Energy Potentials of Briquette Produced from Tannery Solid Waste

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Abstract

The vast quantity of waste generated from industries is one of the serious outcomes of unplanned development, resulting into quantum of hazardous organic and inorganic waste generating daily. Proper waste management is a challenging issue that must be addressed adequately. This is, therefore, carried out with a view of assessing the energy and combustion quality of tannery solid waste with a view of converting them into briquettes for cooking, heating and small home industries and reducing the menace caused by tannery waste disposal. The results of the experiments showed that the combustion rate ranged between 0.171 and 0.217 g/min, the boiling time ranged between 27.78 to 34.11 minutes, the ignition time was found between 14.2 to 17.4 minutes. The durability test and humidity resistance test showed that the briquettes have durability ranged between 92.12 and 95.04 while the humidity resistance was between 95.34 and 97.95. The carbon content ranged between 40.79 and 45.15%. Other results showed that the fixed carbon ranged between 89.93 and 95.46%, volatile matter 1.61 to 4.56% and the calorific values were found between 18.03 and 21.86 MJ/kg. The fleshing has better quality than the other three wastes studied.

Keywords: calorific value, combustion rate, energy, solid waste, tannery

1. Introduction

The rapid increase of costs associated with energy supply, waste disposal, and increasing concerns about environmental quality degradation, conversion of waste to energy is becoming an economically viable solution [1]. Worldwide, in urban and rural areas, huge amounts of organic wastes are produced every day from different sources such as livestock, industries, agriculture and households. Leather industry has been classified as one of the highly polluting industries because of the huge amount of waste generated in the sector, such as the sludge from tannery wastewater treatment, gas and odor pollutions emitted into the atmosphere, and solid waste like tannery shavings, trimmings and buffing dusts that emerging during the transformation of hides and skins into leathers which have negative impacts on the environment. The leather production process has multiple steps from receiving to final commercialization. According to Cámara, et al. [2], this process needs approximately 15
stages. Tanning is one of the unit operations where tanning agents react with the collagen matrix, stabilizing the protein and the collagen [3]. Some of these stages produce solid waste and waste water. Thus, according to Kolomaznik, et al. [4], processing one metric ton of raw hide generates 200 kg of final leather product, 250 kg of non-tanned solid waste, 200 kg of tanned wastes and 50 tons of waste water. This means that tanned wastes corresponds to 20% weight of the final production. The management of solid wastes, especially tanned leather waste, is a challenging problem. Globally, the tannery industries generates about 0.8 million tons of chromium tanned shavings per year [5]. In order to overcome these problems, these wastes need to be managed and utilised in an appropriate means. There are many studies on the treatment of tannery wastes in literatures. Most of these works concern the extraction of chromium from wastes to re-use in the tanning process [6]-[9] and isolation of protein fractions [10],[11]. There are also studies related to pyrolysis of tannery wastes [12]. On the other hand, Abdulrazak, et al. [13] used activated carbon from Moringa Oleifera pods for the treatment of tannery wastewater and they prepared the activated carbons by carbonization in nitrogen at 900 °C followed by activation at 825 °C in carbon dioxide of chromium-tanned leather. Masilamani, et al. [14] were able to develop biodegradable packing materials from gelatin that extracted from Tannery solid waste.

