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Research Article

Food Waste Biomass-Derived Hydrochar by Hydrothermal Carbonization for Solid Biofuel Production

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Energy catalyzes economic development, with research into energy technologies essential for identifying alternatives that could mitigate against the reliance on fossil energy and its aggravating environmental impacts. This study explored the conversion of food waste (FW) biomass into hydrochar achieved via hydrothermal carbonization (HTC) technology. The research focused on evaluating the merits and demerits of using mixed FW feedstock, especially rice, potatoes, vegetables, and/or animal byproducts such as meat and fish at varying water-to-biomass ratios and through the implementation of water recirculation in the HTC process. This approach aimed to decrease water consumption while assessing its impact on the fuel characteristics of the resultant hydrochar. The hydrochar produced demonstrated an enhanced carbon content, which is conducive to combustion, while also exhibiting improved fuel properties such as elevated heating values, improved energy densities, and reduced volatile components. Conditions exceeding 200°C, with a reaction time of 6 h, were found to be sufficient to attain an average carbon content of above 70% and a heating value of around 30 MJ/kg. Moreover, decreasing the water-to-biomass ratio enabled a reduction in initial water usage by up to 50%, without significantly impairing the carbon content and fuel attributes of the hydrochar. Thermogravimetric analysis (TGA) indicated a comparatively elevated combustion temperature of 600°C for the hydrochar generated at an HTC temperature of 220°C, which corresponded with a substantial increase in the carbon content of hydrochar up to 70.65% from initial 48% in the parent biomass. Consequently, the hydrochar generated from FW under different HTC reaction conditions, including water volume reduction and recirculation, demonstrated the potential for minimal water consumption. This method represents a promising strategy for enhancing HTC as a renewable energy technology.

Keywords: biomass waste; hydrochar; hydrothermal carbonization; renewable energy

1. Introduction

The escalating global demand for energy, coupled with the urgent need to address climate change, has spurred an intense research drive into sustainable and renewable energy sources. This research aims to curb the excessive consumption of fossil fuels which causes a series of environmental problems, that include greenhouse gases (GHG), photochemical smog and acidification of aquatic systems [1]. For these reasons, clean and renewable fuels are essential substitutes for fossil fuels, which can promote sustainable development. Biomass, from plants, animals and their derived waste, is increasingly recognized as a significant and more environmentally friendly alternative to fossil fuels [2, 3]. However, the conversion of biomass into energy still releases CO_2, but this emitted CO_2 is the same carbon that facilitated the plant growth, resulting in a nearly neutral carbon balance [4] when combusted.

Food waste (FW) biomass is characterized by its composition of cellulose, lignin, protein, and starch and it is readily available as municipal organic waste that could be utilized as a substrate for carbon-neutral energy [4]. Using FW biomass as an energy resource could serve as a waste management strategy, diverting materials from landfills, and helping reduce the generation of methane produced from anaerobic

decomposition in landfills [5, 6]. This approach also contributes to climate change mitigation. FW occurs across the entire agricultural supply chain (during production, post-harvest handling and storage, processing, and distribution). This loss presents a substantial economic and environmental problem, where, annually, the value of discarded food exceeds USD 400 billion [5]. Per capita, FW varies averaging 107 kg/year in developed countries down to 56 kg/year in developing countries [7]. According to Thi et al. [5], the total global FW generation is estimated to be roughly 1.3 billion tons annually, with a nearly even split between developed (670 million tons) and developing countries (630 million tons). Therefore, using FW as renewable energy feedstock can advance a circular economy and address the environmental and economic challenges of waste disposal.

To effectively utilize biomass as solid fuels, hydrothermal technology has been developed to upgrade feedstocks and recover energy in the presence of water [1]. Compared to hydrothermal liquefaction and gasification, hydrothermal carbonization (HTC), a thermochemical conversion process discovered by Bergius in 1913 [8–10], stands out among biomass conversion technologies. This is due to its ability to convert wet biomass directly into solid biofuel without pre-drying, technical simplicity, reduced energy penalties, and the capability to process mixed biomass feedstocks without prior pretreatment. HTC of raw biomass has been shown to enhance its fuel properties by reducing volatile matter (VM), increasing carbon content, and lowering ash content [2, 9, 11–13]. Consequently, HTC is emerging as a promising renewable energy technology.

The mechanisms driving the thermal decomposition of raw biomass by HTC involve a complex interplay of chemical reactions. These reactions, which transform the biomass components (lignin, cellulose, and hemicellulose) into a carbon reach solid, known as hydrochar, include hydrolysis, dehydration, retro-aldol condensation, isomerization and aromatization, and polymerization [9], typically conducted in pressurized water (2–6 MPa) [8]. For simplicity, the mechanism of cellulose decomposition is used to elucidate the biomass decomposition mechanism during the HTC reaction [13] (Equation 1):

$$(C_6H_{10}O_5)_n \xrightarrow{H_2O,\text{heat}} x\,C_nH_4O_{0.5} + y\,CO_2 + H_2O, \qquad (1)$$

where n denotes the degree of polymerization, and x and y are stoichiometric coefficients. However, HTC yields not only hydrochar but also a variety of other products [14, 15]. These include phenolic, organic, and furan derivatives such as acetic, formic, glycolic, and levulinic acids, and 2,5-hydoxyl-methyl-furfural (HMF), which result from the breakdown of biomass polymers. Since they are water soluble, they are found in the HTC water phase. 2,5-HMF is an important and adaptable chemical with the potential to serve as a substitute for numerous petroleum-derived products because it can be converted into 2,5-dimethylfuran (DMF) [16, 17]. Both 2,5-HMF and DMF represent valuable products derived from biomass.

The use of water as the reaction medium in HTC may present a significant industrial challenge due to the continuous demand for water. For example, a 50% yield of hydrochar at a 1:6 solid-to-liquid ratio would consume 12 t (1 t = 1 metric tons = 1000 kg) of water to produce 1 t of hydrochar [8]. This demand for process water may outweigh the advantages of using HTC technology. Integrating HTC with water-saving strategies, such as water recirculation and volume reduction, could improve overall synthesis efficiency. Therefore, effective water management becomes critical for establishing HTC's competitiveness in renewable energy production.

This study investigated the feasibility of converting kitchen FW into hydrochar via HTC. The primary objective was to optimize water consumption by the HTC process, thereby maximizing its energy advantages while fostering environmentally responsible practices and contributing to carbon neutrality.

2. Materials and Method

2.1. Feedstock Preparation. This study used mixed kitchen FW collected from the Mensa Cafeteria at the University of Oldenburg, Germany. The FW comprised various food residues, including rice, potatoes, vegetables, and/or animal proteins such as meat and fish, rendering it an appropriate candidate for HTC feedstock as it mirrored most ingredients utilized in conventional culinary recipes. FW was homogenized with deionized water, with the volume of water varying from 40 to 100 mL/10 g FW. No additional sample pretreatment was necessary for the HTC process. A portion of FW (10 g) was desiccated in an oven at 80°C and subsequently subjected to element analysis to assess the characteristics of parent biomass before the HTC reaction.

