

## Article

# Hydrothermal Carbonization of Sewage Sludge into Solid Biofuel: Influences of Process Conditions on the Energetic Properties of Hydrochar

Siti Zaharah Roslan <sup>1</sup>, Siti Fairuz Zainudin <sup>2</sup>, Alijah Mohd Aris <sup>2</sup>, Khor Bee Chin <sup>2</sup>, Mohibah Musa <sup>1</sup>, Ahmad Rafizan Mohamad Daud <sup>1,\*</sup> and Syed Shatir A. Syed Hassan <sup>1</sup>

<sup>1</sup> School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, Shah Alam 40450, Malaysia

<sup>2</sup> Indah Water Konsortium Sdn Bhd, No.1 Jalan Damansara, Kuala Lumpur 60000, Malaysia

\* Correspondence: ahmad2057@uitm.edu.my

**Abstract:** Hydrothermal carbonization (HTC) is an attractive, green technology for the management of sewage sludge. In this study, low-value secondary sewage sludge was subjected to an HTC treatment in a 1 L batch hydrothermal reactor and transformed into a high-energy-density hydrochar under varying HTC conditions (temperature of 150–300 °C, carbonization time of 30–150 min and a solid loading of 10–30%). The resulting hydrochar fuel characteristics were analyzed for ultimate and proximate analyses, functional group composition and energetic parameters. It was found that the hydrochar yield decreased with the increasing HTC temperature and reaction time, primarily due to the loss of organic volatile matter and functional groups. Under the optimum conditions of 150 °C, 30 min of carbonization time and 30% solid loading, 80.56% of the hydrochar was recovered, providing a maximum energy yield of 90.32% and a high heating value of 18.49 MJ/kg. Compared to the raw sewage sludge (H/C ratio of 2.67 and O/C ratio of 0.51), the hydrochar also had lower H/C and O/C atomic ratios of 1.42 and 0.18, respectively. The results suggest that significant dehydration and decarboxylation during the HTC treatment of sewage sludge have resulted in the formation of carbonaceous hydrochar with energetic properties close to the sub-bituminous coals.

**Keywords:** hydrothermal; carbonization; sewage sludge; biofuel; hydrochar



**Citation:** Roslan, S.Z.; Zainudin, S.F.; Mohd Aris, A.; Chin, K.B.; Musa, M.; Mohamad Daud, A.R.; Syed Hassan, S.S.A. Hydrothermal Carbonization of Sewage Sludge into Solid Biofuel: Influences of Process Conditions on the Energetic Properties of Hydrochar. *Energies* **2023**, *16*, 2483. <https://doi.org/10.3390/en16052483>

Academic Editors: Dimitrios Kalderis and Constantinos Noutsopoulos

Received: 22 January 2023

Revised: 13 February 2023

Accepted: 27 February 2023

Published: 5 March 2023



**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/>).

## 1. Introduction

Sewage sludge is a semi-solid material produced inevitably as a byproduct of industrial or municipal wastewater treatment plant operations. In line with the global trend, Malaysia, as a developing country, has seen an increase in sewage sludge production resulting from population growth, urbanization and industrialization. To date, Malaysia produces approximately 1.25 million m<sup>3</sup> of sewage sludge per annum, and the number is expected to reach 10 million m<sup>3</sup> per annum by 2035 [1,2]. Due to the high concentration of organic constituents and biological activity, sewage sludge exhibits poor dewatering properties, retaining a moisture content typically greater than 65% through mechanical dewatering; this limits its final disposal options to mainly land dumping, incineration, biogas (methane) generation and agricultural use (soil fertilization) [3,4]. However, due to stricter environmental regulations, land scarcity and growing environmental and health concerns, the traditional method of treating sewage sludge with agricultural and landfill treatments is now deemed impractical, if not impermissible [5]. These techno-environmental challenges are compounded by the high costs of sewage-sludge handling and disposal, which are currently estimated to contribute between 50 and 60% of the total operating costs of a wastewater treatment plant [6].

As nations progress towards achieving sustainable development goals, there is a need to leverage eco-friendly technologies to manage readily available resources, such as using

sewage sludge as a green biofuel. Thermochemical conversion can effectively convert sewage sludge into value-added end products, i.e., solid biofuel, liquid bio-oil and syngas, with the proportion varying depending on the process used. This technology offers the potential to massively reduce the volume of sewage sludge, destroy harmful pathogenic materials, and recover energy embedded in the sewage sludge. However, most traditional thermochemical conversion processes, e.g., combustion, pyrolysis and gasification, typically require the sludge to contain less than 10% moisture, thus necessitating an energy-intensive pre-drying step that makes it challenging for the overall process to attain a positive net energy balance.

Recently, another class of thermochemical process called hydrothermal carbonization (HTC), or wet pyrolysis, has been introduced as a promising clean technology to convert wet biomass and biosolids into carbonaceous materials called hydrochar [7]. Unlike the traditional thermochemical processes, this artificial coalification process does not require energy-intensive drying to convert wet feedstock into hydrochar at relatively high yields (60–80%). In the past, HTC has been employed to convert a variety of lignocellulosic biomasses into solid biofuels, including empty fruit bunch [8], palm shells [9] and corn-stalk [10]. The technology has also been extended to treat more complex wet biosolids, such as paper sludge [11], food waste [12] and sewage sludge [13,14]. Hydrochar produced from the HTC has been shown to have potential applications as biofuels and functional carbon materials [15]. Fundamentally, HTC is a wet-heat chemical process carried out at a mild temperature range of 180–300 °C and an autogenous pressure above the water saturation pressure. Water is kept in a liquid state throughout the process. Depending on the target end product, the treatment can proceed in either an inert atmosphere or in the presence of limited oxygen [16]. It has been established that water, as an environmentally benign solvent at an elevated temperature and pressure, is an attractive medium for biomass and biosolid disintegration due to its enhanced solubility and ability to promote ionic reactions of non-polar organics [16,17].

Previous studies suggested that the HTC process is driven by a series of coalification reactions involving hydrolysis, dehydration, decarboxylation, polymerization and aromatization [15], which are influenced by temperature and reaction time. In principle, major sewage sludge constituents such as proteins, polysaccharides and lipids solubilize in heated water before depolymerizing into monomers and oligomers via hydrolysis at approximately 150 °C. Subsequently, the depolymerized entities decompose into reactive fragments in the liquid phase, primarily through dehydration and decarboxylation reactions. The removal of hydroxyl groups by water formation via dehydration is favored at HTC temperatures below 180 °C, whereas the decarboxylation responsible for the liberation of carboxyl and carbonyl groups by the formation of CO<sub>2</sub> becomes important at a higher temperature. The coalification process improves with an increase in HTC severity (temperature and reaction time), wherein recombination and condensation polymerization occur to produce hydrochar with higher aromaticity and hydrophobicity features. While it is true that hydrochar particles surrounded by water during hydrothermal treatment require an additional dewatering step before they can be employed as a solid biofuel, dewatering the hydrochar is considered less energy intensive as most of the bound water in the sewage sludge has been converted to free water.

The HTC-accelerated coalification process of wet biosolids generates an energy-densified hydrochar with a more enhanced combustion performance than the untreated sewage sludge in terms of ignitability and burning stability [18]. The heating value, fuel ratio, energy yield and aromaticity of the hydrochar structure have also been shown to improve significantly compared to the untreated biosolids. It has been reported that the calorific value for hydrochar obtained from sewage sludge at 180–300 °C ranges from 10 to 20 MJ/kg, equivalent to the low-rank coals such as peat, lignite and sub-bituminous [19,20] coal. More recently, Silva et al. [21] showed that a high energy yield of over 80% and a calorific value of 13–16 MJ/kg could be obtained from HTC treatment at a relatively low temperature and a short carbonization time of 100 to 200 °C and 0 to 60 min, respectively. In

another work, Hansen et al. [22] concluded that the HTC of sewage sludge under extended HTC conditions and an increasing severity (a higher HTC temperature and longer reaction time) did not contribute to the further improvement of the hydrochar fuel properties and quality due to high organic devolatilization and higher ash content.

For the practical conversion of sewage sludge into solid biofuel, less-severe HTC conditions are deemed important to limit excessive devolatilization and decarboxylation reactions, thereby allowing most of the carbon in the sewage sludge to be retained in the hydrochar matrix. Additionally, the release of volatile organics into process water can also be limited to obtain a high hydrochar yield. Therefore, considering the importance of process conditions on the energetic properties of hydrochar, this study investigated the influence of reaction temperature, carbonization time and solid loading on the course of the sewage-sludge transformation under moderate HTC conditions. A laboratory-scale batch hydrothermal reactor system was used in this study to convert secondary sewage sludge from selected sewage treatment plants in Malaysia.

