

# Comparative Evaluation of Physiochemical Properties of a Solid Fuel Derived from *Adansonia digitata* Trunk using Torrefaction

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The effect of temperature on the physiochemical characteristics of a solid fuel or biocoal derived from the dried trunk of *Adansonia digitata* (Baobab) was studied using torrefaction processes. The chemical composition of the solid fuel or char obtained by wet (HTC) and dry torrefaction processes were determined by elemental and thermogravimetric (TGA) analyses. The Brunauer-Emmett-Teller (BET) surface area analyzer measured the porous texture and surface area of the prepared samples. The changes in the surface morphology and crystallinity of the prepared samples were evaluated by field-emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). The torrefaction process successfully improved the energy content from 16.8 MJ/kg to 22.0 MJ/kg, which was evidently higher than the starting precursors. The maximum energy yield obtained was 90.0% using dry torrefaction at 250 °C. The energy densification ratio was also higher for the char produced by the dry torrefaction process. However, the char produced by the HTC process at 250 °C showed the highest surface area. The pore diameter was higher for HTC-char produced at the same temperature. Overall the results revealed that the torrefaction of lignocellulosic biomass is beneficial for upgrading the fuel quality and energy densification of char residues.

*Keywords:* Mild pyrolysis; Biomass; Solid Fuel; Torrefaction; Carbonization; Char

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## INTRODUCTION

The rising demand for non-renewable fossil fuels has led to a global energy crisis (Chowdhury *et al.* 2016a,b). The burning of fossil fuel contributes to the emission of the greenhouse gases, which further initiates a major environmental challenge to be resolved. Biomass substrate has already proved its versatile application as a renewable energy source. These substrates can deliver an interminable energy supply by yearly planting and harvesting (Chowdhury *et al.* 2012a,b, 2013). By utilizing biomass, carbon can be recycled from the atmosphere (Ragauskas *et al.* 2006). The biomass can be transformed into various solid (char) and liquid biofuels using thermo- and biochemical processes. Until recently, different types of technologies have been developed to convert biomass into solid, liquid, and gaseous fuels that have higher energy contents (Kaygusuz 2009; Chowdhury *et al.* 2012a,b, 2013). These technologies include combustion, torrefaction, pyrolysis, liquefaction, digestion, fermentation, and gasification processes. Among all the

processes, torrefaction and pyrolysis are regarded as thermochemical methods. The direct combustion of biomass has few technical problems. The transportation and storage of biomass residues are difficult, as these have low energy density and can easily undergo deformation. Furthermore, due to its fibrous texture, pulverization of biomass is far more difficult when compared to coal (Esteban *et al.* 2006). The high moisture and oxygen contents, with low bulk density of the biomass residues, create difficulties during transportation, handling, and storage. These limitations generate obstacles for its expansive utilization. Also, it contains high contents of alkalis and chlorine, which causes failures of boilers due to corrosion, fouling, and slagging during the combustion and co-combustion processes (Hardy *et al.* 2012). To address these problems, dry and wet torrefaction—often referred to as hydrothermal carbonization (HTC), can be used, because these techniques can transform biomass into a potential solid fuel. Torrefaction was earlier performed for different biomass samples, and it was observed that it could yield solid fuel or char (Felfli *et al.* 2005). The char produced by torrefaction is usually hydrophobic and contains less moisture (Sadaka and Negi 2009). The torrefaction process in the presence or absence of water can considerably increase both energy density (Prins *et al.* 2006; Yan *et al.* 2009; Rousset *et al.* 2011) and higher heating values (HHV) (Bridgeman *et al.* 2008; Couhert *et al.* 2009; Deng *et al.* 2009; Yan *et al.* 2009) of biomass substrates.

Torrefaction, in the absence of water, is sometimes also referred to as mild pyrolysis. It is usually performed under an inert gas flow at temperatures ranging from 200 °C to 300 °C. The end products of dry torrefaction are solid char and gaseous fuels. The process not only helps to lower the oxygen level but it also increases the proportional content of carbon inside the char matrix. Overall about 60% to 80% of mass yield can be obtained (Lynam *et al.* 2011) during this process. The hemicellulose present in the biomass depolymerizes during the torrefaction process and releases volatile components that have lower energy values. Therefore, the remaining solid obtained after torrefaction always has high energy density values (Basu *et al.* 2014).

Although dry torrefaction increases the calorific values with better grindability and hydrophobicity of the resultant char, wet torrefaction appears to have a few additional and significant advantages (Yan *et al.* 2009). Wet torrefaction (HTC) is conducted at approximately 180 °C to 250 °C (Pala *et al.* 2014) and under a pressure of approximately 4.6 MPa (Lynam *et al.* 2011), due to the water vapors and evolved gases. Within the HTC reactor the temperature reaches above 200 °C. The water remains in a liquid phase due to the high pressure. In these subcritical conditions, water has a high concentration of ions that have an influence on biomass transformation, just like an acid or a base catalyst (Lynam *et al.* 2011). Due to this unusual property of water, it is often referred to as the “green catalyst” for the thermochemical conversion process. Torrefaction using water takes place through a series of hydrolysis, condensation, decarboxylation, and dehydration reactions (Funke and Ziegler 2010). Wet torrefaction (HTC) of lignocellulosic residues usually produces gases (mostly CO<sub>2</sub>), aqueous chemicals (primarily sugars and organic acids), and char (often called HTC biochar or hydro char) (Reza *et al.* 2013). The HTC process requires a lower temperature and it can be used for biomass having a high content of moisture that normally requires an intensive drying process. It can reduce ash content through washing it out with hot compressed water (Pala *et al.* 2014). Additionally, previous literature shows that wet torrefaction was more effective when considering the upgrading of energy densification in comparison to

