



## Experimental investigation of heating values and chemical compositions of selected fuel woods as bio-fuel sources in developing countries

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### ABSTRACT

Agro-waste disposal is a serious environmental problem in developing countries like Nigeria since there are insufficient waste management systems in place. However, it is possible to produce sustainable energy from these biomass wastes, which will lessen environmental damage. The heating value of biomass determines its energy content. The aim of this study was to determine experimentally the higher heating value (HHV) of five selected indigenous fuelwood sawdust and to assess the chemical composition of the pyrolysis yield products using a gas chromatography-mass spectrometry (GC-MS) analyzer. Results of the experimental analysis show that the HHVs of the selected fuel woods: *Adansonia digitata* (Ad), *Terminalia ivorensis* (Ti), *Khaya ivorensis* (Ki), *Mansonia altissima* (Ma), *Okoubaka aubrevillei* (Oa) are respectively, 21.02, 20.78, 20.75, 19.95, 19.80 and 20.46 MJ kg<sup>-1</sup>. According to ultimate analysis-based correlation equation, the HHVs were found to be 18.56, 18.48, 18.42, 18.39 and 18.36 MJ kg<sup>-1</sup> for Ad, Ti, Ki, Ma and Oa, respectively. While the proximate analysis-based correlation equation gave HHVs of 18.08, 18.12, 18.25, 18.16 and 18.37 MJ kg<sup>-1</sup> for Ad, Ti, Ki, Ma and Oa, respectively. The mean square error (MSE) was used to compare the deviation of the computed results from the experimental data. The statistical analysis indicates comparative agreement between the computed HHVs and the experimental data. The GC-MS analysis shows the presence of phenolic, ketone, fatty acid, ester, and alcohol compounds in the sawdust samples which is evidence that they have chemical and fuel compositions suitable for use as feedstocks in the pharmaceutical and dye industries as well as for the production of biodiesel for internal combustion engines. It can be inferred that the woody biomass residues can be useful sources of biofuels for developing nations' sustainable energy development if adequately processed with suitable technologies.

### 1. Introduction

Increasing interest in renewable biofuels has been fueled by rising energy prices, rising energy imports, fears about oil shortages, and greater awareness of the environmental impact of fossil fuels. To be a viable option, biofuels must provide net energy advantages, ecological benefits, economic competitiveness, and mass production without depleting the food supply. Biofuel manufacturing necessitates the use of energy to cultivate crops and convert them to biofuels [1]. One of the most promising energy sources for addressing the growing energy demand while protecting the environment and food crops is biomass

waste. In many developing countries with sizable agricultural and forested areas, biomass waste makes about 40 to 50 percent of the energy supply [2]. Carbon, hydrogen, oxygen, nitrogen, and trace amounts of inorganic species produced from waste or animal manure make up the majority of biomass components. Every year, tons of wood wastes like shavings, chips, and sawdust are produced. Even while this massive volume of solid waste, primarily sawdust, has the potential to be an energy source, it frequently stresses the environment [3]. In addition to meeting SDG-7's need for affordable and clean energy, harvesting usable energy from agricultural waste also has the potential to alleviate waste mismanagement problems, thereby tackling SDG-6, SDG-11 and SDG-13 in the process. To fully realize the promise of agrowaste-to-energy,

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Nomenclature			
AC	Ash content	VMC	volatile matter content
ASTM	American Society for Testing and Materials	BKLP	beetle-killed lodgepole pine
BSI	British Standards Institution	BPT	Biomass Power Technology
C	Carbon (wt %)	GHG	Greenhouse gas
c	Cellulose	NNPC	Nigerian National Petroleum Company
EDX	Energy dispersive X-ray	R&D	Research and Development
EN	European Standard	BET	Bioenergy technology
FC	Fixed carbon	WSD	Wood sawdust
FTIR	Fourier transformed infrared	GC	Gas Chromatography
GC-MS	Gas chromatograph mass spectrometer	GC-MS	Gas Chromatography-Mass Spectrometry
GC-TCD	Gas chromatography-thermal conductivity detector	Ad	Adansonia digital
H	Hydrogen (wt %)	Ti	Terminalia ivorensis,
HC	Hydrocarbon	Ki	Khaya ivorensis
HHV	Higher heating value (MJ/kg)	Oa	Okoubaka aubrevillei
L/S	Liquid-solid ratio (wt/wt)	MSE	mean square error
		MAPE	mean absolute percentage error

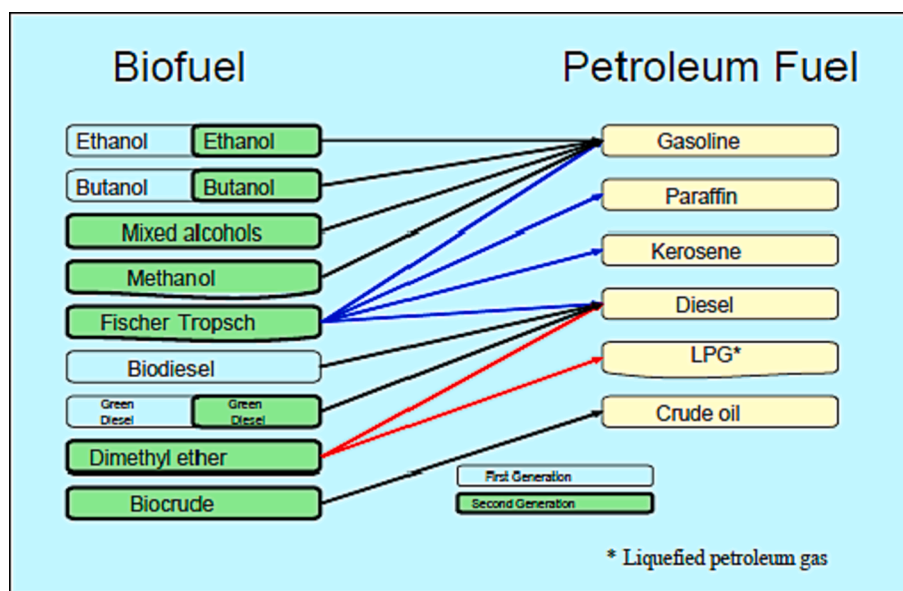


Fig. 1. Potential Replacement of biofuels with petroleum-derived fuels (UNCTAD, 2008).

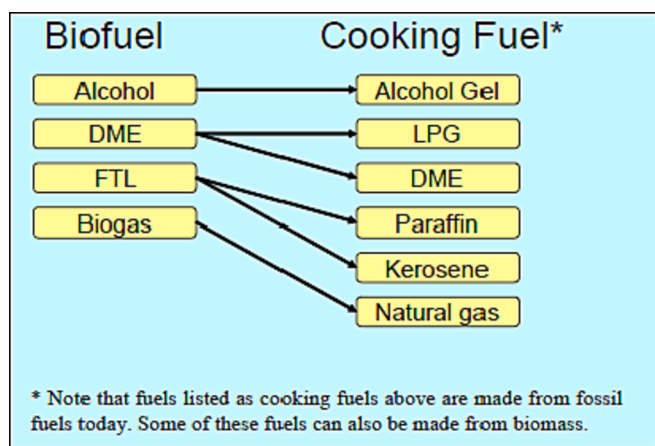


Fig. 2. Potential Replacement of biofuels for fossil fuels used for cooking (UNCTAD, 2008).

however, concerted efforts would be needed to successfully link technology, economics, and political economy of livelihood through appropriate energy policy approaches [4].

As a practical substitute for fossil-derived fuels that can reduce energy costs, ensure energy security, and reduce global warming concerns, biofuels are gaining popularity [5]. Biofuels are divided into four groups based on the feedstock: first, second, third, and fourth generation biofuels. The first generation of biofuels is made up of plants that produce oil, sugar, and starch. The growth of genetically modified yields has accelerated in the two decades since their introduction. A few countries already produce first-generation fuels in significant commercial volumes. Non-edible lignocellulosic biomass, such as non-edible food crop residues (such rice husks or maize stalks) or non-edible whole plant biomass (e.g. agricultural waste or residues, forestry, grasses or trees grown specifically for energy), is used to make second-generation biofuels. Due to its availability and sustainability, lignocellulosic biomass is most likely to become a crucial renewable resource for the manufacture of cost-effective biofuels and bioproducts. In addition to becoming a significant replacement for fossil fuels, the production of bioenergy from lignocellulose biomass now accounts for around 9 % of the world's

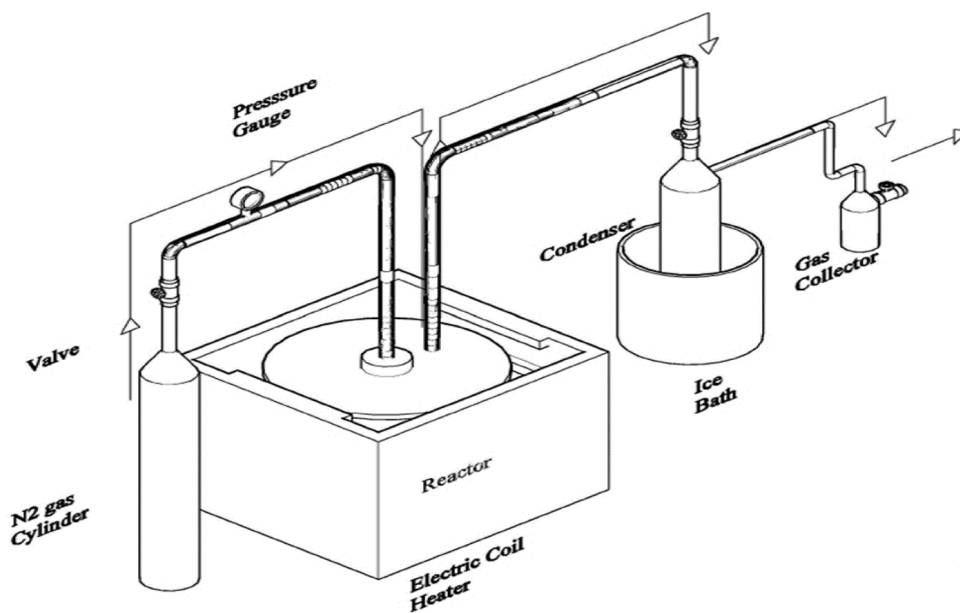


Fig. 3. Pyrolysis experimental set-up.

**Table 1**  
Experimental Heating values of wood samples.

Sawdust sample	Run 1	Run 2	Run 3	Average value of HHV (MJ/kg)
Adansonia digitata	20.90	21.05	21.07	21.01
Terminalia ivorensis	20.70	20.85	20.78	20.78
Khaya ivorensis	20.82	20.78	20.65	20.75
Mansonia altissima	19.90	19.98	19.96	19.95
Okoubaka aubrevillei	19.78	19.82	19.80	19.80

energy supply [6]. No nation has yet begun to market second-generation fuels. Third generation biofuels made from algae are gaining attention because they can be produced in large quantities, absorb CO<sub>2</sub>, and require little effort to refine. The fourth generation of biofuels, a recent development with rapid expansion, uses engineered cyanobacterial development [7].

