver higher CH_4 yields in practice. Theoretically, higher CH_4 yields of hydrothermally treated OFMSW compared to raw OFMSW can be explained through lower O contents as O reduces CH_4 yields in stoichiometric calculations according to Equation (1). Therefore, low-temperature HTT of OFMSW leads to solid products with higher energy yields per kg_{oDM}. However, mass losses and statistically significant lowered oDM contents during HTT processes have to be considered. Energy yields of raw OFMSW with the highest oDM contents but lowest specific CH_4 yields probably equal the potential energy yields from HTT OFMSW with lower oDM contents but higher specific CH_4 yields. Upgrading OFMSW by HTT for the utilization in AD is not suitable considering only potential energy yields, especially due to the energy use that is necessary for HTT. However, HTT also effects TE profiles and leads to enrichments or reductions. Therefore, HTT OFMSW variants could be beneficial from a TE perspective regarding inhibitory and promotional TE for AD. In addition, the ratio of C/N (relevant for the process efficiency of AD) is affected positively through HTT. Furthermore, oDM within coals such as anthracite or high-temperature HTC biochars are considered as not bioavailable or degradable via AD. Due to low-temperature HTT, oDM within OFMSW could still be available for microorganisms in AD. This could be investigated in further research. Based on stoichiometric CH_4 yields of 0.5 to 0.6 m^3/kg_{oDM}, approximately 5 to 6 kWh/kg_{oDM} can be provided. By converting oDM-based stoichiometric CH_4 values to DM as a reference unit (based on Table 2), raw OFMSW achieved 397 L/kg_{DM} while HTT variants reached 423 (150 °C), 445 (170 °C) and 418 L/kg_{DM} (185 °C). This led to energy yields of approximately 4 to 4.5 kWh/kg_{DM}. This equaled the measured values for the LHV and HHV (Table 2 and Figure 2), which is consistent since a complete combustion should deliver similar energy yields as a complete AD. Although HTT could potentially upgrade the substrate of OFMSW prior to AD, the HTT of OFMSW-based digestates seems more promising.

As displayed in Figures 3 and 4, the concentrations of TE in the OFMSW biochar varied depending on the temperature level of HTT. Certain TE (Al, Fe, Ti, Ba, Cu, V, Cr, Ni, Co, Mo, Cd, Zn) accumulated while others decreased (Ca, K, Si, Na, Cl, P, Mg, S, Mn, Zn, Sr, Pb, Li, As) compared to raw OFMSW. For some TE, such as Zn, an accumulation as well as a decrease (depending on the HTT variant) was observed. This phenomenon can be validated by results in Blümel et al. [24] where concentrations for TE such as, Cr, Cu, Pb, Ni or Zn accumulated during HTC at 180 to 220 °C while others such as Cl, K or Hg decreased. Hg was not included in the ICP-OES method; thus, Hg was not measured in this study. However, it can be assumed that Hg contents are possibly reduced by low-temperature HTT as well. Depending on reaction parameters, HTC processes deliver solid, liquid and gaseous products in varying ratios, e.g., due to mass losses

at higher HTT temperatures (Table 2). This was confirmed within another study [24]. However, solids with lower TE concentrations lead to process water with higher levels of TE. From an elemental perspective, it can be estimated (Figures 3 and 4) that the HTT process water mainly contains TE in the amount of the difference between raw OFMSW and the biochars. Detailed analyses (e.g., by gas chromatograph-mass spectrometry and through the evaluation of mass balances) of the OFMSW-based HTT-process waters could be performed in further research. However, by subtracting the reduced TE concentrations of treated OFMSW from raw OFMSW, the total amount of leached TE per kg_{DM} input can already be estimated.

4. Conclusions

Low-temperature and thus low-energy hydrothermal treatment (HTT) of OFMSW has shown several beneficial effects and may generate suitable solid fuels. In this study, low carbonization rates were achieved through HTT. In further research, the solid products and low-temperature HTT could therefore be evaluated in comparison to products from torrefaction processes. Hydrothermal processes, although mainly applied and researched in a lignocellulosic context, may complement the conversion options for composting and AD of OFMSW. The low-temperature treatment of OFMSW offers potential, especially in decentralized and rural areas since energy inputs and technical efforts are minimized. In addition, a wider range of waste heat sources might also be considered as suitable due to lower temperature levels. From a combustion perspective, it can be assumed that HTT leads to improved fuel properties concerning ash melting, corrosion stress and emission behavior. Negative consequences of the HTT process are higher contents of ash in the biochar as well as accumulated heavy metals. However, combustion tests within further research would be advisable. The utilization of raw OFMSW in hydrothermal processes leads to a competition between AD, composting and HTT. Instead of competing for the same resource, the combination of those waste utilization approaches should be further investigated. In the sense of a bioeconomy and from an energy system perspective, it could be beneficial to convert raw OFMSW into a storable energy carrier (CH_4) followed by HTT of the resulting digestate from AD to generate solid fuels for a second energetic utilization via combustion or for material use. The combustion behavior can be estimated based on chemical analyzes but is influenced by the combustion design. Characteristics of OFMSW-based solid fuels in real-life operations should be investigated in further studies. By using HTT solids as fuel, different ash fractions are generated. Those ashes could be used as fertilizer but may also be interesting from an urban mining perspective regarding the leaching of valuable elements. Additionally, the HTT process water could be used as fertilizer or may serve as a platform chemical for material use in the chemical industry. However, the concentrations of elements such as heavy metals that tend to accumulate in the biochars have to be considered for the application as fertilizer.

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Abbreviations

AD	anaerobic digestion
DM	dry matter
DT	deformation temperature
DW	distilled water
FM	fresh mass
FT	flow temperature
HHV	higher heating value
HTC	hydrothermal carbonization
HTT	hydrothermal treatment
ICP-OES	inductively coupled plasma-optical emission spectroscopy
LHV	lower heating value
oDM	organic dry matter
OFMSW	organic fraction of municipal solid waste
TE	trace element(s)
WC	water content

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