Production and Phytochemical Analysis of Bio-based oil obtained from Nigerian *Bambusa vulgaris*

Amalate Ann Obuebite,[1*] and Obumneme Onyeka Okwonna [2]

[*1]*Department of Petroleum Engineering, Niger Delta University, PMB 071, Wilberforce Island, Bayelsa State, Nigeria.*
[2]*Department of Chemical Engineering, University of Port Harcourt, PMB 5323, Port Harcourt, Rivers State, Nigeria.*

Abstract: *Bambusa vulgaris was used as a feedstock in this study to create pyrolysis liquid (bio-oil) utilizing pyrolysis technology. A reactor heated the bamboo to 320°C over the course of 240 minutes. The pyrolysis data demonstrate that as temperature rises, more product is produced. The characteristics of the bio-oil was studied experimentally. The process of pyrolysis was conducted at high temperature of 320°Cafter which the volume of the resultant product was determined. Gas chromatography (GC) analysis of the oil revealed the presence of over 16 distinct chemical compounds with multifunctional groups, including generated paraffins, isoparaffins, olefins, naphthalene, aromatics, and polyaromatics. Fluoranthene, which makes up most of the bio-oil has a high ratio of 211.328.Phytochemical analysis of Nigerian bamboo-based bio-oil shows a high composition of flavonoids (phenols), carboxylic acids, and ketones. The result indicates that the created biofuel may be utilized as substitute to diesel as its (produced biooil) shares similar physical attributes with diesel.*

Keywords*: Bamboo, Pyrolysis, Chromatography, biomass.*

I. Introduction

A sustainable, organic source of renewable or green energy is *Bambusa vulgaris*, commonly referred to as Bamboo in Nigeria. It is the only bio-based source capable of generating fuels in the different phasesas opposed to other renewable energy source[1]. Pyrolysis is a potential method for turning organic materials into solid, gaseous, and liquid compounds by heat breakdown in the absence of oxygen, resulting in the production of fuel. A pyrolysis technique known as conventional or slow pyrolysis typically produces charcoal. Additionally, the initial stage of gasification is pyrolysis. Rapid pyrolysis is a modified pyrolysis technique that has recently been employed to liquefy the production of bio-oil [2]. The fundamental properties of rapid pyrolysis to produce bio-oil include extremely high heat transfer and heating rates at 500 °C controlled temperature, vapor phase temperatures within 400 ˚C to 450 °C, relatively short vapor retention time of about twoseconds [3].

Perennial bamboo belongsto the Poaceae grass family. A woody, hollow, spherical, straight, and jointed stem gives it away. Bamboo generally grows quickly, with some species reaching heights of up to 30 centimeters and others reaching 91 centimeters daily at a rate of about 4 centimeters every hour. Depending on the species, the height range for most bamboo varieties planted in the United States is between 10 and 15 cm. A significant woody grass, bamboo is used for a variety of purposes including the manufacture of biofuels, furniture, animal feed, and carbon (C) sequestration. In Nigeria, Bambusa vulgaris is available and widely distributed in southern region of Nigeria. Ogunwusi and Onwualu [4] claim that several issues prevent the industrialization of bamboo, impeding its potential for generating money and lowering property rights in developing nations like Nigeria.

According to Ladapo [5], there is a pervasive dearth of knowledge among policymakers regarding the industrial potential of bamboo. The national forestry strategy that includes bamboo pays little to no attention to its development. Contrary to China's bamboo industry, which is known to be successful, this neglect has led to the underdevelopment and underutilization of the enormous potential of this prolific, widely available plant in Nigeria. As a result, bamboo cannot be developed to the point where it might feasibly serve as a source of raw materials or as a market for the export of bamboo goods to generate foreign cash [4]. Atanda [10] reported on the environmental benefits associated with the use of bamboo in Nigeria. Several studies [11,12] have reported the use of this versatile raw material in diverse industry from construction, textile, pharmaceutical, interior décor, paper production and recently the energy industry as a possible energy source.

