Conversion of Spent Tea Waste for Solid Carbon Fuel via Hydrothermal Carbonization Process

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ARTICLE INFO	ABSTRACT
	This research aimed to study the effect of hydrothermal carbonization (HTC) process constraints like reaction temperature and contact time of the hydrochar produced via conversion of spent waste tea (SWT), at the time of removing the environment of the pollutant SWT, then to study the hydrochar produced by the HTC process. At the range of temperatures, the SWT feed amount was 5 g, 2 MPa N_2 pressure, with a constant contact time of 45 min, with various temperatures of 150, 175, and 200 °C, respectively. At the range of residence times, the 5g of SWT, 2 MPa N_2 pressure, at constant temperature at 200 °C (the finest degree it was found), and the various contact durations at 30, 45, and 60 minutes, respectively. The characterization process was carried out via physical properties, higher heating values (HHV_s), proximate and ultimate analysis, energy recovery (ER), and energy yield (EY). The results showed that the SWT reached carbon contents and the highest HHV. The conversion of SWT by the HTC process could be used as a solid carbon fuel for energy generation and to rid the environment of pollutant materials.

Introduction

The optimal utilization of agricultural waste as an energy source for decentralized power generation and heating applications can help rural communities meet escalating energy demands. Forests, agricultural produce, residential garbage, animals, food processing, industrial activity, and other sources all produce different biowastes [1]. Tea drinking is the most popular beverage after water, consumed by more than two-thirds of the global population [2]. Tea is one of the items consumed globally and contributes significantly to reusable garbage. Tea is a

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dried leaf-infused beverage made from the leaves of Camellia sinensis L. It is the world's second-best-selling non-alcoholic beverage [3]. Excessive use of fossil fuels has largely contributed to global warming and the looming energy crisis, which requires promoting and developing alternative energy sources to achieve green energy or energy neutrality. Recently, scientific researchers developed pioneering units to increase production efficiency through scientific research, like thermochemical conversion processes, which included (hydrothermal carbonization, pyrolysis, and microwave processes [4]. Over 90% of tea is wasted after ingestion [5]. Tea leaf brewing waste is a lignocellulosic biomass waste generated during tea-brewing. Tea brewing trash can be generated in residential or industrial procedures [6]. Tea trash, such as trimmed branches, seed shells, and tea remnants, includes lignin, cellulose, hemicellulose, and other organic components, which are conducive to the formation of a heating value and large surface area during the hydrothermal carbonization process [7]. Tea waste can be turned into solid carbon fuel or activated carbon using various thermochemical techniques, including pyrolysis, hydrothermal carbonization, and microwave processes [8]. Chemical agents have also been widely employed to increase surface properties, surface functional groups, and new biochar or activated carbon structures.

The HTC method produces a large amount of treated water with significant dissolved organic molecules, minerals, and nutrients. Processed water contains around 15% of the feedstock's energy, 20–50% of biomass organics, and high levels of phosphorus and nitrogen [9]. Converting waste biomass to energy greatly impacts solid waste management [10]. Thermochemical conversion processes are characterized by quick, easy, and low-cost processes, designed with minimal equipment, resulting in solid carbon fuel [11]. Hydrochar is a solid carbonaceous material obtained by thermochemical carbonization of biomass in an oxygen-non environment [12].

The research objectives were to prepare and characterize SWT and determine the suitability to undergo the hydrothermal carbonization HTC process to produce solid carbon fuel under the effect of reaction temperatures and residence times and to rid the environment of pollutant materials.

Materials and Methods

Spent Waste Tea Preparation

The spent waste tea (SWT) sample used in this work was collected from the Household waste resulting from the daily tea consumption. The experiments were done on dried SWT samples at 105°C for two h [13]. Then, it was manually crushed and ground into powder to obtain a similar form and a small size.

