Studies on Physical, Thermal and Chemical Properties of Wood Gliricidia sepium for Potential Bioenergy Production

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Abstract

Price increase and combustion effects of conventional fuels on environmental health have caused a paradigm increase in demand for wood fuel. Hence, a study on the utilization potential of some woody biomass to serve as an alternative to fossilized fuel has become important. Moisture content, density, lignin content, Gross Calorific Value (GCV), proximate and ultimate analyses were determined following standard procedures. Moisture content was 13.39±1.07 while wood density, lignin content, gross calorific value were 992.95±21.40 kgm-3, 26.26±1.26 %, 19.55±0.16 % respectively. Acetone extraction reduced the GCV of *G. sepium* by 17.85%. Ash content (1.28±0.14%), volatile matter (73.138±0.145%), Nitrogen content (0.48±0.01%), Sulphur content (0.03±0.01%) of *Gliricidia sepium* reveals that it could be considered adequate and suitable for use as feedstock in bioenergy production.

Keywords: Bioenergy, Calorific Value, Proximate Analysis, Ultimate Analysis, FTIR, Gliricidia sepium

Introduction

The use of wood as fuel cannot be over-emphasized. Its use is traditional and continues to thrive as the most important universal fuel for most rural areas of developing countries. As forecasted [1], an increase in the price of the underground fuel, as well as the devastating effects of the combustion of the conventional fuels, will enormously cause a paradigm increase in the demand for wood fuel in the future. Wood is renewable; its production will sustain because it is the most accessible and cheapest source of energy for most of the rural inhabitants [2].

About half of the world's population cook with biomass fuels and this accounts for about 35 percent of energy supplies in the developing nations of the world [3]. According to the United Nations Environmental Programme [4], the global consumption of marketed energy from all sources will continue to increase over the coming decades. As projected by Food and Agriculture Organisation (FAO) by 2030, the contribution of oil and other petroleum-based products in the energy consumption is projected to fall from 38% in 2004 to 34% in 2030. This reduction in the oil share is mostly associated with foreseen increases in prices of this energy source over the coming years. Biomass resources have several well-known advantages as an energy source.

Woody biomass plays a unique role as a renewable and expandable resource and as one of the world's important raw materials. It substantially reduces carbon emissions if sustainability aspects of the resources are carefully managed. It is also a proven technology that can function as a reliable base-load capacity, and in many applications are relatively capital-light [5]. As widely reported, biomass constitutes an important feedstock in the current world energetic scenario [6, 7, 8]. It also presents some environmental benefits which include low gaseous CO_2 emissions [9], as well as low NO_x and SO_2 emissions [10, 11].

Gliricidia sepium is one the biomass residue, grows to a height of 2-15 meters with a medium crown, either single or multi-stemmed with a diameter up to 30 cm. Studies have shown that *G. sepium*, a fast-growing tree species and a nitrogen fixer can yield over 5.4 tha-1 yr-1 of copied biomass [12].

Since wood biomass is a versatile material, people have used it in many ways for a long time. It is however essential and important to provide further information on the utilization of some woody biomass for energy by examining their bioenergy properties as this would further assist in understanding their suitability for use as an alternative energy source, which is the overall aim of this study.

Experimental

2.1 Materials

Materials and Sample Preparation

Wood materials were obtained from the base, middle and top position of the tree stem of the selected species (*Gliricidia sepium*) and prepared following the description made in Figure 1. The experimental procedure for the extraction of wood includes preparation of sample, extraction process and drying of the residue [13]. For this study, Soxhlet Extraction method was used with Acetone as the extraction solvent. Each sample was allowed to stay in the condenser tube for 8 hours after which the extracted samples were air-dried to allow for volatilization of the extraction solvent.

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Extractive content was calculated by percentage difference in the initial weight of the sample and final weight after extraction using the formula (Equation 1).

$$\text{Extractive} = \frac{\text{Initial Weight - Final Weight}}{\text{Initial Weight}} \text{ x } 100 \qquad (1)$$

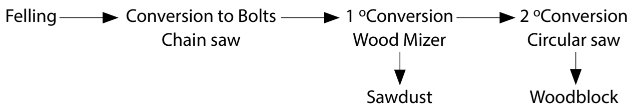

Figure 1 Sample Preparation

2.2 Methods

2.2.1 Physical Properties

Moisture Content

Fifteen clear samples of dimensions 20mm x 20mm x 60mm were prepared from the heartwood and sapwood region of the stem along three different positions of the stem (base, middle and top). The wet weight of each wood sample was determined before drying them to a constant weight in an oven at 103±2°C.