2.2. Experiment Procedure. Twelve HTC experiments were performed under varying reaction parameters including temperature, duration, water-to-biomass ratio, and water recirculation to optimize the yield and energy properties of the resultant hydrochar product (Table 1). Initially, 10 g of FW was combined with 80 mL of deionized water, which was later varied to identify the optimal reaction conditions. Following the mixing process, the reaction mixture was promptly transferred to a high-pressure batch reactor (250 mL Teflon-coated stainless-steel autoclave), which was then subjected to heating in an oven at 200°C. Upon completion of hydrothermal treatment, the reactor was cooled to ambient temperature and the resulting hydrochar was isolated as a solid through vacuum filtration. The solid was thoroughly washed with deionized water until a clear filtrate was achieved, and the solid residue was oven-dried at 100°C overnight before characterization analysis.

The experiment was repeated at different temperatures (180–240°C), HTC_180, HTC_200, HTC_220, and HTC_240 with a residence time of 6 h for each. The optimal conversion temperature was determined from this, followed by a new set of HTC experiments at different reaction times (4–8 h), HTC_4 h, HTC_6 h, and HTC_8 h, to identify the optimal reaction time. A new set of experiments follows this to determine the optimal water-to-solid ratio (mL/g) (100 to 40 mL/10 g of biomass: HTC_100, HTC_80 mL, HTC_60 mL, and HTC_40 mL). A

Table 1: Experimental variables per run.

Run	Code	Experimental conditions		
		T (°C)	Biomass/water ratio (mL/g)	Time (h)
1	HTC_180	180	100/10	6
2	HTC_200	200	100/10	6
3	HTC_220	220	100/10	6
4	HTC_240	240	100/10	6
5	HTC_4 h	220	100/10	4
6	HTC_6 h	220	100/10	6
7	HTC_8 h	220	100/10	8
8	HTC_100 mL	220	80/10	6
9	HTC_80 mL	220	80/10	6
10	HTC_60 mL	220	60/10	6
11	HTC_40 mL	220	40/10	6
12	HTC_REC	220	80/10	6

final experiment (HTC_REC) was performed using the water (recirculated) from the previous HTC experiment.

2.3. Characterization. The analytical methods and equipment employed in this study included a EuroEA Elemental Analyzer (HEK GmbH) and a total organic content (TOC) Analyzer (Shimadzu's-TOC V CPH) to measure the organic and inorganic content (IC) of hydrochar and HTC process water, respectively. Scanning electron microscopy (SEM) (Hitachi S3200N Microscope) was used to examine the surface morphological properties of the hydrochars. Fourier transform electron spectroscopy (FTIR) (Bruker Tensor Spectrometer) was conducted to evaluate the hydrophobicity of the untreated and treated biomass. Additionally, thermogravimetric analysis (TGA) was performed to analyze the combustion properties of the hydrochar using an SDT 650 Simultaneous Thermal Analyzer DSC/TGA System, where samples were heated to 700°C under a nitrogen purge (60 mL/min) at a rate of 20°C/min.

2.4. Fuel Properties Calculations. The hydrochar fuel properties, such as the higher heating value (HHV), could be calculated according to Yuan et al. [18] Equations (2) and (3).

$$\mathrm{HHV} = 0.3383 \times 96\,\mathrm{C} + 1.422 \times [96\,\mathrm{H} - (96\,\mathrm{O}/8)] - 0.0151\mathrm{N}, \tag{2}$$

where C, H, and N are carbon, hydrogen, and nitrogen content (wt.%) given by the element analysis. The oxygen (O) content was determined from N, H, and C contents Equation (3).

$$[\mathrm{O}] = 100 - ([\mathrm{N}] + [\mathrm{H}] + [\mathrm{C}] + [\mathrm{Ash}]). \tag{3}$$

3. Results

A photo of the collected FW is shown in "Supporting Information Figure S1a". The HTC treatment of FW resulted in a blackish solid that resembled hydrochar (*Supporting Information* Figure S1b). This material's appearance differs much from that of the initial FW, indicating that the conversion from biomass to hydrochar has occurred.

3.1. SEM Analysis. An SEM analysis was performed to illustrate the morphological characteristics of hydrochars obtained from different processing conditions "Supporting Information Figure S2a–f)". Most hydrochars exhibit a porous and rough skeleton structure. Micrographs *a* and *b* depict the hydrochar derived from the initial HTC process, where a volume of 80 mL of water was used per 10 g biomass, shown at both low and higher magnifications. In contrast, micrographs *c* and *d* display the hydrochar produced with a lower water volume of 40 mL/10 g of biomass), while micrographs *e* and *f* show the hydrochar generated using recirculated water, presented as well at low and higher magnifications. Micrographs *e* and *f* show less pores compared to those in micrographs *a*. This difference may be due to the accumulation of excessive organic and inorganic materials trapped in hydrochar from recirculated HTC water. Rather, the set of SEM images from both pairs, *a* and *b*, as well as *c* and *d*, showed highly porous surfaces, with the low magnification micrographs (*a* and *c*) offering a clearer view of the porous structure. Some pores exhibited smaller diameters, while others displayed relatively larger diameters. This irregular porous structure of hydrochar creates numerous active binding sites, which may present opportunities for various applications in environmental remediation [19]. Whilst the pore structure might not interfere with energy applications of hydrochar, highly VM reduces the fuel quality of hydrochar [20]. Beyond HTC's energy applications, the highly porous nature of the hydrochar, which is ascribed to the significant decomposition of hemicellulose and cellulose because of HTC treatment [19], makes it a suitable candidate for use as an adsorbent in various applications, including nutrient retention for soil amendment [21] and wastewater treatment [22].

3.2. Element Analysis

3.2.1. Effects of Varying the HTC Temperature on Carbon Content, Hydrogen-to-Carbon (H/C) and Oxygen-to-Carbon (O/C) Ratios, and Energy Properties. Temperature change had considerable effects on the product's hydrochar properties. The

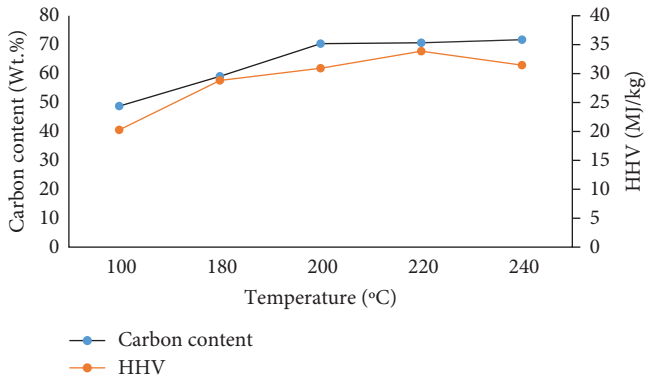

Figure 1: Effects of temperature on carbon content and HHV.