HTC Processes of SWT

The SWT samples were put in the crucibles and heated at 105 °C in an oven for 2 hours to eliminate residual status. Then, they were ground in a mortar and pestle to produce the same powder. On the one hand, hydro char with a temperature range of 5 g SWT feed quantity, 2 MPa N_2 pressure, contact period of 45 min, and a variety of temperatures at 150, 175, and 200°C were labeled (HTC@45min-150 °C, HTC@45min-175 °C, and HTC@45min-200 °C, respectively). This run found that the best temperature was 200 °C, and the highest calorific value was 14.77 kJ/kg, as shown in Table 1. On the other hand, hydrochar yield with a range of contact time feed amount 5 g of SWT, 2 MPa N_2 pressure, at a constant temperature at 200 °C optimum temperature it was originated the previous run, and the difference of the contact time

at 30, 45, and 60 minutes were labeled (HTC@200 °C-30min, HTC@200°C-45min, and HTC@200 °C-60min), respectively. Furthermore, throughout this run, the best residence time was 75 minutes, and the greatest HHV was 14.95 kJ/kg, as shown in Table 1. HTC runs were performed with a 100 ml batch reactor autoclave, stainless steel, and the reactions occurred under N_2 gas pressure. The reactor operated without a mixer, and a 1.0 kW jacket electric heating power source heated the autoclave reactor. The reactor automatically cools to room temperature after the reaction takes place. For subsequent analysis, the hydrochars generated were dried at 105°C for 2 hours and milled into fine powder [14]. At least six times, all experiments were repeated.

Analysis Methods

The raw material, spent waste tea (SWT), was prepared and characterized according to the details described in the next sections. The HHV, according to (ASTM E711), is determined using a Bomb calorimeter [15]. The amount of solid yield was calculated by dividing the yield by the feed [16]. Promoting the SWT property as a fuel by energy properties was investigated via equations from one to five [17]. The CHN-O elemental contents (weight percent) of element components were measured with an analytical instrument (Flash EA 1112). The volatile matter was evaluated using the ASTM E872–82 [18]. The ash content was investigated in an electric muffle furnace, and the ash was estimated using D1102-84 [19]. The estimated value of fixed carbon (FC) was calculated by adding ash and volatile matter and removing 100% [20]. The enhancement of SWT qualities as a fuel by energy characteristics was investigated.

$$Hydrochar\ yield\ (\%) = \frac{Hydrochar\ weight}{-SWT\ weight} \times 100 \tag{1}$$

$$Fuel\ Ratio = \frac{Fixed\ carbon}{Volatile\ matter} \tag{2}$$

$$HHV\ Improvement\ (\%) = = \frac{HHV\ of\ Hydrochar - HHV\ of\ SWT}{HHV\ of\ SWT} \times 100 \tag{3}$$

$$Energy\ Recovery = = \frac{HHV\ of\ Hydrochar}{HHV\ of\ SWT} \tag{4}$$

$$Energy\ yield = Hydrochar\ yield \times Energy\ Recovery \tag{5}$$

Result and Discussion

Hydrochar Yield of SWT

The solid yield was calculated as Eq. 1. The HTC processes of SWT by various temperatures and residence times were investigated to enhance the hydrochar produced. Table 1 and Fig. 1 show the solid formed by hydrochar at different temperatures and contact times. The HTC process of SWT was initially initiated by using 5 g of SWT, setting the residence duration at 45 minutes, and varying the reaction temperatures at 150, 175, and 200 °C, as indicated in Table 1 and Fig. 1a. The hydrochar fluctuates from one batch to the next due to temperature fluctuations during the process. Increasing the temperature to 200 °C has been demonstrated to decrease the hydrochar production. HTC@45min-150°C yielded 3.65 g - 71.2%, followed by HTC@45 min-175 °C yielded 3.22 g - 64.4%, and HTC@45min-200 °C yielded 3.11 g – 62.2 %. The highest hydrochar was 3.65 g – 71.2% at 150 °C and 45 min [21]. At last, under the effect of the residence times, the HTC technique of SWT was added 5g of SWT, constant temperature at 200 °C (best temperature was found) with different ranges of residence time of 30 min, 45 min, and 60 min as shown in Table 1 and Fig. 1b [14]. The hydrochars were close to each other due to the changes in residence times. Raising the residence time to 60 min has been detailed to decrease the hydrochar yield. The arrangement of hydrochar yield, highest to lowest, was HTC@200°C, 30 min = 3.18 g – 63.6%, HTC@200°C, 30 min = 3.2 g – 64%, and

HTC@200°C, 45 min = 3.22 g – 64.4 %. The highest hydrochar was 3.22 g – 64.4% at 45 min and 200°C. The solid yield percentage of hydrochar indicated that the SWT was rich in carbon compounds and organic complexes, which showed a slightly lowest weight loss of about 37.8% at 200°C reaction temperature and 45 min residence time. In comparison, the maximum weight loss was 36.4 % at 60 minutes of contact time and 200 degrees Celsius.