Density

Density was determined in accordance with ASTM D2395–2007a [14]. The oven-dried masses of the specimen were determined. After that, the wood samples were dipped one by one in paraffin wax and then kept in a desiccator. The volume displacement method which employs the use of Eureka can and a measuring cylinder was used to determine the volumes of the specimen. The overall density of each specimen was then computed using the mathematical expression in Equation 2.

$$\text{Density}\left(\frac{kg}{m^3}\right) = \frac{\text{Mass of Specimen}}{\text{Volume of Specimen}} \qquad (2)$$

2.2.2 Lignin Content

Lignin content of the species was determined using Klason method of lignin content determination following standard procedure [15], which is believed to be appropriate and reproducible [16]. The carbohydrates in the wood were hydrolyzed and solubilized by sulfuric acid; the acid-insoluble lignin was then filtered off, dried, and weighed.

2.2.3 Gross Calorific Value

The gross calorific value of each wood species to be studied was determined following standard procedure [17], where 0.4g of each sample was burnt until full combustion in an adiabatic bomb calorimeter. The gross calorific value was calculated using the mathematical expression in Equation 3.

$$Q = \frac{(C_{water} - C_{cal})\ (T_2 - T_1)\ ^{o}C}{W_f} \qquad (3)$$

Where,
Q = Calorific value of sample (kJ/kg);
W_f = Weight of the biomass material sample (kg);
C_{cal} = Heat capacity of the bomb calorimeter;
$T_2 - T_1$ = Rise in temperature;
C_{water} = Heat capacity of water (Joules)

2.2.4 Proximate Analysis

Percentage Ash Content

From each sample, 2g of the ground sawdust was weighed and put in a porcelain crucible which was placed in the furnace to burn at 600°C for four hours to attain full combustion [18]. After full combustion, the samples were allowed to cool in a desiccator. The crucible containing the sample was weighed and subtracted from the initial weight of the crucible to obtain the weight of the ash.

Percentage Volatile Matter

A volatile matter of each sample was determined following standard procedure [19] where 2g of each sample was placed in a porcelain crucible and kept in a furnace at a temperature of 550°C for 10 minutes and weighed after allowed to cool in a desiccator.

Percentage Organic Carbon (POC)

Percentage Organic Carbon (POC) was calculated using the formula in Equation 4.

$$\text{Organic Carbon Content} = \frac{M_{organic\ matter} * 0.58}{M_{oven\text{-}dry}} x100 \qquad (4)$$

Where,
$M_{organic\ matter} = M_{oven\text{-}dry} - M_{ash}$
$M_{oven\text{-}dry}$ = mass of the oven-dried sample

2.2.5 Ultimate Analysis

The important chemical constituents of the wood species namely Nitrogen, Sulphur and Hydrogen were determined through ultimate analysis. Nitrogen content of the samples was determined using the Kjeldahl method for the quantitative determination of Nitrogen in chemical substances as described [20]. The Sulphur content was determined by the turbidimetric method [21]. For Hydrogen content, 2g of each sample was burnt in Leibig-pregle chamber containing Magnesium percolate and sodium hydroxide and calculated (Equation 5). The samples were burnt to produce carbon dioxide and water. The CO_2 was absorbed by NaOH while the water absorbed by Magnesium percolate. Then, the difference in amount of water and CO_2 was calculated.

$$\%\ H = \frac{b \ x\ 0.117}{weight\ of\ sample}\ x\ 100 \qquad (5)$$

Where, b = Quantity of H_2O

2.2.6 Fuel Value Index (FVI)

The selection of ideal fuelwood species is based on its FVI calculated using calorific value, wood density, moisture content and ash content [22]. Fuel Value Index of the species was calculated using the formula presented in Equation 6.

$$\mathrm{FVI} = \frac{CV * bDen}{\% Ash * \% MC} \tag{6}$$

Where;
CV = Net Calorific Value ($MJkg^{-1}$)
bDen = Wood basic density
Ash = Percentage ash content
MC = Percentage moisture content

2.2.7 FTIR and Gas Chromatography–Mass Spectrometry (GC-MS) Analysis

As a follow-up test, the wood extracts from the samples were subjected to various elemental analysis. According to Guangyo and Pirjo[13], for identification of individual components of extractives, gas chromatographic methods in combination with mass spectrometry play a key role. Gas Chromatography–Mass Spectrometry (GC-MS) was carried out on the acetone extracts of the wood species. Fourier Transformed Infrared Spectrometry (FTIR) analysis was also carried out to support the GS-MS analysis.