dry torrefaction (Yan *et al.* 2009). However, HTC needs more advanced reactors to function at elevated pressures. Previously, few works were devoted to the characterization of products arising from the wet torrefaction treatment of biomass fuels. This includes pine sawdust (Yan *et al.* 2009), agricultural residues (Oliveira *et al.* 2013), corn stalk, forest waste (Xiao *et al.* 2012), or eucalyptus sawdust, and barley straw (Sevilla *et al.* 2011).

The baobab tree and its correlated species belong to the Malvaceae family and the *Adansonia* genus. The African baobab has versatile applications and it is big with a large trunk (up to 10 m in diameter). The tree can grow up to 25 m in height and it can live for hundreds of years (Kaboré *et al.* 2011). The plant is grown profusely throughout the hot and drier regions of tropical Africa (Kaboré *et al.* 2011). Previously no studies have been reported to perform the torrefaction of the *Adansonia digitata* (Baobab) trunk to yield char. This research studied the important solid fuel properties of char with its chemical composition using ultimate and proximate analyses, crystallinity index, surface-morphological changes, and mass yield including energy content and energy densification values after dry and wet torrefaction processes.

## EXPERIMENTAL

### Materials

The dried chips obtained from the trunk of *Adansonia digitata* (Baobab) were purchased from Pilot Furniture Manufacturers (PTY) Ltd. (Babelegi, South Africa). The samples were labeled as BT and were then ground to a fine powder using a ball mill (MTI-SFM, Richmond, USA). After ball milling, the samples were sieved using a 70-mesh screen to obtain a fine powder with homogenous particle size. The powdered sample was washed vigorously with hot deionized water. Next, it was dried at 110 °C for 24 h and kept in a closed plastic bottle before initial characterization and torrefaction.

### Methods

#### *Wet and dry torrefaction process*

Wet torrefaction, or HTC, of the dried BT sample was performed at 200 °C, 230 °C, and 250 °C. For this purpose a mixture of BT and water (BT:water = 1:30, w/v) was placed in a Teflon-lined autoclave. The autoclave was closed and kept in an inert atmosphere by passing N<sub>2</sub> gas through the reactor. The flow rate of the N<sub>2</sub> gas was kept constant at 5 L/min for 30 min to evacuate the oxygen from inside. Then the reactor was heated slowly at a rate of 5 °C/min until the desired temperature was reached. A magnetic stirrer was used to agitate the mixture at 500 rpm inside the reactor. The HTC process was performed for 120 min. After 120 min, the heating process including the agitation of the mixture was stopped. The sample inside the reactor was then allowed to cool to room temperature under the nitrogen flow. Vacuum filtration was performed to separate the solid char from the liquid byproducts. The wet torrefied solid samples were washed carefully with acetone to remove any organic residual liquids. The samples were then oven-dried for 6 h at 105 °C. Based on the HTC temperature, the samples were labeled as WBT-200, WBT-230, and WBT-250. The samples were then used for further characterization.

Dry torrefaction of BT powder was performed using a quartz tubular reactor. Next, 5 g of sample was placed into a small porcelain crucible, and the crucible loaded with the sample was positioned inside the middle of the reactor at room temperature. The reactor was then heated at a rate of 5 °C/min. Nitrogen gas was passed throughout the reaction time to ensure an inert atmosphere. The samples were heated to reach the desired temperature (200 °C, 230 °C, and 250 °C). After reaching the targeted temperature, the samples were kept there for 120 min. Through the flow of nitrogen gas the samples were cooled to ambient temperature. The samples were further washed and oven-dried at 105 °C for 6 h. The dry torrefied samples obtained were labeled as DBT-200, DBT-230, and DBT-250 and were used for further characterization.

#### Analytical methods

The char yield was calculated as the ratio of the produced hydrochar weight (after washing and drying) to the dry ash free weight of BT subjected to wet and dry torrefaction at different temperatures under investigation using Eq. 1 (Kalderis *et al.* 2014),

$$\text{Yield (\%)} = \frac{W_2}{W_1} \times 100 \quad (1)$$

where  $W_2$  is the hydrochar weight after washing and drying (g) and  $W_1$  is the dry ash free weight of starting biomass (g).