Nonrenewable sources have been and remains a driving source of energy production and consumption globally [8] despite the increasing concerns regarding its continuous use. The first drawback is its scarcity and unsustainability. Secondly, since it emits too many greenhouse gases, its usage has adverse impact on the environment and animal life with an increasing rate of carbon dioxide (CO_2) emissions [9]. It is crucial to develop non-fossil fuel sources (renewable sources) to lower CO_2 emissions. Biomass is the only source of liquid, solid, and gaseous carbon fuel, unlike other renewable energies (such as wind, solar, etc.). There are various thermochemical processes that enables the transformation of biomass sources into usableenergy such as pyrolysis process. Rapid pyrolysis is thought to be a good option for producing liquid bio-oil with a high yield that can be transported and stored while also having the potential to be used as an energy source.This research reports the devolatilization process ofNigerian bamboo to produce a more sustainablebiofuel. The study will provide an alternative energy source from Nigeria's bamboo biofuel production.

II. Materials and Methods

2.1 Materials

Nigerian bamboo waste was gathered at Etche LGA, 5.0632 N, 7.0498 E in Rivers State. Apparatus used include Viscometer, Steel reactors, Thermocouple, pH strips, Screw feeder,Condensers, Coolant water at 25 °C, Insulators, measuring cylinders for receiving oil, biomass feeder and a heating furnace which served as the heat medium. To appropriately condense the acquired product, a constructed steel reactor with an attached funnel coupled to a glass condenser was thoroughly insulated. The Nigerian bamboospecie used in this study is shown in Figure 1.

Figure 1: Sawn Nigerian bamboo

2.2 Experimental Procedure

The sample (bamboo waste) was gathered from an open dump, dried, and chopped into smaller pieces of fixed dimensions; 15 mm wide by 15 mm thick and 108 mm long. Following that, 500 g of the bamboo is weighed and fed into the reactor through the reactor funnel while making sure the hopper is completely covered. Before the experiment begins, standard measures must be taken to make sure there are no leaks. With the absent of a catalyst, the pyrolysis process starts, and the heater is turned on until just the last drop of oil is left in the graduated cylinder. Water at 25 °C is used to cool the condensate from the reactor in the glass condenser, which is intimately attached to the reactor. Figure 2 shows a schematic diagram of the pyrolysis set up. To determine the impact of temperature on the products generated, pyrolysis was subsequently done at varied temperatures ranging from 25 °C to 320 °C, respectively. The amount of fuel oil generated was observed in relation to temperature and time. The resultant product from the pyrolysis process was subjected to further evaluation to determine its phytochemical composition and properties

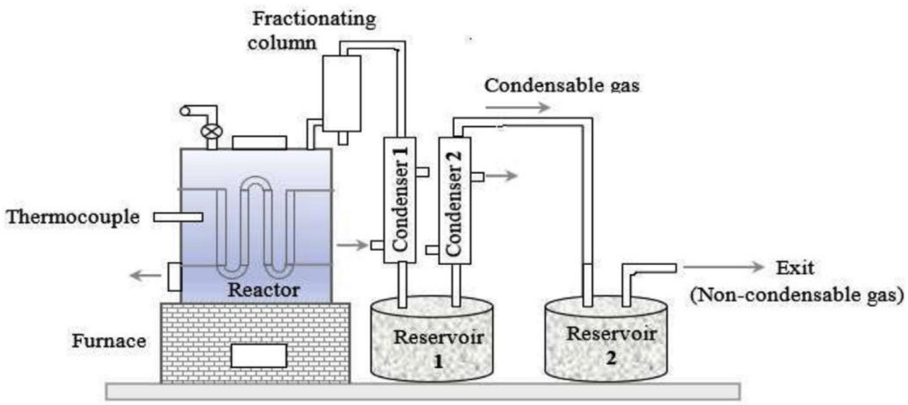

Figure 2: Schematic diagram of Pyrolysis process setup [14].

2.3 Bio-oil analysis

The physio-chemical properties of the produced oil studied include the following

Oil density: The density of crude oil is defined as mass per volume. This occurs less frequently for kilograms/m^3 and more frequently for oils in grams/ml. Bitumen and other fuel oils may have densities higher than 1.0 g/ml, all new crude oils and most fuel oils have densities below 1.0 g/ml. The density of the oil produced was estimated using the expression in equation 2.

