

Physicochemical and Thermal Properties of Some Key Tropical Sawdust Woods for Energy Production

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Abstract

In South Saharan countries, 85% of the population uses biomass as a primary energy source. Cameroon presents one of the highest biomass energy and sawmills produce important sawdust resources which are not used and are burnt in piles leading to significant air toxic emissions. Therefore, we have to valorize industrially these available sawdusts. This study focuses on the physicochemical and thermochemical analysis of Ayous, Sapelli and Tali sawdust. The proximate and ultimate analysis, particle size, structural composition, as well as heavy metal content and calorific value were determined. In addition, the thermogravimetric mass losses were also estimated. The results showed that high water contents (24% - 41%) were recorded in the raw sawdust, and the thermal treatment reduced these contents from 78% to values in the range of 4% - 9%. The values for ash and volatile matter content were respectively between 0.25% - 0.74% and 68% - 76%. The LHV is higher in Ayous (17.5 MJ/kg) and Sapelli (16.8 MJ/kg) than that of Tali (15.7 MJ/kg). The concentration of heavy metals is very low in each species. Extractives are more present in Tali (16.06%) than in the other sawdusts. Pyrolysis of sawdust shows the typical decomposition of hemicellulose (270°C - 325°C), cellulose (325°C - 400°C) and lignin (200°C - 550°C) with a maximum loss of 75% at 370°C and the melting point is 320°C. The results of the sawdust parameters determined in the paper can be valorized to reduce pollutants emissions by developing the efficiency and effectiveness of biomass energy processes and promoting the use of biomass as a sustainable alternative to traditional fossil fuels.

Keywords

Wood, Sawmills, Sawdust, Combustion, Energy

1. Introduction

Most of the world's energy needs have long been supplied by conventional energy sources such as fossil fuels and nuclear energy [1] [2]. Fossil fuels are the foremost channels for the emission of greenhouse gases, which significantly contribute to increased environmental pollution and global warming [3] [4]. Therefore, renewable energy sources, and biomass, are well established as the most widely exploited fuel source after coal and oil are developed as substitute due to their relative environmentally friendly potential [5] [6] [7]. In Africa, more than 85% of the population uses biomass to produce primary and secondary energy [8] [9]. Actually, among the countries in the Congo Basin, Cameroon possesses one of the greatest potentials of under-exploited wood energy source [10] [11]. Sawmills produce nearly 2.5 million m3 of wood waste each year and sawdust accounts for 25% which corresponds to about 150 - 200 kT [11] [12]. These sawdust resources under valorizing, are generally burnt in open air piles leading to an important waste of tropical wood resources and the release of significant toxic gas emissions as particles, polycycles, and aromatics hydrocarburs [10]. Recovering this sawdust to produce energy represents an important advantage for better environmental and energy management in Cameroon [13] [14]. Biomass energy derives from the photosynthetic transformation of solar energy by the walls of plant cell tissues into useful energy [3] [5]. It is stored in the polymers of lignin, cellulose and hemicelluloses of the plant [15] [16]. The physicochemical composition of the biomass influences their energy potential [17] [18]. More importantly, their fixed carbon content, ash content, moisture and density influence their energy potential [19] [20]. It is worth mentioning that the ecological conditions and the origin of the species also influence their physicochemical and energy properties [8] [21] [22].

Classified as hardwood species, Ayous (*Triplochiton scleroxylon*), Sapelli (*Entandrophragma cylindricum* Sprague) and Tali (*Erythrophleum suaveolens* or *Erythrophleum ivorense*) are the most widely exploited woods, with a significant proportion of sawdust in wood processing plants in East region of Cameroon [10] [23]. To date, a great number of research projects have focused on the use of sawdust waste in Cameroon. As an example, the formulation of wood-cement composite materials for building applications and the activated carbons derived from sawdust from Ayous sawdust have been applied for the elimination of organic and inorganic pollutants in wastewater [24] [25]. Others have investigated sawdust extractives from Sapelli and Tali for the synthesis of antioxidants [26]. However, to the best of our knowledge, no research has been conducted yet on the physicochemical and thermal characterisation of sawdust from East Came-

roon and its use as bioenergy. This study aims at the investigation of the physicochemical and thermal properties of sawdust from three species of Ayous, Sapelli and Tali sampled in industrial sawmills from the East Cameroon region to assess their potential as energy valorization. Cameroon, like many other countries in Africa, generates large amounts of sawdust as a byproduct of various industries. The good knowledge of the physicochemical and thermal properties of these sawdust wastes can be used as a source of efficient energy production through combustion, pyrolysis, pelletization or gasification processes. And to impulse proper management of sawdust wastes crucial for environmental sustainability which can be used in developing eco-friendly disposal methods to decrease biomass waste pollution.