2.2.8 Statistical Analysis

The analyses were carried out in triplicate and the averages and standard deviation of the measures were calculated. The ANOVA test was applied to evaluate the difference between the averages of the bioenergy properties and posthoc tests to show the effect of the different factors on the bioenergy properties.

Results and Discussion

3.1 Moisture Content

Variations were observed in the moisture content between species (Table 1). The moisture content slightly increases from the base to top which could be a result of juvenility of wood which increases longitudinally. As a result of more cellular activity within the sapwood, the moisture content of the sapwood is higher than heartwood and there is a significant difference between the moisture content of these two regions (sapwood and heartwood) with $p<0.05$. This variation is in agreement with a report [23]. *Gliricidia sepium* had an average moisture content of 10.96±0.71% though a lower average moisture content of 8.62% was reported [24]. This marked difference could be attributed to the age of the species. The low moisture content of biomass impacts the process of combustion by increasing the flame temperature and/or the working efficiency of the boiler [25]. Moisture content is known to also have a significant impact on the fuel properties of solid biomass [26]. It is also a variable for determining the Fuel Value Index (FVI) of any biomass material with potential use as fuel. In a study on fifteen (15) commonly used species for fuel, an increase in moisture content caused a reduction in their fuel value index [27].

3.2 Density

The density of *Gliricidia sepium* reduced from base to top; this follows the same trend as reported [28]. From Table 2 and Figure 2, there is no significant difference between the sapwood and heartwood density of *G. sepium* with $p>0.05$. Density has been reported to greatly affect the calorific value of woods used as fuel and this justifies the local preference of species for bioenergy [29]. Comparing with other species used for fuel as reported by [30], the density of *G. sepium* 992.95±27.23 kgm^{-3} is higher than densities of *Casuarina equisetifolia*, *Nauclea spp* and *Leucaena leucocephala* with densities of 866 kgm^{-3}, 588 kgm^{-3} and 696 kgm^{-3} respectively.

Table 1 Physical Properties (Moisture Content and Density) of *Gliricidia sepium*

Position	Moisture Content	Density
BS	11.73^{a}±0.34	1021.17^{a,b}±29.95
MS	15.38^{c}±0.80	937.85^{a},b±3.48
TS	13.05^{a,c}±1.37	945.72^{a},b±13.71
BH	7.82^{b}±0.35	1079.29^{b}±40.93
MH	8.96^{b}±0.36	1052.59^{a,b}±14.01
TH	8.85^{b}±1.23	921.08^{a}±96.24

Duncan: Mean values with the same alphabet (along the row) are not significantly different at $\alpha_{0.05}$
BS, MS, TS = Base Sapwood, Middle Sapwood, Top Sapwood respectively
BH, MH, TH = Base Heartwood, Middle Heartwood, Top Heartwood respectively
(±) Standard Error