Due to its nontoxic, sulfur-free, biodegradable nature and renewable source, biofuels are being considered as replacement for fossil-derived fuels. Biofuels can replace fossil-derived fuels in the transportation, industry, and household (cooking) sectors due to their chemical composition, thermophysical qualities, and increased heat value (HHV). The utilization of various biofuels to replace petroleum-based fuels is depicted in Fig. 1. In spark-ignition engines, alcohol fuels can be used instead of gasoline, whereas compression-ignition engines can use biodiesel, green diesel, and DME. Fig. 2 depicts the use of biofuels for cooking, particularly in developing countries rural areas. In all cases, cooking with biofuels releases less (or significantly fewer) pollutants

**Table 2**  
Proximate analysis of wood samples.

Sawdust samples	Elemental Analyzer values				Calculated values			
	MC (%)	VM (%)	FCC (%)	AC (%)	MC (%)	VM (%)	FCC (%)	AC (%)
Adansonia digitata	8.50 ± 0.2	75.49 ± 0.1	14.09 ± 0.4	1.88 ± 0.2	8.55	75.35	14.17	1.93
Terminalia ivorensis	8.70 ± 0.2	75.22 ± 0.1	14.20 ± 0.4	1.88 ± 0.2	8.68	75.40	14.15	1.77
Khaya ivorensis	8.55 ± 0.1	74.90 ± 0.2	14.80 ± 0.2	1.75 ± 0.1	8.62	75.01	14.48	1.89
Mansonia altissima	8.70 ± 0.1	75.47 ± 0.2	14.22 ± 0.3	1.60 ± 0.1	8.65	75.46	14.17	1.72
Okoubaka aubrevillei	8.88 ± 0.2	75.24 ± 0.1	14.79 ± 0.4	1.08 ± 0.2	8.78	75.09	14.80	1.33
<b>Average Values</b>	<b>8.67 ± 0.16</b>	<b>75.26 ± 0.14</b>	<b>14.42 ± 0.34</b>	<b>1.64 ± 0.16</b>	<b>8.66</b>	<b>75.26</b>	<b>14.35</b>	<b>1.73</b>

Where: VM = Volatile matter MC = Moisture content FCC = Fixed carbon content, AC = Ash content.

than cooking with solid fuels. Over 4.5 billion people cook with solid fuels in underdeveloped nations, and the accompanying indoor air pollution has serious health consequences [1,2]. As a result, biofuels can improve the health of billions of people in underdeveloped nations.

The aforementioned issues call for full utilization of alternative energy sources. Woody biomass is one of the most significant renewable energy sources, and it can be converted into bioenergy [8]. Wood waste is all over Sub-Saharan Africa, especially in Nigeria, and it pollutes the environment. These wood wastes can be converted into valuable goods and are found in sawmills and other wood-related businesses. However, it is possible to determine these wood wastes' higher heating value (or calorific value) in order to assess their conversion potential to bio-oil, bio-char, pyroacids, and pyro-gas, which can be used in a variety of

**Table 3**  
Ultimate analysis of wood samples.

Sawdust samples	C (%)	H (%)	N (%)	O (%)	S (%)
<b>Adansonia digitata</b>	45.82 ± 0.3	5.98 ± 0.3	0.29 ± 0.1	42.88 ± 0.2	0.01 ± 0.3
<b>Terminalia ivorensis</b>	45.82 ± 0.3	5.88 ± 0.3	0.28 ± 0.1	42.80 ± 0.2	0.01 ± 0.3
<b>Khaya ivorensis</b>	45.56 ± 0.1	5.90 ± 0.3	0.24 ± 0.2	42.55 ± 0.1	0.01 ± 0.1
<b>Mansonia altissima</b>	45.30 ± 0.1	5.98 ± 0.3	0.27 ± 0.2	42.60 ± 0.1	0.01 ± 0.1
<b>Okoubaka aubrevillei</b>	45.22 ± 0.3	5.96 ± 0.3	0.30 ± 0.1	42.57 ± 0.2	0.01 ± 0.3
<b>Average values</b>	45.54 ± 0.02	5.94 ± 0.3	0.28 ± 0.14	42.68 ± 0.16	0.01 ± 0.02

**Table 4**  
Comparison of Experimental HHVs and the Correlated HHVs for the Selected Wood Samples.

Sawdust samples	HHV(MJ/kg) from Ultimate Analysis	HHV (MJ/kg) from Proximate Analysis	HHV (MJ/kg) from Experimental Analysis
Adansonia digitata	18.56	18.08	21.01
Terminalia ivorensis	18.48	18.12	20.78
Khaya ivorensis	18.42	18.25	20.75
Mansonia altissima	18.39	18.16	19.95
Okoubaka aubreillei	18.36	18.37	19.80
<b>Average value of HHV(MJ/kg)</b>	<b>18.44</b>	<b>18.20</b>	<b>20.46</b>

**Table 5**  
Products of pyrolysis expressed as wt% of input feed stock.

Product yield	Sample	450 °C	500 °C	550 °C	600 °C
Bio-oil (wt.%)	Adansonia digitata	40.10	44.75	42.01	39.70
	Terminalia ivorensis	40.20	43.80	41.90	39.80
	Khaya ivorensis	39.90	42.90	41.95	39.75
	Mansonia altissima	40.00	43.95	41.75	39.50
	Okoubaka aubreillei	39.98	44.01	40.50	39.65
	Bio-char (wt.%)	Adansonia digitata	40.01	36.80	34.70
Terminalia ivorensis		40.10	35.10	34.75	31.50
Khaya ivorensis		40.05	35.05	34.50	31.20
Mansonia altissima		40.25	35.30	34.00	31.40
Okoubaka aubreillei		40.20	35.60	34.30	30.90
Bio-gas (wt.%)		Adansonia digitata	19.89	15.45	23.29
	Terminalia ivorensis	19.70	21.10	23.35	28.70
	Khaya ivorensis	20.05	22.05	23.55	29.05
	Mansonia altissima	19.75	20.75	24.25	29.10
	Okoubaka aubreillei	19.82	20.39	25.20	29.45

Calculated as 100 – (x + y).

static applications like boilers, furnaces, engines, and turbines for the production of electricity [9]. According to studies, certain wood wastes can also be used to create a variety of compounds [10]. Food flavorings, resins, agrochemicals, fertilizers, and emission control substances fall under this category. A wide range of biomass feedstocks have been devised and developed into a variety of conversion processes. Pyrolysis is a technology included in this list. Char and ash are produced during the pyrolysis process, along with liquids like tar (a mixture of heavy hydrocarbons) and gases like H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>. The world is paying a lot of attention to pyrolysis technology, which is still in its early stages of development [11].

The idea of employing pyrolysis to extract biofuels from biomass wastes has been the subject of numerous investigations. Mohammed et al. [11] investigated the pyrolysis of groundnut shells in a vertically fixed bed reactor and found that the product yields are suitable for usage as an energy source and as starting materials for chemical synthesis. On a fixed bench-scale reactor, Tinwala et al [9].’s investigation into the pyrolysis of wastes and agro-industrial biomass mixes. They discovered biochar production of 27.5–40 % and bio-oil yield of 20.5–47.5 %. Due to its low moisture level and high energy content, Guanqun and Fernando [9] suggested beetle-killed lodgepole pine (BKLP) as a feedstock for quick pyrolysis. Two dedicated bioenergy crops growing on reclaimed coal-mine soils in West Virginia were reported and their pyrolysis products were defined by Oginni et al. in their study [10]. The manufacture and analysis of pyrolysis oil (bio-oil) produced from certain hardwood chips (Mahogany, Swietenia macrophylla) were disclosed by Chukwunke et al. [11]. The pyrolysis of wood chips from oak, beech, fir, cherry, walnut, and linden was studied by Kozani et al. [12] at equal mixing fractions between 240 and 650 °C in a fixed bed reactor. They discovered that increased heating rates and reaction temperatures promote higher pyrolytic gas yields while reducing yields of bio-oil and char. The quick pyrolysis of hazelnut cupula was studied by Keleş et al. [13] using a fixed-bed reactor while varying the pyrolysis temperature from 400 to 700 °C, the sweeping gas flow rate, and the particle size. According to the study, the highest oil output was achieved at 600 °C and gas flow rate of 200 mL/min for diameters ranging from 0.150 mm to 0.425 mm. In a batch reactor, the pyrolysis of beech wood at temperatures between 350 and 450 °Celsius was studied by Bajus [14]. The data study revealed an average of 44.3 percent liquids, 30.6 percent biochar, and 25.1 percent gas, with acetic acid, formic acid, furfural, and lactic acid being the most prevalent liquid products. Using a fixed-bed tube reactor, Demirbas [15] examined the effects of pyrolysis on

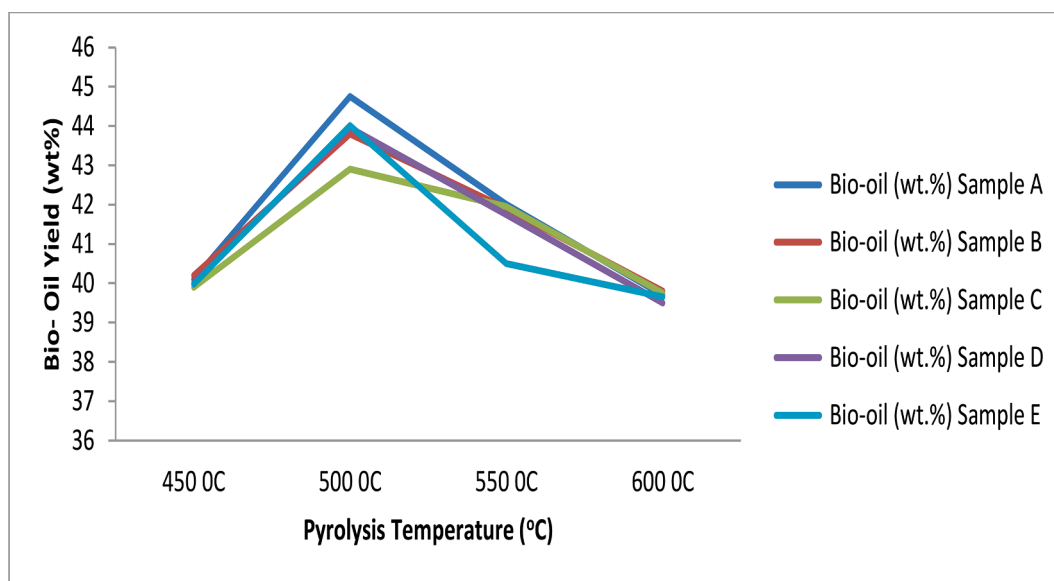


Fig. 4. Variation of Bio-oil yield with pyrolysis temperature.

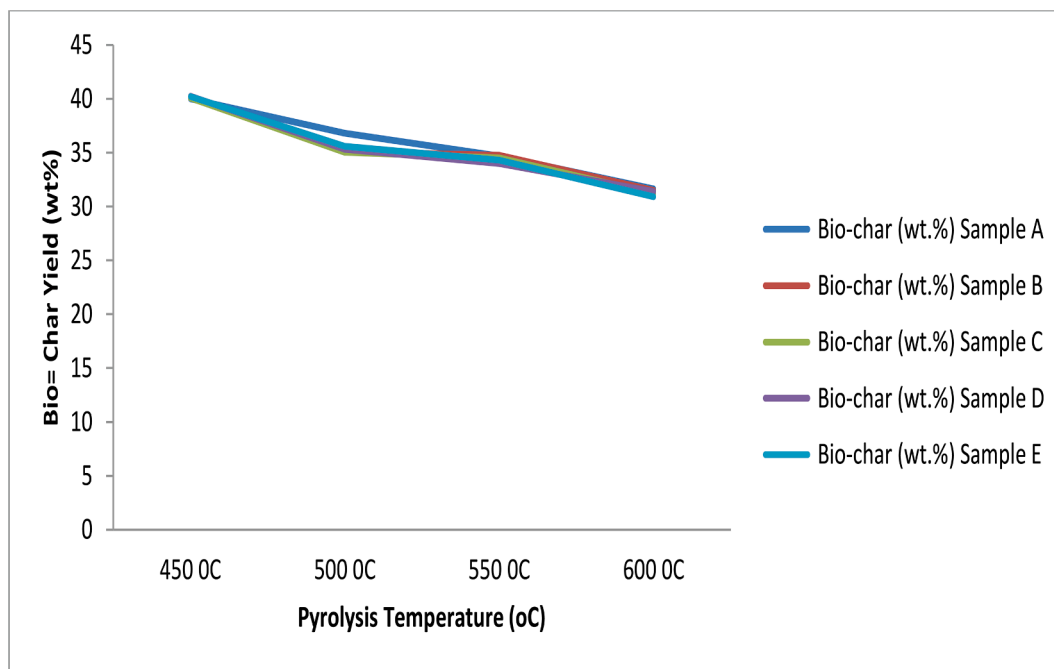


Fig. 5. Variation of Bio-char yield with pyrolysis temperature.

