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Research Article

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Danta Wood Saw Dust Characterizations for Pyrolysis Oil Production potentials

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Abstract Researchers led by rise in energy demands, exhausting fossil fuel resources and consequent environmental management problems, are in search for solution, in recent times. Fast pyrolysis process has commanded most intensive interest for solving the above research problems amongst other alternative fuel technologies. In this present work, DWSD feedstock characterization was carried out via proximate, ultimate, chemical compositions and FTIRS analyses and it was observed that DWSD has the following properties: the proximate analysis indicates high volatile (83.2 wt. %), low moisture (8.2 wt. %),) and low ash (wt. %), contents; the ultimate analysis indicates C,H,N,O content values as 50.50,5.82,0.03 and 43.05% respectively; the chemical composition found cellulose & hemicellulose content was 56.60 wt. %,lignin content, 41.00 wt. %; while the FTIRS shows alkanes, alkenes, aromatics, ketones, alcohol, ether, aldehydes, carboxylic acids, etc contents. Thus, feedstock characterization results show that DWSD sample has great potentials for use in production of pyrolysis oil.

Keywords proximate, ultimate, chemical compositions and FTIRS

1. Introduction

Energy crises and environmental challenges have attracted enormous interests globally among researchers in recent years in order to a find sustainable alternative energy source to fossil fuel. It was estimated that the worldwide energy consumption is of the order 515 X 10^{18} J/year, out of which is supplied from petroleum fuels. This global energy consumption tends to escalate overtime because of the phenomena linked with population rise and increasing demands from emerging countries like Brazil, Russia India and China (BRIC) [1]. With this global increase in population and over-dependence on fast exhausting fossil fuel which also give rise to environmental issues, many studies have been targeted on several technologies to solve the energy and environmental problems. Amongst these emerging technologies are the biological and thermo-chemical conversion processes. Pyrolysis is a subset of thermo-chemical conversion process which can be described as the thermal decomposition of fuel into liquids, gases and char in the absence of oxygen. Pyrolysis products can be used as fuels, with or without prior upgrading, or can be utilized as feed stocks for chemical or material industries. Because of the nature of the pyrolysis process, yield of useful products is high compared to the other renewable energy processes. The materials suitable for pyrolysis processes include coal, animal and human waste, food scraps, paper, card-boards, plastics, rubber and biomass. Nearly 12% of the world's total primary energy consumption is supplied via biomass. Neutral Carbon dioxide (CO_2) emissions are possible from biomass fuel combustion because CO_2 released from the combustion of bio-fuels can be recycled by plants in photosynthesis [2, 3]. The benefits of biomass pyrolysis technology include the following: biomass pyrolysis generates bio fuels which help to mitigate the effects of global warming by reducing the utilization of fossil fuels; it motivates good forestry practices and technologies to the wellbeing of the society and

the environment; the plants are made flexible to deal with available waste feed stocks and this flexibility allows the plant for advantageous adaptation to industrial changes; the pyrolysis process produces multiple useful products, much like the petroleum industry and this value added product stream maximizes the benefits of biomass pyrolysis technological applications; pyrolysis oil is similar to synthetic diesel fuel and can be used as a fuel which has a fuel value that is 50-70% that of petroleum based fuels making it more cost effective to transport than raw biomass; bio-oil can also be used in boilers or upgraded to a transportation fuel [4]. Although, biomass pyrolysis process involves three products, presently fast pyrolysis for liquid production is notably gaining more and intensive research interests commercially as the liquid products have wider value-added applications in comparison to the other products. Fast pyrolysis involves decomposition of biomass very quickly to produce mostly a dark brown homogeneous liquid when wood or a low ash biomass is used as feedstock. The liquid possesses heating value about 40 % that of fossil fuel oil or 60 % that of convectional fuel on the basis of weight or volume basis respectively. Fast pyrolysis produces a high yield up to 75 wt. % (dry feed basis) with most low ash biomass such as wood [5]. It is important to note that the yield and the quality of the fast pyrolysis oil largely are dependent on wood based biomass availability and pyrolysis reactor technology.

Wood is one of the important forest products and wastes. It is reported that up to 11.3% of Nigerian total land is made up of forests. The forest can be classified under fresh water swamp forest, riparian forest, mangrove forest, savanna woodland forest, montane forest, and lowland rain forest and which are spread across twenty-eight states of the country, Nigeria [6]. Apart from the main wood tree materials, the processing of biomass wastes to energy open up opportunities for a good waste management in Sub Saharan Africa [7]. In Nigeria, the agro-forestry industry generates approximately 13 million tones of agro-forestry residues yearly [7]. The characteristics that define biomass as energy resource are proximate, chemical composition, ultimate and thermo-gravimetric analysis among others. The proximate and ultimate analysis describe the combustion properties of the biomass sample: the amount of volatile content in the sample is crucial, since it describes type of the flame produced during combustion. For instance, the biomass sample that contains high volatile produces a thick and bright flame, while those with less volatile burn with a dim and transparent flame [8]. Hence high volatile content of a biomass sample signifies its suitability for the production of pyrolysis oil. Also the Lignin and higher extractives contents contribute to a high heating value [9-10], while ash is considered as an undesirable material in wood for pyrolysis oil production [10, 11]. Recently, several researchers keyed-into the availability and the potentials of varying wood biomass species for fast pyrolysis for the production of pyrolysis oil [12, 13, and 5]. However, no study was performed to verify the candidacy of DWSD for the production of pyrolysis oil via adequate biomass characterization processes. This present research work is aimed at investigating the pyrolysis oil fuel potentials from DWSD which is one of the most important agro-forestry wastes in Nigeria.