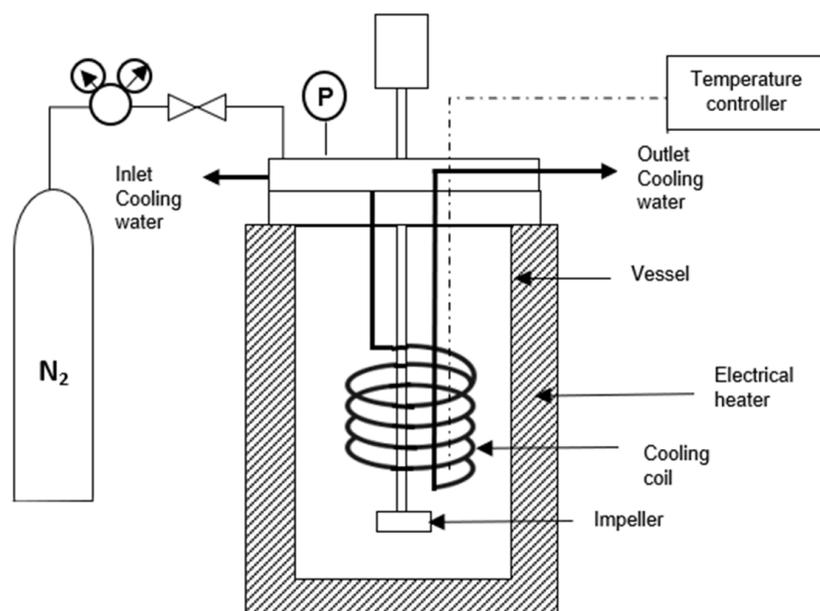
## 2. Materials and Methods

### 2.1. Sewage Sludge Sample Preparation

The raw, dewatered sewage sludge samples were collected from three sewage sludge treatment plants (STPs) located in the urban areas of Selangor and Kuala Lumpur, Malaysia. The STPs are operated by the national sewage treatment company, Indah Water Konsortium. The dewatered sludge cake is comprised of the waste biosolids obtained after secondary treatment and requires disposal in a landfill. Upon collection, the sewage sludge samples were dried in an oven for 24 h at 105 °C (ASTM D1762-84) before being ground into homogeneous particles of less than 1 mm diameter in a grinder (SM 300, Retsch, Germany). The moisture-free, ground sewage sludge samples were labelled as STP1, STP2 and STP3. They were stored in sealed plastic bags and kept in a desiccator before being used in the HTC experiments.

### 2.2. HTC Experiment

The HTC of the sewage sludge was carried out in a 1 L stainless steel cylindrical reactor with an internal diameter of 9 cm and height of 18 cm. The high-pressure batch reactor was designed to operate at a maximum temperature of 350 °C and an autogenous pressure of up to 250 bars. The reactor was equipped with a mechanical stirrer, a pressure gauge and a K-type thermocouple. Heating was provided by an external electric furnace heater that had a temperature controller. A schematic diagram of the hydrothermal carbonization reactor is presented in Figure 1. In each experiment, the dried sewage sludge samples of 50, 100 and 150 g were dispersed in 500 mL of distilled water to achieve 10, 20 and 30 wt.% solid loading. After the HTC reactor was assembled, it was leak-tested using high-pressure nitrogen gas. A gentle nitrogen gas flow was then supplied at a rate of 1 L/min for 30 s to create an oxygen-free atmosphere inside the reactor. The dried sewage sludge and distilled water mixture was heated at 4 °C/min to the desired carbonization temperature and stirred at 150 rpm. The reaction time was taken immediately after the temperature inside the reactor reached the desired carbonization temperature, and the corresponding reaction pressure was recorded from the pressure gauge. Variations in the HTC experimental conditions involving temperature, reaction time and solid loading were investigated using a one-factor-at-a-time approach, as tabulated in Table 1. At the end of each run, the heater was immediately switched off and detached from the reactor body. Cooling water was supplied to quench the reaction and bring the reaction products down to room temperature. The residual pressure was subsequently released, after which the solid hydrochar and liquid-phase reaction mixture were carefully collected and separated in a centrifuge at 4000 rpm for 20 min. The obtained hydrochar was dried at 105 °C for 24 h and characterized. In this work, gaseous products were not collected and analyzed. All experiments were carried out in triplicate, and the average values were reported together with experimental error bounds of one standard deviation interval.



**Figure 1.** Schematic diagram of the 1 L hydrothermal carbonization reactor.

**Table 1.** Overall sewage sludge HTC experimental plan.

Temperature (°C)	Solid Loads (wt.%)	Reaction Time (min)
150, 200, 250, 300	10	30
150	20, 30	30
150	30	60, 90, 120, 150

### 2.3. Sewage Sludge and Products Characterization

A proximate analysis was performed to determine the volatile matter (VM), ash and fixed carbon (FC) composition. The ash and VM tests were conducted following ASTM D3174-02 [23] and ASTM D3175-07 [24] standard methods, respectively. The FC percentage was calculated by difference using Equation (1). Meanwhile, the elements of carbon, hydrogen, nitrogen and sulphur (ultimate analysis) in the sewage sludge and hydrochar were determined using a CHNS Vario Elemental Analyser III in accordance with the ASTM D3176-89 method [25]. The oxygen content was calculated by difference using Equation (2).

$$FC (\%) = 100\% - moisture(\%) - VM(\%) - ash(\%) \quad (1)$$

$$O(\%) = 100\% - C(\%) - H(\%) - N(\%) - S(\%) - ash \quad (2)$$

A Perkin Elmer Spectrum One Fourier Transform Infrared Spectrometer (FTIR) was used to qualitatively analyze the surface functional groups of the sewage sludge and hydrochar samples using KBr palletization method at hydrochar:KBr ratio of 1:100. The FTIR spectrum was accumulated at a wave number range of 4000–400  $\text{cm}^{-1}$  with 10 scans per sample.

### 2.4. Fuel Properties of Hydrochar

The hydrochar yield was calculated using Equation (3). Energy densification, referring to the relative increase in the energy content of the hydrochar, was evaluated according to Equation (4). Consequently, the energy yield was obtained using Equation (5).

$$\text{Hydrochar yield } (\%) = \frac{\text{Mass of hydrochar}}{\text{Mass of dry sludge}} \times 100\% \quad (3)$$

$$\text{Energy densification} = \frac{\text{HHV of hydrochar}}{\text{HHV of raw sludge}} \quad (4)$$

$$\text{Energy yield/recovery (\%)} = \text{Hydrochar yield} \times \text{Energy densification} \quad (5)$$

The higher heating values (HHVs) of the raw sewage sludge and the hydrochar samples were determined using an IKA C5000 BASIC bomb calorimeter in accordance with the ASTM D2015-00 standard method [26] and the well-established Dulong formula (Equation (6)), respectively.

$$\text{HHV} = 0.3383C + 1.422 \left( H - \frac{O}{8} \right) \quad (6)$$

where C, H, and O represent carbon, hydrogen, and oxygen, respectively. The HHV was reported on a dry basis in MJ/kg.

### 3. Results and Discussion

#### 3.1. Characteristics of Raw Sewage Sludge

The ultimate and proximate compositions and the higher heating values of the dewatered sewage sludge samples collected from the STP1, STP2 and STP3 sewage treatment plants are presented in Table 2. The moisture content in these samples, measured on an as-received basis, was found to range between 73.0 and 83.7%. The obtained values corresponded well with the moisture content of sewage sludge from other sewage treatment plants reported in the literature [5]. Fundamentally, moisture exists in sewage sludge in the forms of (i) free (or bulk) water, (ii) interstitial, (iii) vicinal (or surface) and (iv) chemically bound (or hydration) water. During the thickening and dewatering stage, the free and interstitial water was mainly removed, leaving behind the water trapped and bound to the solid particles. Note that the moisture measured here mainly represents the surface and bound water. Due to the high moisture content, a window of opportunity exists for directly applying HTC to convert the sewage sludge into hydrochar. As can be seen from Table 2, the volatile matter (52.5–61.0%), fixed carbon (10.3–12.6%) and ash (28.7–34.9%) content of the dewatered sludge samples were comparable, if not superior to other regional sewage sludges [21,27–30]. The relatively high percentages of fixed carbon and volatile matter are particularly important for the utilization of sewage sludge as a solid biofuel. As with other regional sewage sludges, such as those from Ratmalna, Sri Lanka [21] and Shanghai, China [31], in which the ash contents were reported to be 30.6% and 31.2% respectively, the ash content was found to be considerably high, mainly due to the presence of ash-forming constituents of inorganic minerals and heavy metals. As shown in Table 2, all sludge samples were enriched with the major ash-forming elements Si, Al, Fe, Ca and Mg, all of which are capable of catalyzing certain carbonization and pyrolysis reactions. Alkali metals, including sodium (Na) and potassium (K), were also present in all the investigated sewage sludge samples. In traditional thermochemical processes, these elements may react with silica from the ash at high temperatures to produce a sticky, mobile, liquid-phase material that causes blockages in the equipment and affects the thermal conversion process, especially in a boiler or furnace. In addition, some heavy metals (Cr, Ni, Cu, Zn, Pb, Cd, and Hg) have also been found in the sewage sludge [32], contributing to a high percentage of ash in the sewage sludge. The heavy metals in sewage sludge may originate from various sources, including industrial wastewater, runoff, corrosion of sewerage systems, medicine, detergents, cosmetics and personal care products.