An advance bomb calorimeter (CAL-2K, Gauten, South Africa) was used to determine the energy content of the dried ash free char sample using a method described in previous literature (Saqib *et al.* 2014), where 1 g of dried ash free char was placed inside the bomb and was ignited in the presence of oxygen. Equations 2 and 3 were used for the calculation of the energy densification ratio and energy yield (Saqib *et al.* 2014),

$$\text{Energy Densification Ratio} = \frac{\text{Energy content of char}}{\text{Energy Content of Feedstock}} \times 100 \quad (2)$$

$$\text{Energy Yield} = \text{Yield of Char} \times \text{Energy Densification Ratio} \quad (3)$$

The process for determining the pH, electrical conductivity (EC), and cation exchange (CEC) properties of char was described in the authors' previous work (Chowdhury *et al.* 2016). The method to determine the pH of the prepared char sample was described earlier by Novak *et al.* (2009). Approximately 2 g of char sample was mixed with 40 mL of deionized water, and the mixture was shaken for 30 min. The powdered char sample settled after 15 min. The pH of the clear solution was then measured using the pH electrode 827 pH Lab (Metrohm, California, USA). About 1 g of fresh char sample was agitated with 10 mL of deionized water for 24 h in a conical flask. After the sample had settled at the bottom, the electrical conductivity was measured using a conductometer (Jenway 4510, Liverpool, UK). The values for the cation exchange capacity (CEC) of the prepared char samples were determined by the ammonium acetate (NH<sub>4</sub>OAc) extraction methods described in previous literature (Song and Guo 2012; Melo *et al.* 2013). For this measurement approximately 0.5 g of char sample was mixed with 40 mL of 1 M ammonium acetate (NH<sub>4</sub>OAc) solution, and it was placed in a 50-mL glass centrifuge tube. The mixture was agitated for 20 min at room temperature. The

sample was filtered using a glass fiber filter-using (0.45  $\mu\text{m}$ ) vacuum. The char residue on the filter was further washed with two 20-mL portions of 1 M  $\text{NH}_4\text{OAc}$  solution, followed by three 30-mL portions of isopropanol. Lastly, it was washed with four 50-mL portions of 1 M potassium chloride KCl solution. The rinsate thus obtained was diluted with deionized water to make up a volume of 250 mL. The Kjeldahl method was used to measure the  $\text{NH}_4^+$  ions concentration (Melo *et al.* 2013). The CEC ( $\text{mmol}\cdot\text{kg}^{-1}$ ) of the char sample was calculated by standardizing the amount of  $\text{NH}_4^+$  in the rinsate with the mass of char sample used (0.5 g).

The changes in the surface morphological features for the starting BT sample along with its torrefied samples were observed using a scanning electron microscope (SEM, Model Leo Supra 50VP Field Emission, London, UK). The starting samples (BT) and the prepared char samples after torrefaction were analyzed using a CHNOS elemental analyzer (PerkinElmer-2400, Tokyo, Japan). Thermogravimetric analysis (Mettler Toledo Star SW901, Tokyo, Japan) was performed to determine the moisture, volatile material, fixed carbon, and ash contents of the prepared sample. The crystalline properties of the BT samples and the chars were observed using X-ray diffraction (XRD) analysis (D5005 apparatus, Bruker, Germany) at 40 kV and 40 mA with a Cu-K $\alpha$  radiation source. The Brunauer-Emmett-Teller (BET) surface area, pore volume, and pore size distribution of the prepared char samples along with the starting biomass were analyzed with an Autosorb 1 Quantachrome Autosorb (Tokyo, Japan) automated gas sorption system.

## RESULTS AND DISCUSSION

### Influence of Temperature on Mass and Energy Yield during Wet and Dry Torrefaction

The mass yield of the char decreased with increasing temperature of the wet (HTC) and dry torrefaction process, as illustrated in Table 1. The maximum yield obtained for wet torrefaction was 71.25% at 200  $^{\circ}\text{C}$ , and it decreased to 63.78% at 250  $^{\circ}\text{C}$ . The dry torrefaction process gave a maximum yield of 65.76% at 200  $^{\circ}\text{C}$  and a minimum yield of 57.99% at 250  $^{\circ}\text{C}$ . Under the same temperature and retention time, the mass yield for dry torrefaction was comparatively lower than the HTC process. This illustrated that the torrefaction in the presence of water could yield more char under the same experimental conditions. In both processes, the char yield decreased with increasing temperature (Brachi *et al.* 2016). A similar trend was observed during torrefaction of tomato peels by previous researchers.

**Table 1:** Mass Yield, Energy Yield, Energy Content and Energy Densification Ratio of the Char

Sample	Mass Yield (%)	Energy Content (MJ·kg <sup>-1</sup> )	Energy Yield	Energy Densification Ratio
BT	100	22.35	-	-
WBT-200	71.25	24.85	79.08	1.11
WBT-230	68.78	25.09	77.03	1.12
WBT-250	63.78	27.06	79.73	1.25
DBT-200	65.76	25.66	74.96	1.14
DBT-230	61.49	26.69	73.17	1.19
DBT-250	57.99	27.54	70.74	1.22

At lower temperatures, the disintegration of cellulose and hemicellulose took place, which caused lignin to disintegrate to some extent. However, much of the lignin decomposed at a higher temperature due to its stable chemical nature. Later on, the successive increase in temperature promoted the cracking of long chain-like, high molecular weight volatile compounds. This would result in the formation of smaller chain organic compounds with less molecular weight. Further devolatilization would yield gaseous products rather than char itself (Thangalazhy-Gopakumar *et al.* 2010). Therefore, the enhancement of dehydration and elimination reactions with increasing temperature would cause reduced char yield (Brachi *et al.* 2016; Bacaoui *et al.* 2001; Lua and Yang 2004; Adinata *et al.* 2007). The phenomenon of perceived lessening of the char yield with increasing temperature was evident, and it has been described in other literature as well (Garcia-Perez *et al.* 2008; DeSisto *et al.* 2010; Keiluweit *et al.* 2010; Saquib *et al.* 2014).