2. Experimental

Sawdust from Ayous, Sapelli and Tali were collected by simple random sampling in August 2021 at the Société de transformation du Bois du Cameroun (STBC) located in the town of Abong Mbang in the East Cameroon region (**Figure 1**). The average age of the trees assessed by the STBC varied between 60 - 70 years.



Source : data base PSFE 2021 Designe and realization : BAKAIRA Markus and FIWA KAOKE Davy, novembre 2021

Figure 1. Map of the East Cameroon localization zone of sampling sawdust wood.

2.1. Physicochemical Analysis

The sawdust samples were stored at room temperature. The physicochemical analysis consisted in determining the particle size distribution, proximate and ultimate analysis, heavy metals, structural composition analysis, Fourier Transform Infrared Spectroscopy, the free sugar content and thermal analysis behaviour of the sawdust sample.

2.2. Particle Size Distribution

The particle size distribution of the sawdust was determined after sieving using the EN P 18-560 method. A column of AFNOR 11-501 sieves of decreasing size (2, 1, 0.6, 0.4, 0.125 mm) up to the collector was installed. To this end, 500 g (M) of sample were deposited at the top of the sieve stack, which was vibrated at 70 Hz for 25 min on a Merck vibrator. Particles are smaller than the sieve mesh size pass through (M_i), while those are larger than the mesh size are retained (M_j). All the fractions were weighed to determine the particle size distribution (D_g) for each sample according the Equation (1).

$$D_g = \frac{\sum_{i=0.125}^{3} M_i}{M} \times 100$$
 (1)

2.3. Proximate Analysis

Proximate analysis was performed in order to evaluate the major substances of the sawdust sample such as the water content, ash content, volatile matter content, fixed carbon content and calorific value.

2.4. Determination of Moisture Content

Moisture content was determined according to the protocol of standard AFNOR 14774 in considering samples of wet raw material and dry material (after treatment at 105°C for 48 hours). 3 g of sample was squarely distributed in an aluminium disk and weighed successively using an analytical balance. The disk was removed from the oven and placed in the desiccator until a constant mass was obtained. The samples were weighed and the moisture content was determined.

2.5. Determining of Ash Content

The ash content (TC) of the biomass corresponds to the solid fraction remaining after complete combustion. It was obtained on the various sawdust samples using the kiln calcination method. 3 g of anhydrous sample was weighed into porcelain crucibles. The crucibles were placed in a Carbolite GWF1100 muffle furnace at room temperature. The heating temperature had an intermediate stage at 250° C for one hour with a temperature ramp of 5 K·min⁻¹. A second ramp of 10° K·min⁻¹ was applied to reach the final temperature of 550° C, temperature at which the sample was left for five hours. The percentage of ash was calculated from the mass of the residue after incineration.

2.6. Determination of Volatile Matter Content

The volatile matter content (T_{VM}) was determined using the protocol of standard EN15148. 02 g of sample with a particle size of 0.125 mm was dried in an oven at 105°C for 24 hours. The powder obtained was calcined in an analytical muffle furnace (Naberterm L/LT 1300) under nitrogen gas at 950°C for 45 minutes. The volatile matter content was determined by using Equation (2).

$$T_{VM} = \frac{m_1 - m_2}{m_1} \times 100$$
 (2)

with: T_{VM} : volatile matter content (%), m_1 : mass of sample (g), m_2 : mass of ash after calcination (g).

2.7. Determination of Fixed Carbon Content

The fixed carbon content (T_{FC}) was estimated by taking the difference between the sums of the Volatile Matter Content (T_{VM}), the Moisture Content (T_H) and the Ash Content (T_A) according to Equation (3) [27].

$$T_{FC} = 100 - (T_{VM} + T_A + T)_H$$
(3)

with: T_{FC} : Fixed carbon content (%), T_{VM} : Volatile matter content (%), T_A : Ash content (%). T_{H} : Moisture content (%).

2.8. Determination of Higher Heating Value

The Higher Heating Value (HHV) is the quantity of heat, in joules per gram, obtained after complete combustion of a unit mass of fuel by fully recovering the latent heat. It was obtained by considering the biomass completely anhydrous, using the method set out in standard NF M 03-005. The semi-automatic 6100 isoperibolic calorimeter bomb was used for this purpose. Ignition is controlled by a wire placed between two electrodes. This ignition was burns once in contact with the biomass sample. The HHV is obtained at the end of the experiment and the results were obtained and stored digitally.