Another means of making waste management sustaina ble is to use the organic wastes as sources in renewable energy production, to produce fuel briquettes for utilisation of the waste into heat and power generation. The tannery industry in Nigeria is the country’s largest external income earners. Consequently, during the past 30 years the industry has had significant government’s support and has multiplied throughout the country. The major source of energy in the rural community in sub-Saharan Africa is fuel wood as other sources of energy but it is either not available or grossly inadequate. The demand for fuel wood is expected to rise due to the increasing population, while the supply however, will decrease due to the present pressure on wood for fuel for both wood and charcoal fuels. Increasing pressure on forest resources for energy has led to what is called “other energy crisis of wood fuel” [15]. This has led to environmental degradation, desertification, deforestation, and misuse of soil forests and water resources. The unrestrained level of cutting of wood for firewood, charcoal for combustion, for other domestic and industrial uses is becoming a serious problem that not only in Nigeria but other West African countries. Total annual consumption of wood in Nigeria is estimated about 50–55 million cubic meters, which 90% is firewood, while estimated shortfall of fuelwood in the northern part of the country is about 5–8 million cubic meters [16]. While the annual deforestation of the wood lands in the northern part of Nigeria runs to about 92,000 hectare a year. The fuel wood extraction rate in the country is estimated to be about 3.85 times the rate of regrowth or afforestation. Energy is a complex system; hence, energy-production and energy-conversion require systemic thinking, for which firstly a change of aspect is necessary. The primary view-point is to satisfy the energy demands with the lowest possible stress on the environment. Furthermore, ecological thinking should prevail increasingly during the planning and operating of the different kinds of technical equipment and facilities [17]. One of the processes which these residues could be converted to useful products is briquetting. Wilaipon [18], described briquetting as a process of compaction of residues into a product of higher density than the original material, while Kaliyan and Morey [19] expressed briquetting as a densification process. Briquetting technology is not yet commercialized in Nigeria, because of the technical constrains involving lack of knowledge to adopt the technology suit with local conditions and ensuring the quantity of the raw material which are crucial factors in determining its commercial success. This kind of energy sources should be should be accessible to low income class of the society.

Taking the above considerations, the aim of this work is to evaluate the energy and market potential of the solid tannery waste with a view of adding value to the solid wastes and decreasing the environmental impact.

2. Materials and Methods

Sample collection and preparation. Solid waste samples from pre-fleshing, lime fleshing, shaving, buffing and trimming, randomly selected among piles from the various leather operation units in a Company in Challawa Industrial estate, Kano, were examined. Overall, 1000 kg of the waste were collected for the study. The feedstocks were sorted manually to remove impurities such as pieces of wood, bone, metal and any other unwanted material. Hair, Pre-fleshing and lime fleshing wastes from the air were dried to reduce the moisture content (up to 10% moisture content) and mixed and dried in oven at 105 °C. While the Chrome shavings and buffing dust from tanned leather wastes were oven-dried at 105 °C according to Ozgunay, et al. [20]. The local starch used as binder was obtained from local market in Kano. The biomass was then reduced in size by milling until it could pass through a screen of 1mm. Sieve mesh while the hair waste was reduced to 0.5 mm since it is very light. 500 g of each dried samples were put in a crucible and placed in an oven at 450 °C for 30 min. The calcined samples were then transferred into a silver plate to reduce the temperature and avoided further combustion.

The waste was macerated to provide uniform consistency (slurry). Maceration of the carbonised buffing dust
Preparation of the briquette samples. The four samples BD, CS, FS and HR were milled and labelled prior to briquetting. The samples were weighed using digital weighing balance with an accuracy of 0.1 g. The different concentrations were loaded into the mould compartment using motorized operated briquetting machine. A maximum of 16 briquettes were obtained at each operation of the machine. BD, CS, FS and HR briquettes were produced under this condition while maintaining the pressure at 9.00 MPa throughout production and a dwell time of 80 seconds.

The proximate analysis of the briquette samples was carried out to determine the percentage of volatile material content, % ash content, and % content of fixed carbon. The procedure of ASTM standard D3173–5 was adopted. The briquette was allowed to cool and dry for 19 days before carrying out proximate and mechanical analysis.

Proximate and ultimate analysis of materials. The proximate and ultimate analyses of the solid tannery waste and the briquettes formed were conducted in accordance with American Society of Testing and Materials (ASTM). The moisture content (MC) was determined based on American Society for Testing and Materials Standards [22], the volatile matter (VM) was determined based on American Society for Testing and Materials Standards [23]. The ash content (AC) was determined based on American Society for Testing and Materials Standards [24]. While the fixed carbon content (FC) was calculated by subtracting the sum of volatile matter, moisture content and ash from 100 [25].