Table 1 illustrates the energy content, energy densification ratio, and energy yield trends of the prepared char and the torrefaction temperature. At the higher temperatures the mass yield was reduced but the energy content was higher. The hydrochar derived from microalgae had an energy content of 30 MJ/kg to 32 MJ/kg (Heilmann *et al.* 2010). The energy content of *Adansonia digitata* (Baobab) Trunk was calculated as 22.4 MJ/kg. However, after torrefaction it increased subsequently with increasing temperature. The energy content of char produced by dry torrefaction was slightly higher than that from the HTC process (Yan *et al.* 2009). The energy content of the char obtained by the dry torrefaction process at 250 °C was highest near 27.5 MJ/kg. Also, the other energy profile of the prepared char sample, including the densification ratio and energy yield, were higher for dry torrefaction compared to the wet torrefaction process (Table 1). The highest energy densification ratio observed was 1.22 with an energy yield of 70.7% at 250 °C during the dry torrefaction process.

### Influence of Temperature on Physiochemical Characteristics of Char during Wet and Dry Torrefaction

#### Ultimate (CHNOS) analysis

The elemental composition of BT and the char obtained by wet and dry torrefaction processes are shown in Table 2.

**Table 2.** Characteristics of *Adansonia digitata* (Baobab) Trunk and the Torrefied Char at Different Temperatures

Sample	Ultimate Analysis (wt.%)							pH	EC	CEC
	C (%)	H (%)	N (%)	O (%)	S (%)	H/C	O/C			
BT	43.16	5.78	0.54	50.47	0.05	0.13	1.17	4.98	1798	298.32
WBT-200	43.99	5.02	0.43	50.53	0.03	0.11	1.15	5.23	815	197.89
WBT-230	44.53	4.86	0.41	50.18	0.02	0.10	1.13	5.87	843	203.67
WBT-250	46.03	4.11	0.39	49.45	0.02	0.09	1.07	6.03	856	218.78
DBT-200	44.23	5.34	0.51	49.89	0.03	0.12	1.12	5.89	898	165.77
DBT-230	45.67	4.78	0.45	49.06	0.04	0.11	1.07	6.08	934	145.76
DBT-250	46.98	4.09	0.42	48.48	0.03	0.08	1.03	6.22	967	141.66

The results exhibited the increasing trend of carbon inside the char matrix from 43.2% to 46.0% with increased wet torrefaction temperature. A similar trend was also observed for the dry torrefaction process. This illustrated that the extent of carbonization increased by enhancing the torrefaction temperature (Chun *et al.* 2004; Chen *et al.* 2012). However, the hydrogen and oxygen contents decreased successively with increasing temperature during the HTC process. This was attributed to the breaking of weaker bonds during the carbonization process (Demirbas 2004).

The reducing trend observed in the torrefied char samples in the hydrogen and oxygen contents was ascribed to the decline in the -OH groups and other oxygen-containing functional groups that formed with the increased temperature (Phanphanich and Mani 2011). However, in both torrefactions, the hydrogen and oxygen contents decreased slightly with increased temperature. The hydrochars produced between 200 °C and 250 °C showed H/C ratios of 0.11 to 0.09 and O/C ratios of 1.15 to 1.07. These ratios were clearly different from those obtained with swine manure (H/C = 1.50, O/C = 0.57) (Cao *et al.* 2011), digested maize silage (H/C = 1.26, O/C = 0.24), and cellulose (H/C = 1.17 and O/C = 0.35) (Mumme *et al.* 2011). The differences may have been due to the differences in the starting material composition and the torrefaction process conditions.

Figure 1 displays the H/C and O/C atomic ratios with respect to torrefaction temperature. By determining these two ratios of the carbonaceous sample, the extent of aromaticity and carbonization was elucidated (Krull *et al.* 2009). A substantial reduction of the H/C and O/C atomic ratios was observed compared to the starting biomass of the BT with increasing temperature. Lesser O/C ratios in char indicate its stability in the soil (Melo *et al.* 2013). The BT biomass sample had low aromaticity. Therefore, it had a relatively high H/C atomic ratio. A higher temperature initiated an increased rate of organic reactions, such as dehydration, decarboxylation, and decarbonylation of the sample (Kim *et al.* 2011; Chowdhury *et al.* 2016a). These results were similar with the observation previously depicted for producing graphitic black carbon, switch grass, and pine-based woody bio-char (Schmidt and Noack 2000; Kim *et al.* 2011).