Table 1. Hydrochar yield, calorific value of the SWT, hydrochar yield at different temperatures, and various contact times

|	SWT	Hydrochar @ 45 min, different temperatures, °C			Hydrochar @ 200 °C, various residence times, min		
		150	175	200	30	45	60
Hydrochar yield, g	-	3.56	3.22	3.11	3.20	3.22	3.18
Hydrochar yield, %	-	71.2	64.4	62.2	64	64.4	63.6
HHV, kJ/kg	4.2	6.21	6.51	6.88	5.95	6.51	6.95
HHV improvement	-	47.85	55.00	63.81	41.66	55.00	56.90
Energy recovery (ER)	-	105.21	99.82	104.52	90.66	99.82	105.74
Energy yield (EY)	-	74.91	64.28	65.01	58.02	64.28	67.25

As a result, the hydrochar yield produced has a constant temperature of 200°C and residence durations of 30, 45, and 60 minutes, as seen in Table 1 and Fig. 2b. The yield was obtained using equation one. The solid yield of hydrochar varies depending on its residence period. Rising contact time has been shown to increase the fraction of hydrochar at 45 minutes, then decrease till 60 minutes. From highest to lowest hydrochar yield, HTC@200°C-45min = 3.2 g - 64.4%, HTC@200°C-30min = 3.20 g - 6.4%, and HTC@200°C-60min = 3.18 g - 63.6%. The maximum hydrofuel yield was 3.22 g (64.4%) after 45 minutes at 200°C. The consequences revealed a considerable ratio of hydrochar production, showing that the SWT was high in carbon-based and carbon components, with the lowest weight loss of 35.6% at 45 minutes and 200 degrees Celsius. In comparison, the lowest weight loss was 36.4% during a residence duration of 60 minutes and a temperature of 200 degrees Celsius [22]. Hydrochar yields decrease with rising temperatures and contact time, owing to the higher hydrolysis response of organic materials at the highest temperature in SWT. The results illustrate the efficiency of the decarboxylation procedure and the reaction of the SWT to the thermochemical conversion approach used by the HTC process [23].
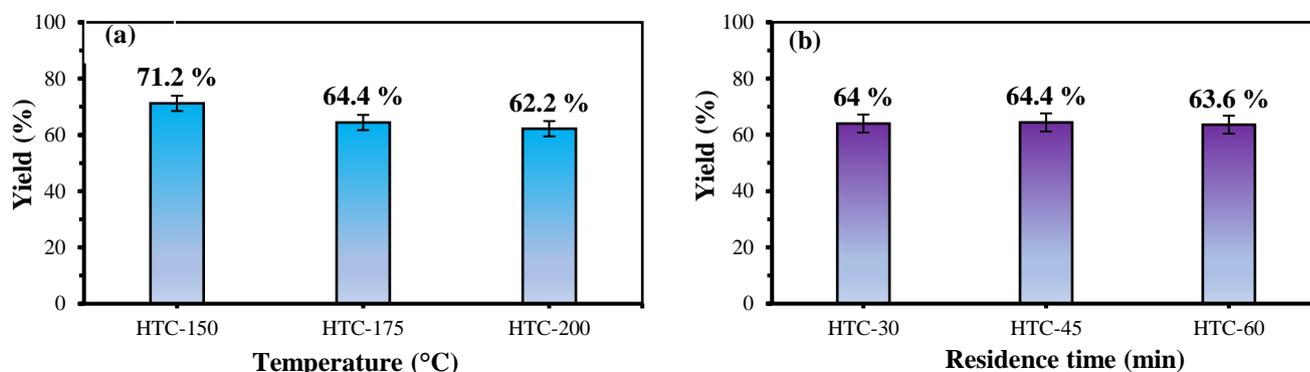
Fig. 1. Hydrochar produced by the SWT via HTC processes, (a) hydrochar produced at different temperatures, (b) hydrochar produced at different residence times