Density= M/V

Density of oil $= \frac{mass\ \ of\ oil - mass\ \ of\ empty\ \ pycnometer}{Volume\ \ of\ oil}$(2)

Density water $= \frac{mass\ \ of\ water\ - mass\ of\ empty\ \ pynometer}{Volume\ \ of\ oil}$ (2)

Specific gravity: The weight or density of a liquid is compared to water using its specific gravity, which is sometimes referred to as relative density. A unitless measurement, specific gravity is the ratio of the weight or density of a particular fluid to the weight or density of water. Given that density changes with temperature, temperature was considered while calculating specific gravity using the expression in equation 3.

Specific gravity= $\frac{\rho_{oil}}{\rho_{water}}$ (3)

API gravity: A petroleum fluid's relative weight to water is determined using the American Petroleum Institute (API) gravity scale. An API gravity of higher than 10 is light, whilst a value less than 10 is considered heavy. It is applied to gauge how dense different petroleum liquids are. Specific gravity (Spgr.) and gravity from the American Petroleum Institute are two densities widely employed in relation to oil characteristics (API).

The API gravity is evaluated using equation 4:

API gravity $= \frac{141.5}{SG} - 131.5$ (4)

pH measurement: pH is a measure of the acidity or alkalinity of a solution. The pH value of a solution shows the amount of hydrogen ions (H+) present, thus, the higher the concentration of H+, the more acidic the solution and the lower the pH.To determine the pH of bio-oil, the tip of the pH strip is dipped in the bio-oil for a few seconds, thereafter the strip is removed, the obtained color of the pH strip is correlated to the provided color chart and the value is then read.

Viscosity: Is a measure of a substance's capacity to resist movement under an applied force, expressed in centipoise (Cp) or millipascal seconds (mPa-s). A viscometer was employed to ascertain the bio-oil viscosity at ambient temperature.

Flash point: Bio-oil is heated in a container to determine its flash point, which is then measured experimentally by placing a tiny flame slightly over the surface of the liquid Over time, a flash or ignition occurs, and the corresponding temperature is referred to as flash point. With the aid of "pensky martens" flash point measurement equipment, flash point was calculated.

Pour point: The temperature below which a liquid loses its ability to flow is known as the pour point of that liquid. For measuring the pour point of biological oils, ASTM D97Standard test procedure is utilized.

Volatile matter: Volatile matter is an unstable matter that quickly vaporizes when the right conditions are met resulting in a drop in mass. The volatile matter of the bio-oil was estimated using eq. (6)

$$volatile\ matter = \frac{final\ weig\ ht - initial\ \ weig\ ht}{final\ \ weig\ ht} \times 100 \qquad (6)$$

Fixed carbon: After the carbon particles are heated and the volatiles are released, fixed carbon is the flammable solid residue that is left over. To ascertain the amount of fixed carbon in the product, the expression in equation (7) was used.

$$\text{Fixed carbon} = \text{mass of oil volume oil} - moisture\ content \times volatile\ matte \qquad (7)$$

Chemical composition: By using gas chromatography (GC) (HP CHEM1 PAH-2) and helium as the carrier gas at a flow rate of 1.0 mL min-1, temperature of 270 °C, and pump volume of 1 L, the chemical composition of the produced bio-oil was examined. The analysis start temperature was 40 °C, the heating rate was 1.5 °C min-1 at 46 °C, and gradually increased to 4 °C min-1 until the end temperature of 209 °C was attained. Equation (8) was used to compute the production of both biochar and bio-oil:

Yield (%) = (product weight/dry biomass weight) × 100% mass (8)

III. Results and Discussion

3.1 Pyrolysis Results

The effect of heating time and temperature on the products obtained from pyrolysis of bamboo is shown in Figure 3. At temperatures of 20^{o}C to 100^{o}C and time between 0 to 10minutes, no product was formed from the pyrolysis process.At an increased temperature of 95^{o}C and a reaction time of 7 minutes, the first tiny drop of product was observed. After areaction temperature of 130^{o}C, and reaction time of 20 minutes, the volume of product formed from the pyrolysis process was 90ml. Atreaction temperatures between 160^{o}C to 210^{o}C and time 30 to 90 minutes, the volume of product formed was 276ml. At higher temperatures between 215^{o}C to 320^{o}C and time between 120 to 240minutes, the volume of product formed was 370ml using a total mass of500g of bamboo. The mass of bamboo char formed by the pyrolysis process was 140g.