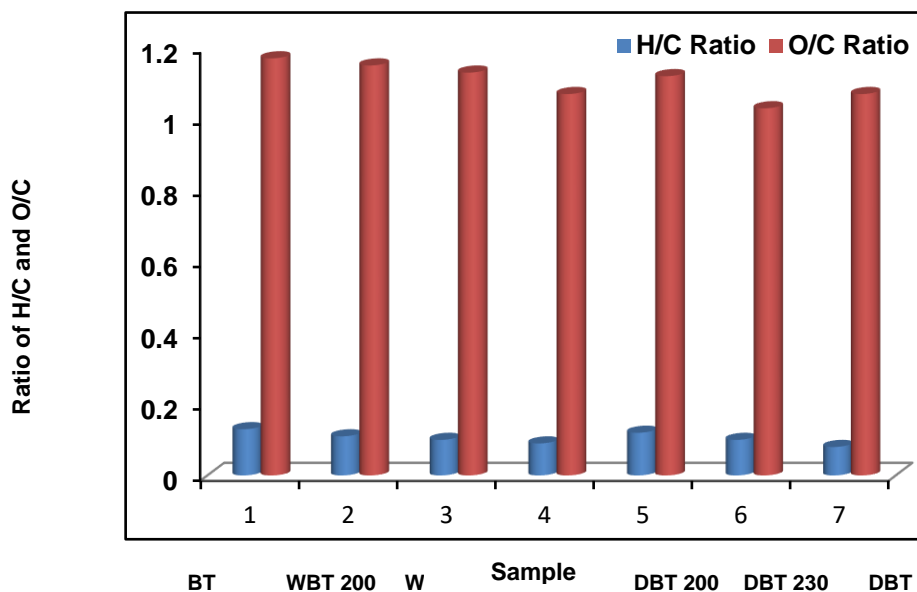


Fig. 1. Comparison of H/C and O/C ratios of BT and chars produced at various temperatures

A higher torrefaction temperature led to higher pH values of the resultant char (Yuan *et al.* 2011). This was attributed to the existence of more ash residues in the char sample produced at higher torrefaction temperatures (Melo *et al.* 2013). The feedstock had a pH of 4.98, which increased to 6.03 at 250 °C during the HTC process, whereas in dry torrefaction, the maximum pH was approximately 6.22 at 250 °C. Once the maximum was reached, it only slightly decreased with increasing temperature.

The EC values represent the salinity of the char sample. Salinity can adversely influence the growth rate of plants. Char samples that had high EC values would decrease the water uptake of plants, which results in lower nutrient consumption (Chan *et al.* 2008). The EC values of the prepared char sample increased slightly with the increasing temperature for both types of torrefaction process. The cation exchange properties (CEC) of the prepared char declined with consecutive enhancement of torrefaction temperature. This might have been due to the lower number of acidic groups present (Gaskin *et al.* 2008; Sing *et al.* 2010; Mukherjee *et al.* 2011; Song and Guo 2012).

#### Proximate analysis

The proximate analysis of the starting biomass and the torrefied char sample was examined by a thermo-gravimetric analysis. The representative parameters of the thermal degradation analysis are listed in Table 3.



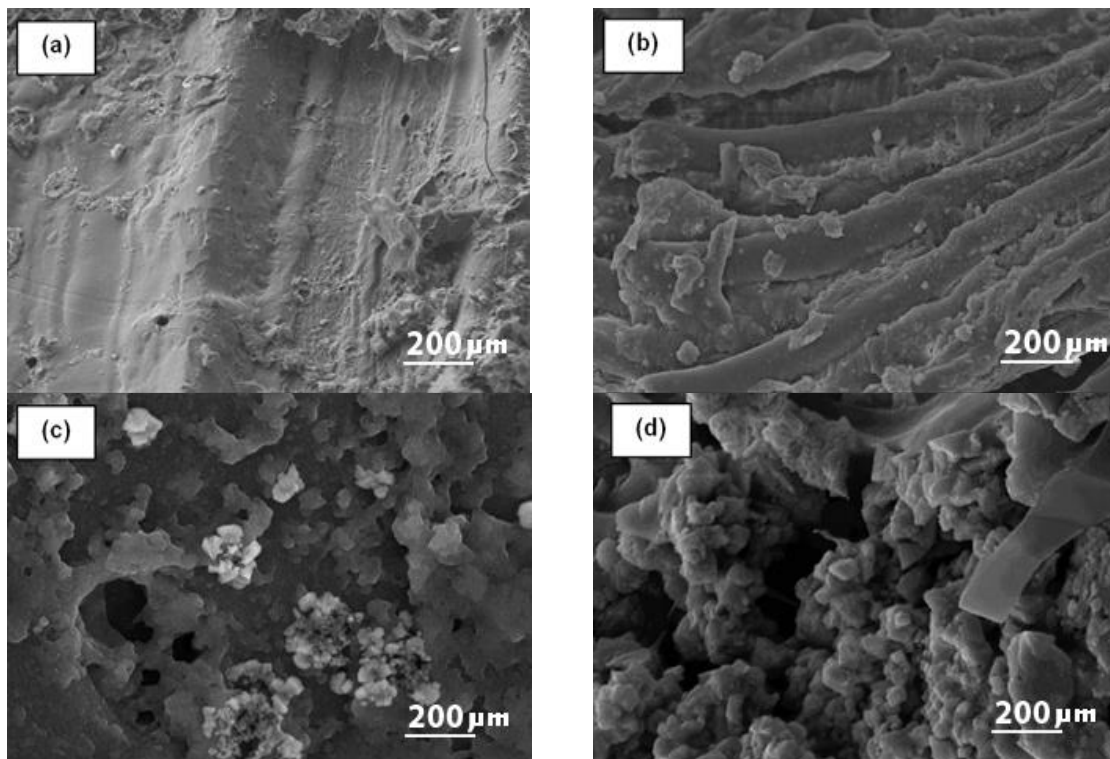
**Table 3.** Proximate Analysis of *Adansonia digitata* (Baobab) Trunk and the Torrefied Char at Different Temperatures