Calorific value. Leco AC-350 Oxyburn Bomb Calorimeter interfaced with a microcomputer was used to assess the heat values of the produced briquettes. 2 g of the briquettes was measured and the screw mould bracket was used to re-mould the briquette to the appropriate calorimeter bucket size. 10 mL of distilled water was poured into the bomb and the industrial oxygen cylinder was connected to the bomb. The valves were opened and bomb was filled slowly at pressure range of 2.5–3.0 Mpa for a minute. The bomb was placed inside a canister bracket containing the distilled water and the bomb lid was covered. The switch was turned on and the microcomputer was set for the determinations which automatically calibrated and measured the energy values as well as displayed the values on the screen for recording after feeding the necessary data on the briquettes. The data and result of the experiment were displayed on computer screen [26].

Determination of carbon, hydrogen, nitrogen, sulphur. A LECO Truspec CHN Analyzer was used to determine carbon, hydrogen and nitrogen content by ASTM D5373-08. The SC-632 Sulphur Determinator, a non-dispersive infrared and digitally controlled instrument designed to determine sulphur in a variety of organic and inorganic materials was used for the determination of sulphur [27]. The sample was combusted at 1350 ± 50 °C in an atmosphere of pure oxygen. The sulphur was oxidized to sulphur dioxide and quantified by infrared absorption. Thereafter, the oxygen content was determined within the results of hydrogen, nitrogen, sulphur, carbon and ash contents [27].

Oxygen Content. The percentage oxygen content was determined as follows:

\[
\% \text{ Oxygen} = 100 - (C+H+N+S) \]  \quad (1)

Where:

- C = % carbon content in the biomass fuel
- H = % hydrogen content in the biomass fuel
- N = % nitrogen content in the biomass fuel
- S = % sulphur content in the biomass fuel

Physical Properties.

Durability test. The durability of the briquettes was determined using a pellet durability tester CEN/TS 15210. 500 g of briquettes was divided into two batches of 250 g each. Each batch was placed in the pellet durability tester for a period of 10 min and operated at 50 rpm. The sample was then placed on a no. 4 sieve (4.75 mm) before and after tumbling and measured for the mass retained on the screen. The pellet durability was then calculated using equation 2.

\[
\text{Durability} = \frac{\text{MAT}}{\text{MBT}} \]  \quad (2)

Where MAT is the mass of the briquettes retained on the screen after tumbling (g), and MBT is the mass of the briquettes retained on the screen before tumbling (g).

Equivalent humidity content (humidity resistance) test. In the equivalent humidity content (humidity resistance) test, the method used by Bilgin [28] was adopted. Briquettes were kept in a room of 20 °C temperature and 50% humidity for 21 days. Each briquette was weighed before and after the test. Depending on weight increase occurred during the storage, humidity resistance was calculated as a percentage.

Thermal properties. The important thermal properties of briquettes were tested included their calorific value,
volatile matter, ash, porosity index, ignition time, burning time and combustion rate.

**Porosity Index (PI).** The porosity of the briquettes was determined based on the amount of water each sample can absorb. The porosity index was calculated as the ratio of the mass of water absorbed to the mass of the sample immersed in the water [28].

\[
PI = \frac{\text{Mass of water absorbed}}{\text{Mass of sample}} \times 100
\]  

(3)

**Ignition time.** Ignition time was determined by burning 200 g of briquettes in charcoal stoves. Since end-point of lighting was subjective and dependent on some judgment according to what stage the ignition has been achieved, two similar charcoal stoves were ignited at the same time by placing equal amount of paraffin on the floor of the charcoal stoves and lit using a lighter. In this process, ignition time was taken as the average time taken to achieve steady glowing fire as recommended in literature [29].