As shown in Figure 3, the product yield is directly proportional to the heating time. It was also observed that as the temperature of the reaction increased from 100^{o}Cto 200^{o}C, the volume of the product also increased. More so, as the heating time increased, from 10 minutes to 150 minutes, the product yield also increased. The product yield at temperatures between 130 to 320^{o}C was analyzed because at this temperature, all the bio-oil had been extracted from the bamboo.

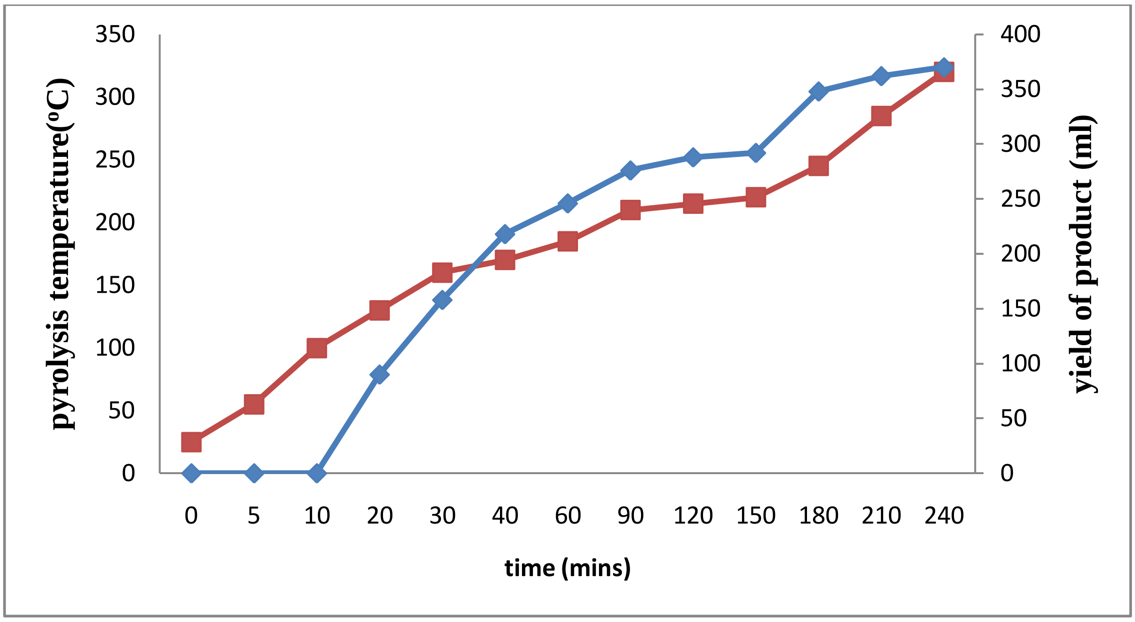

Figure3: Effect of temperature and time on product yield

3.2 Characteristics of the Bio-oil

According to the American Standard for Test Methods and the Standard Table for Fuel Oils, Table 1 outlines the physio-chemical characteristics of the fuel oil obtained. Clearly, the produced bamboo bio-oil has a lower moisture content (7.2%) than wood biomass, which typically has a moisture level between 15 and 30% as noted by Mohan *et al*. [2]. Produced bio-oil has a specific gravity of (0.86), while bio-oil made from wood biomass typically has a specific gravity of between (0.80 and 1.21) [2]. The bio-oil generated from bamboo has an API gravity of (31), which denotes that it is a medium oil at 15 °C. The level of alkalinity and acidity of bamboo bio-oil is (5.3) but pH values between 2.3 and 2.9 is linked to most biomass-based oils, only a few biomass materials, such as almond shells (5.5) and rice straw (4.2), have pH values above 3.0 [2]. Since a boiler might corrode if the pH level is too low, it is crucial for boiler functioning. The generated bio-oil from bamboo had a viscosity of 19.83 mm2.s-1 at 25 °C, which was comparatively greater than that of other biomass sources. An acceptable pour point of (9 °C) was obtained as seen in Table 1. Crude oils having a larger percentage of plant material typically have a higher paraffin content, which is generally correlated with a high pour point (ASTM D5949, 2003). Bio-oil has a flash point of (32°C), which is similar to the flash point of heavy crude oil. The amount of carbon in the generated bio-oil was 0.6 and 86.56 percent fixed, respectively.