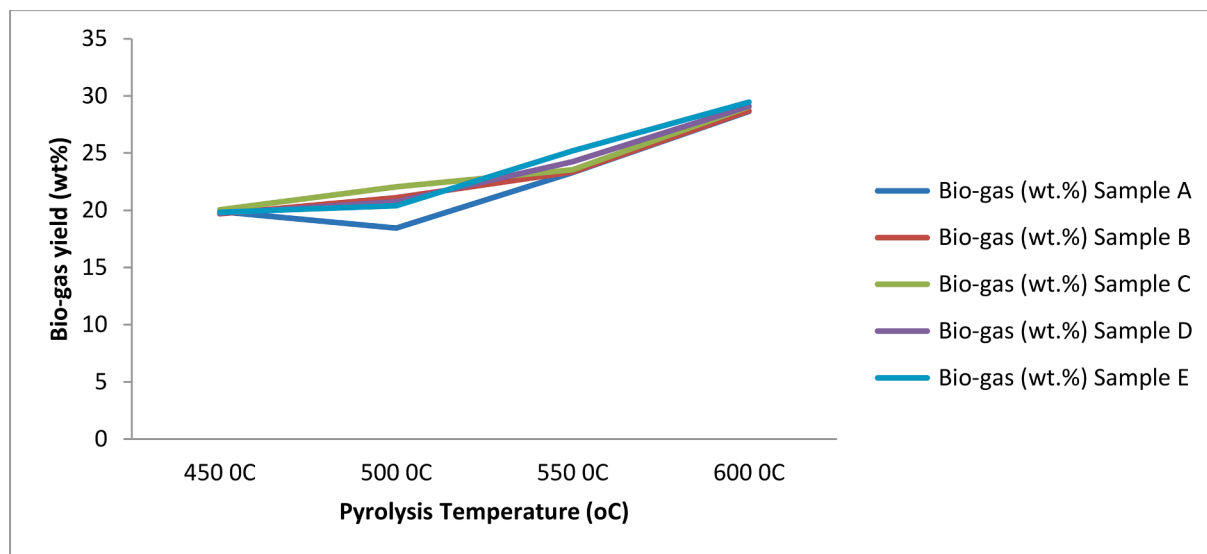


Fig. 6. Variation of Bio-gas yield with temperature.

hazelnut shell, olive husk, beech, and spruce wood samples at various temperatures (350 to 525 °C). High concentrations of 1-hydroxy-2-butanone, acetic acid, 2,6-dimethoxyphenol, 1-hydroxy-2-propanone, methanol, 4-methyl-2,6-dimethoxyphenol, and 2-cyclopentene-1-one were found in increasing percentages of bio-oil 45 wt% at 500 °C.

The prime objectives of this study are to: (i) determine experimentally the higher heating values (HHVs) of five selected fuel woods (*Adansonia digitata*, *Terminalia ivorensis*, *Khaya ivorensis*, *Mansonia altissima*, *Okoubaka aubrevillei*) obtained from South Western Nigeria for effective utilization as bio-fuel and (ii) investigate the chemical composition of the pyrolysis products (bio oils) of the selected fuel wood samples using a gas chromatography-mass spectrometry (GC-MS) analyzer as potential substitute for fossil fuel.

In this study, pyrolysis method is used considering its superior ability to decompose biomass at temperatures between 300 °C and 600 °C and

in the absence of an oxygen-rich atmosphere. Moreover, it is one of the best and most effective processes for degrading biomass. Three distinct products, including bio-oil, biochar, and biogas, can be produced by pyrolysis. Biomass co-pyrolysis is a low-cost and simple to operate method that has the potential to improve biofuel production.

### 1.1. Trends in development of biofuel production technologies in Nigeria

The inconsistency of Nigeria’s electrical supply can be attributed to a lack of diversification and increased energy demand. It is essential to add environmentally friendly green energy sources to the current hydroelectric and thermal power plants in order to offset the pollution caused by the burning of fossil fuels. Nigeria has made very little progress in the switch to renewable energy sources despite its massive population (more than 200 million) and strong agricultural

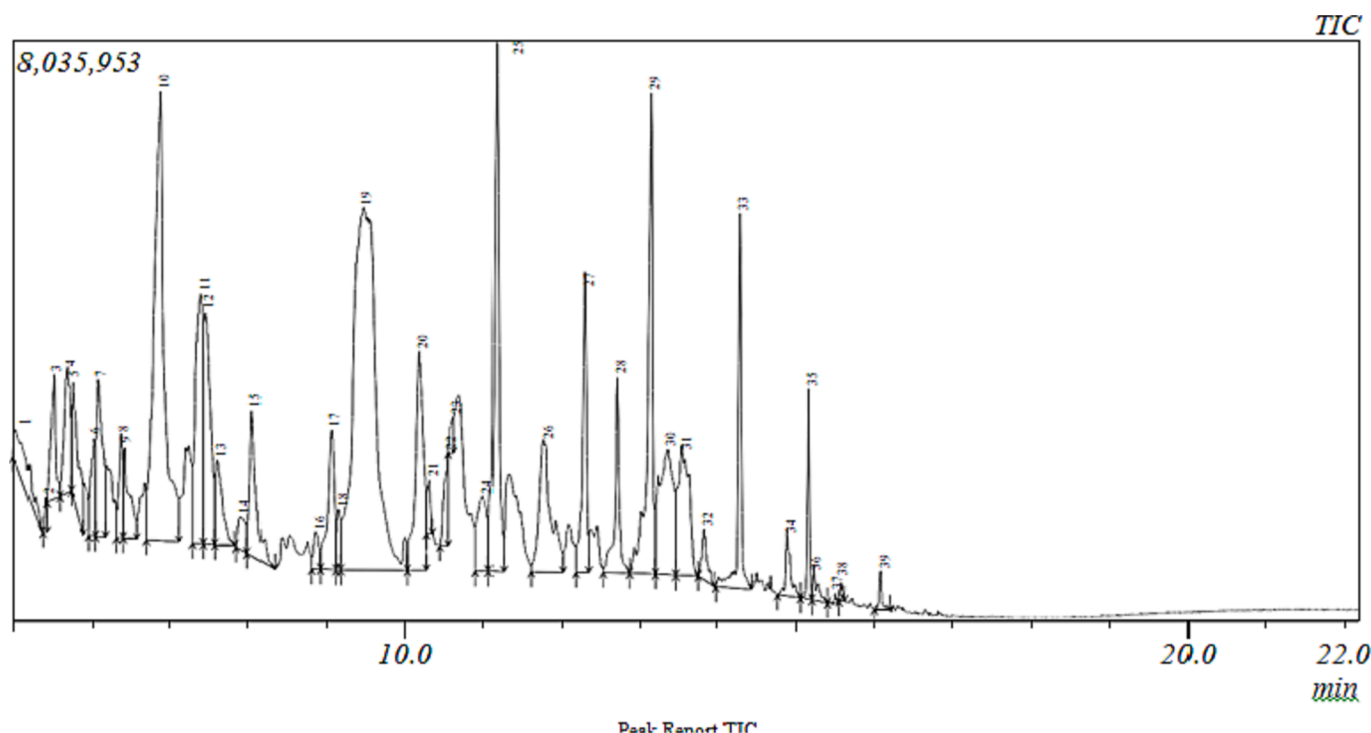


Fig. 7. GC-MS chromatogram for bio-oil from *Adasonia digitata* (Ad).

Table 6

Thermophysical properties and chemical composition of bio-oil yield produced at 500 °C for each sample.

Properties	Diesel	Heavy fuel oil	Bio-oil				
			<i>Adansonia digitata</i>	<i>Terminalia ivorensis</i>	<i>Khaya ivorensis</i>	<i>Mansonia altissima</i>	<i>Okoubaka aubrevillei</i>
Flash point	75	–	79	80	79.05	80.02	80.10
Pour point	–2	–	–7	–7	–7	–7	–7
pH	5.5–8.0	–	4.82	4.73	4.80	4.75	4.70
Density (g/ml) @ 40 °C	0.78	0.94	0.98	0.98	0.98	0.98	0.98
Viscosity (cst (mm <sup>2</sup> /s)@ 40 °C	1.8–4.1	180	4.25	4.30	4.20	4.35	4.30
API gravity	45.0–46.0	40	20.01				
Elemental analysis (db. wt%) of bio-oil							
C	–	–	70.99	70.90	70.16	70.85	69.95
H	–	–	13.40	13.51	14.00	13.45	14.10
N	–	–	0.54	0.55	0.84	0.75	0.95
O	–	–	15.01	14.97	14.95	14.89	14.94
S	–	–	0.06	0.07	0.05	0.06	0.06
HHV (MJ/kg)	45.0–46.0	40	30.77	30.82	30.91	30.77	30.98

production because of financial constraints and a dearth of systematic analyses of readily accessible biomass [16–19]. In Nigeria, fuelwood, crop residues, agricultural crop wastes, animal wastes, energy crops, and other biomass energy resources are all readily available and, if fully developed, will inevitably contribute to the nation’s sustainable energy development, increase national income, create job opportunities for both skilled and unskilled labors, and turn waste into wealth [20–25].

Many developing nations are becoming more interested in biofuels as a way of effective utilization of biomass and expanding access to clean liquid fuels while lowering energy prices, ensuring energy security, and addressing concerns about global warming linked to petroleum fuels. Biomass technology, when used appropriately, provides a compelling foundation for utilizing specific types of biomasses to address both urban and rural energy needs [25–27]. Sustainable biomass energy deployment offers a lot of promise in Nigeria, especially in rural agricultural areas [28–29].

Nigeria as a country in Sub-Saharan Africa has a land size of 923,768 square kilometers. Agricultural land covers around 74,500,000 ha of the

country’s total 91,077,000 ha [30]. In Nigerian mass land, forests, agriculture leftovers, urban and industrial waste products, and other biomass sources. Nearly 200 billion kg of biomass is produced each year. A study found that the biomass resources in Nigeria have the potential to provide up to 62 Mtoe (2.6 billion GJ) of energy. Given Nigeria’s abundance of renewable energy resources and the low access of the populace to clean energy, the conversion of large amounts of biomass resources, primarily in the form of agricultural wastes and residues (animal, food, and municipal), to energy production could potentially increase energy supply while also improving the country’s energy mix and balance. Furthermore, a stable power infrastructure would be in place, and rural areas with an abundance of agricultural waste biomass would have access to electricity [18].