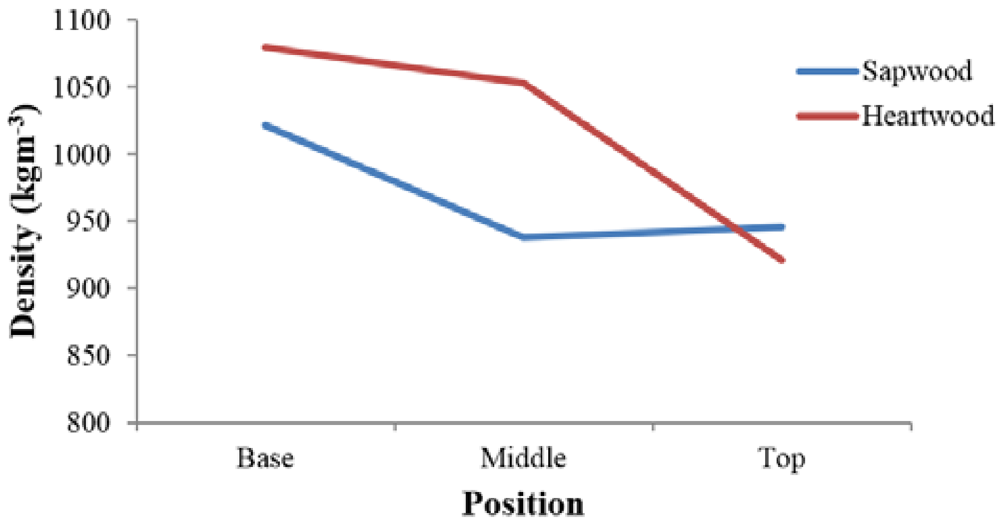

Figure 2 Density gradient (kgm^{-3}) of *Gliricidia sepium*

3.3 Lignin Content

From Table 2, lignin content did not vary significantly (p>0.05) from base to top of the tree stem; this is in agreement with a report that there is no significant variation in lignin content with an increase in tree height and diameter [31]. Considering the type of wood i.e. sapwood and heartwood, there are significant differences in lignin content of the sapwood and heartwood *G. sepium* with the highest lignin content, 26.84±2.13 obtained at the heartwood region while the lowest, 25.68±1.74 was obtained at the sapwood region. Lignin content is known to have a positive correlation with calorific value and hence, higher lignin content in *G. sepium* could possibly cause a high energy value if other factors such as chemical composition and density would favour it.

Table 2 Lignin content (%) of *Gliricidia sepium*

		BS	MS	TS	BH	MH	TH
Lignin Content (%)	Mean	24.25^a±0.40	29.13^b±0.36	23.65^a±0.28	25.58^c±0.38	31.00^d±0.75	23.95^a±0.21
	Max	24.95	29.65	24.15	26.10	32.35	24.25
	Min	23.55	28.45	23.20	24.85	29.75	23.55

Mean values with the same alphabet (along the row) are not significantly different at α = 0.05
BS, MS, TS = Base Sapwood, Middle Sapwood, Top Sapwood respectively
BH, MH, TH = Base Heartwood, Middle Heartwood, Top Heartwood respectively
(±) Standard Error

of *G. sepium* (p<0.05). From Figure 3, unextracted samples of *G. sepium* had an average GCV of 19.55±0.16 MJkg^{-1}, while extracted samples had an average Gross Calorific Value of 16.06±0.08 MJkg^{-1}. Extraction reduced the GCV of the species by 17.85% (Figure 3); this could be because of the presence of extraneous materials (fats, phenols, alcohols, fatty acids, resins, proteins etc.) which are soluble in acetone, a non-polar solvent used for the extraction process. As reported, many wood extraneous materials are highly soluble in acetone [13]. The energy value of *G. sepium* is similar to that of other species commonly used for fuel [30]. In a study on the potential of *G. sepium* as a fuelwood species in Sri Lanka, the wood samples have an average energy value of 21.49MJkg^{-1}±0.47 [32]; this little difference could be as a result of variation in the climatic condition of these two regions. Local climate condition has a direct impact on the growth and formation of physiochemical properties that are chiefly responsible for calorific content of above-ground plant parts [33].

3.3 Gross Calorific Value (MJkg^{-1})

From the results, there is a significant effect of extraction (extracted, unextracted), position (base, middle and top) and type of wood (sapwood, heartwood) on the Gross Energy Value

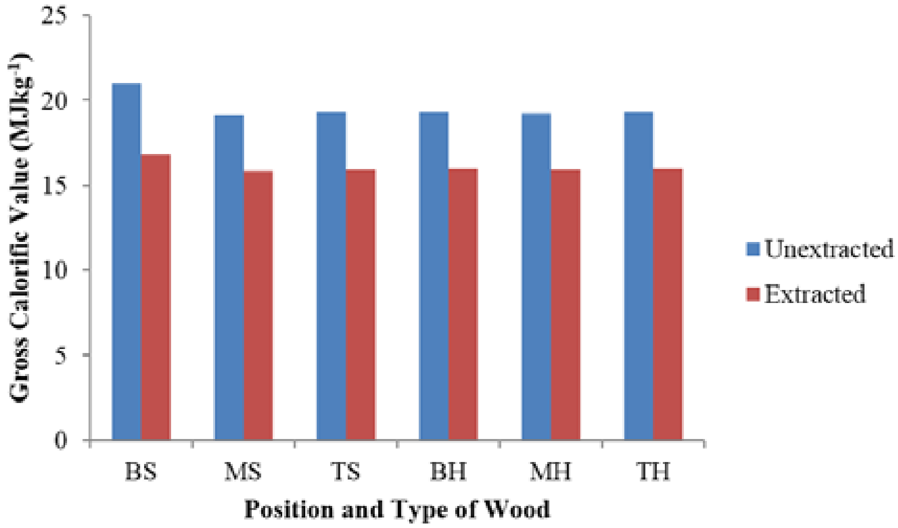

Figure 3 Gross Calorific Value (MJkg^{-1}) of Unextracted and Extracted Samples of *G. sepium*