Table 1: Physio-chemical Properties of the Produced Bio-Oil

Physical properties	Quantity	Unit
Density at 15°C	0.86	g/cm^3
Specific gravity	0.86	-
API gravityat 15°C	31	-
Viscosity	19.83	$mm^2.S^{-1}$
pH	5.3	-
Pour Point	9	°C
Flash Point	32	°C
Volatile matter	0.6	%
Fixed carbon	86.56	%

3.3 Yields of pyrolysis

Interestingly, asides the produced bio-oil, the process resulted in the production of bio- charcoal and non-condensable gas as byproducts. The effectiveness of the three products is shown in Table 2 at 320 °C for pyrolysis. The output of bio-oil also reached 28%. The output of bamboo biochar is 140 g, while the quantity of non-condensable gas is 271.93g.

Table 2: Product yield of pyrolysis process

Mass of bamboo(g)	Mass of liquid(g)	Mass of char(g)	Mass of non-condensable(g)
500	88.07	140	271.93

3.4 Composition analysis of bio-oils

Table 3 provides the composition of bamboo bio-oil as determined by GC analysis. For Nigerian bamboo bio-oil, a total of 16 compounds were found, principal amongst them are phenols, flavonoids, carboxylic acids, and ketones. This implies that complex combinations with multifunctional groups are present in greasy liquids. Based on the analysis by Zhang *et al*. [6], their results are in line with the ratio of the various functional groups in the bamboo bio-oil seen in Table 3. According to chromatographic study, bamboo waste is pyrolyzed in Nigeria at temperatures as high as 320°C, producing paraffins, isoparaffins, olefins, naphthalenes, aromatics, and polyaromatics with carbon atoms ranging from C3 to C34 with high concentrations of C6-C23. This suggests that the fuel oil generated is a mixture of several fuels, such as diesel (C14-C20), kerosene (C10-C16), and gasoline (C5-C10). Due to the presence of branched alkanes, alkenes, and aromatic hydrocarbons, the biodiesel will have good anti-knock properties [7]. Gas chromatography (GC) (HP CHEM1 PAH-2) was then used to evaluate the oil to identify its heavy aliphatic hydrocarbons and polyaromatics. The presence of heavy hydrocarbons in bio-oil (C11–C38) is seen in Figure4. When compared to the concentration of other heavy fats, the bio-oil (C11-C16) concentration with retention period from 4,351 min. to 21,356 min. was high. N-nonadecane, C19, was also present in large amounts. The low concentration of C32-C38 in comparison to other fats shows that all bamboo cellulose was converted to oil above 450 ˚C. The maximum concentration of the polyaromatics in bio-oil determined by gas chromatography (GC) (HP CHEM1 PAH-2) fluoranthene is shown in Table 3 with Pyrene and dibenz(a,h)anthracene having concentrations that are relatively low.

Table 3: Phytochemical analysis obtained from GC evaluation of the produced biomass-based oil

RetTime(min)	Area	Amt/Area	Amount(ppm)	Name
4.351	-	-	-	solvent peak
6.354	49.43186	4.43298	128.51998	Naphthalene
6.553	82.42863	1.71259	54.74163	Acenaphthylene
6.635	44.42140	9.24080	98.15203	Acenaphthene
7.562	63.83014	2.81242	86.00139	Fluorine
9.327	57.72168	5.83108	41.10715	Phenanthrene
9.402	71.83056	1.49301	35.51661	anthracene
11.940	56.52935	8.27159	211.32820	Fluoranthene
12.232	73.15726	4.1752115.21923		Pyrene
15.138	52.80721	2.8113622.8193		Benzo(a)Anthracene
15.282	55.59312	9.82049	48.26031	Chrysene
17.598	63.83269	4.41248	25.75163	Benzo(b)Fluoranthene
18.105	79.41257	1.63114118.80974		Benzo(k)Fluoranthene
20.249	58.52138	6.8215392.82916		Benzo (a) Pyrene
20.580	66.93025	8.82194	29.10283	Indeno(1,2,3 cd)pyrene
20.689	42.25874	2.10025	16.82561	Dibenzo(a,h) anthracene
21.356	-	-	-	Benzo (g,h,i)perylene