Although bioenergy heat and power technologies exist, it is still important to increase the use of the most effective ones while also developing and deploying a number of new technology alternatives for Nigeria’s effective and efficient biofuel production [30,31]. According to Mckendry [32], the kind and quantity of biomass feedstock as well as



**Table 7**  
Chemical Composition of *Adansonia digital* (AD) Bio-oil at 500 °C.

Compounds	Retention Index	Percentage Composition	MF	MW
Tetramethylmethane	434	0.5	C <sub>5</sub> H <sub>12</sub>	72
2-methylfuran	642	1.5	C <sub>5</sub> H <sub>6</sub> O	82
<i>trans</i> -2-octadecadecen-1-ol	2061	15.00	C <sub>18</sub> H <sub>36</sub> O	268
oleic acid	2175	19.0	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	282
3-methylfuran	643	2.0	C <sub>5</sub> H <sub>6</sub> O	82
Trimethylnitromethane	716	0.5	C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>	103
2-pentynal	724	1.5	C <sub>5</sub> H <sub>6</sub> O	82
palmitic acid	1968	6.0	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	256
Dimethylvinylmethanol	600	0.5	C <sub>5</sub> H <sub>10</sub> O	86
4-ethyl-1,3-dioxolane	738	0.5	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	102
vinyl butyrate	775	0.5	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>	114
1-hydroxy-2-butanone	798	1.0	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88
<i>cis</i> -3-octene	823	1.0	C <sub>8</sub> H <sub>16</sub>	112
<i>trans</i> -3-octene	824	1.5	C <sub>8</sub> H <sub>16</sub>	112
2-methoxymethyltetrahydrofuran	825	0.5	C <sub>6</sub> H <sub>12</sub> O	116
2,4-pentadienoic acid	873	1.0	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	98
<i>trans</i> -2-furanmethanol	885	5.0	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	98
5-methyl-3-methylene-5-hexen-2-one	887	1.5	C <sub>8</sub> H <sub>12</sub> O	124
tetrahydro-2-furanmethanol	892	0.5	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	
Corylone	972	1	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>	112
Butylglyoxylate	973	0.5	C <sub>6</sub> H <sub>10</sub> O <sub>3</sub>	130
3-hydroxy-6-methylpyridazine	975	1	C <sub>5</sub> H <sub>6</sub> N <sub>2</sub> O	110
3-methyl-1,2-cyclopentanedione	1003	1.5	C <sub>6</sub> H <sub>8</sub> O	112
methyl-1-cyclohexenyl ketone	1027	5	C <sub>8</sub> H <sub>12</sub> O	124
methyl 2-butyl-2-cyclopropene-1-carboxylate	1057	1	C <sub>9</sub> H <sub>14</sub> O <sub>2</sub>	154
<i>o</i> -guaiacol	1090	2	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	124
Syringol	1279	0.7	C <sub>5</sub> H <sub>8</sub> N <sub>2</sub>	96
2,4-dimethoxyphenol	1279	1.5	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	154
3-nonanoic acid	1290	0.7	C <sub>9</sub> H <sub>14</sub> O <sub>2</sub>	154
1-methyl-3-nitro-2(1H)-pyridinone	1376	1	C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>	154
pelargic acid	1272	1	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	158
<i>cis</i> -10-pentadecen-1-ol	1763	12	C <sub>15</sub> H <sub>30</sub> O	226
<i>n</i> -pentadecanoic acid	1869	2	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	242
9-octadecenal	2007	8	C <sub>18</sub> H <sub>34</sub> O	266
<b>Percentage Total</b>		<b>98.4</b>		

the intended form of energy have an impact on the best biomass conversion technique. The development of biomass conversion systems varies throughout Nigeria; some are at the research stage, some are in the demonstration stage, and only a few are commercially successful. Biofuel production in Nigeria is still in its infancy, with biomass energy technologies like biogas, biofuels, improved woodstoves, and biomass briquetting available to a wide range of end-users [33]. The Nigerian Automotive Biofuel Program, which began in 2005, was a collaboration between the Federal Government, NNPC, Universities, R&D Institutes, commercial investors, and local farmers. The federal government required the NNPC to blend 10 % biofuel with fossil fuels at the country's refineries. Sugar and starchy crop biofuels are available in abundant for commercial or industrial usage in Nigeria, but their feedstocks are first-generation biomass, raising questions about sustainability [18].

Lack of (i) a comprehensive renewable energy strategy and the development of biofuel power technology (BPT), (ii) a supportive environment for the production and development of biofuels, and (iii) biomass technology development investors are the main obstacles preventing Nigeria from producing and developing biofuels on a commercial scale. In addition to the aforementioned factors, low levels of political and public awareness contribute to the poor opinions and attitudes that people have toward emerging renewable energy technology. Lack of skilled local labor, particularly in Nigeria's rural areas, to operate and maintain renewable energy equipment is a significant barrier to the broad adoption of bioenergy technology (BET). Additionally, there is a lack of institutional and financial infrastructure to facilitate the rapid uptake and development of BETs. The development of biofuel energy sources is hampered by the low costs of conventional energy sources (petrol, diesel, natural gas, etc.) [34].

Nigeria is not exempt from the benefits of biofuel because it provides developing nations with the chance to expand new sources of income, lessen their over-dependence on imported fossil fuels, and improve the

environment. Therefore, the government at all levels must prepare to produce biofuel from her enormous biomass resources if Nigeria is to make a significant entry into the biofuels market, with every sector being placed in the usage of cleaner renewable energy. Through the cultivation of arable landmass for the supply of feedstock, this concept is anticipated to strengthen the Nigerian economy. Additionally, the following are crucial to overcoming the obstacles to large-scale biofuel production in Nigeria: (i) The government must put into effect a uniform policy that will serve as a foundation for other stakeholders, including as businesses, non-governmental organizations (NGO), research organizations, and private investors, to contribute their fair share to the development of the biofuel sectors; (ii) Steps that can be done to lower the cost of producing biofuel include localizing the feedstocks, choosing a less expensive way of harvesting, and selecting a less expensive method of transesterification, (iii) It is important to inform the public about the liberal and conservative aspects of using biofuels, particularly the advantages for the economy and environment. This will make it easier for people to accept using biofuel. (iv) In order to increase the output of biofuel production, technological improvement is needed in the fields of oil extraction, transesterification, and fermentation processes. (v) It is important to promote the mass production of non-edible feedstock for biofuel production, such as *Jatropha curcas*, *Madhuca indica*, and *Pongamia pinnata*. In Nigeria, this prevents biofuel feedstock from competing with food. (vi) The federal government must pique the interest of both the public and commercial sectors, particularly their cooperation in research and development [12,18].

## 2. Materials and methods

### 2.1. Samples preparation

The selected wood samples (Sample A (*Adansonia digitata*), Sample

**Table 8**  
Chemical composition of Terminalia ivorensis (Ti) Bio-oil at 500 °C.

Compounds	Retention Index	Percentage Composition	MF	MW
Tetramethylmethane	434	0.4	C <sub>5</sub> H <sub>12</sub>	72
2-methylfuran	642	0.9	C <sub>5</sub> H <sub>6</sub> O	82
trans-2-octadecadecen-1-ol	2061	10.00	C <sub>18</sub> H <sub>36</sub> O	268
oleic acid	2175	20.00	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	282
3-methylfuran	643	0.8	C <sub>5</sub> H <sub>6</sub> O	82
Trimethylnitromethane	716	0.5	C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>	103
2-pentynal	724	1.2	C <sub>5</sub> H <sub>6</sub> O	82
palmitic acid	1968	7.0	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	256
Dimethylvinylmethanol	600	0.5	C <sub>5</sub> H <sub>10</sub> O	86
4-ethyl-1,3-dioxolane	738	0.5	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	102
vinyl butyrate	775	0.5	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>	114
1-hydroxy-2-butanone	798	1.0	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88
cis-3-octene	823	1.0	C <sub>8</sub> H <sub>16</sub>	112
trans-3-octene	824	1.5	C <sub>8</sub> H <sub>16</sub>	112
2-methoxymethyltetrahydrofuran	825	0.5	C <sub>6</sub> H <sub>12</sub> O	116
2,4-pentadienoic acid	873	1.0	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	98
trans-2-furanmethanol	885	4.0	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	98
5-methyl-3-methylene-5-hexen-2-one	887	2.0	C <sub>8</sub> H <sub>12</sub> O	124
tetrahydro-2-furanmethanol	892	0.5	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	102
Corylone	972	1.0	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>	112
Butylglyoxylate	973	0.5	C <sub>6</sub> H <sub>10</sub> O <sub>3</sub>	130
3-hydroxy-6-methylpyridazine	975	1.0	C <sub>5</sub> H <sub>6</sub> N <sub>2</sub> O	110
3-methyl-1,2-cyclopentanedione	1003	0.5	C <sub>6</sub> H <sub>8</sub> O	112
methyl-1-cyclohexenyl ketone	1027	8.0	C <sub>8</sub> H <sub>12</sub> O	124
methyl 2-butyl-2-cyclopropene-1-carboxylate	1057	1.0	C <sub>9</sub> H <sub>14</sub> O <sub>2</sub>	154
o-guaiacol	1090	2.0	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	124
Syringol	1279	1.5	C <sub>5</sub> H <sub>8</sub> N <sub>2</sub>	96
2,4-dimethoxyphenol	1279	3.0	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	154
3-nonanoic acid	1290	0.9	C <sub>9</sub> H <sub>14</sub> O <sub>2</sub>	154
1-methyl-3-nitro-2(1H)-pyridine	1376	1.0	C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>	154
pelargic acid	1272	1.0	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	158
cis-10-pentadecen-1-ol	1763	12.0	C <sub>15</sub> H <sub>30</sub> O	226
n-pentadecanoic acid	1869	2.0	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	242
9-octadecenal	2007	10.0	C <sub>18</sub> H <sub>34</sub> O	266
<b>Percentage Total</b>		<b>99.2</b>		

B (*Terminalia ivorensis*), Sample C (*Khaya ivorensis*), Sample D (*Mansonia altissima*), and Sample F (*Okoubaka aubrevillei*) for this investigation are generally used for furniture in Nigeria. The selected wood samples were obtained from sawmills in Ota metropolis in South Western Nigeria. The wood samples were processed into sawdust at the processing unit, Bells University of Technology, Ota, Nigeria. The samples of sawdust were exposed to the sun for seven days. In line with ASTM C566 and ASTM D1102 standards, the samples were then sieved to a uniform particle size of 0.5 mm (0.0005 m), weighed, and stored at room temperature in polythene bags for proximate and ultimate analysis.

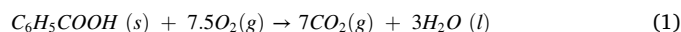
## 2.2. Experimental procedures

### 2.2.1. Determination of higher heating values using bomb calorimeter

Two of the most often used solid biomass fuel sources are wood chips and wood pellets. The recognized indicator of a fuel's energy content is the heating value, often known as the calorific value or heat of combustion. The higher heating value (HHV) of fuels is one of the crucial factors for determining the thermal efficiency of a thermal power plant, such as CHP plants, biomass cogeneration units, and biorefineries. This study used an oxygen bomb calorimeter (Model-IKA C2000) to determine the higher heating values (HHVs) of the selected fuel wood samples in accordance with DIN 51900T3. The bomb calorimeter monitors the heat of a specific reaction or the heating value of the fuels. It has a fixed volume. Bomb calorimeters are designed such that they can resist the intense pressure created by the reaction or burning of fuel inside the calorimeter. Approximately 1.00 g of biomass ingredients were encapsulated in a pellet inside the bomb's crucible. After the device was sealed, oxygen (purity 99.99 %) was poured inside at a pressure of 30 bars in order to remove oxygen and find system leaks. The bomb was put inside the water-filled adiabatic calorimeter, and the sample ignited

electrically. The resultant rise in water temperature makes it possible to determine the sample's HHV. The calorimeter's heat capacity was calculated using benzoic acid as a reference chemical. The equation used for their calculation is as follows.