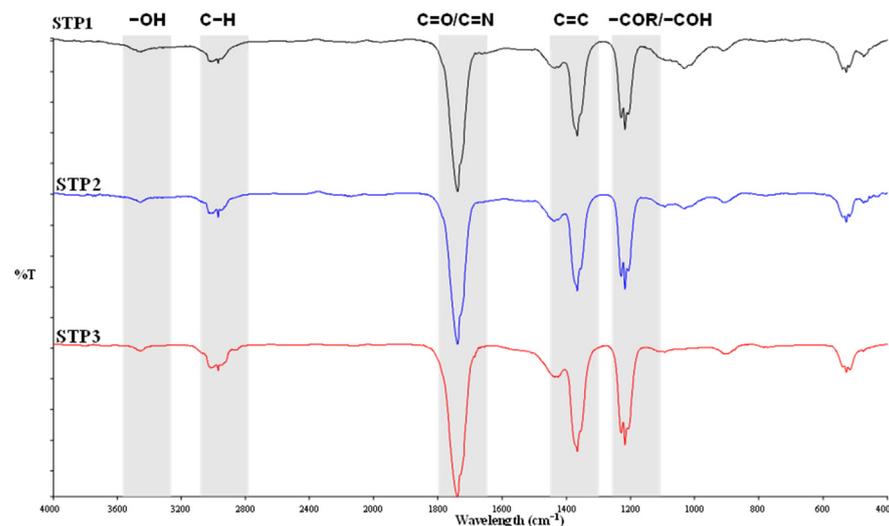
The ultimate analyses indicate that the raw sewage sludge samples contained favorable amounts of elemental carbon (30.9 to 31.8%) and hydrogen (6.8 to 7.8%). The Malaysian sewage sludges were also found to contain a higher concentration of N-containing compounds, most likely originating from protein, peptides, fatty acids and sugar. The presence of oxygen, nitrogen and sulphur is detrimental to potential sewage sludge applications as a solid biofuel as these elements contribute to a lower heating value and release undesirable SO<sub>x</sub> and NO<sub>x</sub> upon combustion. Meanwhile, the higher heating values (HHVs) of the three

sewage samples were almost identical at approximately 13 MJ/kg, within the range of 9.04–15.20 MJ/kg found in the literature [21,27,28].

**Table 2.** Characteristics of dewatered sewage sludge samples.

Analysis		STP1	STP2	STP3
Moisture content (% , as received)		73.03	83.70	80.97
Proximate (wt.%, db)	Volatile matter	61.00	52.52	57.00
	Fixed carbon	10.29	12.58	12.31
	Ash	28.71	34.90	30.69
Ultimate analysis (wt.%, db)	C	31.70	30.90	31.80
	H	7.66	6.87	7.85
	N	5.61	5.06	5.16
	O	25.02	20.99	23.24
	S	1.30	1.28	1.26
HHV (MJ/kg)		13.74	13.10	13.76
Major ash forming elements, (wt.%, db)	Si	5.37	5.60	5.44
	Al	0.73	1.30	1.02
	Ti	0.18	0.20	0.21
	Fe	1.69	2.35	1.90
	Ca	0.55	0.41	0.45
	Mg	0.06	0.04	0.04
	Na	0.09	0.10	0.12
	K	0.12	0.21	0.19
	P	1.38	1.13	1.42

Figure 2 presents the chemical functionalities of the raw sewage sludge samples as observed by the FTIR spectra. Several distinctive absorption bands were observed, having almost similar intensities for all sewage sludge samples irrespective of the sludge origins. The bands at approximately  $3300\text{ cm}^{-1}$  can likely be attributed to the -OH stretching vibrations from the hydroxyl and carboxyl groups. Their presence may be contributed by the proteins and polysaccharides content in the sewage sludge. Meanwhile, the intensities of peaks between  $3000$  and  $2800\text{ cm}^{-1}$  can be associated with the aliphatic C-H<sub>n</sub> groups. The peaks observed at a lower wave number, centered around  $1650\text{ cm}^{-1}$  stretching vibrations, correspond to that of the C=N amides, while a significant presence of C-O-C aliphatic ethers was detected at the wave number of  $1000\text{ cm}^{-1}$ .



**Figure 2.** FTIR spectra of raw, dewatered sewage sludge samples.

Overall, the physicochemical analyses suggest that the characteristics of all raw, dewatered sewage sludge samples investigated in this study closely matched each other. Considering that all samples were collected from STPs located in urban areas, it is likely that the general characteristics of the sewage sludge were influenced by similar local human activities, food consumption patterns, and the surrounding economic and industrial activities. The few differences observed may be attributed to the treatment method used in each STP and the aging of the sludge after the dewatering process.

### 3.2. Effect of HTC Conditions on Hydrochar Characteristics

In order to better understand the effects of the HTC conditions on the upgrading of sewage sludge into biofuel, the raw sludge sample obtained from STP2 was chosen for subsequent investigations. This selection took into consideration the need to assess the applicability and suitability of the HTC technology in upgrading a less-favorable feedstock into a high-quality hydrochar. The effects of temperature, carbonization time and solid loading on the hydrochar yield and its propensity for use as solid biofuel were evaluated primarily by proximate and ultimate analyses, as tabulated in Table 3. The hydrochar recovered after HTC treatment for all conditions investigated appeared as a dark-brown solid with a distinctive, unpleasant, sharp smell.

**Table 3.** Proximate and ultimate analysis of hydrochar.

Sample ID	Proximate Analysis (wt.%, db)				Ultimate Analysis (wt.%, db)				Solid Yield (%)
	VM	FC	Ash	C	H	O *	N	S	
HTC1:150 °C:10%:30 min	41.70	16.30	42.00	39.30	4.68	8.35	3.89	1.78	73.93
HTC2:200 °C:10%:30 min	32.15	16.85	51.00	35.80	4.18	4.55	2.85	1.62	63.09
HTC3:250 °C:10%:30 min	28.10	16.90	55.00	34.70	3.93	2.28	2.64	1.45	57.65
HTC4:300 °C:10%:30 min	23.29	19.71	57.00	33.95	3.85	1.69	2.13	1.38	48.46
HTC5:150 °C:20%:30 min	42.08	16.61	41.31	39.52	4.69	8.78	3.91	1.79	75.97
HTC6:150 °C:30%:30 min	42.96	16.65	40.39	39.78	4.71	9.38	3.93	1.81	80.56
HTC7:150 °C:30%:60 min	40.53	16.76	42.71	39.25	4.62	7.70	3.92	1.80	78.58
HTC8:150 °C:30%:90 min	36.80	17.41	45.79	38.23	4.61	5.68	3.89	1.80	77.35
HTC9:150 °C:30%:120 min	35.69	17.50	46.81	38.21	4.44	5.03	3.75	1.76	76.94
HTC10:150 °C:30%:150 min	35.05	17.02	47.93	38.19	4.38	4.70	3.61	1.63	74.52

\* Calculated by difference.