2.9. Determination of Lower Heating Value

The lower heating value (LHV) obtained by deducting the higher heating value (HHV) and the moisture content of the fuel has an experimental repeatability of less than 0.5%. The relationship in Equation (4) gives the LHV [27]:

LHV = HHV -
$$\left[\frac{(K_{\text{cond}} * K_2 * H_{\text{ech}})}{100} - \frac{(K_{\text{cond}} * W)}{100}\right]$$
 (4)

with: LHV obtained in MJ/kg⁻¹, $E_{cond} = 2511$ J/g the heat of water condensation, K_2 the proportionality factor which is equal to 2 masses of hydrogen present and 8937 masses of water formed, $K = H_{ech}$ (%) the hydrogen content of the sample in given by Equation (8) and the moisture content of the sample (*W*). The hydrogen content of a sample was determined by relation (5) [27]:

$$H_{\rm ech} = H_{\rm anhydre} \times \frac{100 - W}{100} \tag{5}$$

2.10. Structural Composition Analysis

The structural composition analysis consisted of determining the extractable content, the lignin/klason content, the cellulose content and the hemicellulose content. Extractives were determined using the soxhlet extraction method. The procedure followed is similar to that in ASTM 1107-96 5 (ASTM 1998). Lignin content was determined using the lignin/klason method in accordance with Tappi 222 [28]. The cellulose content was obtained by basic hydrolysis. The hemicellulose content was obtained using the equation (6).

$$T_{\rm HEM} = T_{\rm HOL} - T_{\rm CEL} \tag{6}$$

 T_{HEM} : Hemicellulose content (%), T_{HOL} : Hollocellulose content (%), T_{CEL} : Cellulose content (%).

2.11. Determination of Heavy Metals

The X-ray fluorescence spectrometry method was used to analyse the heavy metals present in the sawdust samples, using an AXIOS PWX440.

2.12. Fourier Transform Infrared Spectroscopy Analysis

The Fourier Transform Infrared (FT-IR) Spectroscopy analysis of sawdust was carried out using Thermo Scientific NicoletTM model 6700 infrared Fourier Transform Spectrometer. The infrared spectra were recorded automatically by an MCT detector (6000 - 600 cm⁻¹).

2.13. Determination of the Free Sugar Content

The sugar content was determined by ion chromatography with a pulsed amperometry detector (HPAEC-PAD). It is equipped with a Carboard PA20 DIONEX column (3×150 mm) and a guard column (3×50 mm) used as the stationary phase to separate and identify sugars according to their profiles. The mobile phase was prepared by diluting a NaOH solution (46% - 48%) in ultrapure water. Monosaccharides and ironic acids were separated using isocratic conditions and a linear elution gradient respectively. The samples were performed at 35° C at a rate of 0.4 mL/min. The pulse sequence for pulsed amperometry detection has a potential distribution of +100 mV (0 - 200 ms), +100 mV (200 - 400 ms), -2000 mV (410 - 420 ms), +600 mV (430 ms) and -100 mV (440 - 500 ms). The standards were rhamnose, galactose, arabinose, glucose, mannose, xylose, galacturonic acid and glucuronic acid.

2.14. Thermal Analysis

Thermal analysis consists of determining the degradation of sawdust fibres during heating. The thermogravimetric (TG) methods were used. Pyrolysis of the biomass over time was carried out in accordance with standard NF EN 14 775. The Mettler Toledo ATG/DSC Q50 analyser was used for this purpose. The samples were subjected to a temperature ranging from 30°C to 550°C with a temperature ramp of 10°C/min. Nitrogen was used as the carrier gas.

3. Results and Discussions

3.1. Particle Size Distribution

The particle size distribution of sawdust from Ayous, Sapelli and Tali was determined and displayed in Figure 2. It can be seen that sawdust sizes are generally less than 4 mm and the most abundant particle size distributions are in the range 0.4 - 0.6 mm (35 wt%), 1 - 2 mm (14 wt%), 0.6 - 1 mm (25 wt%), 0.125 -0.4 mm (15 wt%) and 1 - 2 mm (12 wt%). Particle size has a significant influence on the mechanical strength of potentially formulated briquettes or solids biofuel. This influence increases as the particle size becomes finer [19] [26]. The optimal particle size depends on the process of densification which can in general admit larger particles at pelletization processes, for granulation particles are generally below 5 mm in diameter. And in general, a broad variation of particle size is best with respect to pellet quality. However, when a number of fine particles are smaller than 0.2 mm in diameter than in the raw material, it can develop a negative impact on friction and pellet properties. Therefore, the number of fines should not surpass 10% to 20% except for the additional binding agent [29] [30] [31]. The obtained results indicated that the sawdust, in the present study presents particle size (<5 mm) suitable for the production of solid biofuel such as biofuel briquettes, in close agreement with the data from the literature [20] [28].