By measuring the calorific value of benzoic acid (C<sub>6</sub>H<sub>5</sub>COOH), the heat capacity of the calorimeter C<sub>ca</sub> was calculated during calibration. At a temperature of 25 °C, the combustion reaction of benzoic acid is given as follows:



The heat capacity of the calorimeter is computed using Eq. (2) (Gravalos et al., 2016):

$$C_{ca} = \frac{m_{ba} + H_{ba} + m_{ct} \cdot H_{ct}}{\Delta T_c} \quad (2)$$

where m<sub>ba</sub> is the mass of benzoic acid (in grams), m<sub>ct</sub> is the mass of cotton thread (in grams), H<sub>ba</sub> is the calorific value of benzoic acid (in joules per gram), H<sub>ct</sub> is the calorific value of cotton thread (in joules per gram), and ΔT<sub>c</sub> is the observed change in temperature during the calibration experiment (in degrees Celsius).

The heating value of the fuel sample is calculated using Eq. (3):

$$H_{fs} = \frac{C_{ca} \cdot \Delta T_{fs} - m_{ct} \cdot H_{ct}}{m_{fs}} \quad (3)$$

where m<sub>fs</sub> is the fuel sample's mass and ΔT<sub>fs</sub> is the fuel sample's observed change in temperature (°C) during combustion.

The higher heating value (or gross calorific value) of the biomass samples was experimentally determined based on CEN/TS 14918:2005 (2005) standards. The method for determining a solid biofuel's gross calorific value in a bomb calorimeter at constant volume and 25 °C as the reference temperature is described in this Technical Specification.



**Table 9**  
Chemical composition of *Khaya ivorensis* (KI) Bio-oil at 500 °C.

Compounds Name	Retention index	Percentage Composition	MF	MW
beta-Acetylnaphthalene	5.196	0.7	C12H10O	170.21
Cycloheptano[d]imidazolidine, 1,3-dihydro	5.325	0.3	C9H18N2O2	186.25
2-Nonenoic acid	5.556	1.9	C9H16O2	156.22
2,4-dimethyl-Cyclohexanol	5.689	1.2	C8H16O	128.21
3,4-dimethyl- Pyridine	5.945	1.2	C9H9NO4	195.17
1-Silacyclo-2,4-hexadiene	6.112	2.9	C5H6Si	94.19
Bicyclo[2.2.1]heptane-2-carboxaldehyde, 3	6.244	1.3	C11H16O	164.24
Bicyclo[2.2.1]heptan-2-ol	6.509	2.6	C7H12O	112.17
Decanal	6.650	1.9	C10H20O	156.26
2-hydroxy-3-methyl-2-Cyclopenten-1-one	6.921	9.5	C6H8O2	112.13
10-Methyl-3,4,5,8,9,10-hexahydrooxecine-2-one	7.286	1.7	C10H16O2	168.23
2-methoxy- Phenol	7.401	9.0	C7H8O2	124.14
3-Cyclohexene-1-carboxaldehyde	7.629	1.9	C7H10O	110.15
3-ethyl-2-hydroxy-2-Cyclopenten-1-one	8.084	1.9	C7H10O2	126.15
7,7-dimethyl-Bicyclo[2.2.1]heptan-2-ol	8.449	1.1	C9H16O	140.22
2-methyl-5-prop-1-en-2-yl-7-oxabicyclo[4.1.0]heptan-2-ol	8.574	3	C10H16O2	168.23
Streptovitacin A	8.873	2.8	C15H23NO5	297.35
Creosol	9.068	6.0	C8H10O2	138.16
1-Bicyclo[4.1.0]Hept-7-Yl-1-Pentanone	9.176	1.2	C12H20O	180.29
Valeric acid	9.380	3.7	C5H10O2	102.13
2-(hydroxymethyl)-Cyclohexanone	9.533	8.0	C7H12O2	128.169
2-Ethyl-3-methoxy-2-cyclopentenone	10.255	1.7	C8H12O2	140.18
4-ethyl-2-methoxy-Phenol	10.324	2.1	C9H12O2	152.19
Hydroquinone	10.693	4.8	C6H6O2	110.11
2,6-dimethoxy-Phenol	11.194	7.1	C8H10O3	154.16
2-methyl-1,4-Benzenediol	11.325	2.7	C7H8O2	124.14
3-[(E)-but-2-enyl]thiophene	11.818	1.4	C8H10S	138.23
1,2,3-Trimethoxybenzene	12.301	3.8	C9H12O3	168.1
2-methoxy-5-[(E)-prop-1-enyl]phenol	12.392	1.8	C10H12O2	C10H12O2
Apocynin	12.723	1.6	C9H10O3	166.17
N-Methyl-2-phenylethanamine	13.127	4.9	C9H13N	135.21
1,6-anhydro-.beta.-D-Glucopyranose,	13.284	1.5	C12H16O8	288.25
2,6-dimethoxy-4-(2-propenyl)- Phenol	14.675	3.1	C11H14O3	194.23
		99.3		

With the use of the reference reagent, benzoic acid, the calorimeter was previously calibrated. The wood samples were turned into gelatin capsule seals, oil paper seals, powder, pellets, and powder. A small amount of biomass powder is compacted into an immovable pellet to speed up the burning process. The capsule burns quickly, which causes the sample to ignite. The following steps are part of the experimental process:

- A tablet of benzoic acid was used to calibrate and verify the instrument.
- A precision balance was used to weigh the biomass sample, which was between 0.5 and 1.0 g.
- The powdered sample was inserted in the capsule and the capsule was pressed to compact the material.
- The capsule was put into the holder with care.
- The cotton thread was attached and the firing cotton was ensured that lies on top of the capsule.
- The bomb was lowered in the calorimeter and the cover was then closed.
- The test was launched by pressing the start button.

To estimate the mean and standard deviation of the heating values, the HHVs obtained from all of the fuel wood samples were subjected to basic descriptive statistical analysis using the following equations:

$$\text{Average of } x = \bar{x} = \frac{1}{n} \sum_{x=1}^n x_i \quad (4)$$

$$\text{Standard deviation of the mean of } x = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n(n-1)}} \quad (5)$$

### 2.2.2. Pyrolysis experimental Set-up

In this study, the pyrolysis experimental set-up consisted of an insulated reactor, condenser, gas collector, ice bath, inert gas flow system, PID temperature controller, and electric heater. The pyrolysis experiment was carried out in a fixed-bed reactor under nitrogen environment between the temperature ranges of 450–600 °C. A sealed and airtight retort was used to hold sun-dried samples of wood waste of known weight (100 g). A condensate receiver cylinder of known weight (0.50 g) was connected to the retort's outflow to allow gas from the retort to enter it, and it was put in an ice bath to aid condensation of the pyrolysis' condensable volatile. The input of a compressor was linked to the condensate receiver's outlet, which was connected to the gas collecting cylinder's exit. A nitrogen gas cylinder was attached to the retort's intake with the help of a pressure gauge regulator to flush the system, displacing oxygen and creating an inert atmosphere. The retort with sawdust sample were put inside the electric furnace with the nitrogen cylinder connected for 35 min at different temperature three runs per sample, following which the electric furnace was turned off and the retort was allowed to cool fully. The pyro-oil with the cylinder, weight of the pyro-oil, and weight of the char were all determined when the condensate receiver was taken from the ice bath. The experimental set-up for pyrolysis is shown in Fig. 3.

### 2.3. Proximate and ultimate analysis of fuel wood samples

This study used proximate and ultimate analysis to estimate the fixed carbon, ash, volatile matter, moisture content, and percentages of carbon, hydrogen, nitrogen, and organics in the chosen fuel wood samples in accordance with [35]. The samples' moisture content, volatile matter, fixed carbon, and ash percentages were assessed using proximate analysis to determine their fuel characteristics and heating values. On the other hand, the percentages of carbon, hydrogen, nitrogen, and organics

**Table 10**  
Chemical composition of *Okoubaka aubrevillei* (Oa)Bio-oil at 500 °C.

Compounds Name	Retention index	Percentage Composition	MF	MW
beta-Acetylnaphthalene	5.196	0.2	C12H10O	170.21
1,3-dihydro Cycloheptano[d]imidazolidine	5.325	0.3	C9H18N2O2	186.25
2-Nonenoic acid	5.556	2.0	C9H16O2	156.22
2,4-dimethyl-Cyclohexanol	5.689	1.2	C8H16O	128.21
3,4-dimethyl- Pyridine	5.945	1.2	C9H9NO4	195.17
1-Silacyclo-2,4-hexadiene	6.112	0.9	C5H6Si	94.19
Bicyclo[2.2.1]heptane-2-carboxaldehyde	6.244	1.3	C11H16O	164.24
Bicyclo[2.2.1]heptan-2-ol	6.509	4.0	C7H12O	112.17
Decanal	6.650	1.8	C10H20O	156.26
2-hydroxy-3-methyl-2-Cyclopenten-1-one	6.921	9.5	C6H8O2	112.13
10-Methyl-3,4,5,8,9,10-hexahydrooxecine-2-one	7.286	1.8	C10H16O2	168.23
2-methoxy- Phenol	7.401	10.8	C7H8O2	124.14
3-Cyclohexene-1-carboxaldehyde	7.629	2.0	C7H10O	110.15
3-ethyl-2-hydroxy-2-Cyclopenten-1-one	8.084	1.9	C7H10O2	126.15
7,7-dimethyl-Bicyclo[2.2.1]heptan-2-ol	8.449	1.1	C9H16O	140.22
2-methyl-5-prop-1-en-2-yl-7-oxabicyclo[4.1.0]heptan-2-ol	8.574	2.4	C10H16O2	168.23
Streptovitacin A	8.873	0.8	C15H23NO5	297.35
Creosol	9.068	5.0	C8H10O2	138.16
1-Bicyclo[4.1.0]Hept-7-Yl-1-Pentanone	9.176	1.2	C12H20O	180.29
Valeric acid	9.380	3.7	C5H10O2	102.13
2-(hydroxymethyl)-Cyclohexanone	9.533	9.6	C7H12O2	128.199
2-Ethyl-3-methoxy-2-cyclopentenone	10.255	1.7	C8H12O2	140.18
4-ethyl-2-methoxy-Phenol	10.324	2.1	C9H12O2	152.19
Hydroquinone	10.693	4.8	C6H6O2	110.11
2,6-dimethoxy-Phenol	11.194	6.8	C8H10O3	154.16
2-methyl-1,4-Benzenediol	11.325	2.7	C7H8O2	124.14
3-[(E)-but-2-enyl]thiophene	11.818	1.4	C8H10S	138.23
7,Bicyclo[2.2.1]heptane-1-carboxylic acid	11.923	0.5	C22H25N3O5	411.5
2,3-Dimethylhydroquinone	12.105	0.5	C8H10O2	138.16
1,2,3-Trimethoxybenzene	12.301	2.8	C9H12O3	168.1
2-methoxy-5-[(E)-prop-1-enyl]phenol	12.392	0.8	C10H12O2	C10H12O2
Apocynin	12.723	0.6	C9H10O3	166.17
N-Methyl-2-phenylethanamine	13.127	4.9	C9H13N	135.21
1,6-anhydro-.beta.-D-Glucopyranose,	13.284	0.5	C12H16O8	288.25
2,6-dimethoxy-4-(2-propenyl)- Phenol	14.675	4.5	C11H14O3	194.23
		99.3		

were determined via ultimate analysis.