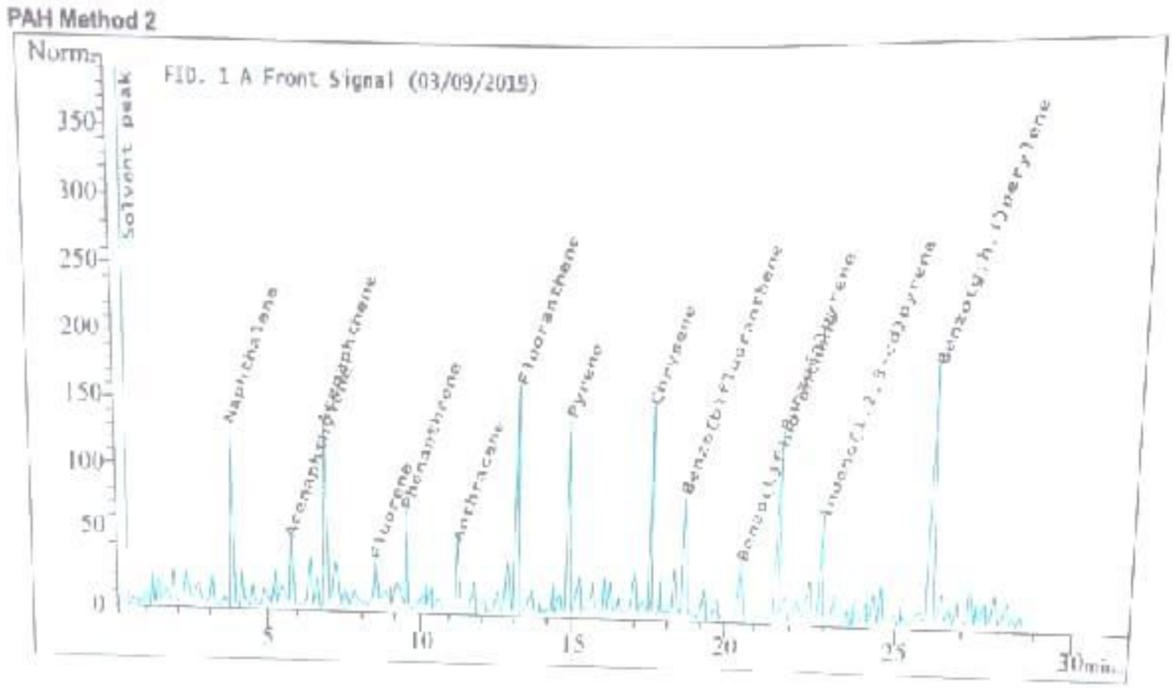

Figure4: Chromatography of heavy aliphatics in fuel oils produced up to 320℃(GC) (HP CHEM1 PAH-2)

3.5 Comparative analysisof the Produced Bio-Oil and Gas Oil (Diesel)

The generated fuel oil's physical characteristics are displayed in Table 4 according to American Standard Test Methods and Standard Tables for Bio-oil. When compared to other oils, the qualities of the fuel oil generated are favorable when compared to petroleum (diesel) (a type of petroleum for automobiles). It is utilized in agricultural and construction machines as well as diesel-fueled automobiles. It has a strong diesel and flammable gasoline odor. Table 4 compares the characteristics of fuel oils generated at temperatures up to 320 °C in correlation with diesel oil properties obtained from Demirbas [13].