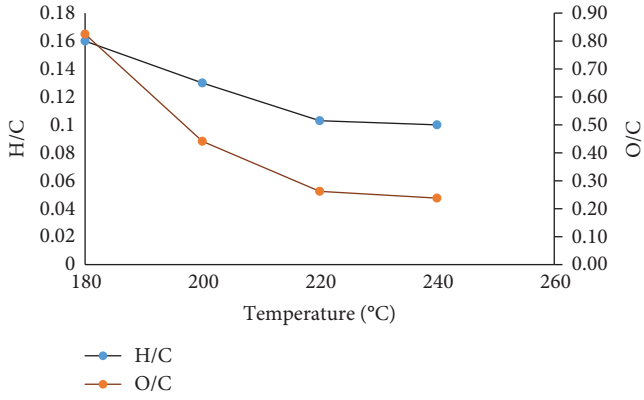

Figure 2: Effects of temperature on O/C and H/C ratios.

carbon content increased significantly from around 48.8% in the parent biomass to approximately 72% when the temperature increased to 240°C (HTC_240) (Figure 1). However, the hydrochar yield decreased from approximately 38.6% in the original biomass to around 30% as the HTC temperature increased from 180 to 240°C. The decline in hydrochar yield with rising HTC temperature was anticipated; Higher temperatures, during biomass conversion, result in more VM being released from the biomass [15], which produces a more carbon-rich solid fuel. Likewise, the HHV at 220°C increased to 33.87 MJ/kg (HTC_220) from 28.8 MJ/kg (HTC_180). The HHV value of 33 MJ/kg is significantly higher than those reported by Mohammed et al. [15] and Reza et al. [23] (ranging from 15.57 to 17.58 MJ/kg) under different HTC conditions and feedstocks such as corn stover, miscanthus, switchgrass, and rice husk. This shows that FW biomass is a good feedstock for biomass conversion.

Raising the HTC temperature to 220°C significantly impacted H/C and O/C ratios (Figure 2). The observed decrease in the H/C atomic ratio from 0.16 in the parent biomass to 0.10 and O/C ratio from 0.82 in the parent biomass to 0.24 in hydrochar, because of HTC treatment, correlates to increased energy densification and HHV (Table 2). This indicates that the biomass has undergone dehydration and decarboxylation reactions during HTC [12], which highlights the degree of carbonization tailoring the fuel properties of hydrochar becoming more carbon-rich [2, 24]. During the HTC reaction, organic materials experience dehydration and hydrolysis leading to the elimination of volatile components, including water and oxygenated functional groups [2, 20]. This was further validated by the acidification of residual HTC process waters, which were found to be relatively acidic (with pH values of 3.7–4.5) compared to the initial HTC process water used (pH of around 7). The decrease in pH of the HTC process is associated with the production of organic acids, such as acetic and levulinic acids, that leak into the water due to the hydrolysis of biomass during the HTC reaction [20].

The trend of producing less volatile hydrochar indicates a notable enhancement in fuel quality and an improvement in the efficiency and effectiveness of combustion, while offering important environmental benefits. This is supported by Poomsawat and Poomsawat [20], who state that the reduction in hydrochar volatility is linked to lower pollutant emissions during combustion, thereby enhancing the environmental impact of fuel utilization and increasing the ignition temperature of hydrochar. This finding underscores the importance of optimizing fuel production methods for both quality and sustainability.

3.2.2. Effects of Varying the HTC Duration on Carbon Content, HHV, and H/C and O/C Ratios. Figure 3a,b suggest that the duration of HTC has impacted the effectiveness of biomass conversion, although Gao et al. [25], Röhrdanz et al. [21], and Assis et al. [26] initially believed that HTC time had minimal effect on the biomass-to-hydrochar conversion. Visual inspection of the HTC product processed for less than 4 h revealed a yellow-brownish substance that did not resemble the typical black hydrochar (Figure S1b). This observation indicated that the conversion of biomass to hydrochar had not essentially occurred. Consequently, further analysis was not pursued, and an alternative reaction was initiated with an extended synthesis period.

The carbon content after 4 h of reaction (HTC_4 h) was just under 50% and the HHV was only 21 MJ/kg (Figure 3a). This confirms the significant influence synthesis time has on the effectiveness of the HTC process. A HTC time of 6 h proved to be optimal for converting FW biomass resulting in the highest carbon content of 70.64% and HHV of 33.87 MJ/kg. Extending the reaction time, beyond 6 h, did not lead to further increases in carbon content or HHV.

As noted in Figure 3b, the HC ratio decreased from 0.11 to 0.10, and the O/C ratio declined from 0.30 to 0.24 when comparing the initial HTC duration with a 6-h HTC (HTC_6 h). The observed decline in both H/C and O/C ratios suggests that the HTC process, even with a relatively short duration increase, is more complete, facilitating a more carbon-rich structure in the hydrochar. Figure 3b indicates that the HTC_6 h provides the ideal reaction duration for HTC, as extending the duration failed to sustain the lower H/C and O/C ratios. Although these changes appear minor, lower H/C and O/C ratios correlate with higher energy density (Table 1) and hold significant implications for the fuel properties of the resulting hydrochar

Table 2: Summary of hydrochar characteristics and fuel properties by elemental analysis.

Sample	Hydrochar yield (%)	Elemental analysis (wt.%) N	C	H	O	H/C	O/C	HHV (MJ/kg)	ED
Dry FW	—	2.14	48.77	7.67	40.23	0.16	0.82	20.26	—
Varying temperature (180–240°C) at 6 h, biomass-water ratio (mL/g = 8)									
HTC_180	38.646	4.21	59.05	9.47	26.06	0.16	0.44	28.81	1.43
HTC_200	30.855	2.72	70.34	7.31	18.44	0.13	0.26	30.92	1.53
HTC_220	32.020	2.22	70.64	9.12	16.82	0.10	0.24	33.87	1.67
HTC_240	32.464	2.49	71.70	7.23	17.38	0.10	0.24	31.45	1.55
Varying time (4–8 h) at 220°C, biomass-water ratio (mL/g = 8)									
HTC_4 h	14.595	3.09	48.48	5.92	41.32	0.11	0.30	21.79	1.07
HTC_8 h	27.303	2.64	68.26	7.34	20.56	0.10	0.35	29.88	1.47
Varying biomass-water ratio (40–100 mL/g) at 220°C, 6 h.									
HTC_40 mL	39.567	2.51	69.42	7.40	19.48	0.10	0.28	30.54	1.51
HTC_60 mL	29.689	2.28	67.35	7.08	22.09	0.11	0.33	28.92	1.43
HTC_100 mL	23.141	2.47	66.56	7.31	22.46	0.11	0.34	28.92	1.43
Water recirculation at 220°C, 6 h, biomass-water ratio (mL/g = 8)									
HTC_REC	47.447	2.25	69.82	8.14	18.59	0.12	0.27	31.90	1.04