### 2.3.1. Determination of moisture content

The sawdust samples were weighed to determine their initial weight and were then oven-dried at a temperature of about 100–102 °C for 90 min. Then the samples were allowed to cool down in the oven and put in an air-tight container before determining its new weight on a digital weighing balance. The moisture content was determined using Eq. (6), given as

$$\text{Moisture content} = \frac{WS_{Wet} - WS_{Dry}}{WS_{Dry}} \times 100\% \quad (6)$$

Where:  $WS_{Wet}$  = wet sawdust weight (g),  $WS_{Dry}$  = dry sawdust weight (g) at 102 °C.

### 2.3.2. Determination of volatile matter and fixed carbon content

Pyrolysis of dried sawdust obtained during the moisture content determination was carried out at a temperature range of 350–500 °C for about 45 min to extract char in a closed reactor. The char (carbon) was then measured to determine its weight/ mass percentage composition. The volatile matter and carbon content percentage were obtained using Eqs. (7) and (8).

$$\text{Volatile matter} = \frac{WS_{Wet} - WS_{Dry}}{WS_{Wet}} \times 100\% \quad (7)$$

Where:

$WS_{Wet}$  = wet sawdust weight (g),  $WS_{Dry}$  = dry sawdust weight (g)

$$\text{Fixed Carbon content} = \frac{WS_{Dry} - WS_{Pyro}}{WS_{Dry}} \times 100\% \quad (8)$$

Where:

$WS_{Dry}$  = dry sawdust weight (g),  $WS_{Pyro}$  = pyrolyzed sawdust weight (g).

### 2.3.3. Determination of ash content

The ash content is determined by using Eq. (9)

$$\% \text{ Ash} = \frac{M_{AR}}{M_s} \quad (9)$$

Where:

$M_{AR}$  = Ash residue weight (g) obtained from pyrolysis.

$M_s$  = Sample weight (g).

### 2.3.4. Determination of elemental composition and heating values using correlations

The elemental compositions of the selected fuel wood samples were determined using Eltra elemental analyzer according to ASTM D3176 – 09 and ASTM D7582.

The Higher Heating Values (HHV) of the raw fuel wood samples were estimated from a correlation equation based on ultimate analysis and proximate analysis. Equation (10) was used to compute the HHV based on ultimate analysis as follows [36].

$$HHV_{DRY} (Mj/kg) = -1.3675 + 0.3137C + 0.7009H + 0.0318O \quad (10)$$

Where:

C - Carbon.

N - Nitrogen.

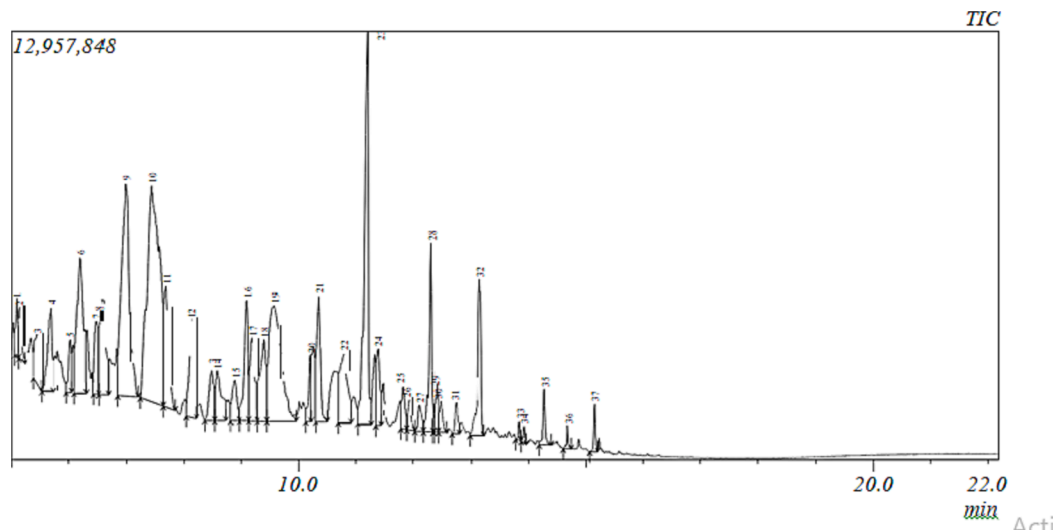
H - Hydrogen.

O - Oxygen.

Eq. (11) was used to compute the HHV of the fuel wood samples

**Table 11**  
Chemical composition of *Mansonia altissima* (Ma) Bio-oil at 500 °C.

Compounds Name	Retention index	Percentage Composition	MF	MW
6,10-dimethyl (E5,E9)-Dodecadien-2-one	5.025	0.4	C18H30O2	278.4
1-nitroso-2,5-dihydropyrrole	5.154	0.7	C4H6N2O	98.1
3,4-dihydro-2H-Pyran	5.524	2.2	C5H8O	84.12
1,4,5-trimethyl- Imidazole	5.674	5.0	C14H28N2	224.39
1,4-Dioxaspiro[5.5]undecan-2-one	6.089	2.7	C9H14O3	170.21
Exo-Norborneol methyl ether	6.384	2	C8H14O	126.2
Bicyclo[2.2.1]heptan-2-ol	6.495	1.0	C7H12O	112.17
2-hydroxy-3-methyl-2-Cyclopenten-1-one	6.902	8.8	C6H8O2	112.13
3,3-dimethyl-Cyclohexanecarboxaldehyde	7.230	0.75	C7H12O	112.17
Mequinol	7.617	10.3	C7H8O2	124.14g
5-methyl-Pyrimidine-4,6-diol	7.917	0.3	C5H6N2O2	126.11
3-ethyl-2-hydroxy-2-Cyclopenten-1-one	8.063	1.1	C7H10O2	126.15
Z-8-Methyl-9-tetradecenoic acid	8.213	0.24	C15H28O2	240.38
7,7-dimethyl-Bicyclo[2.2.1]heptan-2-ol	8.460	0.7	C9H16O	140.22
Streptovitacin A	8.974	1.5	C15H23NO5	297.35
Creosol	9.159	5.4	C8H10O2	138.16
Catechol	9.575	10.4	C6H6O2	110.11
5-Hydroxymethylfurfural	9.764	1.4	C6H6O3	126.11
2-Ethyl-3-methoxy-2-cyclopentenone	10.210	3.5	C8H12O2	140.18
4-ethyl-2-methoxy-Phenol	10.337	2.6	C9H12O2	152.19
2-ethylcyclohexyl ester	10.733	3.5	C14H19NO2	233.31
2,6-dimethoxy-Phenol	11.209	9.3	C8H10O3	154.16
2-methyl-1,4-Benzenediol	11.329	2.1	C7H8O2	124.14
Vanillin lactoside	11.803	4.9	C20H28O13	476.4
1,2,3-Trimethoxybenzene	12.321	4.7	C9H12O3	168.19
Apocynin	12.735	1.5	C9H10O3	166.17
Homovanillic acid	13.145	2.8	C9H10O4	182.17
1,6-anhydro-beta.-D-Glucopyranose	13.666	6.5	C6H10O5	162.14
3,4-diethyl-, dime 2,4-Hexadienedioic acid	13.924	0.3	C6H6O4	142.11
Methyl-(2-hydroxy-3-ethoxy-benzyl)ether	14.270	0.6	C10H14O3	182.22
2,6-dimethoxy-4-(2-propenyl)- Phenol	14.683	0.3	C11H14O3	194.23
3,5-Dimethoxy-4-hydroxyphenyl acetic acid	15.155	0.7	C10H12O5	212.2
3-Allyl-6-methoxyphenyl	15.236	0.1	C10H12O2	164.2
		98.3		



**Fig. 8.** GC–MS chromatogram for bio-oil from *Terminlina ivorensis* (Ti).

based on proximate analysis as follows [37]:

$$HHV_{dry} = 0.6042FC + 0.4083VM + 0.2442Ash + 0.4107MC - 25.20 \quad (11)$$

Mean Bias Error (MBE) was used in this study to calculate the percentage error between the experimental values of HHV and the computed values of HHV from the established correlations of each selected fuel woods. The MBE is given by [38];

$$MBE = \frac{1}{n} \left( \sum_{j=1}^n \frac{HHV_{mu} - HHV_{mp}}{HHV_{mp}} \times 100 \right) \quad (12)$$

Where subscripts *mu* and *mp* indicate the estimated value from the correlation models and the experimental data, respectively, and *n*, the number of samples.

#### 2.4. Gas Chromatography-Mass spectrometry (GC–MS) analysis

The fuel wood pyrolysis products were analyzed using a Shimadzu Gas Chromatograph Model QP2010 plus for the GC–MS analysis. With detector temperatures set at 220 and 290 °C, the beginning and ultimate temperatures were maintained for 3 and 10 min, respectively. The

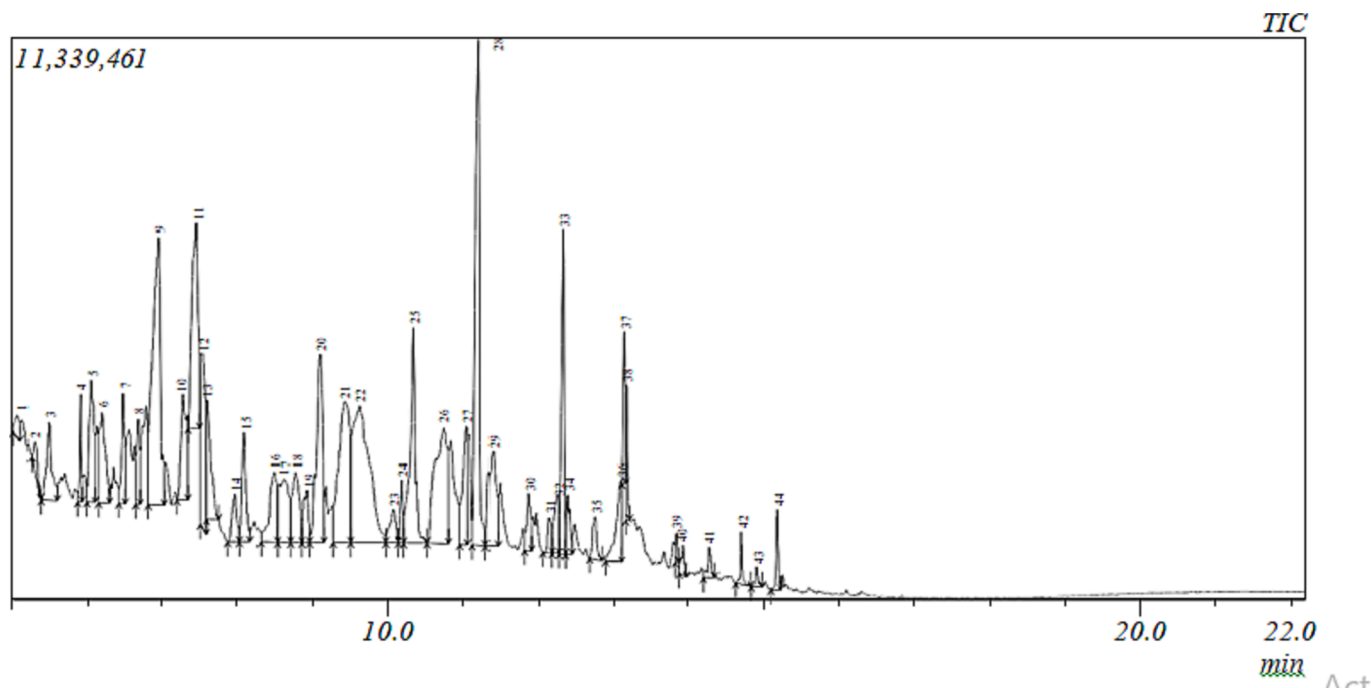


Fig. 9. GC-MS chromatogram for bio-oil from *Khaya Ivorensis* (Ki).