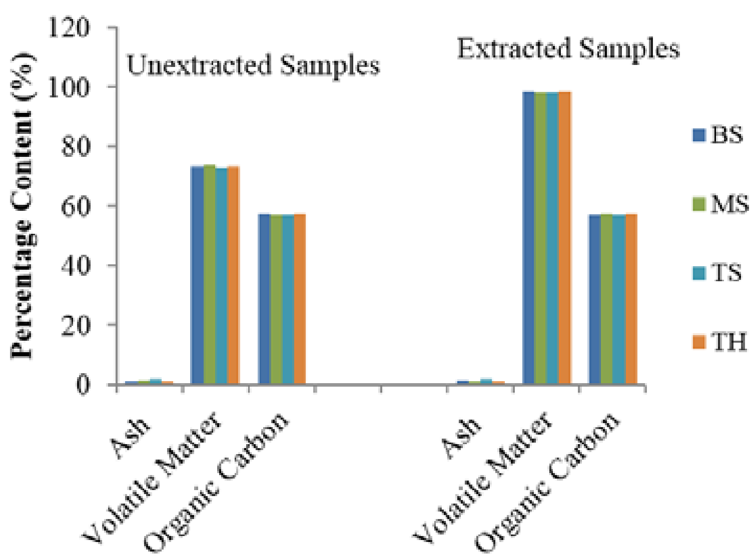

Figure 4 Proximate and Ultimate Analysis of *Gliricidia sepium*

3.4 Proximate Analysis

The results in Table 3 indicated that the unextracted samples of *Gliricidia sepium* had an average percentage volatile matter of 73.138±0.15. Because wood has a low C:H ratio, it has a rather higher volatile content between 73% and 90% [34]; the values obtained for *G. sepium* fall within this range. Acetone extracted samples of *G. sepium* have an average percentage of the volatile matter of 98.31±0.07. The significance of the volatile matter and organic carbon contents is that they provide a measure of the ease with which the biomass can be ignited and subsequently gasified or oxidized, depending on how to utilize the biomass as an energy source. Biomass materials with volatile content up to 78% indicated ignition temperatures between 236°C and 270°C while the lignite with volatile content will ignite at 274°C [35]. *G. sepium* could be considered adequate for fuel pellets since they are greater than the minimum values suggested by Austria and German standards for fuel pellets and briquettes. From Figure 4, unextracted samples of *G. sepium* had a mean organic carbon content of 57.26±0.09% while extracted samples had a mean organic carbon of 56.49±0.63%. Organic carbon content gives a rough estimate of the heating value of fuel and acts as the main heat generator during burning [19]. Thus, the higher the organic carbon content of a biomass fuel the more likely that the species would have higher heating value.

3.5 Ultimate Analysis

From Table 3, the Nitrogen content of the species is 0.48% and it is below the recommended maximum by Austria Österreichisches Normungsinstitut (ONORM) standard but greater than the

Table 3 Fuel Properties of *Gliricidia sepium*, Austria and Germany Standard for Fuel Pellets

Species	*Gliricidia sepium*	Austria ÖNORM[a] M7135	Germany DIN[a] 51731 / DINplus	*Dysoxylum spp.*[b]	*Glochidion spp.*[b]
Gross Calorific Value * ($MJkg^{-1}$)	19.55±0.16	≥18.0	17.5-19.5	19.133 ± 0.601	18.136 ± 1.299
Density* (kgm^{-3})	992.95±21.40			536.02	491.11
Ash Content* (%)	1.28±0.14	< 6.0	<1.5%	2.28 ± 0.41	2.97 ± 0.04
Volatile Matter	73.14±0.15			NA	NA
N (%)	0.48±0.01	< 0.6	< 0.3	NA	NA
S (%)	0.03±0.01	< 0.08	< 0.08	NA	NA
H (%)	2.85±0.67			NA	NA