Figure 2. Particle size distribution sawdust of Ayous, Sapelli and Tali.

3.2. Proximate Composition

The proximate analysis was performed for the overall tropical wood sawdust (Ayous, Sapelli and Tali) and the results are presented in Table 1. From Table 1, it is observed that the moisture content in the raw sawdust is 36.9 ± 0.2

| Proximate composition | Ayous | Sapelli | Tali |
|-----------------------|----------------|----------------|-------------------|
| Т _{мн} (wt%) | 36.9 ± 0.02 | 24.3 ± 0.01 | 41.45 ± 0.03 |
| T _{MS} (wt%) | 7.83 ± 0.02 | 5.46 ± 0.02 | 8.12 ± 0.01 |
| T _A (wt%) | 0.25 ± 0.01 | 0.52 ± 0.03 | 0.74 ± 0.03 |
| T _{VM} (wt%) | 76.03 ± 0.01 | 73.84 ± 0.03 | $68.81{\pm}~0.04$ |
| T _{FC} (wt%) | 15.69 ± 0.03 | 20.18 ± 0.04 | 23.13 ± 0.03 |
| HHV (MJ/kg) | 21.8 ± 0.04 | 20.9 ± 0.05 | 19.6 ± 0.06 |
| LHV (MJ/kg) | 17.5 ± 0.03 | 16.8 ± 0.04 | 15.7 ± 0.05 |

 Table 1. Proximate composition of sawdust.

Avg ± SD: Average ± Standard Deviation.

wt% for Ayous, 24.3 ± 0.5 wt% for Sapelli and 41.45 ± 0.6 wt% for Tali. This result can be explained by the fact that the sawdust was left in the open air and sampled in a wet period. The higher moisture content of these sawdust obtained influence negatively calorific value and significantly limited their use as solid biofuel, particularly for combustion or densification systems. The work of [29] [20] reported that biomass with a moisture content of more than 20% can prevent the solubilisation and condensation of cellulose and lignin via Van Der Waals forces and hydroxide groups, by limiting the mechanical strength of the solid biofuel during the granulation process. After treatment, drying influence positively the moisture content of sawdust for Ayou (29.07 wt%), Sapelli (18.84 wt%) and Tali (32.78 wt%) obtained.

The moisture content of dry sawdust is 5 times lower than the wet samples, and falls within the range (4 - 9 wt%) of the standard value. This result is close to those obtained by [29] [30] [31] who showed that the optimum moisture contents for the granulation in general were found to be between 10 to 15 wt% to produce good stability, mechanical hardness and higher calorific value of the solid biofuel [26] [27] [32]. The thermochemical and mechanical quality of the solid biofuel depends on the densification process which itself is influenced by the moisture content. Several researchers concluded that the energy consumption for granulation was dependent on moisture content. They found that the energy input needed to compact the sawdust and biomass to a constant volume decreased with an increase in moisture content between 9 to 15 wt%. An increase in moisture content for lignocellulosic biomass results in a decrease in the energy required for different components of the granulation process [23] [24] [30].

The ash content of Ayous (0.25 wt%), Sapelli (0.52 wt%) and Tali (0.74 wt%) sawdust is below 1%. These results are similar to those of standard EN14961-2 and corroborate the fact that the ash content of biomasses in these woods is generally below 1%. It has been established that low ash contents indicate a significant potential of the calorific value [20] [33]. The value of volatile matter was very high in the Ayous (76.03 wt%), followed by Sapelli (73.84 wt%) and Tali

(68.81 wt%). Volatile matter has a significant influence on the thermal decomposition and combustion of biomass [34] [35]. This result is similar to of those reported by Olsson *et al.* [36] Orberg *et al.* [37], Holt *et al.* [38]. The high level of volatile matter in the biomass reflects a better calorific value. This result can be explained by the influence of the soil and climate conditions located in the sampling zone. The high fixed carbon content of 15 - 20 wt% justifies the high levels of volatile matter in sawdust. The HHV and LHV of the sawdust of Ayous, Sapelli and Tali samples were shows are presented in Table 1. HHV and LHV are major energy parameters which quantify the total heat present in biomass. The HHV results of Ayous, Sapelli and Tali were 21.5, 20.9, and 19.6 MJ/kg, respectively. This result can be explained in terms of the presence of high moisture and extractable content in Tali, which limits his calorific values [39] [40].