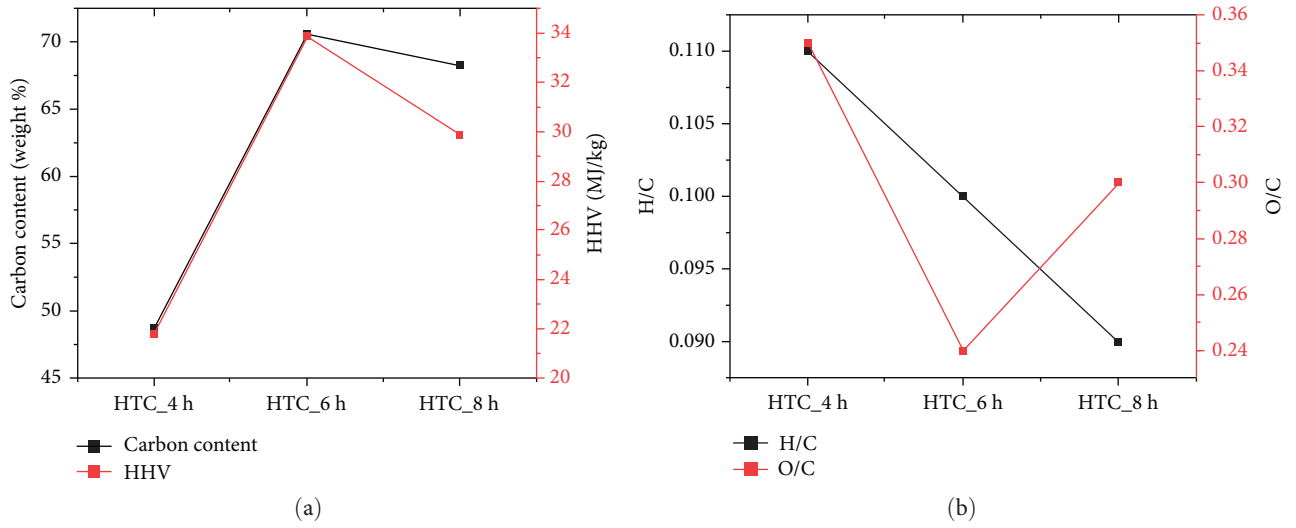

Figure 3: Effects of HTC reaction time (a) on carbon content and HHV, (b) H/C and O/C ratios of hydrochar.

[25, 27, 28] which are desirable characteristics for biofuel applications making hydrochar more suitable as a solid fuel substitute. Interestingly, these results contrast with earlier findings, [21, 25] which implied that reaction time had negligible effects on hydrochar properties. The data presented in Figure 3a,b challenges that notion, emphasizing that even slight modifications in the HTC process duration can have meaningful effects on the chemical composition of the hydrochar.

3.2.3. Effects on Carbon Content, HHV, and H/C and O/C Ratios of HTC Process Water Volume Reduction and Recirculation. The effectiveness of hydrochar production through HTC is affected by several key factors, including carbon content, HHV, and H/C and O/C ratios. Figure 4 depicts the properties of hydrochars produced using various water volumes and recirculation methods, highlighting notable insights on their application as solid fuels.

The hydrochar produced using 80 mL of water (HTC_80 mL) exhibited the most favorable properties, offering the highest HHV of 70.64 MJ/kg and carbon content of 33.87% (Figure 4a). These elevated values are attributable to the optimal conditions provided by larger water volume, which likely facilitated better hydrolysis as the important first step, improving the following carbonization and reducing the presence of oxygenated functional groups. The low H/C and O/C ratios of 0.10 and 0.24, respectively, suggest that this hydrochar is more carbon-rich and has less hydrophilic [20] characteristics what enhance its combustion efficiency [24]. It is somewhat unusual that the hydrochar yield increased, as the water volume decreased, from 23% (HTC_100 mL) to 39.6% (HTC_40 mL). Although reducing water volume can be an effective water-saving strategy for HTC, the rise in hydrochar yield may be linked to higher VM, which could potentially impact the fuel quality of the resulting hydrochar. This will be better

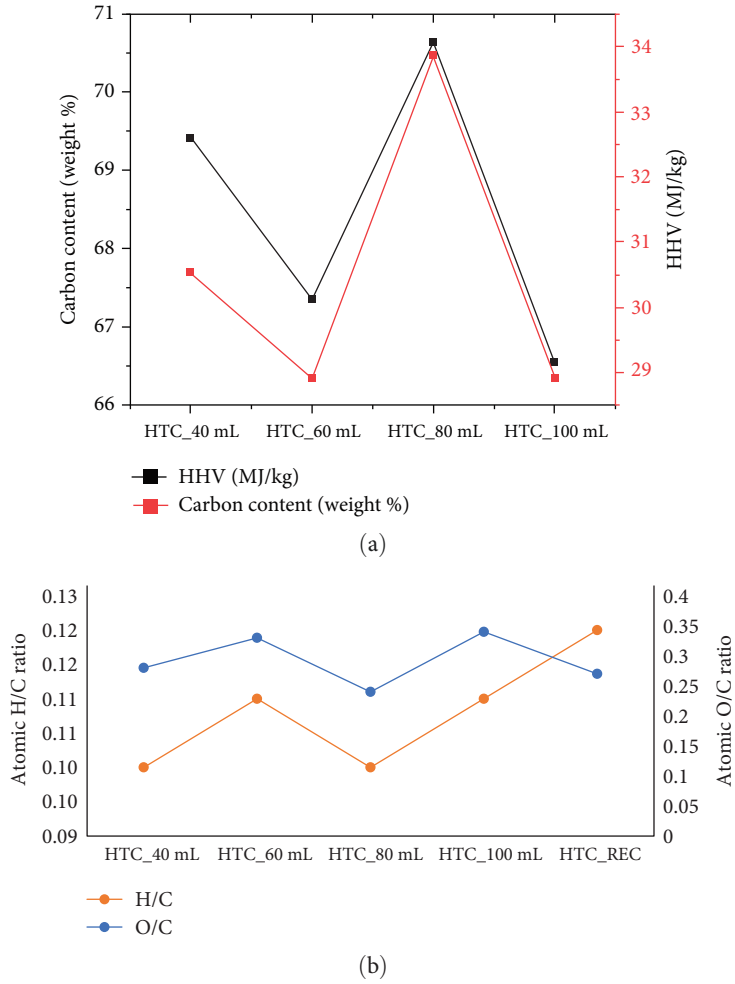

FIGURE 4: Impact of reducing water volume and recirculation in the HTC process on (a) hydrochar carbon content and HHV, and (b) H/C and O/C ratios.

understood through TGA, providing more insights into the combustion properties of the hydrochar produced.

In contrast, hydrochars produced under lower water volumes, namely at HTC_40 mL and HTC_60 mL, as well as with water recirculation (HTC_REC), displayed slightly higher H/C and O/C ratios, resulting in somewhat lower carbon content and (66%–69%) and HHV (28 – 31 MJ/kg) (Figure 4a,b). While these values are lower than those of HTC_80 mL, the differences in combustion performance may not be substantial enough to deter the use of HTC_40 mL or HTC_REC in solid fuel applications, particularly considering the marginal reduction in energy density. Moreover, the observation that increasing water volume to 100 mL has not improved the hydrochar fuel properties supports the notion of optimizing HTC conditions for resource efficiency and the overall environmental impact of HTC technology.