HHV Values

HHV of solid carbon fuel hydrochar yield at different temperatures and contact periods is detailed in Table 1 and Fig. 2. Fig. 2a shows the HHV of SWT and hydrochars at various temperatures. In contrast, Fig. 2b shows the HHV of SWT and hydrochars at varied residence periods. As a result, the temperature had a negative impact [24]. The HHV of the SWT was 2.4 kJ/kg [25]. HTC@60 min – 200 °C = 6.88, HTC@60 min – 175 °C = 6.5, and HTC@60 min - 150 °C = 6.2 kJ/kg were the greatest and lowest HHV values, respectively. The greatest HHV was HTC@60 minutes – 200 °C = 6.88 [26]. At the same time, the lowest HHV was HTC@60 min - 150°C = 6.2 kJ/kg. The reaction duration time of 60 min was appropriate for all reaction temperatures, increasing the HHV. Hydrochar formed at different reaction temperatures was enhanced. The fuels' combustibility was determined by calculating the HHV of the fuel burned [27].
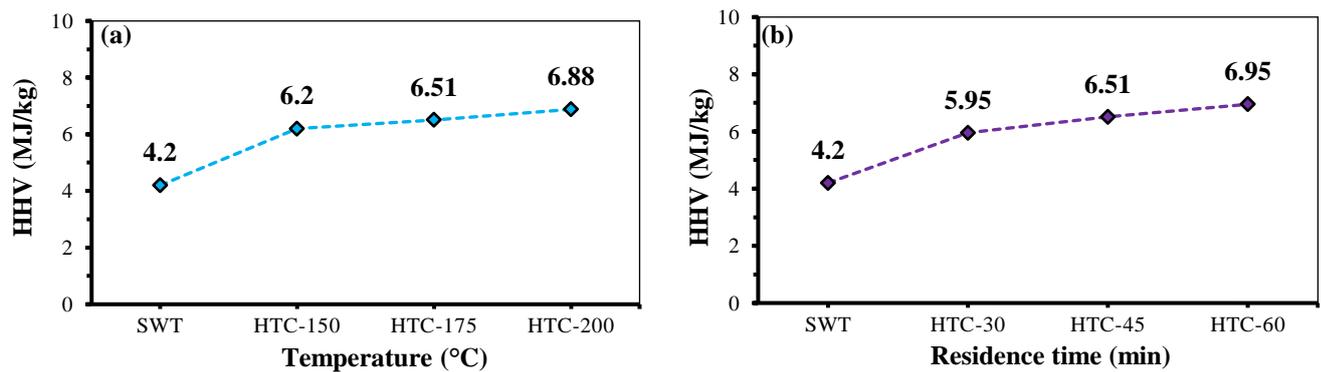
Fig. 2. HHV of SWT and hydrochar, (a) hydrochar produced at various temperatures, (b) hydrochar produced at different residence times

The high heating value of hydrochar at a range of residence duration was sorted from greatest to lowest was HTC@200 °C - 60 min = 6.95, HTC@200 °C - 45 min = 6.51, and HTC@200 °C - 30 min = 5.95. As a result, these findings indicate that the optimal HTC residence time for the production of alternative solid carbon fuel hydrochar is approximately 760 minutes [28]. The reaction temperature of 200°C was adequate for the full reaction residence time, boosting the HHV yield. This study found that SWT-derived hydrochar exhibited a considerable increase in HHV compared to the raw material SWT. The duration of time reaction directly influenced the HHV [29]. The results showed that the HHV has been enhanced [30].

