Comparison of Thermochemical and Physical Properties of Some Indonesian Agricultural Wastes

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Abstract

Indonesia is one of the largest agricultural countries in the world. Two main agricultural sub-sectors in Indonesia are food crops and estate crops. Agricultural waste is one of the biomass energy sources that has the potential to replace fossil energy sources. The weakness of energy sources from different types of agricultural waste is their heterogeneous thermochemical and physical properties. The objective of the experimental study is to compare the thermochemical and physical properties of fourteen selected agricultural wastes in Indonesia. The thermochemical properties that were compared are high heating value (HHV), percentage of lignocellulosic components, and ultimate analysis, while that of physical properties are the grindability, hydrophilicity, and proximate analysis. A material with high fixed carbon, low moisture, and low ash contents is preferred as a solid fuel source. Based on the experimental results of proximate analysis, coffee husk has the highest fixed carbon content (20.85%). Empty fruit bunch has the lowest moisture content (7.04%). Palm kernel shell has the lowest ash content (1.82%). Based on the results of the ultimate analysis, the palm kernel shell is the sample with the highest carbon content (49.42%), while the empty fruit bunch has the highest hydrogen content (6.69%). The coconut shell was identified as containing the lowest nitrogen (0.14%) and sulfur (0.052%). Peanut shell is the easiest to grind, while empty fruit bunch is the hardest to grind materials. The hydrophilicity of sugarcane trash is lower than other samples (9.34%). Coconut shell has the highest percentage of cellulose (47.21%). Several pairs of agricultural waste have similar properties that can be used as considerations for handling management and co-utilization.

Keywords:
Biomass; grindability; HHV; hydrophilicity; lignocellulosic; proximate analysis; ultimate analysis

1. Introduction

Global concern and efforts regarding renewable energy are enormous, with many countries actively implementing strategies to increase the share of renewable energy in their energy portfolios. Encouragingly, the share of renewable energy continued to grow (15%) and account for 7.5% of the world’s primary energy consumption in 2021 [1]. Renewable energy has become a global focal point as countries strive to reduce dependence on fossil fuels and promote sustainable development. Many

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countries are increasingly realizing the need to transition to renewable energy sources to mitigate climate change because renewable energy helps reduce greenhouse gas emissions [2,3]. Global initiatives and agreements, such as the Paris Agreement, emphasize the importance of international collaboration in addressing climate change through increasing the use of renewable energy [4]. Diversifying energy sources is a priority for countries wishing to increase energy security. Diversifying energy sources is a priority for countries wishing to increase energy security. Dependence on limited and geopolitically sensitive fossil fuels can be reduced by incorporating renewable energy technologies. Additionally, the renewable energy sector offers economic benefits, including job creation and innovation opportunities.

Biomass is one of renewable energy sources destined to play a crucial role as an alternative energy source in the future [5]. Biomass is organic material that comes from plants and animals that are still alive or dead, but in this case, it does not include fossilized plants and animals [6]. Biomass is a renewable energy source because it can be developed in a short time so that it can become a long-term and sustainable energy source that is environmentally friendly [7,8]. The energy in biomass is formed through the photosynthesis process in plants. The photosynthesis process converts water, nutrients from the soil and CO₂ in the air with the help of sunlight into carbohydrates. Carbon dioxide absorbed from the air during the photosynthesis process is released when biomass is used as fuel, so the utilization of biomass as fuel does not increase the amount of CO₂ in the atmosphere [9-11]. Therefore, biomass is called a carbon dioxide-neutral fuel. Biomass represents a highly encouraging resource that can substitute for energy generated from fossil fuels. It presents an alternative solution for lowering emissions [12].

Currently, most countries in the world still rely on fossil energy sources, especially petroleum, and coal, so the potential of biomass has yet to be utilized as an energy source. Humans actually have utilized biomass energy sources before other energy sources were used. For example, people have used wood for thousands of years for cooking. Biomass can commonly be classified as woody biomass and non-woody biomass. Woody biomass mainly involves products and by-products derived from the forest, woodland, and tree sectors. Non-woody biomass includes agricultural, agroforestry residue, herbaceous products, animal waste, and tertiary waste [13]. One source of biomass energy that has great potential worldwide is agricultural waste. The process of harvesting and processing agricultural commodities produces waste that has the potential to be used as an energy source.