The key takeaway from these findings is the strategic advantage of using reduced water volumes in the HTC process by successfully producing hydrochars nearly equivalent in fuel properties to that from HTC_80 mL. The HTC_40 mL and HTC_REC methods therefore represent an opportunity for significant water conservation which can alleviate one of the critical bottlenecks associated with HTC technology, enhancing its sustainability profile. Anticipated results from TGA, specifically the ignition temperature and burn-off rates, will ultimately clarify the combustion performance and enhance the understanding of how these hydrochars behave as solid fuels under practical energy applications.

Table 2 provides a summary of the characteristics, highlighting the carbon content, HHV, H/C and O/C ratios, and energy densification of hydrochars generated under different HTC conditions. The values were derived from elemental analysis and Equations (2 and 3).

3.3. The Van Krevelen Diagram. The Van Krevelen diagram (Figure 5) effectively assessed various coal-to-biomass regions (biomass, lignite, peat, and coal) of hydrochars produced under different HTC conditions by plotting H/C against O/C ratios. FW was clearly positioned in the biomass region, while hydrochar produced at 180°C (HTC_180) fell into the peat region, suggesting that lower temperatures are suboptimal for hydrochar production from this feedstock. Hydrochars obtained at 200°C (HTC_200) and with 4 h reaction time (HTC_4 h) cluster in the lignite region, indicating improved production

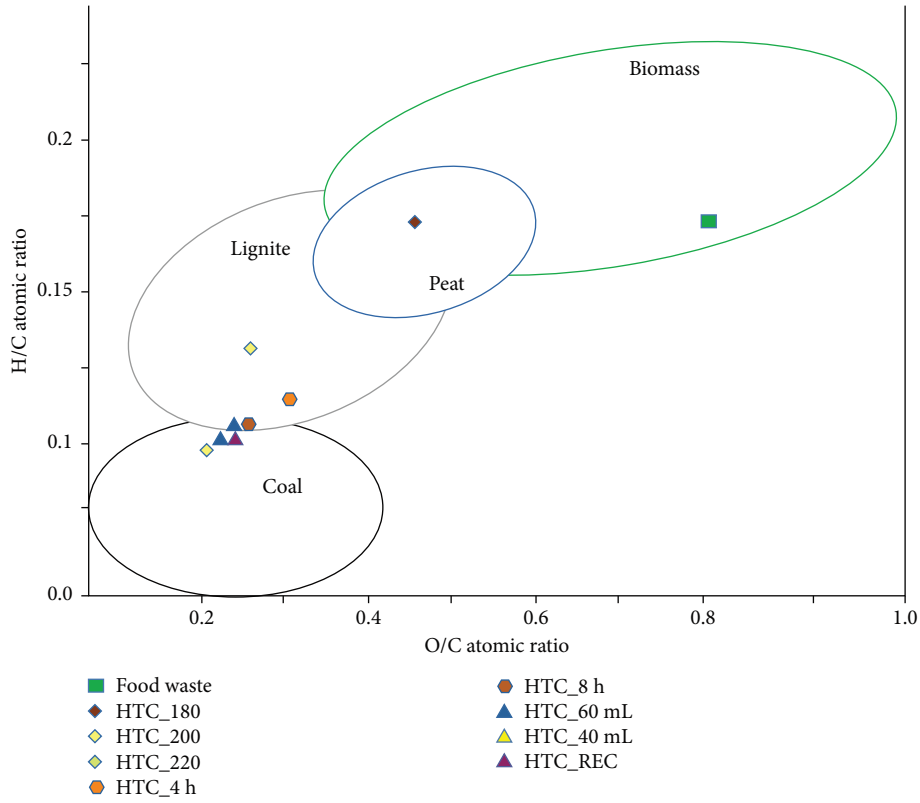

FIGURE 5: The Van Krevelen diagram of hydrochar at varying HTC conditions.

conditions. However, hydrochars from lower water volumes (HTC_40 mL and HTC_REC), produced at 220°C over 6 h, distinctly aligned with the coal region. These findings suggest that high-quality hydrochars can be achieved with minimal water usage when optimal temperatures and relatively longer reaction times are employed.

The Van Krevelen diagram (Figure 5) proved valuable in delineating various biomass-to-coal regions of hydrochars; however, these classifications and regions may not have consistent definitions depending on the specific biomass feedstock utilized [20, 29, 30]. Nevertheless, the diagram offered significant insights into the effectiveness of converting FW biomass, indicating that reducing water volume and recirculating did not substantially influence the quality of the resulting hydrochars, supporting the idea that this approach can be an effective water-saving strategy for HTC technology.

3.4. Analysis of Total Organic and IC and pH of HTC Liquid Phase. Analysis of TOC, IC, and pH proved effective in identifying changes in the HTC liquid phase. There is a notable difference in TOC, IC, and pH levels of HTC residual waters compared to water measurements taken before the HTC reaction (Table 3).

The IC of water before the HTC reaction (freshwater) was slightly higher (25.3 mg/L) compared to the IC in the HTC residual water (Table 3). The decreased IC in residual HTC water could be attributed to the possible uptake of minerals by the hydrochar generated during the HTC reaction, which can function as an adsorbent.[31, 32, 34, 35] The TOC showed a significant increase, from 311 mg/L in freshwater, up to above 2000 mg/L after HTC treatment (Table 3). The TOC in the HTC residual water increased even more (up to 5290 mg/L) when the HTC process water was recirculated (HTC_REC). The increase in TOC could be due to the residual HTC water receiving twice the organic matter from the biomass in subsequent HTC reactions when the HTC process water was reused without pretreatment. The increased TOC was also revealed by the observed decrease in pH of the HTC process water, likely due to the leaked acidic groups.

The pH of residual HTC water ranged from 3.7 to 4.5 (Table 3), showing a considerable decrease from its initial pH of 7.7 in the water used for the reaction. The acidification of residual HTC water is linked to the presence of organic matter and nutrients [36], including acetic acid, clavulanic acid, and formic acid, which are generated from the degradation of sugars and lignocellulosic constituents of biomass through hydrolysis during the HTC reaction [18, 20, 37]. The contamination of HTC process water by organic and inorganic substances turns this into a highly turbid and polluted liquid [23] that cannot be disposed of in its current state without pretreatment, as this would exceed the World Health Organization (WHO) water quality guideline limit of 300 mg/L for total dissolved solids [1].

3.5. FTIR Analysis. The FTIR spectra of raw biomass and hydrochar "Supporting Information Figure S3a,b)" revealed

Table 3: TOC, IC, and pH of residual HTC process waters.