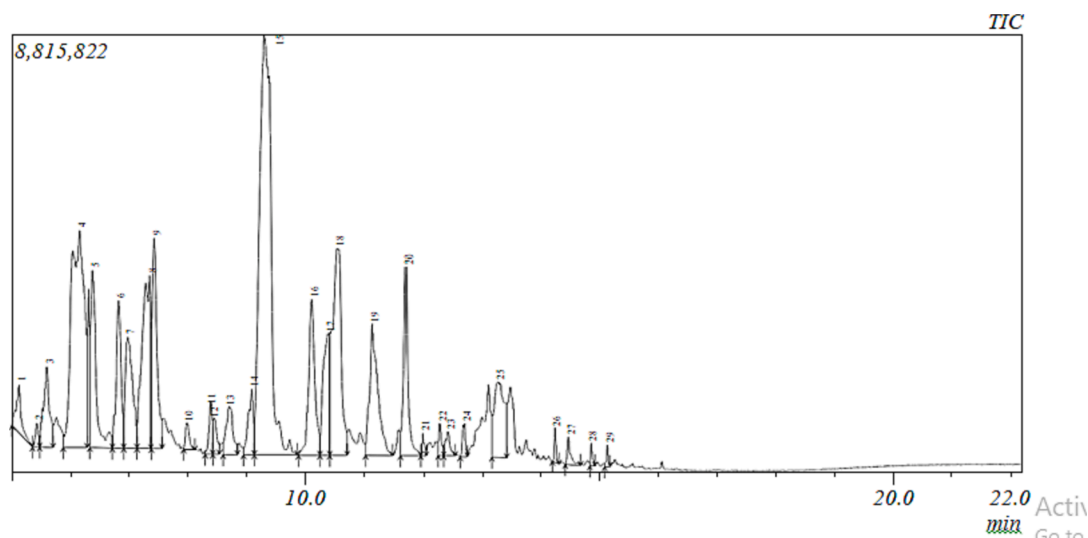


Fig. 10. GC-MS chromatogram for bio-oil from *Okoubaka ambrevillei* (Oa).

temperature in the column oven was set to change from 80 to 220 °C at a rate of 4 °C min<sup>-1</sup>. As a carrier gas, helium was used and pumped at a 1.5 mL min<sup>-1</sup> rate. One liter of the sample was injected in the slit mode (split ratio, 1:100). The gas chromatograph's internal data-handling algorithm was used to finish the quantification. The composition of the results is shown as a share of the total peak area [36].

### 3. Results and discussion

#### 3.1. Results of experimental analysis of HHVs of fuel wood samples

Using an oxygen bomb calorimeter, an experimental assessment of the higher heating value of the selected fuel wood samples was made. Table 1 shows the findings of an experimental investigation of the higher heating values of the five fuel wood samples that were selected for this study. The average values of HHVs for each wood sample

varies from 19.80 to 21.01 MJ/kg. Fuel wood sample - *Adansonia digitata* has the highest heating value of 21.01 MJ/kg while the fuel wood sample - *Okoubaka aubrevillei* has the least heating value of 19.80 MJ/kg. The result of this study is in agreement with that of Adekiigbe (2012) who investigated the heating value of five economic trees residue as a fuel for biomass heating system in Nigeria. The HHVs of the fuel woods ranged from 20 MJ/kg to 29 MJ/kg. Also, the HHVs of hardwood lignin and softwood lining evaluated by Demirbas (2006) are 24.9 MJ/kg and 26.6 MJ/kg, respectively. Moreover, the result of this study is favourably well compared to that of Akkaya (2013) and Cichy et al., (2016) who predicted the maximum Coal heating value to be 24.33 MJ/kg and 28.13 MJ/kg, respectively. The HHVs obtained experimentally from the selected fuelwoods in this present study are found to be sufficiently accurate to be used in an engineering thermal system. This result is significant if the biomass residues can be effectively converted to useful energy source. Considering the quantity available and the higher

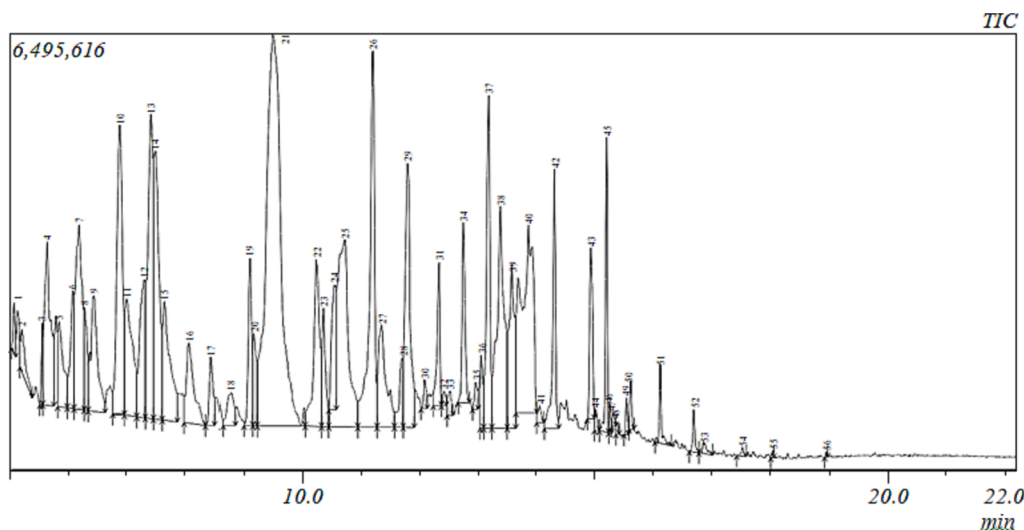


Fig. 11. GC-MS chromatogram for bio-oil from Mansonia altissima (Ma).

**Table 12**  
Validation of Ultimate and experimental heating values for raw samples.

Sawdust samples	HHV(MJ/kg) from Ultimate analysis	HHV (MJ/kg) Experimental Analysis	Bias (%)
Adansonia digitata	18.08	21.01	0.1395
Terminalia ivorensis	18.12	20.78	0.1280
Khaya ivorensis	18.25	20.75	0.1205
Mansonia altissima	18.16	19.95	0.0917
Okoubaka aubrevillei	18.37	19.80	0.0722
Average value of HHV(MJ/kg)	18.20	20.46	0.1105

**Table 13**  
Validation of Proximate and experimental heating values for raw samples.

Sawdust samples	HHV (MJ/kg) from Proximate analysis	HHV (MJ/kg) from Experimental analysis	Bias (%)
Adansonia digitata	18.11	21.01	0.1380
Terminalia ivorensis	18.49	20.78	0.1102
Khaya ivorensis	18.18	20.75	0.1239
Mansonia altissima	18.15	19.95	0.0902
Okoubaka aubrevillei	18.34	19.80	0.0737
Average value of HHV(MJ/kg)	18.25	20.46	0.1072

heating values of the fuelwood samples tested, Nigerian biomass wastes could be a dependable alternate source for thermal energy generation for industrial processing operations.

### 3.2. Results of proximate analysis of fuel wood samples

Table 2 presents the results of proximate analysis of the selected fuelwood samples. Table 2 compares the calculated and elemental analyzer-derived MC, VM, FCC, and AC values. The elemental analyzer-derived MC, VM, FCC and AC vary from 8.50 to 8.88 %; 75.22–75.90 %; 14.09–14.80 % and 1.08–1.88 %, respectively while the calculated values vary from 8.55 to 8.70 %; 75.01–75.46 %; 14.15–14.80 % and

**Table 14**  
Comparison of the HHVs of raw fuelwood samples to bio-oil yields.

Sawdust samples	Raw samples HHV (MJ/kg) from Proximate analysis	HHV (MJ/kg) from Experimental analysis	Bio-oil HHV (MJ/kg) from Experimental analysis
Adansonia digitata	18.11	21.01	30.77
Terminalia ivorensis	18.49	20.78	30.82
Khaya ivorensis	18.18	20.75	30.91
Mansonia altissima	18.15	19.95	30.77
Okoubaka aubrevillei	18.34	19.80	30.98
Average value of HHV(MJ/kg)	18.25	20.46	30.85

1.33–1.93 %, respectively. If the five selected waste saw-dust samples are further treated to greater pyrolysis temperatures, as shown in Table 2 with the average volatile matter of  $75.26 \pm 0.14$  and low ash content of  $1.64 \pm 0.16$ – $1.73$  %, there is possibility for a higher yield of bio-oil from the fuel wood samples. When compared to fixed carbon content available in wood residues (11–15 %), a significant percentage of fixed carbon (14.09–14.80 %) obtained in the wood samples for this study indicates high energy content potential in the wood samples [38,39]. The wood samples' low ash content (1.08–1.93 %) is a desirable characteristic. The mean value  $8.65 \pm 0.12$  for the moisture content obtained in this study is found reasonable [40].

### 3.3. Results of ultimate analysis of fuel wood samples

Table 3 shows the elemental composition of the selected fuelwood samples. From the ultimate analysis, the elemental composition varies as C (45.22–45.82 %), H (5.88–5.98 %), N (0.24–0.30 %), O (42.55–42.88 %) and S (0.01 %). As expected, carbon content has the highest chemical composition in the fuelwood samples investigated. High carbon content is expected to increase the heating value of woody biomass. The mean value of the carbon content obtained ( $45.54 \pm 0.02$ ) agreed with the reported results in the literature putting the carbon content of wood between 45 and 50 % and 0.01 % of Sulphur, confirming biomass energy is environmentally friendly [38–41].



Table 4 presents comparison of the HHVs obtained from experimental analysis to that obtained from correlations by ultimate analysis (Eq. (10)) and proximate analyses (equation (11)). From Table 4, the HHVs obtained from experimental analysis are greater than that obtained from correlations. Moreover, there is no significant difference in the values of HHVs obtained using ultimate analysis and proximal analysis. This suggests that both correlations based on ultimate and proximate analysis can be used to predict the HHVs of biomass fuel. The HHVs from experimental analysis vary from 19.80 to 21.01 MJ/kg while the HHVs from ultimate and proximate analyses vary from 18.36 to 18.56 MJ/kg and 18.12–18.37 MJ/kg, respectively. Higher energy content and amount of heat of combustion released using experimental method is more significance than analytical method. These results agree with that of Cantrell *et al.* [16], which confirmed that the average higher heating value wood residues varies between 18.30 and 21.90 MJ kg<sup>-1</sup>.