Indonesia is one of the largest agricultural countries in the world, with an agricultural land area of 64.6 million ha and more than twenty commodities. Two main agricultural sub-sectors in Indonesia are food crops and estate crops. The primary commodities of the food crop agriculture sub-sector are rice, corn, soybeans, peanuts, and cassava, and those of estate crops are oil palm, coconut, cocoa, sugar cane, and coffee. Indonesia has abundant biomass energy resources to support national energy security, which comes from the waste of various agricultural commodities.

The objective of others previous researches were to compare several agricultural wastes from the author’s countries. This research not only focuses on comparing but also identifying the similarities of fourteen agricultural wastes from Indonesia. The research based on the experimental result of the physical and thermochemical properties of the samples. The physical properties of biomass that were compared included grindability, hydrophilicity and the percentage of moisture, fixed carbon (FC), volatile matter (VM) and ash. Thermochemical properties compared include high heating value (HHV), percentage of lignocellulosic components and ultimate analysis. By comparing the properties of one biomass with another, groups of biomass with almost the same properties can be identified to determine appropriate management and pretreatment processes.
2. Methodology
2.1 Material

The feedstocks used in the experimental study were food and estate crop wastes in Indonesia. Rice, corn, soybean, peanut, and cassava were selected for the food crop commodities in the study. Meanwhile, the wastes from five selected commodities were rice husk, rice straw, corn husk, corn stalk, soybean stalk, peanut shell, peanut stalk, and cassava stem. Oil palm, coconut, cocoa, sugarcane, and coffee were selected for the estate crop commodities in the study. The selected estate crop wastes were palm kernel shell, empty fruit bunch, coconut shell, cocoa pod shell, sugar cane trash, and coffee husk. These commodities were chosen because they are the ten primary commodities in Indonesia. The diagram of the research process is depicted in Figure 1. The all selected agricultural waste are depicted in Figure 2.

![Fig. 1. The diagram of the research process](image1)

![Fig. 2. The agricultural commodities and selected sample of agricultural waste](image2)
2.2 Sample Characteristics

The proximate and ultimate analyses was carried out at Coal Laboratory, Mineral and Coal Testing Center in Bandung. The proximate analysis of each sample was carried out according to the American Society for Testing and Materials (ASTM) 3171, 3174, and 3175 standard testing methods. Volatile matter and ash contents were determined using a muffle furnace (Carbolite AAF 1100) following standard test methods of ASTM 3175 and ASTM 3174, while moisture content analysis was performed by Minimum Free Space (MFS) oven (Carbolite) according to ASTM 3171 standard test methods. The fixed carbon content was calculated by subtracting the moisture, volatile, and ash contents from the total biomass on an air-dry basis. The elemental components (C, H, O, N, S) of each sample were determined by the LECO CHN 628 elemental analyzer according to the standard test method of ASTM D5373. The sulfur content was analyzed using LECO S 632 elemental analyzer according to the standard test method (ASTM D4239). Oxygen content was determined by the difference. Testing the HHV was conducted at Integrated Research and Testing Laboratory, Gadjah Mada University in Yogyakarta. An IKA C6000 bomb calorimeter was used to determine the HHV of all samples. These analyses were conducted twice for repeatability.

The structural analysis was done at The Center for Food and Nutrition Studies, Gadjah Mada University in Yogyakarta. The structural analysis was conducted to determine cellulose, hemicellulose, and lignin contents. The structure of the sample was analyzed using the Chesson-Datta method. The Chesson-Datta method involved a series of steps: Initially, one gram of the sample was refluxed for two hours with 150 mL of H₂O at a temperature of 100 °C to obtain water-soluble components. Next, the sample was refluxed for two hours with 150 mL of 0.5 M H₂SO₄ at 100 °C to extract hemicellulose. Subsequently, the sample was treated in 10 mL of (v/v) H₂SO₄ of 72% for four hours, diluted to 0.5 M of H₂SO₄, and refluxed at 100 °C for two hours to acquire cellulose. The remaining sample residue was dried and heated in a furnace at a temperature of 575 ± 25 °C until the sample was constant to determine lignin. Finally, the ash content was obtained. Furthermore, cellulose, hemicellulose, and lignin content in the substrate was calculated using the following formula.

\[
\text{Hemicellulose} = \frac{(b - c)}{a} \times 100\% \\
\text{Cellulose} = \frac{(c - d)}{a} \times 100\% \\
\text{Lignin} = \frac{(d - e)}{a} \times 100\%
\]

where oven dry weight (ODW) of initial biomass sample (a), ODW sample residue refluxed with hot water (b), ODW of the sample refluxed with 0.5 M of H₂SO₄ (c), ODW residue macerated with 72% H₂SO₄ and diluted to 0.5 M (d), and ashes (e).