Sample	Proximate Analysis (%)				$T_i$ (°C)	$T_{max}$ (°C)	Residue (%)
	Water Content	Volatile Matter	Fixed Carbon	Ash			
BT	11.93	61.23	23.61	3.23	244.54	334.56	22.65
WBT-200	5.98	59.77	29.95	4.30	267.98	342.89	18.65
WBT-230	2.98	57.96	33.94	5.12	276.88	346.54	15.98
WBT-250	2.17	53.98	36.76	7.09	289.76	349.76	14.87
DBT-200	3.80	54.98	34.65	6.57	293.77	331.77	31.32
DBT-230	2.23	48.87	41.67	7.23	298.65	329.65	33.56
DBT-250	1.90	45.33	44.34	8.43	302.34	327.88	36.76

The amount of fixed carbon increased with an increase in the torrefaction temperature. The ash residues indicated the presence of non-volatile and non-combustible materials in the char sample (Mukherjee *et al.* 2011; Angin 2013). The successive increase in temperature formed more ash residue and fixed carbon in both types of char. However, the proportion of volatile components decreased with increased temperature. In a previous study, an analogous observation was reported for the carbonization of seed press cake that was obtained from a safflower sample (Angin 2013). Table 3 shows that the onset temperature of devolatilization ( $T_i$ ), which corresponded to a weight loss of 5% with respect to the final weight loss, increased subsequently with increasing temperature. The temperature values for the maximum rate of devolatilization ( $T_{max}$ ) moved to a higher temperature during the wet torrefaction process. This implies that the thermal stability of wet torrefied BT-based char had been enhanced. However, for the dry torrefied sample, these values slightly decreased with increasing temperature. This phenomenon was further supported by an XRD analysis. During wet torrefaction, the amorphous cellulose domain and smaller crystallites with short chains were selectively removed, while the larger cellulose crystallites remained unaltered. Some of the newly formed intra- and inter-molecular hydrogen bonds between the contiguous cellulose crystallites resulted in the development of larger crystallites (Zheng *et al.* 2014). This enhanced the thermal stability of the wet torrefied char sample. Near 850 °C, there were less of the carbonaceous remains that were obtained for the wet torrefied samples than the starting BT sample. In contrast, the carbonaceous residues for the dry torrefied samples were considerably increased with the successive increase in torrefaction temperature, as shown in Table 3. This can be elucidated from the different chemical configuration of the torrefied sample. The wet torrefied sample contained an increased amount of cellulose and decreased amount of alkali metal inside the char, which resulted in a reduced amount of char residues. However, the increased residues for the dry torrefied sample were endorsed for the increased amount of acid and alkali metal fractions as ash residues (Wannapeera *et al.* 2011).