The results indicate that the hydrochar yield was strongly affected by the HTC temperature. The highest hydrochar yield was observed at the lower end of the HTC temperature investigated (i.e., 150 °C). As the carbonization temperature increased from 150 to 300 °C, the hydrochar yield gradually decreased from 73.9% to 48.5%. The decrease in yield was mainly due to the primary and secondary decomposition of various components in the sewage sludge [8], which were caused by complex and simultaneous reactions involving hydrolysis, dehydration, decarboxylation and condensation. Similarly, temperature–time interactions resulted in lower hydrochar yield, albeit at a smaller yield percentage reduction. Extending the reaction to 150 min exposed the sewage sludge constituents to further degradation. The volatile organic matter that devolatilized and dissolved into an aqueous phase might polymerize at a longer reaction time, resulting in secondary, polyaromatic, structured hydrochar. The proximate analysis showed that the volatile matter of the hydrochar was considerably lower when compared to the raw, dewatered sewage sludge. When the reaction temperature was raised from 150 to 300 °C, the volatile matter content gradually decreased from 41.7% to 23.3%. The mass loss observed in the volatile matter was only partially compensated for by the increase in fixed carbon content. This suggests that the volatile organic matter in the sewage sludge was likely devolatilized and partitioned into process water or released as gases (e.g., CO<sub>2</sub>) during the HTC treatment. Accordingly,

the ash content markedly increased with the reaction temperature due to a higher degree of volatile solubilization and inorganic mineral retention [33,34].

Similar trends involving the evolution of volatile matter and fixed carbon and ash content were observed from experiments investigating the effect of solid loading and reaction time. One exception was the decrease in ash content with an increasing solid load, from 42.0% to 40.4%, indicating a decrease in the amount of carbon dissolved as the solid loading increased, coinciding with the mild increase of the hydrochar produced. On the other hand, the slight changes in the volatile matter content imply that only a small proportion of the light organic components transitioned into the HTC's liquid and gaseous phases. The effect of solid loading on ash content observed in this study is consistent with the findings reported for sewage digestate [14]. Compared to solid loading, the effect of extending the reaction time from 30 min to 150 min on the loss of the volatile matter was more pronounced, and when combined with the minerals retained within the hydrochar structure resulted in an upsurge of the ash content from 40.4% to 47.9%, respectively.

The percentage of elemental CHNOS of the hydrochar was found to decrease steadily with the carbonization temperature and reaction time. It is likely that some organic functional groups bearing the CHNOS elements were lost together with the volatile matter during the HTC treatment, as confirmed by the FTIR analyses in Section 3.4. In a typical HTC treatment, sewage sludge constituents, including protein, polysaccharides, lipids and humic substances, have been shown to undergo dehydration, decarboxylation, condensation and depolymerization reactions, resulting in the sewage sludge decomposition into hydrochar and liquid and gaseous products. The loss of carbon content may be explained by the transfer of carbon from the solid phase into the liquid and gas phase, mainly via decarboxylation. Meanwhile, the decreasing trend for the hydrogen and oxygen contents may be attributed to dehydration and decarboxylation reactions. Reductions of the N and S heteroatoms content were likely related to the dissolution of N- and S-containing compounds. It was reported that the hydrolysis of N-containing compounds during HTC encouraged the build-up of ammonium constituents in the process water [35]. A longer carbonization time (up to 150 min) resulted in lower carbon, oxygen and hydrogen concentrations. Due to the dehydration and decarboxylation reactions, the oxygen concentration dropped significantly from 9.4% to 4.7%. The N content of the hydrochar was substantially reduced to 3.6% after 150 min of HTC treatment. The hydrolysis and dissolution of protein components into soluble proteins, amino acids, amide and  $\text{NH}_4^+$  was the primary cause for the substantial fall in the N content. The HTC reaction time had very little effect on the S content of hydrochar, evidenced by the slight reduction in the S content.

In contrast to the other reaction parameters investigated, increasing the solid loading from 10% to 30% only slightly changed the elemental CHNOS concentrations of the hydrochars produced. This indicates a low elemental yield dependency on the feedstock composition [36] and a lack of strong association with its impact on dehydration and decarboxylation processes. This is consistent with the results of Zabaleta et al. [37].

### 3.3. Fuel Characteristics

Figure 3 illustrates the influence of the HTC parameters on the hydrochar fuel properties. The HHV of the hydrochar was found to have increased considerably from approximately 13 MJ/kg for the raw dewatered sewage sludge to approximately 16–18 MJ/kg after the HTC treatment, a 23–38% improvement. The highest HHV value of 18.49 MJ/kg was obtained from the experiment at 150 °C, a 30 min reaction time and a 30% solid load. It is clear that the HTC was able to convert low-heating-value sewage sludge into coal-like hydrochar with an HHV ranging from 15 to 19.36 MJ/kg [38,39]. The HHV results showed a downward trend with an increasing HTC temperature and reaction time (Figure 3a,c); however, the opposite was observed for the solid loading experiments. These trends were closely attributed to the changes in the concentrations of the heat-contributing elements of carbon, hydrogen and ash contents of the hydrochar as a result of the variations in the HTC parameters. As the HTC condition severity was raised, higher amounts of carbon and

hydrogen were driven off the hydrochar, primarily via decarboxylation and dehydration mechanisms at temperatures above 150 °C [22]. Dehydration is often attributed to the removal of hydroxyl groups, while decarboxylation is the thermal breaking of long-chain carboxylic acids. As these mechanisms were temperature-related, the degree of HHV loss was more pronounced for the HTC temperature than the reaction time. Meanwhile, the inorganics and minerals were concentrated in the hydrochar, leading to a higher ash content and therefore lowering the HHV. The impact of solid loading on the HHV value was limited, mainly due to a lack of improvement in the carbon and hydrogen contents of the hydrochar even at a 30% solid loading, as tabulated in Table 3. Moreover, there was no clear association between the changes in solid loading and its impact on dehydration and decarboxylation reactions that would significantly influence the HHV by altering the hydrogen and oxygen compositions in the hydrochar. Such observations were in agreement with the published results [14].

The fuel properties for hydrochars obtained at various HTC conditions were evaluated using the energy densification, fuel ratio (FC/VM) and energy yield. The results are presented in Table 4. Clearly, the HTC temperature exerts considerable influence on the fuel characteristics of the hydrochar compared to the effects of solid loading and carbonization time. Interestingly, the results showed that a satisfactorily high energy recovery of over 80% was recorded at the lower end of the HTC temperature investigated, i.e., 150 °C, with a maximum observed at a solid loading of 30% and a 30 min reaction time. Given that energy densification remained almost stable at this temperature, this implies that hydrochar was produced at a greater mass yield under these conditions than those obtained at higher temperatures.

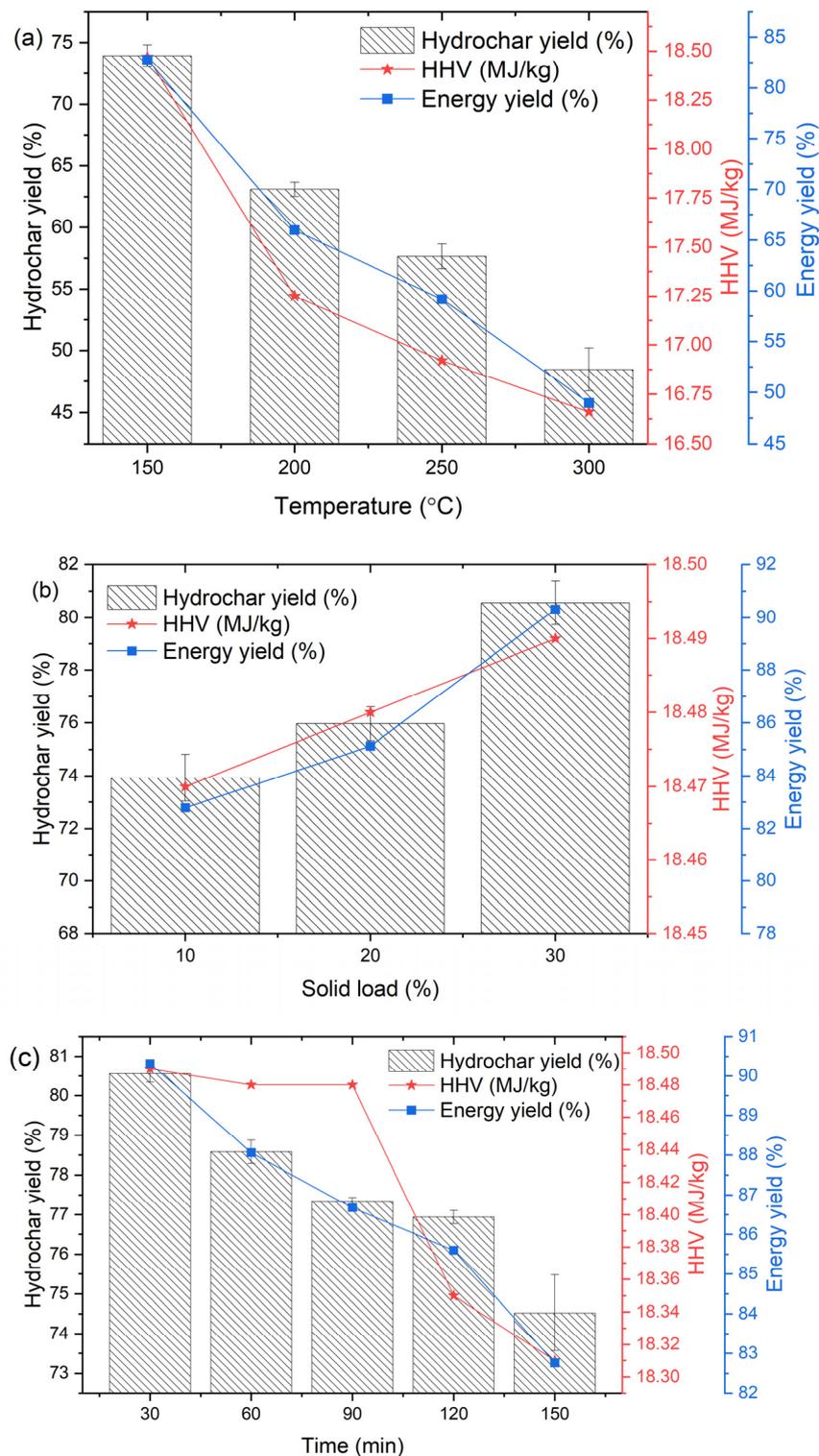
**Table 4.** Fuel characteristics of hydrochar.