The hydrophilicity and grindability tests conducted at Renewable Energy Laboratory, Janabadra University in Yogyakarta. Equilibrium moisture content (EMC) was used to investigate the hydrophilicity properties of the samples. The hydrophilicity test was initiated by reducing the sample size to below 177 μm (80 meshes) through grinding, then drying the sample at 105 °C for two hours. Subsequently, hydrophilicity analysis was performed by placing 2 grams of each sample into an airtight container. A saturated sodium chloride (NaCl) solution was employed to maintain a relative humidity level of approximately 75% within the container as a humidity control [14]. A humidity meter KW06-291 (Krisbow) was used to monitor the relative humidity in the container. Hydrophilicity
analysis was conducted by letting the sample absorb moisture in a container and weighing it every 12 hours until there was no more increase in weight.

The general grindability testing method for coal is the HGI standard. There is no grindability testing standard for biomass. There are several methods used to evaluate the grindability by previous researchers, including the volumetric HGI test, the energy consumption, and particle size distribution method [15-19]. In this work, grindability test was done based on particle size distribution. Fifty grams of each sample with 8 - 20 mesh particles was placed in a mini ball mill. The mini ball mill has a cylindrical pan with an inner diameter of 14 cm and a height of 14 cm, which contains 30 steel balls (diameter of 20 mm and mass of 1075 grams). In this process, the rotational speed of the mill was 150 rpm for 15 min. After grinding, the sample was sieved to get the particle size distribution with a series of sieves of 200 (75 μm), 100 (150 μm), 40 (425 μm), and 30 (600 μm) mesh sizes. Sieving was carried out by a sieve shaker with a frequency of 20 Hz for 10 min. Particle size distribution was determined by weighing the material on each sieve. After that, the cumulative weight was calculated after the shaking was completed.

3. Results

Each type of biomass has specific properties. The heterogeneous nature of agricultural wastes, a critical problem of using them as a resource, requires a comprehensive analysis of their physicochemical properties. The results of proximate analysis, ultimate analysis, heating value, particle size distribution, hydrophilicity and lignocellulosic composition revealed that some significant differences exist in the chemical and structural properties of agricultural wastes. The proximate analysis provides moisture content, volatile matter, fixed carbon, and ash content, and the ultimate analysis includes the elemental composition (Carbon, Hydrogen, Nitrogen, Sulfur, Oxygen) of all samples presented in Table 1. The higher heating value of all the samples is presented in Figure 3. Figure 4 and Figure 5 show particle size distribution and hydrophilicity of fourteen specimens. The lignocellulosic composition of each selected agricultural waste is illustrated in Figure 6.

3.1 Proximate Analysis

Knowing the water content in agricultural waste is essential to determine the process selection before using it as fuel. The moisture content of agricultural wastes varies based on length of time, particle size, and drying method. It plays a crucial role in determining the cost of drying and the energy content of the final product. The moisture content of the material after drying can also change depending on the storage method. Higher moisture content is particularly problematic for thermal processes, as it needs more energy for water evaporation, resulting in decreased calorific value and unnecessary transportation weight. Additionally, increased moisture content in the feedstock leads to substantial heat loss during evaporation [20]. The moisture content is a principal characteristic of biomass. It affects the mechanical, physical, and thermal properties of biomass fuels. Consequently, it holds great significance in selecting the appropriate biomass conversion technology. Low water content in agricultural wastes is beneficial for the thermal conversion process, while those with higher moisture content are more fitting for biochemical processes like fermentation conversion or hydrothermal process [21,22].