HHV Improvement

The percentage of HHV improvement hydrochar yield at different temperatures and contact times was detailed in Table 1 and Fig. 3. Fig. 3a shows the percentage of HHV improvement hydrochars produced at various temperatures, and Fig. 3b shows the percentage of HHV improvement hydrochars produced at different residence times [31]. The resultant percentage of HHV improvement was consistent with upgraded fuel characteristics. HTC@200 °C - 60 min showed the highest percentage of HHV improvement (65.9%). Consequently, the percentage of HHV enhancement via diverse residence times was superior to various reaction temperatures [32]. The highest percentage of HHV improvement was HTC@60 min – 200 °C = 45. The percentage of HHV improvement was compatible with upgraded fuel properties [25]. The results of HHV improvement indicated that these results were suitable for developing the fuel properties [33].
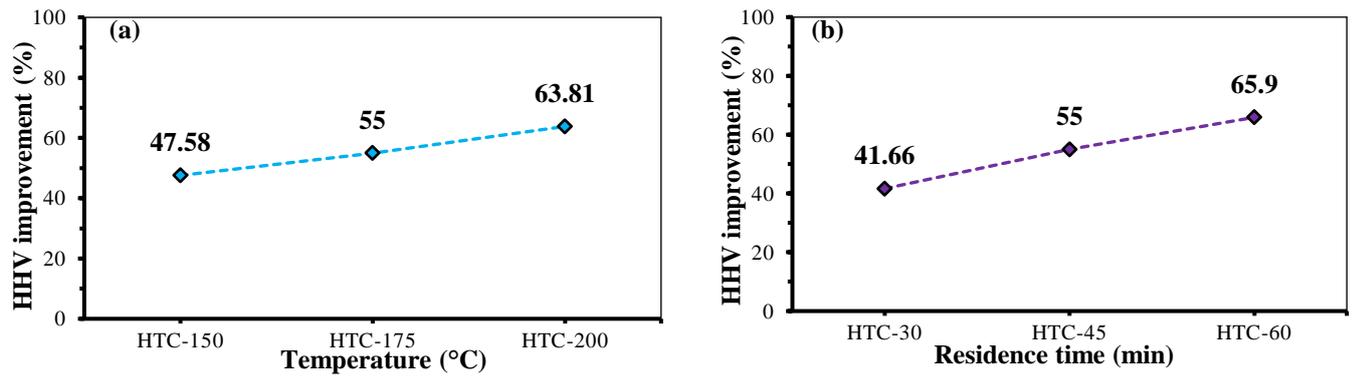
Fig. 3. HHV improvement of hydrochars (a) hydrochar produced at various temperatures, (b) hydrochar produced at different residence times

Proximate and Ultimate Analysis

Table 2 details the proximate and ultimate analysis of SWT hydro cars. The proximate analysis is an appraisal of the relative quantities of fixed carbon (FC), volatile matter (VM), and Ash, while the ultimate analysis evaluates the relative content of individual rudiments such as C, H, N, S, and O [34]. The results demonstrate that the SWT has low volatile metals (40.60%), low ash (25.2%), and a high carbon content (29.69%). Perhaps reactions in HTC processes, such as decarboxylation and dehydration, will occur quickly [35].

Table 2. The proximate, fuel ratio, and ultimate analysis of SWT and optimum hydrochars

Characterizations		SWT	HTC@45 min – 200 °C	HTC@200 °C - 60 min
Proximate analysis	VM%	41.60	40.11	39.45
	Ash%	25.20	28.31	27.75
	FC%	28.69	31.58	32.80
Fuel ratio	FC/VM	0.68	0.78	0.83
Ultimate analysis	C %	38.16	41.22	41.15
	H %	8.15	6.12	6.22
	N%	4.32	3.72	3.15
	O%	49.37	48.94	49.48

Upgrading the SWT Properties as a Solid Fuel

Fig. 4 depicts the fuel ratio FR (FC/VM) of SWT and hydrochar produced across a range of contact times. The highest fixed carbon percentage of the hydrochar generates a less angry flame and supports stable combustion; nevertheless, the high VM concentration of hydrochar causes unstable combustion due to poor heat balance burning [36]. The fuel ratio of hydrochar increased as the reaction temperature rose. This could be owing to a considerable fall in VM at higher treatment temperatures, whilst the upsurge in FR can be interpreted as an enhancement in fuel properties through hydrothermal treatment. Given the product hydrochar yield and energy-related qualities connected with the produced high-quality fuel, it is reasonable to conclude that the attributes of hydrochar were improved during HTC [37]. The FR of SWT to hydrochar yield was raised from 0.68 SWT to 0.78 HTC@200 °C for 45 minutes and 0.83 HTC@60 minutes at 200 °C. The highest FR was 0.83, which resulted in a 22.06% rise at 200°C