Sample ID	Energy Densification	Fuel Ratio (FC/VM)	Energy Yield (%)
HTC1:150 °C:10%:30 min	1.12	0.39	82.79
HTC2:200 °C:10%:30 min	1.05	0.52	65.98
HTC3:250 °C:10%:30 min	1.03	0.60	59.16
HTC4:300 °C:10%:30 min	1.01	0.85	48.96
HTC5:150 °C:20%:30 min	1.12	0.39	85.13
HTC6:150 °C:30%:30 min	1.12	0.39	90.32
HTC7:150 °C:30%:60 min	1.12	0.41	88.06
HTC8:150 °C:30%:90 min	1.12	0.47	86.68
HTC9:150 °C:30%:120 min	1.11	0.49	85.60
HTC10:150 °C:30%:150 min	1.11	0.49	82.76

Meanwhile, Table 5 compares the hydrochar yield, HHV and energy yield obtained from this work to other conventional carbonization methods, including torrefaction and pyrolysis. As can be seen, the conversion of sewage sludge into a solid biofuel using HTC at a lower process severity showed superior performance compared to torrefaction and pyrolysis. This indicates that HTC could be a preferred treatment approach for sewage sludge carbonization.

The fuel quality of the hydrochar was assessed by the Van Krevelen diagram (Figure 4), which characterizes the evolution of the H/C and O/C atomic ratios after HTC treatment. The diagram depicts the degree and pathway of coalification and compares the fuel quality of the hydrochar produced against several traditional solid fuels such as coal, peat, lignite and biomass. The hydrochars produced in the present study showed a progressive degree of coalification with increasing severity of HTC temperature and reaction time. As shown by the ultimate analyses, the carbon content was mostly retained in the hydrochar. Meanwhile, the H/C and O/C atomic ratios of the hydrochar were markedly lower than the starting raw sewage sludge (H/C 2.67 and O/C 0.51), even for hydrochars produced at the low HTC temperature of 150 °C and short reaction time of 30 min. By increasing the reaction

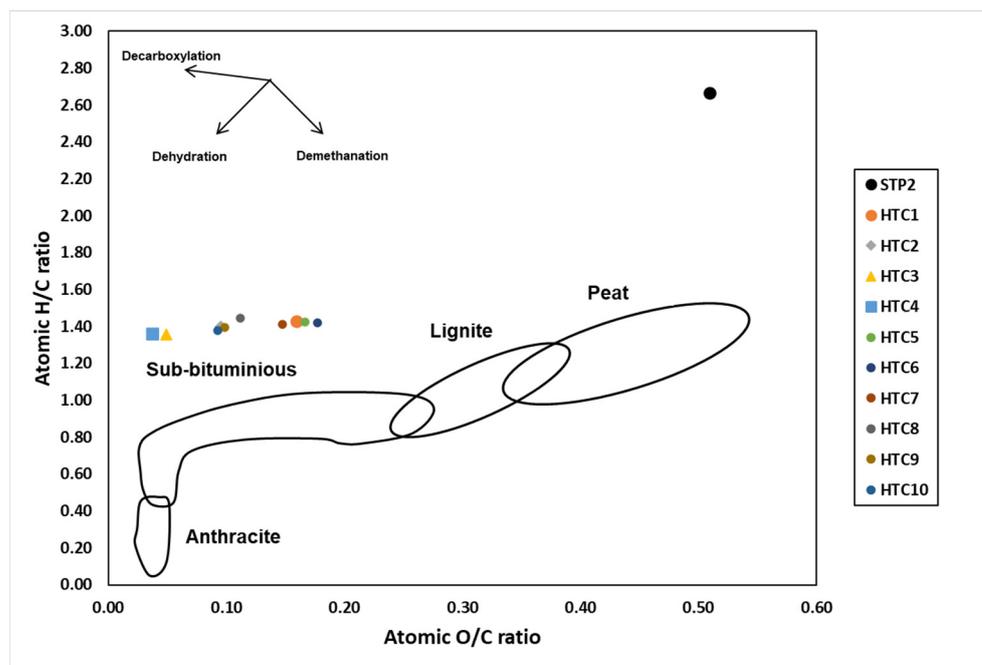
temperature further to 300 °C and extending the reaction time up to 120 min, the respective atomic ratios continued to decrease, approaching those in the sub-bituminous coal region, albeit at a slightly higher H/C ratio.



**Figure 3.** Effects of HTC conditions on solid yield, HHV and energy yield; (a) temperature at fixed 10% solid loading and 30 min; (b) solid loading at fixed temperature 150 °C and 30 min; and (c) reaction time at fixed temperature 150 °C and 30% solid loading.

**Table 5.** Comparison of HHV of hydrochar/biochar under different operating parameters and carbonization method.

Sludge Sample Location	Carbonization Method	Condition	Solid Yield (%)	HHV (MJ/kg)	Energy Yield (%)	References
Shah Alam	Hydrothermal carbonization	Temperature:150 °C Time: 30 min Solid load: 30%	80.56	18.49	90.32	This study
Changsha, China	Hydrothermal carbonization	Temperature:150 °C Time: 30 min	58.51	12.06	64.32	[33]
Jastrzebie-Zdrój, Poland	Torrefaction	Temperature: 240 °C Time: 60 min Time: 50 min	-	12.06	-	[40]
London, Ontario, Canada	Slow pyrolysis	Temperature: 300 °C Time: 30 min	50	18.6	65.96	[41]
Dehradun, India	Pyrolysis	Temperature: 500 °C Time: 60 min	58.70	10.04	50.41	[42]

**Figure 4.** Van Krevelen diagram of raw sewage sludge and hydrochar produced at different HTC conditions.

The observed progression of the hydrochar coalification primarily follows the dehydration and decarboxylation pathways, resulting in the liberation of hydroxyl and carboxylic groups, respectively [18,43,44]. The results indicate that the chemical dehydration pathway (resulting in lower H/C) predominated at mild HTC conditions of 150 °C and 30 min. On the contrary, simultaneous dehydration and decarboxylation pathways, by which the sewage sludge was carbonized by decreasing the H/C and O/C ratios [36], predominated at higher HTC temperature and longer reaction time. Hydrochar produced at the extended reaction time exhibited a lower O/C ratio, implying the loss of oxygen functional groups. This lead to increased carbon aromaticity and hydrophobicity [45]. The trends were in agreement with the results of previous studies on the HTC of sewage sludge [46] and saccharides (e.g., glucose, sucrose and starch) [16]. The O/C values for a 10%, 20% and 30% solid loading were approximately 0.16, 0.17 and 0.18, respectively, indicating an increasing

degree of hydrochar carbonization with an increasing solid load, similar to those observed for the agro-industrial waste hydrochar [47].