**Combustion rate.** Burning time was obtained by observing the mass changes recorded on mechanical balance and also by using stop watch. It is the time for the biomass combustion to be completed. With known amount of total burnt briquette and burning time, average combustion rate can be calculated using the following formula [30].

\[
CR = \frac{\text{Total Mass of Burnt Briquette}}{\text{Burning Time (min)}}
\]  

(4)

3. Results and Discussion

The Result of Proximate Analysis of Briquette Samples. As shown in Table 1 HR briquettes have the lowest average moisture content of 4.3871% followed by BD briquettes with the average moisture content of 4.5121%. The observably moisture content might be due to its polymeric and fibrous nature. FS briquettes have the highest moisture content of 6.2417%. This might be due to the presence of excess fat and collagen substances. CS has an average moisture content of 6.0767%. The values obtained for the four samples were good for storability and combustibility of the briquettes as recommended by Grover et al. [31]. The value obtained was also corroborated by Wamukonya and Jenkins [32] who reported a moisture content of 5% for durable briquettes of sawdust. Moisture content is one of the attributes that determines the quality of briquette. When the moisture content is low, the briquettes will easily be ignited, with no slagginess during burning and for this reason higher calorific values will be expected from the fuel. With high moisture content in the briquette, much of the heat will be used to vaporize the surplus water and sometimes briquettes tear into pieces with low burning rate and less heat is generated with too much smoke emitted [33]. From the above statement, it can therefore means the four samples meets the moisture requirement of a good briquette. BD briquettes have the least volatile matter of an average of 1.6135% followed by CS briquettes with an average of 1.7312% while HR briquettes have the highest value of an average of 4.5556% followed by FS with an average of 2.1117%. This implies that more energy will be required to burn off the volatile matter in HR briquettes before the release of heat energy. HR briquettes as seen in Table 1, has the highest ash content of 5.0143% followed by CS briquettes with an average value of 2.8811%. The lowest ash content was observed in BD briquettes with an average of 2.4157% while CS briquettes have an average of 2.4249%. Ash content is an important factor in the burning rate and ignition time of briquettes. The higher the fuel’s ash content, the lower its calorific value since it influences the burning rate due to minimization of the heat transfer to fuel’s interior parts and diffusion of oxygen to the briquette surface during char combustion [34]. The tolerance level of ash content for fuel is below 4% [32]. From the above, it implies that all the briquettes except HR briquettes have better qualities in terms of the ash content. The results fall below values obtained for rice hulls (17.4%), coal (10.3%), pomace (2.7%) and apple pomace (4.0%) [34]. The results of ash content are the amount of inorganic substance that would remain after burning. As shown in Table 1, BD briquettes have the highest percentage of fixed carbon of 95.4587%, followed by CS and FS briquettes with 94.3217% and 94.2211% respectively. HR briquettes have the least average value of 88.84%. The fixed carbon of a briquette is a percentage of solid fuel available for char combustion after volatile matter is distilled off or lost to the atmosphere. Therefore, fixed carbon gives a rough estimate of the heating value of fuel and acts as the main heat generator during burning [35]. The fixed carbon in the tanned wastes is very high, making it potentially useful in terms of the energy stored, based on the fact that materials with high fixed carbon exhibit higher heating values [36].

Table 1 reveals that the mean calorific values of the waste samples ranges between 18.0297 and 21.8635 MJ/kg. FS briquettes were observed having the highest calorific value of 21.8635 MJ/kg which is probably due to the lower ash content. BD and CS briquettes were next
having 20.1750 and 19.8236 MJ/kg respectively, this could probably be due to their high carbon content. HR briquettes have the least calorific value of 18.0297 MJ/kg, this could be as a result of its higher ash and volatile matter compared to the other three briquettes since sample with the least volatile matter is expected to have the highest energy value vice versa. This energy value is sufficient enough to produce heat required for household cooking and small scale industrial cottage applications. The calorific value of the briquettes in this study was compared with 19.534 kJ/kg for briquettes from a mixture of palm kernel cake (PKC) and sawdust and 18.936 kJ/kg for sawdust of some hardwood species [37]. This value was also compared with that reported by Oladeji [38], who studied the heating value of five briquettes produced from corncob, groundnut shell, melon shell, cassava and yam peels and were found to be 20,890, 18,634.34, 21,887, 12,765, and 17,348 kJ/kg, respectively. These energy values obtained for the whole samples are sufficient enough to produce heat required for household cooking and small scale industrial cottage applications. Combustion characteristics based on the figures above fulfill the minimum requirement of calorific value for making commercial briquette (>17500 J/g), as stated by DIN 51731 [39].