The results presented in Table 1 indicate that these Indonesia agricultural wastes have moisture contents between 7.04 wt.% (empty fruit bunch) and 13.92 wt.% (peanut shell), hence more suited for thermal conversion technology such as torrefaction or pyrolysis methods. The result obtained
from the proximate analysis shows that empty fruit bunch, sugarcane trash, palm kernel shell, and cocoa pod shell have low moisture content (< 10.00 wt.%).

<table>
<thead>
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<th>Table 1</th>
<th>Proximate and ultimate analyses</th>
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<tbody>
<tr>
<td>Biomass</td>
<td>Proximate analysis (wt%, adb)</td>
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<tr>
<td></td>
<td>Moisture</td>
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<tr>
<td>Palm kernel shell</td>
<td>8.16</td>
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<td>Empty fruit bunch</td>
<td>7.04</td>
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<tr>
<td>Cocoa pod shell</td>
<td>9.64</td>
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<td>Coconut shell</td>
<td>11.87</td>
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<tr>
<td>Sugarcane trash</td>
<td>7.72</td>
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<tr>
<td>Coffee husk</td>
<td>11.52</td>
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<tr>
<td>Rice husk</td>
<td>10.31</td>
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<td>Rice straw</td>
<td>11.2</td>
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<tr>
<td>Corn stalk</td>
<td>10.36</td>
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<tr>
<td>Corn husk</td>
<td>11.74</td>
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<tr>
<td>Peanut shell</td>
<td>12.26</td>
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<tr>
<td>Peanut stalk</td>
<td>13.92</td>
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<tr>
<td>Soybean stalk</td>
<td>10.76</td>
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<tr>
<td>Cassava stem</td>
<td>10.52</td>
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</table>

Fixed carbon is one of the parameters used to characterize the quality and properties of solid fuel. It is an important property that describes the amount of carbonaceous material remaining in solid fuel after volatile matter and moisture have been driven off through a heating process. It is an essential indicator of the energy content and is used in calculating the calorific value. High fixed carbon content generally indicates a higher energy content and better solid fuel quality.

From the research results, agricultural waste samples in this study can be grouped based on their fixed carbon content into three groups, namely low FC (< 15%), medium FC (15% - 18%), and high FC (> 18%). High FC include palm kernel shell, cocoa pod shell, coconut shell, and coffee husk. Medium FC consists of a peanut shell, empty fruit bunch, soybean stalk, corn stalk, and cassava stem. Low FC includes peanut stalks, rice husks, rice straw, and sugar cane trash. Evaluating the FC percentage, the sample with the highest FC percentage is coffee husk (20.85%), while the sample with the lowest is sugar cane trash (11.73%).

Volatile matter is also a significant parameter in the analysis of biomass materials. VM is the largest component in biomass material. It consists of various parts that can vaporize as gases when the material is heated in the absence of air. It is usually a hydrocarbon, hydrogen, oxygen, carbon monoxide, and noncombustible gases [23]. Biomass having a greater content of volatile matter is more likely to provide a high concentration of bio-oil. The high percentage of volatile matter firmly has an effect on its combustion behaviour and thermal decomposition [22]. Volatile matter is combustible, and high volatile matter content makes the fuel more active and easier to burn [24]. Gasification from material containing high amounts of volatile matter is unfavourable as it releases more tar, which triggers complications in the engine [23]. Table 1 shows that most of the samples have a VM percentage between 60 - 70%. Sugarcane trash has the highest percentage of VM (71.39%), while rice straw contains the lowest VM (53.56%).

Ash content is an important parameter for solid fuels as it is a by-product of combustion. For solid fuels such as biomass, the ash content is an essential factor in determining its quality and combustion characteristics. Higher ash content can lead to operational challenges in combustion systems, as the ash can lead to fouling and slagging, as well as reducing the efficiency of the process [25].
Additionally, high ash content can contribute to increased particulate matter emissions and other pollutants. For efficient energy production and environmental sustainability, it is essential to consider the ash content alongside other parameters when evaluating the suitability of biomass for solid fuels. The results obtained from the proximate analysis show that ash content in agricultural waste varies between 1.82% to 22.12%. Palm kernel shell has the lowest ash content (1.82%), whereas rice straw shows the highest (22.12%).