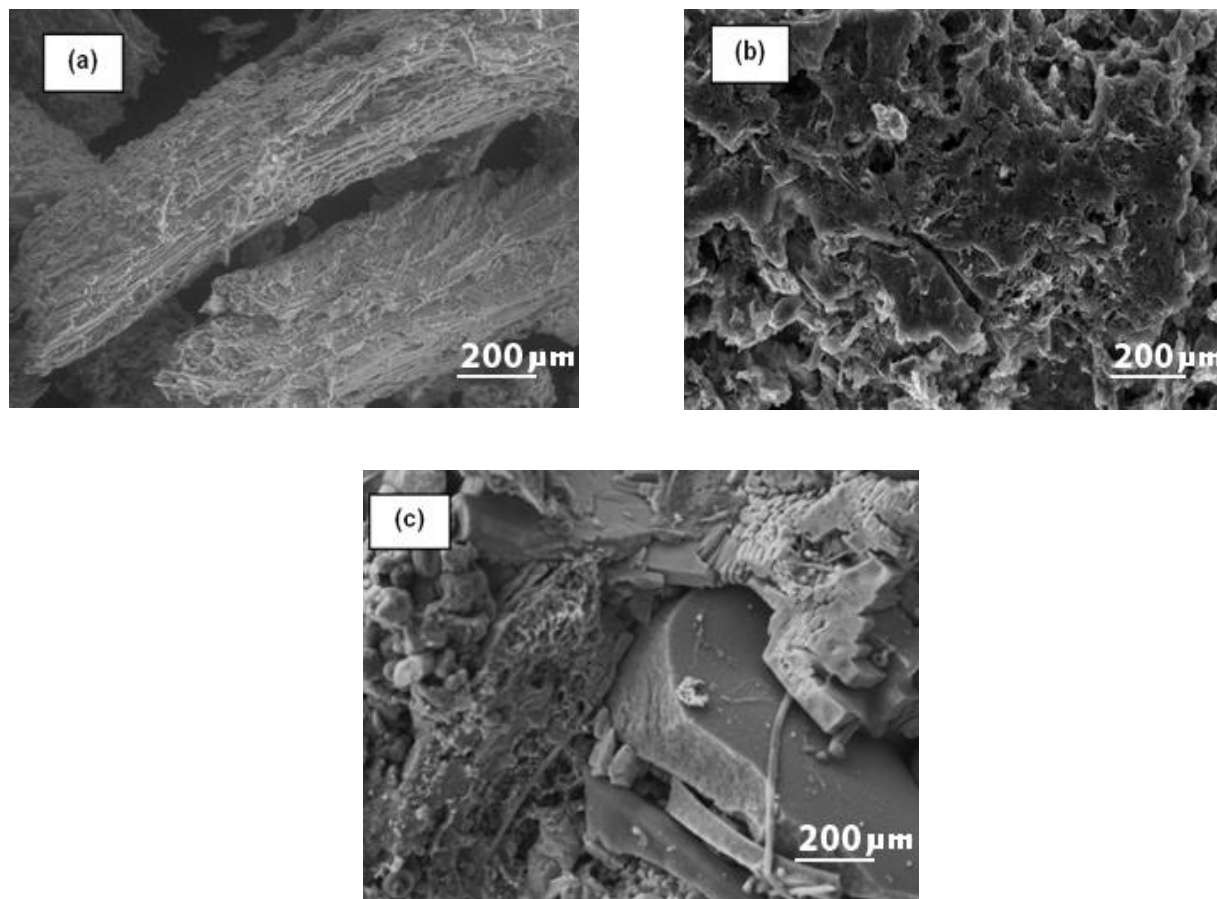
#### SEM image analysis

The SEM images of BT and the corresponding char sample after wet torrefaction (HTC) at various temperatures are illustrated Fig. 2. The morphological features of the original feedstock (BT) clearly altered after both types of treatments. The surface of the original BT sample was regular, smooth, and compact, which exhibited its intact morphology (Fig. 2a).



**Fig. 2.** SEM images of (a) BT; (b) WBT-200; (c) WBT-230; and (d) WBT-250 (Magnification 12000 x, 20 kV, Low vacuum)

The hydrothermal carbonization around 200 °C resulted in defibrillation, to yield separate microfibrils with occasional deposition over the surface (Fig. 2b). A further increase in HTC-temperature to 230 °C caused a serious breakdown of the lignocellulosic structure; thereby several cracks were observed (Fig. 2c). Tiny aggregates of uneven shaped pores were detectable on the surface between the tiny microspheres of lignin droplets (Fig. 2c). At an HTC temperature of 250 °C, substantial destruction of the feedstock was noticeably observed (Fig. 2d). The surface was visibly rough with uneven folds. The number of spherical-shaped droplets increased (Kristensen *et al.* 2008). This might have been attributed to the partial melting of lignin and wax materials at 250 °C under compact pressure with consequent condensation. The HTC treatment disrupted the complex network of lignocellulosic biomass mainly by dissolving the hemicelluloses within. Thus at lower temperatures, the micro-fibrillar cellulosic texture was still conserved (Fig. 2b). Some lignin polymers along with some carbohydrates also may have been deposited onto the surface of the cellulose fibers (Zhu *et al.* 2009). At lower temperatures, the microfibrils of the BT sample were not entirely separated, initially, but they were somewhat twisted due to the partial removal of hemicellulose and lignin. These types of structural changes were observed in previous literature (Selig *et al.* 2007; Xu *et al.* 2007; Zeng *et al.* 2007; Donohoe *et al.* 2008). The char obtained after dry torrefaction at different temperatures is shown in Fig. 5.



**Fig. 3.** SEM images of (a) DBT-200, (b) DBT-230, and (c) DBT-250 (Magnification 12000 x, 20 kV, Low vacuum)

After torrefaction at 200 °C, certain portions of the hemicellulose were burnt as gases, and the BT sample was defibrillated (Fig. 3a). With an increased temperature of 230 °C and 250 °C, the sample was fragmented into small pieces, and some pores also were developed over its surface (Figs. 3b and 3c). The porous texture was advantageous for upgrading the quality of the soil for growing microbes (Thies and Rilling 2009). This showed that both the wet and dry torrefaction treatments for BT were effective in producing well-defined mesopores on the surfaces of the char sample.

#### *Surface area with pore size distribution analysis*

The BET surface area, BJH cumulative surface area, total pore volumes, and pore diameter of the prepared char samples are listed in Table 4. When the HTC temperature increased from 200 °C to 250 °C, the BET and BJH cumulative surface area of the char sample considerably increased. Additionally, at a higher hydrothermal temperature of 250 °C, the BET surface area was enhanced up to 2.565 m<sup>2</sup>/g which was more than two fold the surface area of the starting feedstock BT sample (1.034 m<sup>2</sup>/g).