The Result of Ultimate Analysis of Briquette Samples. As seen in Table 2, the organic carbon content of the tannery waste ranged from 40.792% to 45.153%. CS has the highest carbon content (45.153%), with BD, FS having 43.634%, 40.811% respectively while HR have the least of 40.782%. The result obtained in this study was compared with results obtained by Forero-Núñez et al. [36] whom reported 42.5% carbon content after thermal decomposition at 180 °C of tannery waste. Carbon content of 47.80% was reported by [40], while Gil, et al. [41] reported 48.2%. Nitrogen content is a good indicator of the amount of nitrogen based toxic components that can be formed during combustion [42]. Nitrogen is oxidized to nitrogen oxide (NOX) during combustion process. Stillman, [43] wrote that exposure to nitrogen oxides increases the risk of respiratory infections as it is highly toxic and irritating to the respiratory system. The nitrogen content of tannery waste studied ranged between 13.157 to 15.570%. The values obtained are higher than that obtained by Gil et al. [41] of 7.5% and 10.70% obtained by BLC [42] but similar to that obtained by Forero-Núñez et al., [36] whom reported 16.14% nitrogen content after thermal decomposition at 180 °C of tannery waste. The result is higher than the limit set by the German national standard for fuel pellet, Germany DIN 51731/DIN plus (i.e. Nitrogen content ≤0.3%) and that set by the Austria national standard for pellet and briquettes, Austria ÖNORM M7135 (i.e. Nitrogen content ≤0.6%).

The hydrogen contents of the tannery waste briquettes studied varied between 5.317% for HR and 6.885% for FS (Table 2). Higher hydrogen content leads to a higher heating value [44]. This might be the reason why the calorific value of FS is higher than the rest. However, the hydrogen content of the briquettes is similar to the results of BLC [42] of 6.40% and 5.80% for Gil et al. [41] and higher than that obtained by Forero-Núñez et al., [36] whom reported 4.88% hydrogen content after thermal decomposition at 180 °C of tannery waste. The sulphur contents of the briquettes studied varied between 2.215% for BD and 2.668% for FS while CS and HR have sulphur content of 2.317 and 2.417% respectively. The results are higher than that obtained by BLC [42] of 1.43 and that of Gil et al., [41] and lower than that obtained by Forero-Núñez et al., [36] whom reported 2.66% nitrogen content after thermal decomposition at 180 °C of tannery waste. The sulphur content of the briquettes is higher than the limits set by the Austria and German national standards for fuel pellet and briquettes (Sulphur content ≤0.08%). This means that if the briquettes are used as fuel it is much likely that they would emit sulphur compounds more than the accepted limits into the atmosphere which would have adverse effects on both human and environment.

Results of some physical properties. Durability, also known as abrasive resistance, is an indication of briquette quality. It is the ability to produce fewer fines during transportation storage etc. The results of the durability test on the briquettes as shown in Table 3, reveals that the durability of FS was the highest at 95.04%. The durability of tannery waste briquettes ranges from 892.12–95.04%. The result reveal that tannery waste studied will not disintegrate easily during transportation, handling and storage. From Table 3 it shows that the briquettes were not relatively affected by ambient humidity when they were

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>S (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD</td>
<td>43.634</td>
<td>6.218</td>
<td>13.157</td>
<td>2.215</td>
<td>34.776</td>
</tr>
<tr>
<td>CS</td>
<td>45.153</td>
<td>5.782</td>
<td>12.766</td>
<td>2.378</td>
<td>30.921</td>
</tr>
<tr>
<td>FS</td>
<td>40.811</td>
<td>5.885</td>
<td>15.357</td>
<td>2.668</td>
<td>35.279</td>
</tr>
<tr>
<td>HR</td>
<td>40.792</td>
<td>6.317</td>
<td>15.510</td>
<td>2.417</td>
<td>34.964</td>
</tr>
</tbody>
</table>

Where: C = % carbon content in the biomass fuel, H = % hydrogen content in the biomass fuel N = % nitrogen content in the biomass fuel, S = % sulphur content in the biomass fuel BD- buffering dust, CS- chrome shavings, FS- fleshing, and HR- hair.