3.3. HHV and LHV Energy Comparison with Fossil Fuels Feedstock

The HHV and LHV were obtained by the degradation of biomass, which is an indicator of the energy potential of the biomass feedstock [41] [42]. The high TC, T_{H5} T_{FC} and T_{VM} content present in biomass describe higher energy yields which result in an important HHV [43]. Thus, biomass with higher T_{FC} and T_{VM} content and less ash content will offer a higher heating value because poor HHV impacts the speed of the heating rate and, thus, decreases the desired energy yield [44]. The HHV and LHV of Ayous were higher than that of Sapelli and those for Tali and in comparison, to petroleum feedstock (**Figure 3**), as natural gas (50.84 - 45.86 MJ/kg), gasoline (46.94 - 44.15 MJ/kg), diesel (45.60 - 42.91 MJ/kg), and kerosene (45.99 - 43.69 MJ/kg) the HHV and LHV for sawdusts was lowest [14]. This could be explained by the presence of the lower concentration of hydrochar in the biomass than in the petroleum feedstocks. The petroleum resources are one of the greatest causes of environmental pollution which enhances global climatic heating [45].



Figure 3. Comparison of Higher Heating Values (HHV) and Lower Heating Values (LHV) of sawdust samples and petroleum feedstocks.

3.4. Ultimate Compositions

The ultimate chemical composition of dry matter samples of sawdust is presented

in **Table 2**. The C, H and O are the most abundant chemical elements in lignocellulosic biomass [33]. The carbon content (50 - 56 wt%) is very high in sawdust materials, followed by oxygen (36 - 43 wt%) and hydrogen (6.08 - 6.67 wt%), while nitrogen (0.15 - 0.23 wt%) is present in the trace. These results differ from those of Mckendry *et al.* [46] and Parascanua *et al.* [47], who obtained carbon values for O, H and N varying from 45 to 55 wt%, 40 to 49 wt%, 5 to 6%(wt) and 0.1-0.5 wt% respectively. This difference can be explained by the soil and climate conditions and the varieties of wood used [35]. Furthermore, when biomass has higher content in C and H and a lower O content, is strongly favourable for liquid or solid biofuel products because C and H can be transformed into aromatic compounds that produce biofuel [43] [47]. During combustion, Carbon and Hydrogen are oxidised in an exothermic reaction leading to the formation of CO_2 , CO and H_2O [46]. The low content of N in the sample may lead to low N-fuel formation [39].

Table 2. Ultimate composition of sawdust.

| Samples | Content of CHON elements (wt%) | | | | | |
|---------|--------------------------------|---------------|----------------|---------------|---------------|--|
| | С | н | 0 | N | C/H | |
| Tali | 50.71 ± 0.02 | 6.08 ± 0.04 | 43.06 ± 0.02 | 0.19 ± 0.04 | 8.34 ± 0.05 | |
| Sapelli | 55.73 ± 0.01 | 6.46 ± 0.01 | 37.67 ± 0.02 | 0.15 ± 0.03 | 8.63 ± 0.02 | |
| Ayous | 56.53 ± 0.03 | 6.67 ± 0.02 | 36.59 ± 0.03 | 0.23 ± 0.02 | 8.47 ± 0.01 | |

Avg \pm SD: Average \pm Standard Deviation.



Figure 4. A van Krevelen diagram of the H/C and the O/C ratios oof Ayous, Sapelli, Tali, coal and petroleum feedstocks.

The H/C and O/C atomic ratios of the sawdust woods are presented in a van Krevelen diagram in **Figure 4**. These atomic ratios of H/C and O/C were com-

pared with the lignite, sub-bituminous, semi-anthracite and anthracite. The main purpose of H/C and O/C atomic ratios is to provide the degree of hydrogenation and deoxygenation to offer data about the thermal efficacy of the biomass [48]. The H/C, and O/C atomic ratios obtained from Ayous (1.81 - 0.67), Sapelli (1.52 - 0.48) and Tali (1.68 - 0.59) sawdust were higher than those of coal lignite (1.08 - 0.22), sub-bituminous (0.83 - 0.17), semi-anthracite (0.45 - 0.04), and anthracite (0.34 - 0.07) [47]. And were smaller compared to research made on methane (4.0 - 0.1), kerosene (2.1 - 0.3) diesel (2.1 - 0.2), and gasoline (2.1 - 0.1) by [49]. Thus, higher H and C ratios can increase the yield of biochar and solid biofuel. The atomics ratios of the sawdusts depend on the variation of the thermal degradation which can decrease H, C, and O ratios because of the loss of the hydroxyl groups and the deoxygenation, dehydration, and dehydrogenation reactions [50]. The lower atomic H/C and O/C ratios of biomass indicate the efficacy of thermal degradation of the biomass due to higher aromatic and carbonaceous formation at above 400°C.