**Table 4.** BET Surface Area Analysis of *Adansonia digitata* (Baobab) Trunk and the Torrefied Char at Different Temperatures

Sample	BET Surface Area (m <sup>2</sup> /g)	BJH Surface Area (m <sup>2</sup> /g)	Total Pore Volume x 10 <sup>-3</sup> (mL/g)	Average Pore Diameter (nm)
BT	1.034	1.006	1.991	5.687
WBT-200	1.567	1.204	3.452	8.018
WBT-230	1.878	1.583	4.793	7.594
WBT-250	2.565	2.324	5.394	6.566
DBT-200	1.632	1.123	1.590	6.234
DBT-230	1.353	1.432	1.871	6.876
DBT-250	0.987	1.097	1.214	7.087

This surface area change was associated with the reduction of organic compounds through the volatilization process during char formation (Cantrell *et al.* 2012). The consecutive increase in the temperature during the HTC process expedited the release of more volatile materials. This would result in a larger surface area with substantially enhanced pore volume of the prepared char sample. A larger surface area is preferable for char because it upsurges the moisture holding capacity of the soil (Theis and Rilling 2009; Shaban *et al.* 2013). However the opposite trend was observed for the torrefied char, for which the surface area decreased with increased temperature. This might have been due to the deposition of ash residues inside the pores. Based on the internal diameter; the pores could have been classified as micropores (less than 2 nm), mesopores (from 2 nm to 50 nm), and macropores (larger than 50 nm) (Rouquerol *et al.* 1999). The char prepared in this study were meso-porous. The diameter and volume of the pores obtained by the HTC process were greater compared to the dry torrefaction process.

#### *X-Ray diffraction (XRD) analysis*

The crystallinity index (CrI) of the BT sample was comparatively less (around 31.6%). However, after the wet torrefaction process, the HTC char showed higher CrI values. The CrI increased with the elevated temperature from 37.0% for WBT-200 to 48.7% for WBT-250 sample. This revealed that the HTC process could considerably improve the crystallinity degree of the BT sample.

**Table 5.** Crystalline Parameters of *Adansonia digitata* (Baobab) Trunk and the Torrefied Char at Different Temperatures

Parameter	BT	WBT-200	WBT-230	WBT-250	DBT-200	DBT-230	DBT-250
CrI (%)	31.55	36.99	43.78	48.67	35.87	39.12	36.78
$\beta$ (nm)	2.98	2.78	2.09	1.76	2.47	2.22	1.65
$L_{002}$ (nm)	6.76	7.56	8.12	8.98	7.23	6.28	5.98

During the HTC process, the bio-macromolecule of hemicellulose and amorphous regions of cellulose with certain parts of lignin were disintegrated to yield liquid chemicals. However, a major portion of the crystalline domain of cellulose remained undamaged and consecutively formed solid char (Yu and Wu 2010). This affected the crystallinity index of the HTC char sample. The dry torrefaction could also enhance the crystallinity degree as demonstrated by the increased CrI of DBT-200, DBT-230, and DBT-250. Nevertheless, at severe conditions, when the torrefaction temperature was increased from 200 °C to 250 °C, the disintegration of the crystalline region of cellulose started to take place. Thus, the CrI of DBT-250 decreased to 36.78%. It was reported earlier that certain smaller least ordered cellulose crystallites could have been degraded during the HTC process because they are reactive, but the bulky and impeccable cellulose crystallites will persist as unaltered (Xiao *et al.* 2011). Therefore, the crystalline size ( $L_{002}$ ) of the HTC char was enhanced. Conversely, the bigger cellulose crystallites that were present in the BT sample may have been disorderly arranged themselves, and later on disintegrated due to harsh conditions during the dry torrefaction at 250 °C. Therefore, the crystallite size of DBT-250 was decreased to 1.65. The full width at half maximum of (002) peak ( $\beta$ ) in the XRD profiles of the HTC char sample decreased successively with increased temperature.

## CONCLUSIONS

This research explored the potential of *Adansonia digitata* (Baobab) trunk to produce char using dry and wet torrefaction (HTC) methods. Both dry and wet torrefaction (HTC) processes were promising methods to transform the lignocellulosic biomass to high-energy solid fuel or char for subsequent application. Temperature considerably affects the mass and energy yield, and physio-chemical properties of solid fuel products from both the processes. The conclusions can be summarized as:

1. The mass loss percentages with energy content were higher for the dry torrefaction process. Thus, the HTC process was able to produce a greater amount of char with less energy content.
2. The proportion of carbon and ash contents increased subsequently with temperature for both types of char. The increased trend of carbon showed better fuel properties of the prepared char.
3. The char obtained by the dry torrefaction process showed a greater energy densification ratio with higher energy yield compared to the HTC process.

4. The surface area, pore volume, and pore diameter values of the HTC process were higher than the dry torrefaction process. Thus, the HTC char indicated greater potential to retain moisture in soil and thereby proved to be more beneficial for plant growth than the char obtained from dry torrefaction process.
5. The cation exchange capacity (CEC) of the prepared char was reduced somewhat with increased temperature. Nevertheless, the electrical conductivity (EC) and pH values showed an opposite trend with an elevated temperature in the wet and dry torrefaction processes.
6. The crystallinity index (CrI) for both types of char increased after both the wet and dry torrefaction process. However, after a certain limit, increased temperature in the dry torrefaction process showed a lower crystallinity index, which was due to a severe disintegration of crystalline cellulose at higher temperature.

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