[a] [39], [b] [30]

* Fuel Value Index (FVI) = 1314.05; NA- Not Available

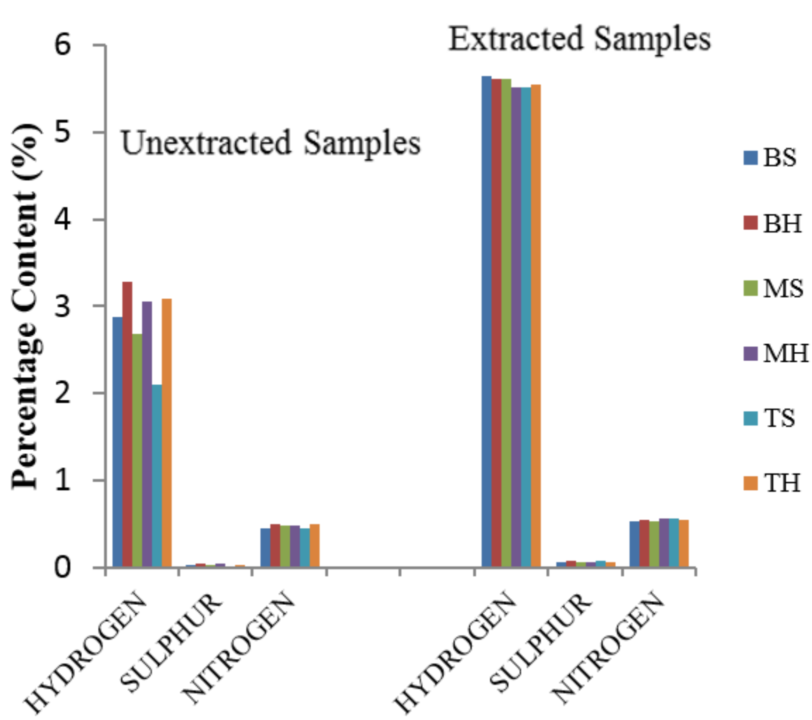

Figure 5 Ultimate Analysis of *Gliricidia sepium*

recommended maximum by German standard. Nitrogen content is a good indicator of the amount of nitrogen-based toxic components that can be formed during combustion. During the combustion of wood fuel, nitrogen is oxidized into nitrogen oxide (NO_x). When emitted from combustion facilities at relatively low levels, NO_x may have a useful fertilizing effect on the forests. However, as emission levels increase, NO_x produces adverse health effects and increases the acidification of water and soils. Exposure to nitrogen oxides increases the risk of respiratory infections as it is highly toxic and irritating to the respiratory system [35]. When NO_x and volatile organic compounds react in the presence of sunlight, they form photochemical smog, which is a significant form of air pollution [36]. The Sulphur content of the species is 0.03±0.01 and it is below the maximum suggested by Austria and Germany standards for fuel pellets. There is a significant effect of extraction on the Nitrogen and Hydrogen content of *G. sepium* while it has no significant effect on the Sulphur content of the species (Figure 5). For different extractives and other biochemical compounds soluble in acetone, the extraction process could have caused a transformation in the organic compounds (mostly carbohydrates) which would make other hydrocarbons chemically active, a probable reason why extraction had a significant effect on the Hydrogen and Sulphur content of *G. sepium*.

3.6 Fourier Transformed Infrared Spectrometry (FTIR)

Figure 6 shows the spectral diagram of bioactive compounds of *Gliricidia sepium* (Heartwood and Sapwood). Functional groups identified in both the sapwood and heartwood of *G. sepium* confirmed the presence of Alcohol, Alkyne, Aldehyde, Amine, Alkyl Halide, Acid, Alkene, Alkane and aromatic compounds. Studies on the leaf extract of *G. sepium*, similar compounds were discovered [37]. The inherent chemical compositions of this species (*G. sepium*) could be a clear definition of why it exhibits good bioenergy properties. Figure 7 shows the different functional groups identified in the species.

3.7 Fuel Value Index (FVI)

As presented in Table 3, the Fuel Value Index (FVI) of *Gliricidia sepium* is 1314.05. By comparison, FVI of *G. sepium* is higher than some other recommended species used as bioenergy such as *Balanites aegyptiaca* (881), *Ziziphus mauritiana* (907) and *Combretum glutinosum* (1191) [38]. This implies that *G. sepium* could also recommended for use as fuel with the fact that it is low in ash, moderate Nitrogen content, high energy value and low sulphur content.