### 3.4. Surface Functionalities of Hydrochar

Figure 5 compares the FTIR spectra of the raw sewage sludge with those of the hydrochars obtained at varying carbonization temperatures, solid loading ratios and reaction times. The accumulated spectra appeared identical in the infrared absorption bands detected, suggesting that the hydrochars retained most of the original chemical functionalities observed in the raw sewage sludge. Several important absorption band peaks centered around wavenumbers of  $3400\text{ cm}^{-1}$ ,  $3000\text{--}2800\text{ cm}^{-1}$ ,  $1800\text{--}1650\text{ cm}^{-1}$ ,  $1360\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$  were identified. The peak at around  $3400\text{ cm}^{-1}$  corresponds to the -OH stretching vibrations from hydroxyl and carboxyl groups which could have originated from the protein and polysaccharide constituents [48,49]. The -OH peak intensity was lower at higher reaction temperatures and longer carbonization times, suggesting that dehydration and decarboxylation may have been promoted under these conditions. The peaks between  $3000$  and  $2800\text{ cm}^{-1}$  represent the aliphatic C-H<sub>n</sub> groups [33]. Compared to the raw sewage sludge feedstock, these peaks in the hydrochar became slightly intensified as the solid load rose. The C-H<sub>n</sub> peak intensity, however, was not influenced by the HTC temperature and reaction time, indicating the relative strength of the bond. A distinctively broad peak was observed at lower wavenumbers between  $1650$  and  $1800\text{ cm}^{-1}$  and stretching vibrations corresponding to that of C=O carboxyl and C=N amides [50,51]. Following the HTC process, this peak showed a lower intensity. It has been suggested that the C=N functional group is prone to a hydrolysis reaction during HTC treatment [33]; hence the downward trend under more severe HTC conditions. The bands at  $1360\text{ cm}^{-1}$  showed -C=C stretching in aromatic ring carbons. As carbonization time increased, their intensity remained almost constant with the increasing temperature and solid loading. The analysis also revealed a strong occurrence of C-O-C aliphatic ethers and -COH in alcohol identified at the wavenumber centered around  $1200\text{ cm}^{-1}$  [52,53]. The increasing intensity at higher temperatures was ascribed to the alcohol dehydration reaction. Low signal peaks below  $800\text{ cm}^{-1}$  could be interpreted as those of aromatic fingerprints; however, this is inconclusive.

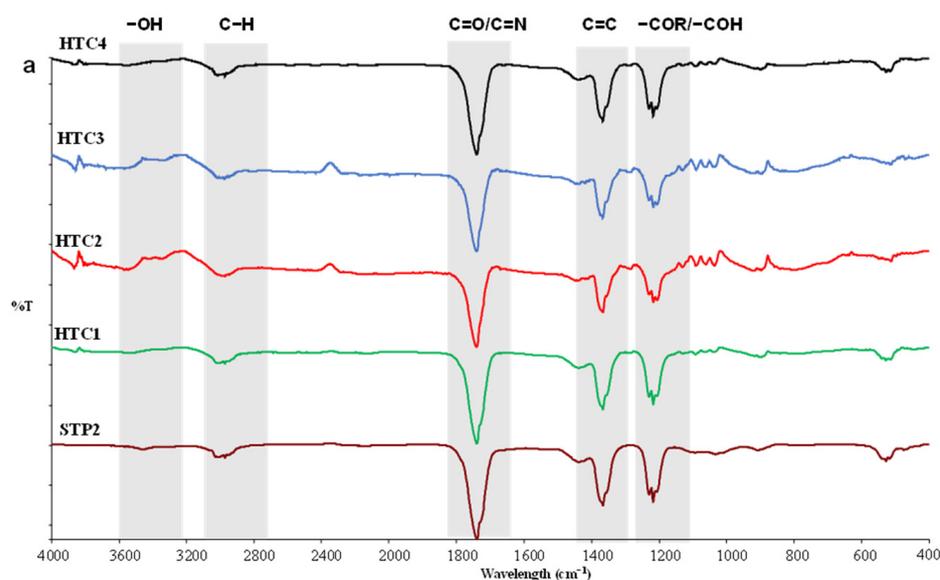
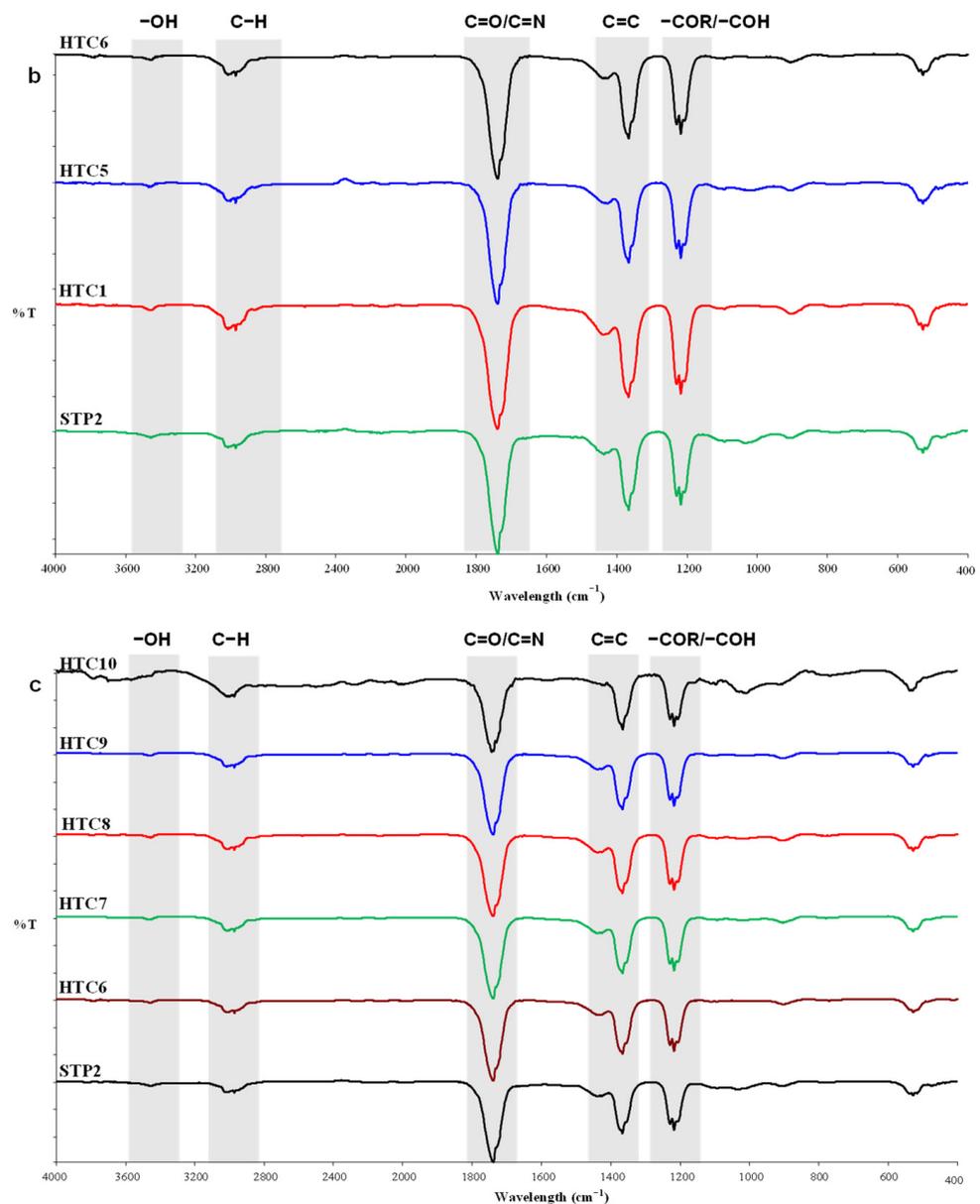


Figure 5. Cont.



**Figure 5.** FTIR spectra of hydrochar obtained at different (a) HTC temperatures; (b) solid loading ratios and; (c) reaction times.

#### 4. Conclusions

In this study, the effects of HTC operating conditions on the fuel properties of hydrochars produced from wet sewage sludge were investigated. HTC treatment was found to improve the physicochemical properties of the raw sewage sludge significantly. Unlike solid loading, the carbonization temperature and time affected the fuel characteristics of the produced hydrochar more, mainly due to dehydration and decarboxylation reactions. At mild HTC conditions of 150 °C and 30 min of carbonization time, a hydrochar with a good fuel quality was obtained at a high yield of 80.56%. The hydrochar exhibited a high heating value (18.49 MJ/kg), low H/C and O/C atomic ratios that approached those of sub-bituminous coal grade, and low N and S contents. With an energy recovery as high as 90.32%, HTC is a promising approach for converting wet sewage sludge into a sustainable, solid biofuel. These results highlight the potential of the HTC treatment to produce a solid biofuel compatible for co-firing with low-ranked coal for less harmful SO<sub>x</sub> and NO<sub>x</sub> gas emissions. However, the high ash levels remain a technical challenge.