3.2 Ultimate Analysis and Heating Value

The ultimate analysis presented in Table 1 is useful for analyzing the elemental composition content in selected samples that consist of C, H, N, S, and O. Total carbon (C) derived from the ultimate analysis differs from the fixed carbon amount of the proximate analysis. Fixed carbon does not include organic carbon, which escapes during combustion as a volatile matter, but total carbon from the ultimate analysis consists of this [15]. The highest carbon content in agricultural waste samples is 49.42% (palm kernel shell), and the lowest is 31.03% (rice straw). The range of hydrogen in all the samples is between 5.29% (rice straw) and 6.69% (empty fruit bunch). Nitrogen and oxygen are found in the range of 0.14 - 1.42% and 38.83 - 50.7%, respectively. The minimum nitrogen has been obtained from the coconut shell, while the maximum of that is from the coffee husk. Empty fruit bunch contains the lowest oxygen, while corn husk is the opposite. The percentage of sulfur lies in the range of 0.052% (coconut shell) to 0.22% (peanut stalk).

The most important parameter of biomass as a fuel is the heating value. One of the weaknesses of biomass is low heating value because not all components in biomass contain calories, such as water and a part of the VM. Therefore, sometimes pre-treatment is needed to increase the heating value. Figure 3 depicts the HHV of the study sample. It has been seen that agricultural wastes can be divided into three groups based on their heating value. First, a group with a heating value greater than 17 MJ/kg; second, a group with a heating value ranging from 15 – 17 MJ/kg; and last, a group with a heating value less than 15 MJ/kg. Materials with HHV higher than other agricultural waste types include palm kernel shell, coconut shell, empty fruit bunch, peanut shells, and cassava stems. Palm kernel shell has the highest HHV (19.64 MJ/kg).

![Fig. 3. The HHV comparison various kind of agricultural wastes](image)
3.3 Physical Analysis

One of the weaknesses of agricultural waste is its fibrous nature, which makes it difficult to grind. Grindability of solid biofuels is crucial, mainly in pulverized combustion systems [26]. The original nature of fibrous material causes higher energy consumption for grinding. This work used the particle size distribution method to assess the grindability. The grindability of different agricultural wastes is presented in Figure 4. Based on grindability, selected agricultural waste can be grouped into three: easy, medium, and difficult to grind. Materials that are easy to grind are characterized by a greater percentage of small particles when conducting grindability tests. The cocoa pod shell, rice straw, corn husks, peanut stalks, and peanut shells are classified as easy to grind, while empty fruit bunch, coconut shell, sugar cane trash, and coffee husk are categorized as easy to grind materials.

Fig. 4. Comparison of grindability of various agricultural wastes

The other disadvantage of biomass is that it tends to absorb atmospheric moisture (hydrophilic nature). The greater the ability to absorb water, the more likely the moisture content in biomass increases again when stored in an open area, even after drying beforehand [27]. Increasing moisture content within biomass diminishes the heating value, grows fungus more easily, and contributes to higher expenses for transportation and handling [28]. Comparison of the hydrophilicity of the sample can be seen in Figure 5. Cocoa pod shell reached its maximum hydrophilicity of 18.21 wt.% while sugarcane trash obtained its minimum of 9.38 wt.%. Based on hydrophilicity, the sample can be grouped into three different classes, namely low hydrophilicity (< 10 wt.%), medium hydrophilicity (10 – 14 wt.%), and high hydrophilicity (> 14 wt.%). Sugar cane trash, coconut shell, palm kernel shell, and empty fruit bunch are materials with low hydrophilicity, while rice husks, rice straw, peanut stalks, corn stalks, and peanut shells are materials with medium hydrophilicity. The materials with high moisture absorption ability include corn husks, cassava stems, soybean stalks, coffee husk, and cocoa pod shell.
3.4 Lignocellulosic Analysis

Agricultural wastes are generally lignocellulosic biomass consisting of three major constituents: hemicellulose, cellulose, and lignin. Very small quantities, such as ash and protein, are also contained in lignocellulosic biomass since the ash and proteins are negligible. Lignocellulosic material is a fibrous part of biomass [2,28,29]. The results of this study showed that all agricultural wastes have various percentages of lignocellulose composition. Cellulose, hemicellulose, and lignin are found in the range of 20.89 - 70.23%, 1.33 - 41.33%, and 8.83 - 35.28%, respectively. Cellulose is the main component of most agricultural waste. Figure 6 shows that nine of the fourteen samples of agricultural wastes contained more cellulose than hemicellulose and lignin, including palm kernel shell, coconut shell, sugarcane trash, rice husk, rice straw, corn stalk, peanut shell, soybean stalk, and cassava stem. This result is in accordance with the result of previous research by Awogbemi and Kallon [29]. Peanut stalk contains more hemicellulose than other components. In comparison, empty fruit bunch, cocoa pod shell, coffee husk, and corn husk contain more lignin.
3.5 Similarity Analysis