3.5. The Functional Groups by FTIR

The main functional groups present in Ayous, Sapelli and Tali sawdust are shown in **Figure 5**. The observations made show that the trend in the signals from the functional groups is the same infrared spectra in the sawdust. They formed bands located between 3000 and 3800 cm⁻¹ corresponding to the elongating of hydroxyl (OH) groups, with the band recorded between 2790 and 3000 cm⁻¹ corresponding to CH₃ groups. The peak at 1650 cm⁻¹ corresponds to the C=O groups, with the corresponding elongating vibration at 1500 - 1620 cm⁻¹. The elongating of signals at 1200 - 1500 cm⁻¹ are attributed to the CH₂ groups, with a



Figure 5. Infrared spectra of sawdust from Ayous, Sapelli and Tali.

peak at 1480 cm⁻¹. Higher elongating characterises the COOH group, which has a peak of 1000 cm⁻¹, located in the elongating vibration of 6800 - 1210 cm⁻¹ [50] [51]. The characterisation of lignocellulosic biomass by FTIR makes it possible to identify the main functional groups present in their constitution with the aim of understanding the crystalline structure of cellulose and lignin and the influence of the crystalline and amorphous domains on the properties of the biomass during its transformation into solid biofuel. Biomass consists of pure linear hydrocarbons, including hexane and pentane, which are the main components of cellulose and lignin [34]. Thus, sawdust samples have a greater quantity of functional groups, CH, C=O, C-OH. It has been reported that the functional groups of carbon and hydroxides have an effect on the mechanical and chemical properties during densification, due to the increase in intermolecular forces linked to the surface of the molecule [20]. Carbon functional groups are also thought to have a profound influence on boiling, melting and flash points during the conversion of sawdust into solid biofuels. As intermolecular forces increase with carbon number, density, boiling point, melting point and flash point increase. Thermal pre-treatment of biomass could therefore increase the thermal and energy properties of solids biofuels [41] [48].

3.6. Structural Composition in Macromolecules

The structural composition obtained from sawdust samples composition in macromolecules is shown in **Table 3**. It can be seen that the celluloses contents are between 37 - 43 wt%, the hemicellulose content is in the range 17 to 23 wt% and the lignin content is between 29 - 32 wt%. These results reveal that the cellulose, hemicellulose and lignin compounds in sawdust are significantly higher in all the sawdust samples. Cellulose is a carbohydrate made up of a chain of D-glucose units linked by $\beta(1,4)$ osidic bonds [52]. It has a crystalline form made up of micro-fibrils that are surrounded by amorphous celluloses inside plant cells. This structure is maintained stable by hydrogen bonds from hydroxyl groups [53]. Considered an abundant source of carbon, it is not a suitable adhesive to play the role of binder in the biomass densification process. This limitation can be overcome by heat treatment and the addition of a binder, which will make the cellulose molecule more flexible during densification [54].

Lignin is a complex macromolecule and chemical compound most often derived from lignocellulosic biomass and is an integral part of the secondary walls of plants and algae [55]. It is a random system polymer with a variety of linkages

 Table 3. Structural composition of sawdust (g/100g).

| Samples | Holocelluloses | Celluloses | Lignines | Hemicelluloses | Extractibles |
|---------|------------------|----------------|------------------|----------------|----------------|
| Ayous | 67.6 ± 0.02 | 43.17 ± 0.04 | 29.09 ± 0.01 | 24.43 ± 0.03 | 3.31 ± 0.04 |
| Sapelli | 58.83 ± 0.01 | 38.31 ± 0.03 | 30.31 ± 0.02 | 20.52 ± 0.02 | 10.86 ± 0.03 |
| Tali | 54.32 ± 0.02 | 37.32 ± 0.02 | 29.43 ± 0.01 | 17.06 ± 0.04 | 16.19 ± 0.02 |

Avg ± SD: Average ± Standard Deviation.

of hydroxide and hydrogen bonds that provide the mechanical hardness of the biomass [54]. The lignin molecule has structural functions, such as adhesion to cellulose fibres, and plays a crucial role in water conduction in plant stems due to the high hydrophobicity of the cell walls, which helps to improve mechanical behaviour during storage [56] [57]. In addition, the composition of lignin promotes the formation of binders and the inter-diffusion of fibres when the structure reaches the glass transition temperature, it is a glue which creates solid bridges binder between molecules particles during the briquette densification process [54]. There is a correlation between mechanical hardness and the lignin content of pellets: When the lignin level increases, the mechanical strength of the briquette also increases. Lignin is an excellent fuel, releasing more energy during combustion than cellulose, and it helps to build solid bonds at higher temperatures by acting as a bulking and rigidifying agent [57]. As a result, highly lignified biomass is more sustainable and makes a good feedstock for solid biofuels, as its energy yield is higher than that of cellulose. The presence of lignin in sawdust means that it can be pelletised without the addition of a binder. Shanka et al. [20] have reported that lignin exhibits thermosetting properties at temperatures below 140°C and acts as an intrinsic resin binder, making it easier to formulate more robust briquettes. Higher levels of lignin are thought to be a good lead to stiffer binder to produce pellets.