Table 4: Variation in the physiochemical properties of the produced bio-oil and diesel oil

Properties	Unit	Produced bio-oil	Gas oil(diesel)
API	-	31	30-35
Density at 15oC	g/cm^3	0.86	0.84-0.89
Pour point	℃	9	3-9
Flash point	℃	32	35-50
Physical state	-	Liquid	Liquid
Flammability -	-	Flammable@Room Temp	Flammable
Colour	-	Brownish	Light Red
Constituent	-	Paraffins Isoparaffins Olefins Naphthlenes Aromatics	Paraffins Isoparaffins Naphthlenes Aromatics And Polyaromatics

IV. Conclusion

Bamboo biomass from Nigeria was gathered, sawn, and pyrolyzed in a reactor for this study. At a pyrolysis temperature of 320°C, bio-oil was produced from the bamboo biomass. Experimental results indicated a directly proportional relationship between the heating temperature and the product's yield. However, more than 16 distinct chemical compounds with multifunctional groups were discovered when the bio-oil was investigated by GC. With a high ratio of 211,32820, fluoroanthene is the primary chemical in the bio-oil. The well-distributed phenols, flavonoids, carboxylic acids, and ketones are the major constituents of Nigerian bamboo bio-oil. In addition to the bio-oil that was produced, the bio charcoal and non-condensable gas were produced as byproducts.These products have a lot of potential. Physiochemical results indicate that the biofuel obtained is a likely substitute to diesel in a diesel-powered engine since the physical qualities of the generated fuel oil are superior to gas oil (diesel). Similarly, petroleum products such as kerosene, gasoline etc. may be produced under low temperature pyrolysis. This bamboo pyrolysis from Nigeria has demonstrated that bamboo is an effective biomass for producing bio-oil and that bamboo bio-oil may be used as a substitute energy source. Pyrolysis up to 320°C achieves a 28% conversion rate in catalyst-free pyrolysis.

References

[1] Bridgwater, A. V., & Peacocke, G. V. C. (2000). Fast pyrolysis processes for biomass. *Renewable and sustainable energy reviews*, *4*(1), 1-73.

[2] Mohan, D., Pittman Jr, C. U., & Steele, P. H. (2006). Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy & fuels*, *20*(3), 848-889.

[3] Bridgwater, A. V. (2003). Renewable fuels and chemicals by thermal processing of biomass. *Chemical engineering journal*, *91*(2-3), 87-102.

[4] Ogunwusi, A., &Onwualu, A. (2013). Prospects for multi-functional utilisation of bamboo in Nigeria. *Prospects*, *3*(8).

[5] Ladapo, H. L., Oyegoke, O. O., & Bello, R. O. (2017). Utilization of vast Nigeria’s bamboo resources for economic growth: A review. *Journal of Research in Forestry, Wildlife and Environment*, *9*(2), 29-35.

[6] Dong, Q., Zhang, S., Zhang, L., Ding, K., & Xiong, Y. (2015). Effects of four types of dilute acid washingon moso bamboo pyrolysis using Py–GC/MS. *Bioresource technology*, *185*, 62-69.

[7] El-Gendy, N. S., & Nassar, H. M. N. (2018). *Biodiesel sulfurization in petroleum refining*. John Wiley & Sons.

[8] Yildiz, I. (2018). Fossil Fuels. *Comprehensive Energy Systems, 1,* 521- 567.

[9] Cheng, L., Adhikari, S., Wang, Z., Ding, Y. (2015). Characterization of bamboo species at different ages and bio-oil production. *Journal of Analytical and Applied Pyrolysis*, 116, 215-222.

[10] Atanda, J.O. (2015). Environmental Impacts of Bamboo as a Substitute Constructional Material in Nigeria. *Case Studies in Construction Materials*, 3, 33-39.

[11] Xiang, Z. (2010). China’s Bamboo Industry Booms for Greener Economy. China English News, Global Edition.

[12] Yu, Y., Tian, G., Wamg, H.K., Fei, B.H., Wan, G. (2011). Mechanical characterization of single bamboo fibers and nanoindentation and microtensile technique. Holzforschung 65 (1), 113-119.

[13] Demirbas, A. (2008). Biodiesel: A Realistic Fuel Alternative for Diesel Engines. 1st Edition, Springer, pp. 141-160.

[14] Aziz, M.A., Rahman, M. A., Molla, H. (2018). Design,fabricationandperformancetestofafixedbedbatchtypepyrolysisplantwithscraptireinBangladesh. *Journal of Radiation Research and Applied Science*,https://doi.org/10.1016/j.jrras.2018.05.001.