**Author Contributions:** Conceptualization, investigation, methodology, and writing—original draft preparation, S.Z.R. and A.R.M.D.; formal analysis and data curation, S.Z.R. and M.M.; writing—review and editing, S.S.A.S.H.; supervision, A.R.M.D., S.S.A.S.H., K.B.C. and S.F.Z.; funding acquisition, A.R.M.D., S.S.A.S.H., K.B.C., A.M.A. and S.F.Z. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was jointly supported by Universiti Teknologi MARA and Indah Water Konsortium Sdn Bhd through a Strategic Research Partnership grant: grant numbers 100-RMC 5/3/SRP PRI (028/2020) and 100-RMC 5/3/SRP (004/2020).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data reported in this research may be found in the publication.

**Acknowledgments:** The authors are grateful for the laboratory facilities and the technical and financial assistance provided by the School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA Shah Alam and the Indah Water Konsortium Sdn Bhd throughout the research duration.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Roslan, S.N.; Ghazali, S.S.; Asli, N.M. Study on the Characteristics and Utilization of Sewage Sludge at Indah Water Konsortium (IWK) Sungai Udang, Melaka. *Int. J. Environ. Ecol. Eng.* **2013**, *7*, 544–548.
2. Spinosa, L. *Wastewater Sludge: A Global Overview of the Current Status and Future Prospects*, 2nd ed.; IWA Publishing: London, UK, 2011; Volume 10, ISBN 9781780401195.
3. Chojnacka, K.; Skrzypczak, D.; Szopa, D.; Izydorczyk, G.; Moustakas, K.; Witek-Krowiak, A. Management of Biological Sewage Sludge: Fertilizer Nitrogen Recovery as the Solution to Fertilizer Crisis. *J. Environ. Manag.* **2023**, *326*, 116602. [[CrossRef](#)] [[PubMed](#)]
4. Kacprzak, M.; Neczaj, E.; Fijałkowski, K.; Grobelak, A.; Grosser, A.; Worwag, M.; Rorat, A.; Brattebo, H.; Almås, Å.; Singh, B.R. Sewage Sludge Disposal Strategies for Sustainable Development. *Environ. Res.* **2017**, *156*, 39–46. [[CrossRef](#)]
5. Syed-Hassan, S.S.A.; Wang, Y.; Hu, S.; Su, S.; Xiang, J. Thermochemical Processing of Sewage Sludge to Energy and Fuel: Fundamentals, Challenges and Considerations. *Renew. Sustain. Energy Rev.* **2017**, *80*, 888–913. [[CrossRef](#)]
6. Kakwani, N.S.; Kalbar, P.P. Review of Circular Economy in Urban Water Sector: Challenges and Opportunities in India. *J. Environ. Manag.* **2020**, *271*, 111010. [[CrossRef](#)] [[PubMed](#)]
7. Zhai, Y.; Peng, C.; Xu, B.; Wang, T.; Li, C.; Zeng, G.; Zhu, Y. Hydrothermal Carbonisation of Sewage Sludge for Char Production with Different Waste Biomass: Effects of Reaction Temperature and Energy Recycling. *Energy* **2017**, *127*, 167–174. [[CrossRef](#)]
8. Parshetti, G.K.; Hoekman, S.K.; Balasubramanian, R. Chemical, Structural and Combustion Characteristics of Carbonaceous Products Obtained by Hydrothermal Carbonization of Palm Empty Fruit Bunches. *Bioresour. Technol.* **2013**, *135*, 683–689. [[CrossRef](#)]
9. Nizamuddin, S.; Mubarak, N.M.; Tiripathi, M.; Jayakumar, N.S.; Sahu, J.N.; Ganesan, P. Chemical, Dielectric and Structural Characterization of Optimized Hydrochar Produced from Hydrothermal Carbonization of Palm Shell. *Fuel* **2016**, *163*, 88–97. [[CrossRef](#)]
10. Zhang, D.; Wang, F.; Shen, X.; Yi, W.; Li, Z.; Li, Y.; Tian, C. Comparison Study on Fuel Properties of Hydrochars Produced from Corn Stalk and Corn Stalk Digestate. *Energy* **2018**, *165*, 527–536. [[CrossRef](#)]
11. Mäkelä, M.; Benavente, V.; Fullana, A. Hydrothermal Carbonization of Industrial Mixed Sludge from a Pulp and Paper Mill. *Bioresour. Technol.* **2016**, *200*, 444–450. [[CrossRef](#)]
12. Saqib, N.U.; Baroutian, S.; Sarmah, A.K. Physicochemical, Structural and Combustion Characterization of Food Waste Hydrochar Obtained by Hydrothermal Carbonization. *Bioresour. Technol.* **2018**, *266*, 357–363. [[CrossRef](#)] [[PubMed](#)]
13. Danso-Boateng, E.; Shama, G.; Wheatley, A.D.; Martin, S.J.; Holdich, R.G. Hydrothermal Carbonisation of Sewage Sludge: Effect of Process Conditions on Product Characteristics and Methane Production. *Bioresour. Technol.* **2015**, *177*, 318–327. [[CrossRef](#)]
14. Aragón-Briceño, C.I.; Grasham, O.; Ross, A.B.; Dupont, V.; Camargo-Valero, M.A. Hydrothermal Carbonization of Sewage Digestate at Wastewater Treatment Works: Influence of Solid Loading on Characteristics of Hydrochar, Process Water and Plant Energetics. *Renew. Energy* **2020**, *157*, 959–973. [[CrossRef](#)]
15. Wang, L.; Chang, Y.; Li, A. Hydrothermal Carbonization for Energy-Efficient Processing of Sewage Sludge: A Review. *Renew. Sustain. Energy Rev.* **2019**, *108*, 423–440. [[CrossRef](#)]
16. Pauline, A.L.; Joseph, K. Hydrothermal Carbonization of Organic Wastes to Carbonaceous Solid Fuel-A Review of Mechanisms and Process Parameters. *Fuel* **2020**, *279*, 118472. [[CrossRef](#)]
17. Knez, Ž.; Markočič, E.; Hrnčič, M.K.; Ravber, M.; Škerget, M. High Pressure Water Reforming of Biomass for Energy and Chemicals: A Short Review. *J. Supercrit. Fluids* **2015**, *96*, 46–52. [[CrossRef](#)]