Observations made on extractables show that the Tali (16.06 wt%) sawdust was higher than those of Ayous (2.81 wt%) and Sapelli (11.14 wt%) sawdust. This variation of extractable content can be explained by the fact that the sawdust of Ayous and Sapelli has virtually no heartwood. As the heartwood is the non-living part of the tree, it contains great quantities of extractives. Studies carried out on other tropical wood species have reported highly variable levels of extractives, sometimes with high contents between 20 to 22 wt% [58] [59]. These results are significantly different from those obtained by Tchinda *et al.* [26] for extracts of Tali (17.7 wt%) and Ayous (4.4 wt%) from the city of Yaoundé. These differences may be due to the type of species, pedoclimatic origin, organ studied, maturity, harvesting season and storage time. Extractives consist of low molecular weight organic compounds, including fatty acids, waxes, terpenes and tannins [60] [61]. Extractives have been shown to reduce pellet durability by lubricating biomass particles through fibre channels, and to affect densification by blocking hydrogen bonding sites between particles [20]. The higher the extractable content, the poorer the quality of biofuel briquette made without the use of binders [62].

3.7. Composition of Carbohydrates Free Sugar Content

The free sugar content of Ayous, Sapelli and Tali sawdust obtained are the total carbohydrate content shown in **Table 4**. It is composed of consists of Glucose, Xylose, Xylitolose, Cellobiose, Arabinose, Pentose, Galactose, and Mannose of the total weight. It observed that, Glucose (68 - 82 wt%) and Xylose (16 - 20

wt%) are globally the most important sugars in the different samples and, Glucose content is higher in Tali (82.03 wt%) sawdust, followed by Ayous (71.8 wt%), while Xylose is higher in Sapelli (18.63 wt%) than Ayous (20.31 wt%) than in Sapelli (18.63 wt%) and Tali (16.09 wt%). These results obtained can be explained by the higher composition of hemicellulose, cellulose and lignin content obtained from the sawdust of the Sapelli and Ayous [60]. Similar results in excellent agreement have been reported with the earlier study by Tchinda *et al.* [26]. Ayous presents a higher Xylose content in its hemicelluloses and Tali presents a higher cellulose (Glucose) content. Much research shows that Glucose and Xylose seem to be the mains monosaccharides products for the whole free sugar obtained in the lignocellulosic materials and it is found to be crucial raw materials for bioethanol production using fermentation technologies [49] [54].

Table 4. Sugar composition of sawdust.

| | Sugar content (wt%) | | | | | | | |
|---------|---------------------|-------|-------|-------|-------|-------|----------|----------|
| Sciures | Rham | Arab | Galac | Gluc | Xyl | Man | Ac galac | Ac gluc. |
| Sapeli | 0.77 | 1.057 | 2.705 | 68.73 | 18.63 | 3.98 | 3.78 | 0.167 |
| Ayous | 0.744 | 0.88 | 1.188 | 71.82 | 20.31 | 2.96 | 2.86 | 0.14 |
| Tali | 0.282 | 0.58 | 0.838 | 82.03 | 16.09 | 2.163 | 2.054 | 0.18 |

Rham: Rhamnose, Galac: Galactose, Arab: Arabinose, Gluc: Glucose, Man: Mannose, Xyl: Xylose, Ac Gluc: Galacturonic acid, Ac gluc: Glucuronic acid.

3.8. Heavy Metal Composition

The minerals and heavy metals compositions of the Ayous, Sapelli and Tali sawdust samples are represented in **Table 5**. The heavy metals obtained are sulphur (S), lead (Pb), manganese (Mn), cadmium (Cd), copper (Cu), nickel (Ni),

| Table 5. | Composition | of inorganic | species (| $(mg \cdot kg^{-1}).$ |
|----------|-------------|--------------|-----------|-----------------------|