Sample	pH	TOC (mg/L)	IC (mg/L)
Freshwater	7.7	311.0	25.3
HTC_80 mL	3.9	2397.0	26.0
HTC_60 mL	3.9	2365.0	23.1
HTC_40 mL	4.0	2153.0	21.5
HTC_Rec	4.1	5290.0	23.0

that the bands in Figure 3b (for hydrochar) exhibited lower intensity compared to those in Figure 3b (for biomass). According to Da Silva Lima et al. [31], the reduced intensity of bands in hydrochar is due to the loss of volatile functional groups during the HTC reaction. Another significant distinction between the two spectra is the presence of an absorption band at 3304 cm^{-1} in Figure 3a, which is absent in Figure 3b. According to Röhrdanz et al. [21] and Gao et al. [25], the stretching vibrations of the -OH group are indicative of phenols and alcohols usually found between 3200 and 3600 cm^{-1}. Additional vibrations noted in 1000–1450 cm^{-1} range are attributed to phenolic and carboxyl groups, as well as stretching at 1580 cm^{-1} associated with C═C double bonds [31]. These vibrations have also shown a notable decrease in peak intensity compared to those in the biomass spectra. The absence of the ─OH group in Figure 3b suggests an increased level of dehydration and carbonization, resulting in a hydrophobic surface for hydrochar. The hydrophobicity of hydrochar is an important feature that enhances its fuel properties, as it indicates lower moisture content [20].

3.6. TGA. The TGA, which monitors sample mass loss as a function of temperature, was useful for comparing the combustion behavior of raw biomass and the resulting hydrochar products. The normalized weight loss (TG) and derived weight loss (DTG) curves allowed the determination of the three main combustion parameters namely the ignition temperature (Ti), the temperature at maximum combustion rate (Tm), and the burnout temperature (Tb) of the starting biomass and the derived hydrochar, produced under different reaction conditions such as temperature, reaction duration, composition and water recirculation with the temperature program heating from 30 to 700°C at 20°C/min in nitrogen atmosphere (60 mL/min). Several methods could be used to determine the combustion parameters which may slightly differ from different methods. In this study, the Ti, Tm, and Tb (green, blue, and black traces) in Figure 6 were obtained according to the TG-DTG intersection method [25, 30]. The temperature at the intersection of the tangent line and the initial horizontal line of the reaction on the TG curve was used to determine Ti, whereas the tangent line on the TG curve was taken as the peak temperature corresponding to Tm on the DTG curve. The Tb was defined by the temperature at which the combustion rate exceeded −1 wt.%/min on the DTG curve or at the end of the combustion process where the conversion reached above 90% [25].

Figure 6 and d displays the TG-DTG plots of biomass and hydrochars under different reaction conditions such as temperature, water volume reduction and recirculation (HTC_220, HTC_40, and HTC_REC). The Ti shown in Figures 6 is just below 250°C for the biomass and its derived hydrochars. The Ti around 250°C may be sufficiently safe as Ti below 200°C could lead to spontaneous combustion [38], which is a safety hazard in transportation and storage [18]. Yuan et al. [18] also obtained a Ti of 256°C from hydrochar produced from corn and rice straws by HTC. However, it is quite strange for the biomass to have almost the same Ti value as its derived hydrochar, which is usually expected to have a lower Ti value than its derived hydrochar, as it contains a higher proportion of volatile that should normally cause the initial biomass to ignite at lower temperatures [29, 39]. This could be explained by the fact that the TGA of biomass was performed on a dry basis, after predrying the biomass in an oven, which might have somewhat decreased the volatile substances and improved the Ti of the parent biomass.

The hydrochar from HTC_REC gave the highest mass loss rate (85%/min) when using HTC water from the previous process (Figure 6d) which was quite unusual as hydrochar is considered to have a lower mass loss rate than the parent biomass. This could be due to contamination of the hydrochar by the previously used HTC water, suggesting that, in contrast to reducing the HTC water volume, direct recycling of water from one HTC to another without pretreatment affects the fuel properties of the hydrochar. This may not be a viable water conservation strategy for HTC if the hydrochar is produced for energy purposes.

The hydrochar at HTC_220 gave the highest burnout temperature (600°C) compared to its parent biomass (434°C) before the HTC water was reduced or recirculated (Figure 6b). This means that freshwater is an ideal medium for the HTC reaction as it provides the best hydrochar with increased carbon content and higher energy yield. In practice, however, this would only be ideal; producing hydrocarbon from freshwater would put enormous strain on water resources and become a water conservation problem. Therefore, any strategy that minimizes water consumption while maintaining acceptable levels of product quality would be preferable. HTC water reduction (Figure 6c) instead of recirculation has been shown to significantly reduce the amount of water consumed by HTC and has satisfactory combustion characteristics achieved through improved combustion parameters such as relatively lower mass loss rate (53%/min) and improved burnout temperature (540°C) compared to the original biomass. Therefore, reducing HTC water volume provides the opportunity to optimize HTC water consumption with minimal impact on the fuel quality of the resulting hydrochar.