18. Zhao, P.; Shen, Y.; Ge, S.; Chen, Z.; Yoshikawa, K. Clean Solid Biofuel Production from High Moisture Content Waste Biomass Employing Hydrothermal Treatment. *Appl. Energy* **2014**, *131*, 345–367. [[CrossRef](#)]
19. Maniscalco, M.P.; Volpe, M.; Messineo, A. Hydrothermal Carbonization as a Valuable Tool for Energy and Environmental Applications: A Review. *Energies* **2020**, *13*, 4098. [[CrossRef](#)]
20. Djandja, O.S.; Yin, L.-X.; Wang, Z.-C.; Duan, P.-G. From Wastewater Treatment to Resources Recovery through Hydrothermal Treatments of Municipal Sewage Sludge: A Critical Review. *Process Saf. Environ. Prot.* **2021**, *151*, 101–127. [[CrossRef](#)]
21. Silva, R.D.V.K.; Lei, Z.; Shimizu, K.; Zhang, Z. Hydrothermal Treatment of Sewage Sludge to Produce Solid Biofuel: Focus on Fuel Characteristics. *Bioresour. Technol. Rep.* **2020**, *11*, 100453. [[CrossRef](#)]
22. Hansen, L.J.; Fendt, S.; Spliethoff, H. Impact of Hydrothermal Carbonization on Combustion Properties of Residual Biomass. *Biomass Convers. Biorefinery* **2020**, *12*, 2541–2552. [[CrossRef](#)]
23. ASTM D 3174-02; Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal. American Society for Testing and Materials International: West Conshohocken, PA, USA, 2002.
24. ASTM D3175-07; Standard Test Method for Volatile Matter in the Analysis Sample of Coal and Coke. American Society for Testing and Materials International: West Conshohocken, PA, USA, 2007. [[CrossRef](#)]
25. ASTM D 3176-89; Standard Practice for Ultimate Analysis of Coal and Coke. American Society for Testing and Materials International: West Conshohocken, PA, USA, 2002.
26. ASTM D 2015-00; Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter. American Society for Testing and Materials International: West Conshohocken, PA, USA, 2015.
27. Lu, X.; Ma, X.; Qin, Z.; Ke, C.; Chen, L.; Chen, X. Co-Hydrothermal Carbonization of Sewage Sludge with Wood Chip: Fuel Properties and Heavy Metal Transformation Behavior of Hydrochars. *Energy Fuels* **2021**, *35*, 15790–15801. [[CrossRef](#)]
28. Wang, S.; Persson, H.; Yang, W.; Jönsson, P.G. Pyrolysis Study of Hydrothermal Carbonization-Treated Digested Sewage Sludge Using a Py-GC/MS and a Bench-Scale Pyrolyzer. *Fuel* **2020**, *262*, 116335. [[CrossRef](#)]
29. Wang, K.; Zheng, Y.; Zhu, X.; Brewer, C.E.; Brown, R.C. Ex-Situ Catalytic Pyrolysis of Wastewater Sewage Sludge—A Micro-Pyrolysis Study. *Biomass Convers. Biorefinery* **2017**, *232*, 229–234. [[CrossRef](#)] [[PubMed](#)]
30. Becker, G.C.; Wüst, D.; Köhler, H.; Lautenbach, A.; Kruse, A. Novel Approach of Phosphate-Reclamation as Struvite from Sewage Sludge by Utilising Hydrothermal Carbonization. *J. Environ. Manag.* **2019**, *238*, 119–125. [[CrossRef](#)]
31. Deng, W.; Tao, C.; Cobb, K.; Zhou, H.; Su, Y.; Ruan, R. Catalytic Oxidation of NO at Ambient Temperature over the Chars from Pyrolysis of Sewage Sludge. *Chemosphere* **2020**, *251*, 126429. [[CrossRef](#)]
32. Tytła, M. Assessment of Heavy Metal Pollution and Potential Ecological Risk in Sewage Sludge from Municipal Wastewater Treatment Plant Located in the Most Industrialized Region in Poland—Case Study. *Int. J. Environ. Res. Public Health* **2019**, *16*, 2430. [[CrossRef](#)]
33. Peng, C.; Zhai, Y.; Zhu, Y.; Xu, B.; Wang, T.; Li, C.; Zeng, G. Production of Char from Sewage Sludge Employing Hydrothermal Carbonization: Char Properties, Combustion Behavior and Thermal Characteristics. *Fuel* **2016**, *176*, 110–118. [[CrossRef](#)]
34. Zhang, J.H.; Lin, Q.M.; Zhao, X.R. The Hydrochar Characters of Municipal Sewage Sludge Under Different Hydrothermal Temperatures and Durations. *J. Integr. Agric.* **2014**, *13*, 471–482. [[CrossRef](#)]
35. Aragón-Briceño, C.; Ross, A.B.; Camargo-Valero, M.A. Evaluation and Comparison of Product Yields and Bio-Methane Potential in Sewage Digestate Following Hydrothermal Treatment. *Appl. Energy* **2017**, *208*, 1357–1369. [[CrossRef](#)]
36. Funke, A.; Ziegler, F. Hydrothermal Carbonization of Biomass: A Summary and Discussion of Chemical Mechanisms for Process Engineering. *Biofuels Bioprod. Biorefining* **2010**, *4*, 160–177. [[CrossRef](#)]
37. Zabaleta, I.; Marchetti, P.; Lohri, C.R.; Zurbrugg, C. Influence of Solid Content and Maximum Temperature on the Performance of a Hydrothermal Carbonization Reactor. *Environ. Technol.* **2017**, *38*, 2856–2865. [[CrossRef](#)]
38. Setyawati, W.; Damanhuri, E.; Lestari, P.; Dewi, K. Correlation Equation to Predict HHV of Tropical Peat Based on Its Ultimate Analyses. *Procedia Eng.* **2015**, *125*, 298–303. [[CrossRef](#)]
39. Grammelis, P.; Margaritis, N.; Karampinis, E. Solid Fuel Types for Energy Generation: Coal and Fossil Carbon-Derivative Solid Fuels. In *Fuel Flexible Energy Generation*; Elsevier: Amsterdam, The Netherlands, 2016; pp. 29–58. ISBN 9781782423997. [[CrossRef](#)]
40. Pulka, J.; Manczarski, P.; Koziel, J.A.; Białowiec, A. Torrefaction of Sewage Sludge: Kinetics and Fuel Properties of Biochars. *Energies* **2019**, *12*, 565. [[CrossRef](#)]
41. Barry, D.; Barbiero, C.; Briens, C.; Berruti, F. Pyrolysis as an Economical and Ecological Treatment Option for Municipal Sewage Sludge. *Biomass Bioenergy* **2019**, *122*, 472–480. [[CrossRef](#)]
42. Kumar, P.; Kumar, A.; Pandey, J.K.; Chen, W.; Patel, A.; Ashokkumar, V. Pyrolysis of Sewage Sludge for Sustainable Biofuels and Value-Added Biochar Production. *J. Environ. Manag.* **2021**, *298*, 113450. [[CrossRef](#)]
43. Akhtar, J.; Aishah, N.; Amin, S. A Review on Process Conditions for Optimum Bio-Oil Yield in Hydrothermal Liquefaction of Biomass. *Renew. Sustain. Energy Rev.* **2011**, *15*, 1615–1624. [[CrossRef](#)]
44. Wang, G.; Zhang, J.; Lee, J.-Y.; Mao, X.; Ye, L.; Xu, W.; Ning, X.; Zhang, N.; Teng, H.; Wang, C. Hydrothermal Carbonization of Maize Straw for Hydrochar Production and Its Injection for Blast Furnace. *Appl. Energy* **2020**, *266*, 114818. [[CrossRef](#)]
45. He, C.; Giannis, A.; Wang, J.Y. Conversion of Sewage Sludge to Clean Solid Fuel Using Hydrothermal Carbonization: Hydrochar Fuel Characteristics and Combustion Behavior. *Appl. Energy* **2013**, *111*, 257–266. [[CrossRef](#)]
46. Xu, Z.-X.; Xu, L.; Cheng, J.-H.; He, Z.-X.; Wang, Q.; Hu, X. Investigation of Pathways for Transformation of N-Heterocycle Compounds during Sewage Sludge Pyrolysis Process. *Fuel Process. Technol.* **2018**, *182*, 37–44. [[CrossRef](#)]

47. Volpe, M.; Fiori, L. From Olive Waste to Solid Biofuel through Hydrothermal Carbonisation: The Role of Temperature and Solid Load on Secondary Char Formation and Hydrochar Energy Properties. *J. Anal. Appl. Pyrolysis* **2017**, *124*, 63–72. [[CrossRef](#)]
48. Gao, Y.; Wang, X.-H.; Yang, H.-P.; Chen, H.-P. Characterization of Products from Hydrothermal Treatments of Cellulose. *Energy* **2012**, *42*, 457–465. [[CrossRef](#)]
49. Fei, Y.-H.; Zhao, D.; Liu, Y.; Zhang, W.; Tang, Y.-Y.; Huang, X.; Wu, Q.; Wang, Y.-X.; Xiao, T.; Liu, C. Feasibility of Sewage Sludge Derived Hydrochars for Agricultural Application: Nutrients (N, P, K) and Potentially Toxic Elements (Zn, Cu, Pb, Ni, Cd). *Chemosphere* **2019**, *236*, 124841. [[CrossRef](#)]
50. Chen, C.; Liu, G.; An, Q.; Lin, L.; Shang, Y.; Wan, C. From Wasted Sludge to Valuable Biochar by Low Temperature Hydrothermal Carbonization Treatment: Insight into the Surface Characteristics. *J. Clean. Prod.* **2020**, *263*, 121600. [[CrossRef](#)]
51. Liang, W.; Wang, G.; Xu, R.; Ning, X.; Zhang, J.; Guo, X.; Ye, L.; Li, J.; Jiang, C.; Wang, P.; et al. Hydrothermal Carbonization of Forest Waste into Solid Fuel: Mechanism and Combustion Behavior. *Energy* **2022**, *246*, 123343. [[CrossRef](#)]
52. Malhotra, M.; Garg, A. Hydrothermal Carbonization of Centrifuged Sewage Sludge: Determination of Resource Recovery from Liquid Fraction and Thermal Behaviour of Hydrochar. *Waste Manag.* **2020**, *117*, 114–123. [[CrossRef](#)] [[PubMed](#)]
53. Özçimen, D.; Ersoy-Meriçboyu, A. Characterization of Biochar and Bio-Oil Samples Obtained from Carbonization of Various Biomass Materials. *Renew. Energy* **2010**, *35*, 1319–1324. [[CrossRef](#)]

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.