| Elements | Ayous | Sapelli | Tali | Limit values |
|----------|-------|---------|------|--------------|
| Ca | 501 | 518 | 523 | 493 |
| К | 712 | 701 | 709 | 680 |
| Na | 5.82 | 7.23 | 9.4 | - |
| Р | 53 | 67 | 62 | - |
| Mg | 325 | 412 | 485 | - |
| S | 31 | 38 | 33 | 70 - 1000 |
| Pb | 0.23 | 0.41 | 0.35 | 10 |
| Cd | 0.15 | 0.19 | 0.21 | 0.5 |
| Cu | 0.41 | 0.54 | 0.45 | 5 |
| Ni | 0.5 | 1.2 | 2.3 | 10 |
| Zn | 21 | 18 | 23 | 100 |
| Fe | 1001 | 1003 | 1101 | 1000 |
| Cl | 22 | 25 | 27 | 100 |

zinc (Zn), and chlorine (Cl). The elements in trace present in very small quantities in the various sawdust samples included in the standard limit value except iron (Fe) which is higher (1001 - 1101 mg·kg⁻¹). The minerals Calcium (Ca), Magnesium (Mg), Potassium (K), Sodium (Na) and Nitrogen (N) present a concentration relatively higher than the standard limit value. These results would be influenced by the geological cover of East Cameroon, which is made up of ferritic soils, red-brown soils and sandy-clay soils that are rich in a diversity of heavy metals and mineral elements. The work of [48] [62] has shown that sawdust is lower in heavy metals. At high concentrations, these elements would influence the quality of the ash discharged and the gases released during the combustion of solids biofuels [63]. The aggregation of heavy metals inorganics (S, Fer, Cu Zn, etc.) during the combustion of biofuels leads to the formation of aerosols and bottom ash, which can impede the operation of boilers and industrial furnaces, with risks of corrosion and environmental pollution [39].

3.9. Thermal Degradation

The thermal degradation using thermogravimetric (TGA) and differential thermogravimetric (DTG) analysis for Ayous, Sapelli and Tali sawdust samples were represented in **Figure 6** and **Figure 7** respectively. The mass loss shows two main steps, from 200°C - 300°C associated with the mass loss of hemicelluloses and 300°C - 400°C associated mostly to cellulose pyrolysis. Some mass loss still occurs after 400°C (reorganisation of char). Ayous sawdust shows the highest value of mass loss (52 wt%), followed by (50 wt%) for Sapelli and (49 wt%) at 370°C for Tali. Finally, at the end of the thermal degradation different mass fractions in biochar are produced. Thus, biochar for Ayous sawdust was 25.5 wt%, for Sapelli Sawdust 26 wt% and 38 wt% for the sawdust of Tali. These results are



Figure 6. Thermogravimetric analysis of Ayous Sapelli and Tali sawdust.



Figure 7. Differential Thermogravimetry of Sawdust of Ayous, Sapelli and Tali.

in line with the structural analyses, which show that Tali sawdust in particular has more extractive compounds than the other species [64] [65].

4. Conclusion

Herein, key physicochemical and thermal properties of sawdust from Ayous, Sapelli and Tali were studied. The results reveal that the sawdust samples consisted of particle sizes of <3 mm, with a greater distribution in 0.4 - 0.6 mm (35 wt%). In addition, the sawdust displays a high-water content (25 - 41 wt%). Therefore, pre-treatment is required before any thermochemical transformation or solid biofuel production. The ash content (0.25 - 0.74 wt%), as well as volatile matter (68 - 76 wt%) present some differences. Especially Tali presents a higher char yield (38 wt% on anhydrous biomass at 550°C). These 3 woods present similar cellulose, lignin and C, H, O contents. The extractives are in greater proportion in Tali (16.04 wt%) than in the other types of species. A high content of iron was found in the 3 species because of the nature of the soil where wood stems were harvested. The calorific values are very different in the sawdust. Ayous has a higher LHV (17.5 MJ/kg) than those of Sapelli (16.8 MJ/kg) and Tali (15.7 MJ/kg). The 150 - 200 kT of available anhydrous sawdust in East Cameroon represent an energy potential of 2700.056 to 3600.075 TJ. The understanding of the Physicochemical composition and thermal properties of biomass sawdust can lead to optimizing the design and combustion, densification, pyrolysis or gasification of the biomass processes systems. For more efficiently to minimize the formation of harmful pollutants such as particulate matter, nitrogen oxides, and volatile organic compounds. Leading to lower emissions of air pollutants. Also,

by investigating the potential for utilisation of biomass sawdust as a renewable fuel source in industrial processes. Finally, all the Key sawdust exhibits excellent physicochemical and thermal properties, which are highly suitable for valorisation as energy and also the wood energy route needs some incentives to be better structured for their collection and transport for the efficient valorisation of all the wood wastes.

Conflicts of Interest

The authors declare no conflicts of interest.

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