Classification and similarity evaluation of the agricultural wastes is carried out using data normalization of several parameters. Normalized parameters include O/C and H/C ratio atomics, hydrophilicity, grindability, celluloscic content, and fuel volatility. Min-max normalization, one of the most common ways to normalize data, was applied in the study. The minimum value of each datum gets transformed into a 0, the maximum value gets transformed into a 1, and every other value gets transformed into a value between 0 and 1.

Agricultural waste has varied properties. However, various agricultural waste types can be grouped with closely similar properties. The grouping is useful for managing the utilization and handling of agricultural waste as a fuel source. Similarity analysis was begun by normalizing the data for each parameter because each parameter has a different range. Normalizing data was divided into three groups based on the value, i.e., 0 to 0.33, 0.33 to 0.67, and 0.67 to 1. Figure 7 shows the normalized data for several parameters of all samples.

![Fig. 6. Lignocellulosic composition of various agricultural wastes](image-url)
Fig. 7. Normalizing data of various agricultural wastes for similarity analysis

The samples are categorised as close in similarity when more than five parameters of the samples are in the same group. Based on the evaluation of agricultural properties, palm kernel shell and empty fruit bunch have similar properties in O/C atomic ratio, hydrophilicity, fuel volatility, percentages of holocellulose and lignin, as well as HHV. Cocoa pod shell and coconut shell have similarities in several parameters, including O/C and H/C atomic ratios, hydrophilicity, percentages of holocellulose and lignin, as well as fuel volatility. Agricultural wastes of rice straw and corn husk are in the same group of lignin content, O/C and H/C atomic ratios, hydrophilicity, and grindability. Peanut stalk and rice husk have the same properties in O/C and H/C atomic ratios, lignin and holocellulose contents, as well as HHV. The O/C atomic ratio, grindability, HHV, as well as lignin and holocellulose contents of cassava stem and cocoa pod shell are closely similar.

4. Conclusions

In this paper, comparison agricultural waste properties from Indonesia are investigated to provide property information for their potential utilization as feedstock energy sources. The evaluation of agricultural waste includes proximate, ultimate, heating values, particle size distribution, hydrophilicity, and lignocellulosic composition analyses. The study shows that various agricultural wastes have different thermochemical and physical properties. It was known that from the 14 samples studied, the fixed carbon (FC) content was in the range of 11.73 to 20.85%. The highest and lowest FC content samples were peanut stalks and coffee husk, respectively. The majority of the samples have a VM content between 60 and 70%. Rice straw has the lowest percentage of volatile matter (VM) (71.39%), while Sugarcane trash contains the highest VM (53.56%). The ash content in agricultural waste varies between 1.82% to 22.12%. Palm kernel shell and rice straw have the lowest highest ash contents, i.e., 1.82% and 22.12%, respectively. The maximum carbon content
is owned by palm kernel shell (49.42%). The ultimate analysis indicated that empty fruit bunch sample contains more hydrogen content and coffee husk sample contains more nitrogen than other sample. Corn husk has the highest Oxygen content (50.7%), and peanut stalks have the highest sulfur content (0.22%). The sample with the highest HHV is palm kernel shell (19.64 MJ/kg). Peanut shell is the easiest to grind, while empty fruit bunch is the hardest to grind materials. The hydrophilicity of the sample is in the range of 9.34% for sugarcane trash and 18.21% for cocoa pod shell. Cellulose is the highest component of lignocellulosic in most agricultural waste with a range between 20.59% (coffee husk) and 47.21% (coconut shell). Based on similarity evaluation of the agricultural wastes using data normalization of several parameters, it is concluded that agricultural waste with similar properties is palm kernel shell to empty fruit bunch, cocoa pod shell to coconut shell, rice straw to corn husk, peanut stalk to rice husk, and cassava stem to cocoa pod shell.

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