for 60 minutes. This research indicates that SWT's hydrothermal treatment has a strong energy recovery potential. The FR of hydrochar displayed a diverging trend in changing indices. FR grew until the treatment temperature reached 200 °C, 60 minutes, then declined to more than 200 °C, 45 minutes [38]. This finding was consistent with the results of the proximal analysis. A residence time of 60 minutes may be adequate for all reaction temperatures, increasing the ash content while decreasing the VM content of the fuel.
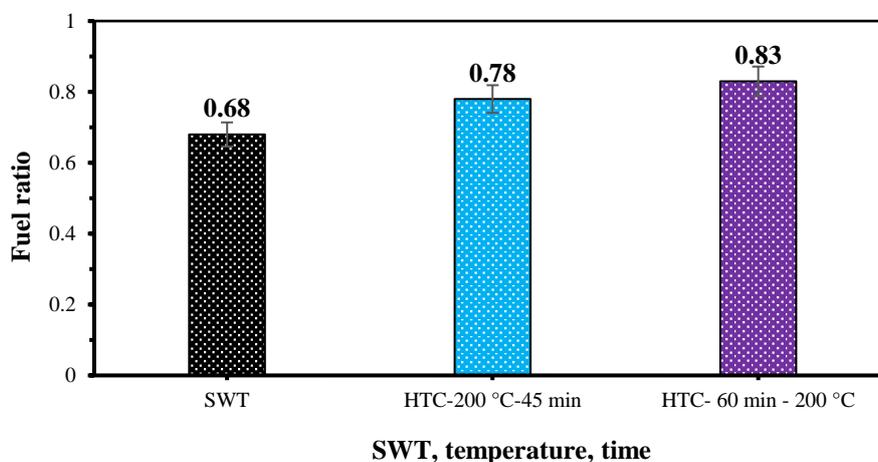

Fig. 4. Fuel ratio of SWT, HTC@200 °C- 45 min, and HTC@60min – 200 °C

Furthermore, to assess HTC's technical efficiency, the enhanced energy of the solid carbon fuel product was evaluated after it was produced by the HTC method [39]. As a result, the HTC technique was evaluated by fuel ratio, which was affected by the decreased product yield and increased heating value [40]. The ER achieved a maximum of 105.74 % at 200°C for 60 minutes. The HTC process caused this because the dehydration and decarboxylation reactions occur at higher temperatures [41]. According to Kambo and Dutta's observations, the SWT's ER generally decreased as the reaction temperature increased [42]. However, after HHV enhancement, HTC@200 achieved a score of 105.21 %, whereas HTC@60 scored 105.74 %. Based on the findings, it can be inferred that HTC can improve the fuel characteristics of hydrochar from the SWT [35].

Energy Recovery

The recovered energy (ER) was calculated after the hydrochar was formed to determine and compare the hydrochar's burn efficiency. Table 1 and Fig. 5 depict the ER of hydrochar formed at different temperatures and residence durations. Fig. 5a illustrates the EY of hydrochar created at different temperatures, while Fig. 5b shows the energy recovered from hydrochar produced at different residence times. This finding implies that the HTC therapy of SWT was quite detrimental in terms of ER potential. SWT's maximum ER potential was 33.43 of HTC at 200 °C for 75 minutes [43]. HTC was treated at a temperature of 200 degrees Celsius. ER and EY enhanced the mixture hydrochar product yield and calorific value. The HTC technique enhanced the hydrochar combustion efficiency compared to SWT. As can be seen, the composition of hydrochar varies with HTC reaction temperature and residence time [44]. The reaction temperature of 200 °C was adequate for all reaction residence times, resulting in a higher ER of the hydrochar. HTC treatment at higher temperatures improves hydrochar formation and ER [45].
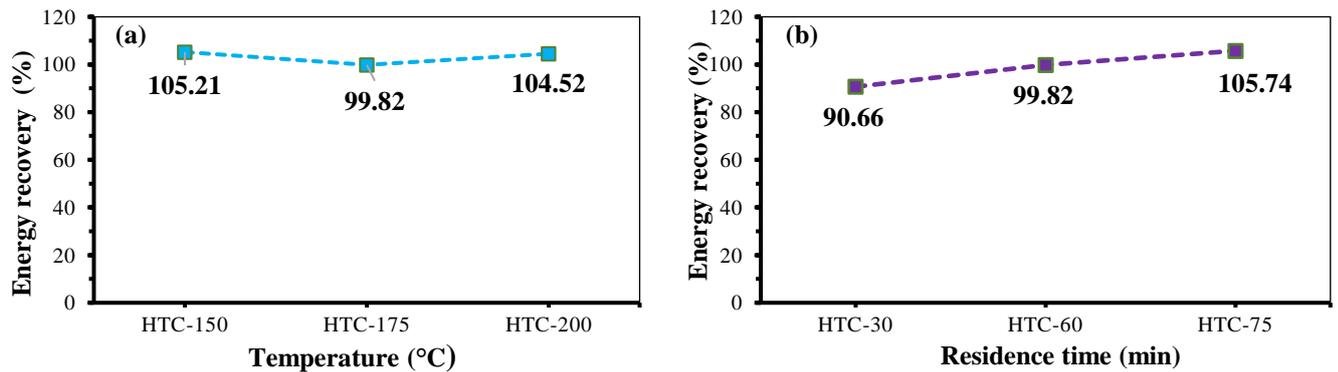
Fig. 5. Energy recovery of hydrochar (a) hydrochar produced at various temperatures, (b) hydrochar produced at different residence times