Acetone extraction reduced the FVI of *G. sepium* by 27.02%. This reduction could be due to a decrease in the calorific value caused by the extraction process. Even at this reduction, the FVI of extracted *Gliricidia sepium* (959) was found greater than that of *Balanites aegyptiaca* (881), *Ziziphus mauritiana* (907) [38]

Conclusion

Stem position and type of wood have a considerable effect on the physical properties, thermal properties as well as chemical properties of the wood. The juvenility of wood which is known to increase longitudinally caused a reduction in density along the axial direction while moisture content increases. Lignin content did not vary significantly along with the tree height but higher in the heartwood than sapwood. The Gross Calorific Value of *G. sepium* could be considered adequate for bioenergy production such as charcoal, briquettes and other bioenergy derivatives e.g. bio-oil, bio-gas and bio-char since they are greater than the minimum values suggested by Austria and German standards for fuel pellets and briquettes (Austria ÖNORM M7135, Calorific value ≥18.0 MJ/kg; Germany DIN 51731 / DINplus, Calorific value 17.5 - 19.5 MJ/kg). Acetone extraction was found to reduce the energy value of *G. sepium*; there is a significant effect of stem position and type of wood on the energy value of the species. The ash content of the species studied is lower than 6%, the value beyond which the ash content of the biomass fuel is considered not adequate according to the Austria ÖNORM M7135 standard. The density (992.95±21.40kgm^{-3}), ash content (1.28±0.14), Nitrogen content (0.48±0.01), Sulphur content (0.03±0.01) and calorific value (19.55±0.16) of *Gliricidia sepium* reveals that it is suitable for use as fuel. Future work should consider exploring other derivative bioenergy products from the species (*G. sepium*) other than wood since the wood has demonstrated good properties for use as bioenergy.