Table 3. Results of some Thermal Properties of Briquettes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Durability (%)</th>
<th>Humidity Resistance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD</td>
<td>93.45</td>
<td>95.34</td>
</tr>
<tr>
<td>CS</td>
<td>94.23</td>
<td>96.12</td>
</tr>
<tr>
<td>FS</td>
<td>95.04</td>
<td>95.77</td>
</tr>
<tr>
<td>HR</td>
<td>92.12</td>
<td>97.93</td>
</tr>
</tbody>
</table>

BD- buffering dust, CS- chrome shavings, FS- fleshing, and HR- hair
kept at 20 °C and in humidity of 50% for 21 days. The humidity resistance values were found to be considerably close for all briquettes. In addition, the briquettes produced was packed in hermetically, and kept at 20 °C and in humidity of 50% for 21 days, and at the end of 21th day, it was detected that there was no change in mass and sizes of the briquettes. The results of water and humidity resistance show that briquettes have to be stored packed and under covered ambient conditions.

**Results of thermal properties.** As observed from Figure 1, HR has the highest volume of water absorbed (35%). This might be because of the presence of larger pores (air spaces) in HR briquettes which has particle size of 1.0 mm, while BD (22%), CS (25%) and FS (24%) have particle sizes of 0.5 mm. This observation might be added to the fact that the larger particle sizes could have more pronoune pore spaces in between the particles than the finer particle size thus support water absorption. It is expected that the HR briquettes will burn properly more than other briquettes because air can easily enter the briquettes through the pores to enhance the burning process. Akowuah et al. [33] wrote that the higher the porosity, the higher the rate of infiltration of oxidant and out flow of combustion/pyrolysis products during combustion and the higher will be the burning rate of the briquette [21].

The ignition time is a function of the volatile matter and particle size. The higher the volatile matter the higher the ignition time since more time is taken to burn off the volatiles before combustion. Also the larger the particle sizes the higher the ignition time. As seen on the Table 4, HR has the highest ignition time of 92 seconds. BD, CS and FS have ignition time of 67, 71, 73 seconds respectively the similarity in the ignition time of BD, CS and FS might be as a result of the briquettes being of the same particle sizes (0.5 mm) and from the same material. HR has higher ignition time though from the same material the reason might be as a result of its large particle size (1.00 mm).

![Water boiling time is a function of the calorific value, volatile matter, and thermal efficiency of a fuel. FS has the lowest water boiling time of 27.78 minutes followed by CS of 28.72 minutes. HR has the highest boiling time of 34.11 minutes followed by BD with 30.98 minutes.](image)

**Figure 1. Result of Porosity Test**

Water boiling time is a function of the calorific value, volatile matter, and thermal efficiency of a fuel. FS has the lowest water boiling time of 27.78 minutes followed by CS of 28.72 minutes. HR has the highest boiling time of 34.11 minutes followed by BD with 30.98 minutes.

Combustion rate is one of the important characteristics to confirm the quality of briquettes, it is the amount of a material that undergoes combustion over a period of time. The briquettes have different compositions hence will have different combustion rate. The result of the combustion rate of briquettes is shown in Table 4. HR has the fastest combustion rate of 0.217 g/min followed by BD with combustion rate of 0.189 g/min. The lowest combustion rate of 0.171 g/min was recorded in CS, with FS recording 0.174 g/min. Combustion rate has a significant effect on briquette application. A briquette with high combustion rate implies that more briquettes will be required in combustion as they burn off readily. The combustion rate in this work which ranged between 0.171 and 0.217 g/min is lower than that reported by Islam et al. (2014) of briquette from Coir Dust and Rice Husk Blend which varies between 0.789-0.945 kg/hour.

**4. Conclusion**

Solid fuel was produced from four solid waste of tannery processing via briquetting using cassava starch as binder. The produced briquettes were subjected ultimate analysis and water boiling test with a view of assessing their combustion quality and suitability. The produced briquettes were found to meet the requirement for household cooking, heating and for used in home industries. Of the four waste studied the fleshing possess the best quality in terms of its combustion characteristics.

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