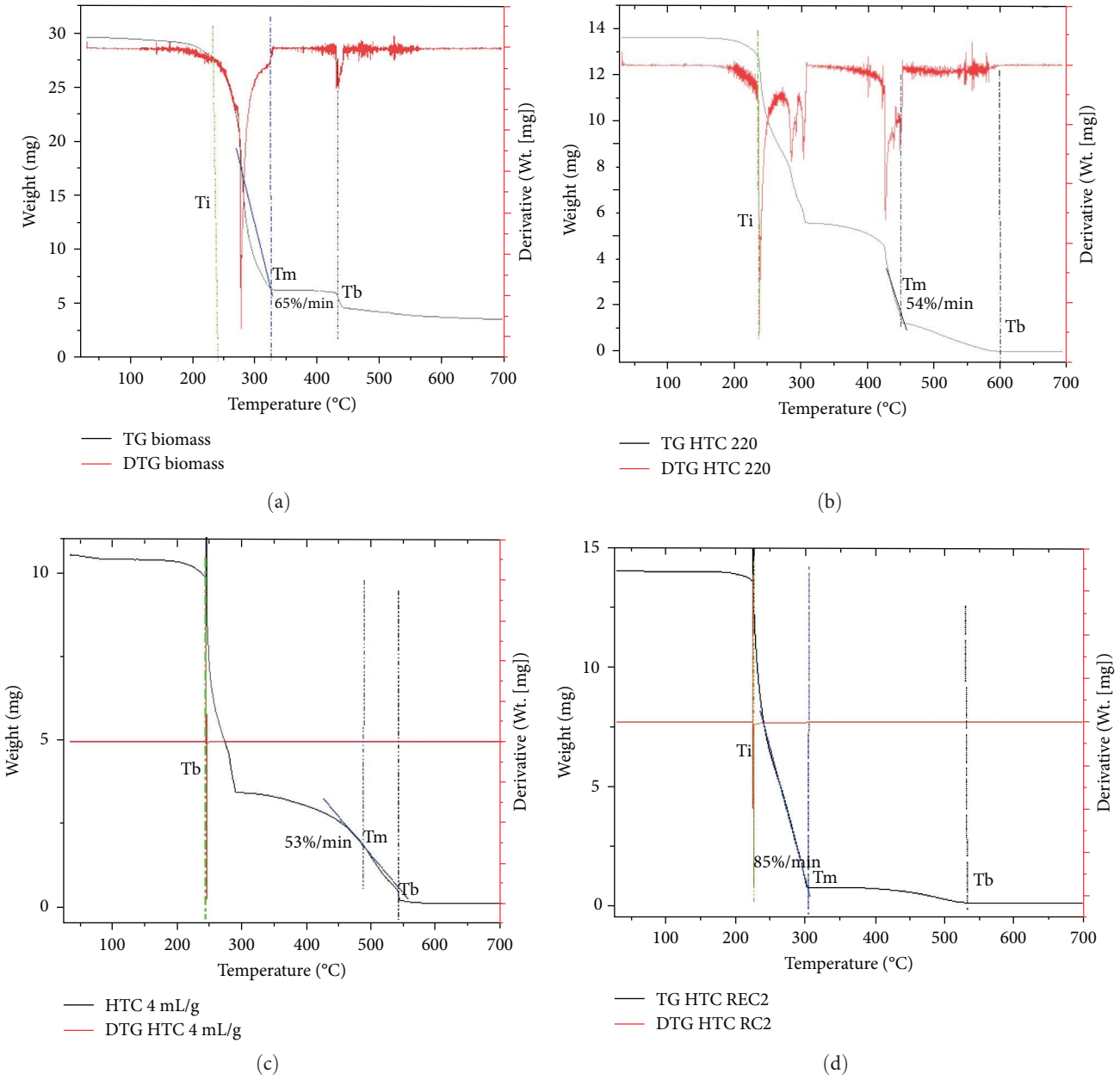

FIGURE 6: TG -DTG plots of (a) raw biomass, (b) hydrochar HTC_220, (c) hydrochar HTC_40, and (d) hydrochar HTC_REC.

4. Conclusions

This study successfully demonstrated the potential of HTC as a viable method of converting FW into hydrochar suitable for solid biofuel production. Optimization of HTC process parameters significantly enhanced the elemental composition and fuel properties of the resultant hydrochar while minimizing water consumption. The optimal conversion conditions identified included a temperature of 220°C and reaction time of 6 h, achieving a carbon content of 70.64%, markedly higher than the biomass value of 48.77%.

The HHV of the hydrochar produced increased from approximately 20.26 MJ/kg in the original biomass feedstock to 33.87 MJ/kg. Thermal analysis showed burnout temperatures ranging from 540 to 600°C, confirming the hydrochar's suitability for energy generation. Reduction of H/C and O/C ratios to 0.10 and 0.24, respectively, further indicated a superior fuel quality of the hydrochar, correlating with increased combustibility and reduced pollutant emission.

By reducing the water-to-biomass ratio from 80 to 40 mL/10 g FW maintained comparable hydrochar characteristics, while halving water input, offering a suitable solution for industrial scalability of HTC. Notably, the hydrochar produced with recirculated HTC water exhibited higher mass loss, suggesting contamination with VM, which may slightly impair the overall fuel quality.

These findings substantiate HTC's role as a renewable energy technology that converts FW into valuable energy

carriers, mitigating landfill-related environmental impacts and aligning with circular economy principles. The approach advances waste valorization strategies, reduces reliance on biofuel crops and fossil energy, thereby supporting the UN Sustainable Development Goals, particularly goals 7 (affordable clean energy) and 13 (climate action). Integrating HTC technology with water-efficient practices presents a compelling pathway for sustainable energy development with environmental and economic benefits.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no conflicts of interest.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. (*Supporting Information*) Supporting Information is appended to this manuscript, including additional figures such as food waste feedstock, hydrochar, and SEM images.

References

[1] X. Zhuang, H. Zhan, Y. Huang, Y. Song, X. Yin, and C. Wu, "Conversion of Industrial Biowastes to Clean Solid Fuels via Hydrothermal Carbonization (HTC): Upgrading Mechanism in Relation to Coalification Process and Combustion Behavior," *Bioresour Technol* 267 (2018): 17–29.

[2] Z. Liu, A. Quek, S. Kent Hoekman, and R. Balasubramanian, "Production of Solid Biochar Fuel From Waste Biomass by Hydrothermal Carbonization," *Fuel* 103 (2013): 943–949.

[3] M. T. Islam and M. T. Reza, "Evaluation of Fuel and Combustion Properties of Hydrochar Derived From Co-Hydrothermal Carbonization of Biomass and Plastic," *Biomass and Bioenergy* 172 (2023): 106750.

[4] K. Jayaraman, M. V. Kok, and I. Gokalp, "Combustion Properties and Kinetics of Different Biomass Samples Using TG–MS Technique," *Journal of Thermal Analysis and Calorimetry* 127, no. 2 (2017): 1361–1370.

[5] N. B. D. Thi, G. Kumar, and C.-Y. Lin, "An Overview of Food Waste Management in Developing Countries: Current Status and Future Perspective," *Journal of Environmental Management* 157 (2015): 220–229.

[6] H. Bayat, M. Dehghanizadeh, J. M. Jarvis, C. E. Brewer, and U. Jena, "Hydrothermal Liquefaction of Food Waste: Effect of Process Parameters on Product Yields and Chemistry," *Frontiers in Sustainable Food Systems* 5 (2021): 658592.

[7] Y. Xu, B. Wang, S. Ding, et al., "Hydrothermal Carbonization of Kitchen Waste: An Analysis of Solid and Aqueous Products and the Application of Hydrochar to Paddy Soil," *Science of The Total Environment* 850 (2022): 157953.

[8] H. S. Kambo and A. Dutta, "A Comparative Review of Biochar and Hydrochar in Terms of Production, Physico-Chemical Properties and Applications," *Renewable and Sustainable Energy Reviews* 45 (2015): 359–378.

[9] I. Oliveira, D. Blöhse, and H.-G. Ramke, "Hydrothermal Carbonization of Agricultural Residues," *Bioresource Technology* 142 (2013): 138–146.

[10] C. Huang, C. Yu, G. Wang, J. Zhang, X. Ning, and C. Wang, "Comparison of Structural Characteristics and Combustibility Analysis About Hydrochar and Pyrochar," *Journal of Thermal Analysis and Calorimetry* 147, no. 19 (2022): 10509–10523.

[11] M. Puccini, E. Stefanelli, M. Hiltz, M. Seggiani, and S. Vitolo, "Activated Carbon From Hydrochar Produced by Hydrothermal Carbonization of Wastes," *Chemical Engineering Transactions* 57 (2017): 169–174.

[12] G. Wang, R. Xu, X. Ning, et al., "Hydrothermal Carbonization of Forest Waste Into Solid Fuel: Mechanism and Combustion Behavior," *Energy* 246 (2022): 123343.

[13] J. A. Libra, K. S. Ro, C. Kammann, et al., "Hydrothermal Carbonization of Biomass Residuals: A Comparative Review of the Chemistry, Processes and Applications of Wet and Dry Pyrolysis," *Biofuels* 2, no. 1 (2014): 71–106.