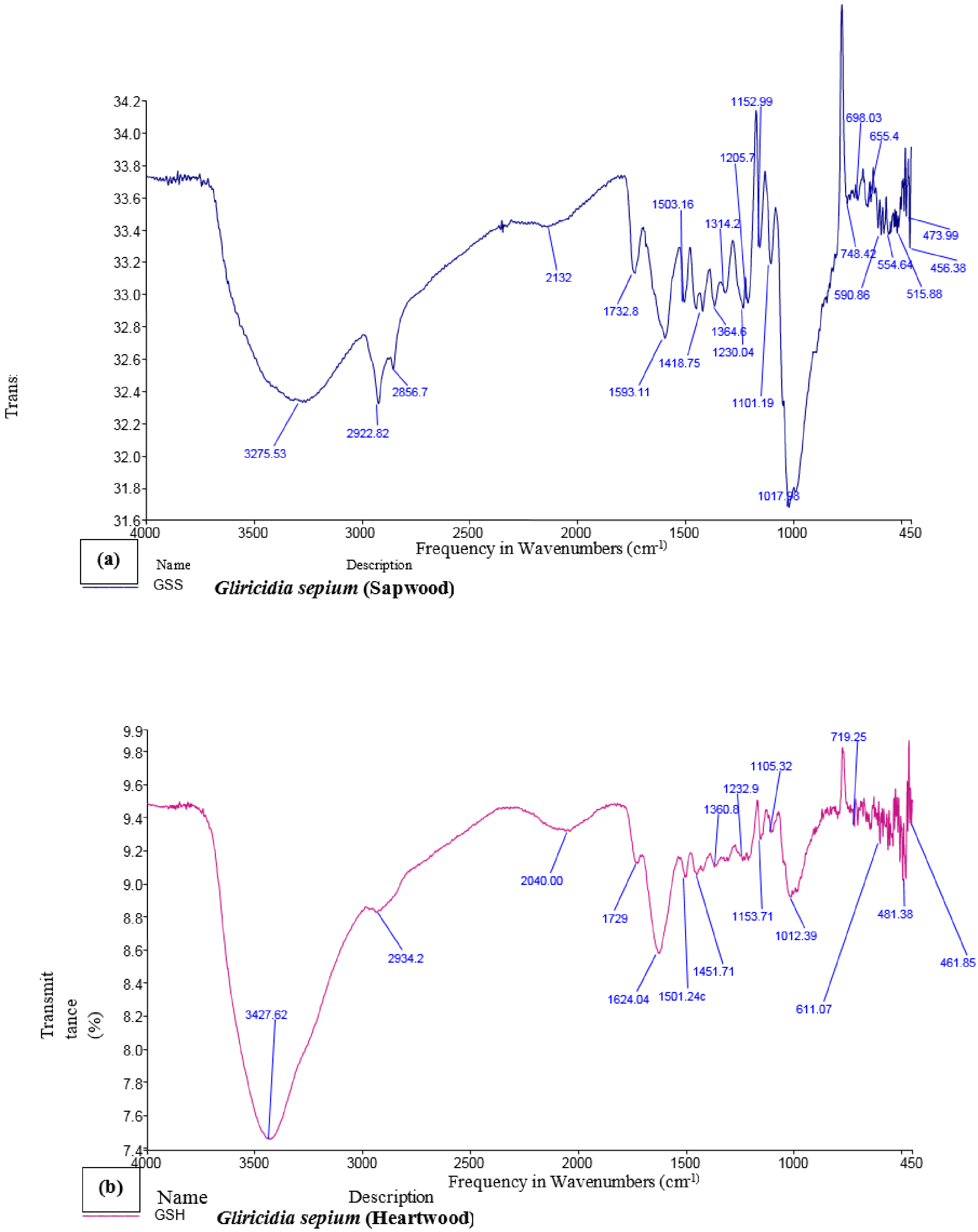

Figure 6 Spectral Diagram of Bioactive Compounds of *Gliricidia sepium*
(a) Sapwood of *Gliricidia sepium*, (b) Heartwood of *Gliricidia sepium*

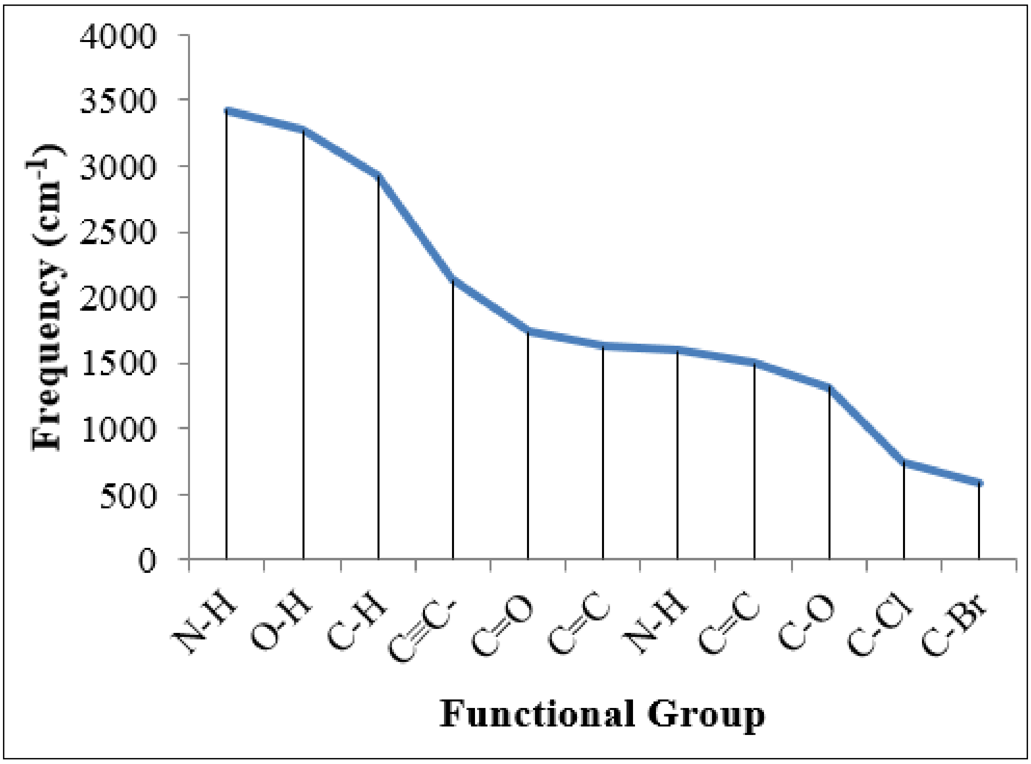

Figure 7 FTIR Analysis of *Gliricidia sepium*

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