Less than 1 % ash of woody biomass typically has a heating value of around 20 MJ/kg, and an increase in each 1 % ash does not contribute to the overall heat released by combustion, even though components in the ash may be catalytic to the thermal decomposition, according to Jenkins *et al.* [18]. In this study, the ash contents for the selected fuelwood samples vary from 1.08 to 1.88 % with *Adansonia digitata* (1.88 %), *Terminalia ivorensis* (1.88 %), *Khaya ivorensis* (1.75 %), *Mansonia altissima* (1.60 %) and *Okoubaka aubrevillei* (1.08 %) these ash contents found in the sawdust samples make them acceptable for production of fuel and chemical. Lower ash content is expected to increase the heating value of woody biomass, and the value of ash content obtained are in agreement with [44–45] that put the ash content of woody biomass between 0.06 and 2.31 %. It was found in this study that positive correlation exists between the HHV and ash content. The regression analysis gave the R<sup>2</sup> of 0.9944. This is higher than the value of R<sup>2</sup> = 0.79 presented by Ogwo *et al.* [42] and Rawat *et al.* [43] with the simple regression equation given as:

$$HHV = 0.187AC + 18.135 \quad (13)$$

The selected fuel wood samples' higher heating value (HHV) and fixed carbon content (FCC) were correlated, and the results demonstrate that HHVs increase as fixed carbon content increase. This is consistent with the conclusions reached by Nasser and Aref [33]. The connection between the HHV and fixed carbon content determined by simple regression analysis in this study indicates that equation (14) best captures the trend of the data for all samples examined.

$$HHV = -0.158FCC + 20.72 \quad (14)$$

Higher FC content suggests longer combustion time, which increases HHV (the heat released when 1 kg of wood is burned) and demonstrates that the wood samples are rich in lignin, the substance in woods that produces heat [46–48].

### 3.4. Effect of temperature Variation on pyrolysis products yields

The effects of temperature variation (450–600 °C) on the product yields of the five selected wood samples are presented in Table 5 and Figs. 4–7. With increase in temperature, there is increase in bio-oil and bio-gas yields while the bio-char yield decrease for all the fuel wood samples. Maximum bio-oil yield was produced at temperature of 500 °C for all the fuel wood samples. The maximum bio-oil yield produced from *Adansonia digitata* (Ad), *Terminalia ivorensis*(Ti), *Khaya ivorensis* (Ki), *Mansonia altissima*(Ma) and *Okoubaka aubrevillei* (Oa) is 44.75 wt%, 43.80 wt%, 42.90 wt%, 43.95 wt% and 44.01 wt%, respectively. The maximum bio-gas was produced at highest temperature of 600 °C and the value varies from 28.6 wt% to 29.45 wt%. *Okoubaka aubrevillei* wood sample produced the highest bio-gas (29.45 wt%) while *Adansonia digitata* produced the least bio-gas (28.6 wt%). As the pyrolysis temperature increases from 450 °C to 600 °C, there is substantial decrease in the bio-char yield. Result of this study is in agreement with that of Giuffre *et al.*, 2017; Guedes *et al.* 2018 and Chuxia *et al.*, 2019.

### 3.5. Fuel properties and chemical composition of bio-oil yield

Table 6 presents the thermophysical properties and chemical composition of the bio-oil yields produced at 500 °C from *Adansonia digitata* (Ad), *Terminalia ivorensis* (Ti), *Khaya ivorensis* (Ki), *Mansonia altissima* (Ma) and *Okoubaka aubrevillei* (Oa). The elemental analysis of the bio-oil yield showed the following chemical composition: Carbon (Ad (70.99 wt%), Ti (70.90 wt%), Ki (70.16 wt%), Ma (70.85 wt%) and Oa (69.95 wt%), Hydrogen (Ad (13.40 wt%), Ti (13.51 wt%), Ki (14.00 wt%), Ma (13.45 wt%) and Oa (14.10 wt%); Nitrogen (Ad (0.54 wt%), Ti (0.55 wt%), Ki (0.84 wt%), Ma (0.75 wt%) and Oa (0.95 wt%); Oxygen (Ad (15.01 wt%), Ti (14.97 wt%), Ki (14.95 wt%), Ma (14.89 wt%) and Oa (14.94 wt%), and sulfur (Ad (0.06 wt%), Ti (0.07 wt%), Ki (0.05 wt %), Ma (0.06 wt%) and Oa (0.06 wt%). The HHVs of the bio-oil yields are respectively 30.77, 30.32, 30.91, 30.77 and 30.98 MJ/kg for *Adansonia digitata* (Ad), *Terminalia ivorensis*(Ti), *Khaya ivorensis* (Ki), *Mansonia altissima*(Ma)and *Okoubaka aubrevillei*(Oa). This study's low sulfur content (0.05 %), which is within the same range of values as that reported by Oyebanji *et al.* [14], Chukwunke *et al.* [15], and Okeunle *et al.* [16], implies a low pollutant influence on the environment. Lower pour points indicate the temperature at which a bio-oil ceases to flow due to the development of wax crystals that enhance its viscosity, but lower flash points indicate good flammability and volatility of the oil. The lowest flash point (79) and pour point (-7) of the bio-oil yield from this study are favorably comparable to the flash point (75) and pour point (-2) of diesel, which are very close to the range of flammability. The pH, density, viscosity, and API gravity coincide with the bio-oil yield from biomass reported by [49–51] while density at 40 °C (0.98 g/cm<sup>3</sup>) have a small variation from that of diesel (0.78g/cm<sup>3</sup>), fuel oil (0.9101 g/cm<sup>3</sup>) and furnace oil (0.92 g/cm<sup>3</sup>) but has close value to heavy fuel oil (0.9888 g/cm<sup>3</sup>). The pH values of the bio-oil yields (4.70–4.82) fall a little below that of diesel (5.5–8.0). The HHVs of the bio-oil yields from this study vary from 30.77 to 30.98 MJ/kg and are a bit lower than that of Diesel and gasoline (42–46 MJ/kg and 44–46 MJ/kg, respectively) [52–53]. Notwithstanding, the bio-oil yields can serve as alternative fuel to the fossil fuel in industrial operations.

### 3.6. Gas chromatography–Mass spectrometry analysis of the Bio-oils produced

The bio-oil yields from the selected wood samples were subjected to gas chromatography (GC) and gas chromatography-mass spectrometry (GC–MS) analyses in order to identify the various bio-fuel components in the bio-oil yields in detail. The results of the analysis are shown in Tables 7 to 11 for *Adansonia digital* (Ad), *Terminalia ivorensis* (Ti), *Khaya ivorensis* (Ki), and *Okoubaka* (Oa), respectively. The retention indices of identified components were established based on their retention times in order to confirm the identification. The retention indices of the composition from the wood dusts are presented in Figs. 7 to 11, respectively. Both the GC and GC–MS analyses were carried out as presented in Oyebanji *et al.* [36]. GC–MS analysis of bio-oil yields at 500 °C identified the presence of Thirty-five compounds in Ad (with Oleic Acid has the highest composition (19 %) and this is followed by trans-2-Octedecaden-1-01 (15 %)); Thirty-seven compounds in Ti (having Oleic Acid with highest composition (20 %) and followed by cis-10-Pentadecent-1-01 (12 %)); Thirty-three compounds in Ki (with 2-hydroxyl-3 methyl-2-cyclopentene-1-one has highest composition (9.5 %) followed by Phenol (9.0 %)); Twenty-nine compounds in Ma (with Catechol has the highest composition (10.4 %) and followed by Mequinol (10.7 %)) and Thirty-five compounds in Oa (has 35-compounds with 2-Methyl-Phenol has highest composition (10.8 %) and followed by 2-hydroxymethyl-cyclohexamore (9.6 %)). The presence of phenolic, ketone, fatty acid, ester, and alcohol compounds in the sawdust samples is evidence that they have chemical and fuel compositions suitable for use as feedstocks in the pharmaceutical and dye industries as well as for the production of biodiesel for internal

combustion engines. The chemical compositions found in the study are consistent with the findings of earlier investigations [54–58].

### 3.7. Validation of results

#### 3.7.1. Performance criteria for error computation

There are several procedures to calculate the quality of a model; however, MSE, MAPE and R are the most common error indicators

(i) The mean square error (MSE) is the average square error between the network output and the desired output. MSE is computed as:

$$MSE = \frac{1}{n} \sum_{j=1}^n (P_{Forecast} - P_{actual})^2 \quad (15)$$

(ii) The mean absolute percentage error (MAPE) is calculated by comparing the relative error in the prediction to the actual value of the variable term by term and is defined as:

$$MAPE = \frac{1}{n} \sum_{j=1}^n \frac{(P_{Forecast} - P_{actual})}{P_{actual}} \times 100 \quad (16)$$

(iii) Correlation Coefficient (R) describes degrees or collinearity between simulated and measured data, ranging from  $-1$  to  $1$ .

Table 12 and 13 present the estimated and experimental HHV values and it can be seen that the average experimental HHV (20.46 MJ/kg) is higher than the calculated HHV (18.20–18.25 MJ/kg). Positive bias error values were revealed in all the samples which imply that the predicted values are close to the actual values. From this study, the wood sample *Adansonia digitata* has the highest HHV (21.01 MJ/kg) while *Okoubaka aubrevillei* has the least HHV (19.80 MJ/kg).

Table 14 presents comparison of the HHVs of the raw fuel wood samples and the bio-oil yields from each fuel sample. The HHVs of bio-oil yields vary from 30.77 to 30.98 MJ/kg and are higher than the HHVs of the raw fuel woods (19.80–21.01 MJ/kg) but are a bit lower than that of diesel and gasoline (42–46 MJ/kg and 44–46 MJ/kg, respectively). Notwithstanding, the bio-oil yields can serve as alternative fuel to the fossil fuel in industrial operations such as in boiler engines. This is an improvement on fossil fuels and is also considerably more environmentally friendly [59].

## 4. Conclusion

In this study, the heating values and chemical composition of five selected fuel wood samples have been investigated experimentally and analytically. The selected fuel wood samples are *Adansonia digitata*, *Terminalia ivorensis*, *Khaya ivorensis*, *Mansonia altissima* and *Okoubaka aubrevillei* collected from Ota, South–West, Nigeria. The proximate analysis shows that the Ash Content, Fixed Carbon Content and Volatile Matter obtained from the selected sawdust vary from: 1.08–1.93 %, 14.09–14.80 % and 74.90–75.80 %, respectively. The high percentage of volatile matter and fixed carbon are responsible for the appreciable HHVs of the samples studied. The experimental result gave HHV for the fuel wood samples in the range of 19.80–21.10 MJ/kg while the correlation equation based on ultimate and proximate analyses gave HHVs in the ranges of 18.36–18.56 MJ/kg and 18.12–18.37 MJ/kg, respectively. Meanwhile, the HHVs of bio-oil samples studied at 500 °C are 30.77, 30.32, 30.91, 30.77, and 30.98 MJ/kg for *Adansonia digitata* (Ad), *Terminalia ivorensis*(Ti), *Khaya ivorensis* (Ki), *Mansonia altissima* (Ma) and *Okoubaka aubrevillei*(Oa), respectively. Result of this study is in agreement with that of Parikh et al. [34] and Sheng and Azevedo [35]. Additionally, this study's GC–MS analysis showed that the levels of phenolic compounds, oleic acid, aromatic hydrocarbons, and nitrogen-containing substances in the five analyzed samples of sawdust varied according to their bio-oil content. Its potential use as a biofuel and a raw material in the chemical industries would be improved by analysis of the chemical compositions of bio-oil generated from woody biomass. Moreover, the results of the GC–MS analysis will help in establishing the stability, fuel-suitability, toxicity, and potential as a source of chemical

components of the bio-oil. We can draw the conclusion that the selected wood residues (sawdust) have the potential to be renewable resources for the production of biofuels and can also be used as a raw material for chemical industries. Based on the result of this study, it is recommended that the Federal Government of Nigeria, policy makers and stakeholders in energy sector encourage researches in production of biofuels from the wood residues studied through adequate funding. Researches in this direction could assist in improving access to clean and cheap energy (SDG 7).

### CRedit authorship contribution statement

Joseph A. Oyebanji: . Sunday O. Oyedepo: Supervision. Olawumi T. Oyebanji: Investigation. Araoyinbo O. Alaba: . Oluwaseun Kilanko: . Joseph O. Dirisu: . Bahaa Saleh: .

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

The authors do not have permission to share data.

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