[14] M. Cozier, "Business Highlights: Collaboration: Bigger and Beta," *Biofuels, Bioproducts and Biorefining* 8, no. 6 (2014): 743–745.

[15] I. S. Mohammed, R. Na, K. Kushima, and N. Shimizu, "Investigating the Effect of Processing Parameters on the Products of Hydrothermal Carbonization of Corn Stover," *Sustainability* 12, no. 12 (2020): 5100.

[16] Y. Su, H. M. Brown, X. Huang, X.-D. Zhou, J. E. Amonette, and Z. C. Zhang, "Single-Step Conversion of Cellulose to 5-Hydroxymethylfurfural (HMF), a Versatile Platform Chemical," *Applied Catalysis A: General* 361, no. 1-2 (2009): 117–122.

[17] A. Urbanowska, M. Kabsch-Korbutowicz, M. Wnukowski, et al., "Treatment of Liquid By-Products of Hydrothermal Carbonization (HTC) of Agricultural Digestate Using Membrane Separation," *Energies* 13, no. 1 (2020): 262.

[18] Y. Yuan, Y. He, J. Tan, Y. Wang, S. Kumar, and Z. Wang, "Co-Combustion Characteristics of Typical Biomass and Coal Blends by Thermogravimetric Analysis," *Frontiers in Energy Research* 9 (2021): 1–11.

[19] X. Luo, H. Du, J. Du, X. Zhang, W. Xiao, and L. Qin, "The Influence of Biomass Type on Hydrothermal Carbonization: Role of Calcium Oxalate in Enhancing Carbon Sequestration of Hydrochar," *Journal of Environmental Management* 349 (2024): 119586.

[20] S. Poomsawat and W. Poomsawat, "Analysis of Hydrochar Fuel Characterization and Combustion Behavior Derived From Aquatic Biomass Via Hydrothermal Carbonization Process," *Case Studies in Thermal Engineering* 27 (2021): 101255.

[21] M. Röhrdanz, T. Rebling, J. Ohlert, et al., "Hydrothermal Carbonization of Biomass From Landscape Management—Influence of Process Parameters on Soil Properties of Hydrochars," *Journal of Environmental Management* 173 (2016): 72–78.

[22] K. Harinisri, B. Thamaraiselvi, R. Gopalakrishnan, and M. Manovina, "Application of Biochar in Wastewater Treatment:

A Review," in *Application of Biochar in Wastewater Treatment: A Review*, (De Gruyter, 2022): 67–88.
[23] M. T. Reza, J. G. Lynam, M. H. Uddin, and C. J. Coronella, "Hydrothermal Carbonization: Fate of Inorganics," *Biomass and Bioenergy* 49 (2013): 86–94.
[24] T. Wang, Y. Zhai, Y. Zhu, C. Li, and G. Zeng, "A Review of the Hydrothermal Carbonization of Biomass Waste for Hydrochar Formation: Process Conditions, Fundamentals, and Physicochemical Properties," *Renewable and Sustainable Energy Reviews* 90 (2018): 223–247.
[25] Y. Gao, X. Wang, J. Wang, et al., "Effect of Residence Time on Chemical and Structural Properties of Hydrochar Obtained by Hydrothermal Carbonization of Water Hyacinth," *Energy* 58 (2013): 376–383.
[26] E. I. N. C. Assis and E. M. N. Chirwa, "Fuel Properties and Combustion Performance of Hydrochars Prepared by Hydrothermal Carbonization of Different Recycling Paper Mill Wastes," *The Canadian Journal of Chemical Engineering* 101, no. 3 (2023): 1123–1137.
[27] Y. Feng, T. Yu, K. Ma, G. Xu, Y. Hu, and D. Chen, "Effect of Hydrothermal Temperature on the Steam Gasification Performance of Sewage Sludge: Syngas Quality and Tar Formation," *Energy & Fuels* 32, no. 6 (2018): 6834–6838.
[28] R. Wang, Q. Jin, X. Ye, H. Lei, J. Jia, and Z. Zhao, "Effect of Process Wastewater Recycling on the Chemical Evolution and Formation Mechanism of Hydrochar From Herbaceous Biomass During Hydrothermal Carbonization," *Journal of Cleaner Production* 277 (2020): 123281.
[29] A. Rivas-Ubach, Y. Liu, T. S. Bianchi, N. Tolić, C. Jansson, and L. Paša-Tolić, "Moving Beyond the Van Krevelen Diagram: A New Stoichiometric Approach for Compound Classification in Organisms," *Analytical Chemistry* 90, no. 10 (2018): 6152–6160.
[30] J. R. Laszakovits and A. A. MacKay, "Data-Based Chemical Class Regions for Van Krevelen Diagrams," *Journal of the American Society for Mass Spectrometry* 33, no. 1 (2022): 198–202.
[31] P. N. Da Silva Lima, A. Ghosh, A. Nascimento, et al., "Advanced Sustainable Carbon Material From Babassu Biomass and Its Adsorption Performance," *Journal of Physics and Chemistry of Solids* 176 (2023): 111188.
[32] M. Gupta, N. Savla, C. Pandit, et al., "Use of Biomass-Derived Biochar in Wastewater Treatment and Power Production: A Promising Solution for a Sustainable Environment," *Science of The Total Environment* 825 (2022): 153892.
[33] S. Kaur, A. Kumar, G. Rakhra, and R. Arora, "Application of biochar for wastewater Treatment," *BioChar: Applications for Bioremediation of Contaminated Systems* (2022): 233–244.
[34] G. Enaime, A. Baçaoui, A. Yaacoubi, and M. Lübken, "Biochar for Wastewater Treatment—Conversion Technologies and Applications," *Applied Sciences* 10, no. 10 (2020): 3492.
[35] P. Regmi, J. L. Garcia Moscoso, S. Kumar, X. Cao, J. Mao, and G. Schafran, "Removal of Copper and Cadmium From Aqueous Solution Using Switchgrass Biochar Produced Via Hydrothermal Carbonization Process," *Journal of Environmental Management* 109 (2012): 61–69.
[36] M. Wilk, A. Magdziarz, K. Jayaraman, M. Szymańska-Chargot, and I. Gökalp, "Hydrothermal Carbonization Characteristics of Sewage Sludge and Lignocellulosic Biomass. A Comparative Study," *Biomass and Bioenergy* 120 (2019): 166–175.
[37] S. Jha, R. Gaur, S. Shahabuddin, and I. Tyagi, "Biochar as Sustainable Alternative and Green Adsorbent for the Remediation of Noxious Pollutants: A Comprehensive Review," *Toxics* 11, no. 2 (2023): 117.
[38] D. Li, N. Zhao, Y. Feng, and Z. Xie, "Thermogravimetric Analysis of Coal Semi-Char Co-Firing With Straw in O_2/CO_2 Mixtures," *Processes* 9, no. 8 (2021): 1421.
[39] C. Tong, X. Yang, G. Chen, et al., "Experimental Investigation for the Combustion Characteristics of Blends of Three Kinds of Coal," *Fuel* 300 (2021): 120937.