Energy Yield

The EY of hydrochar during the HTC process of SWT is illustrated in Table 1 and Fig. 6. Fig. 6a shows the EY of solid carbon produced at several temperatures, and Fig. 6b shows the EY of solid carbon fuel produced at different contact times [46]. With the increase in temperature degree, the EY of hydrochar increased rapidly and then increased slightly, while EY at residence times slightly increased. The EY (104.52%) of hydrochar was produced at 200 °C and 60 min. While the EY of hydrochar produced at different residence times was 67.25 of HTC 75 min, it was the highest in the condition of HTC residence time, which increased by 6.12% [47]. The percentage of increase in reaction temperature was better than in residence time. After the HTC process, the EY change was not obvious because the reactions reached relative equilibrium. The results showed that the EY of hydrochar could be improved during the HTC process [48].
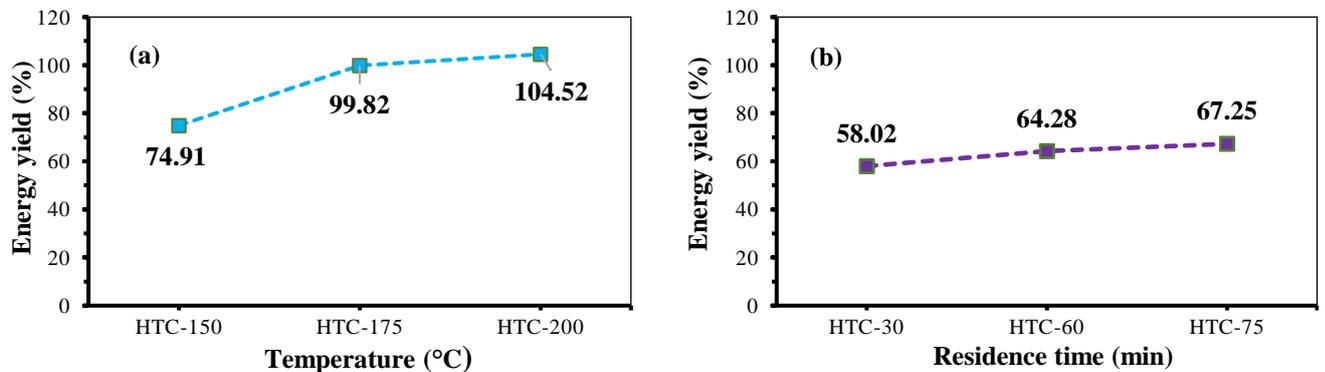
Fig. 6. Energy yield of hydrochar (a) hydrochar produced at various temperatures, (b) hydrochar produced at different residence times

Conclusion

The study addressed the manufacturing of hydrochar and its energy characteristics using SWT's HTC technology. HTC treatment enhanced reaction temperature improved HHV and reduced SWT combustion stage in air combustion. The results showed that temperature affected solid yield up to 200 °C, beyond which it dropped. While the effect of duration time on the solid product was favorable, it was discovered that the solid product grew as the contact time increased, indicating that the impact of residence time was most effective for the longest time attained (60 minutes). The carbon content measurement revealed that the best hydrochar was

achieved at 200 °C for 60 min. The solid result can be used as a fuel for combustion due to the efficiency with which the hydrochar fuel is burned. The researchers did not previously specify that the HTC process must incorporate feed volume, pressure, temperature, and duration. At the start of the experiment, fill the reactor with water and manually mix it in the absence of a mixer, followed by pressure, temperature, and contact duration. The results showed that the HHV of the SWT was increased from 4.2 to 6.95 kJ/kg hydrochar, resulting in a 72.88% recovery, suggesting that the hydrochar produced was converted to an excellent solid carbon fuel. This increase in HHV supports the utilization of SWT converted during the HTC process to provide solid fuel for energy production. The HTC technique for solid carbon fuel production can convert the large amounts of SWT accumulated as greenhouse waste.

CONFLICT OF INTEREST

The authors declare no conflict of interest requiring disclosure in this article.

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