2. Experimental

2.1 Material and Methods

Danta (*Nesogordonia Papaverifera)* Wood Saw Dust (DWSD) was used in this study as the raw lignocellulosic biomass, which is one of the widespread and abundant species in the Nigeria. Danta an important commercial wood can be used for furniture and building materials, which produces large amounts of sawdust and other wood residues every year in Nigeria. The raw sawdust sample was collected from the Department of Wood Scientific Equipment Development Institute, SEDI Enugu, Federal ministry of Science and Technology, Nigeria. The DWSD sample was sieved to particle size between 0.75mm to 1.00 mm and then dried for 24 hours under hot sun to a constant weight prior to use for analysis and pyrolysis samples.

2.2 DWSD Proximate Analysis

The proximate analysis of the biomass sample (DWSD) was performed as per ASTM D-271-48 standards to determine ash content, volatile matter, and fixed carbon. The *moisture content* was determined following ASTM D 4442-92 standard methods.

(i) ***Percentage Ash Content, (PAC)***: A porcelain crucible was weighed and oven dried to a constant weight. A sample weight of 3g was put in the crucible. The crucible and content were then weighed to the nearest 0.001g. The sawdust sample was then ashed at 550 ^{0}C for 4 hours and the crucible was carefully withdrawn and cooled in a desiccators. Finally, it was weighed to the nearest 0.001g. This procedure was conducted in triplicate. The ash content was calculated using Eq. (1).

$$\text{PAC} = \frac{AshWeight \quad (100\ ) \quad \%}{Oven\ dried\ Sample\ \ Weight\ at\ 105^0C} \qquad (1)$$

(ii) ***Percentage volatile Content (PVC) :***

A weight of 3g of sawdust sample was placed into the crucible and was oven dried at 105 ^{0}C for 1 hour. The oven dried sample was cooled in desiccators and re-weighed, then heated at 550 ^{0}C for 10 minutes. Then the sample was withdrawn, cooled and weighed to the nearest 0.001g. This procedure was conducted in triplicate. This was calculated on a percent basis using equation (2)

$$\text{PVC} = \frac{Sample\ weight\ at\ 105^0C - weight\ at\ 550^0C\ (100)}{Oven\ dried\ Sample\ \ Weight\ at\ 105^0C} \qquad (2)$$

(iii) ***Percentage moisture Content,*** $(\boldsymbol{PMC})$ **:** 3g of the sawdust sample was put in a porcelain crucible and dried at 105^0C for 60 minutes. The crucible was weighed to the nearest 0.001g. This procedure was conducted in triplicate. The moisture content is given as:

$$PMC = \frac{3g\ weightof\ Sample - weight\ at\ 105^0C\ (100)}{3g\ Sample\ \ Weight} \qquad (3)$$

(iv) ***Percentage Fixed Carbon, (PFC)****:* This was determined on a percentage basis using Eq. (4).

$$\text{PFC} = 100 - (Ash + PVMC + PMC) \qquad (4)$$

(v) ***DWSD Bulk Density***:

A 100 cm^3 measuring cylinder was filled with the DWSD sample and weighed in a digital weighing balance with accuracy of 0.001g. This experiment was repeated for four times and the mean weight, w was calculated and recorded. Thus the bulk density of DWSD sample, $\delta_B = \frac{w}{100}$ (g/cm^3).

2.3 DWSD Ultimate Analysis:

The ultimate analysis of the biomass sample was carried out using a CHN automatic analyzer (LECO CHN 600) at Ahmed Belo University ABU, Zaria Nigeria following the ASTM D5373-02 Standard Test Methods for Instrumental Determination of Carbon, Hydrogen and Nitrogen, Laboratory Samples of Coal and Coke [14]. The oxygen content of the samples was calculated by difference.

2.4 Chemical Composition Analysis of DWSD

The percentage content of the total extractives, of the sample, DWSD was determined using a Soxhlet extractor following the ASTM D1037 standard methods [15]. The percentage contents of cellulose, hemicelluloses, and lignin were determined also according to the ASTM D1037 standard methods using the meal free-extractive method based on the oven-dry weights for the residue as described below [15].

(i) Water soluble extractives: The sample was placed in a paper tray and dried at 105^{0}C to a constant weight which was recorded. The sample was then put into a porous thimble and placed inside the Soxhlet extractor. 500 milliliter of water was poured into a round bottom flask and placed on a heating mantle. The Soxhlet extraction apparatus was coupled to the 500 milliliter flask and heated for extraction about 4 hours. After the extraction, the supernatant was collected and evaporated to about 15 ml and then was dried at 105 ^{0}C until a constant weight was reached. This residue obtained was measured as the water soluble extractives.

(ii) Ethanol soluble extractives: The same process was repeated as in the above extraction method except that ethanol was used as solvent here. The residue obtained was the ethanol extractives.

(iii) Cellulose Content: The Base-Acid-Base-Acid-Base method was used for the cellulose extraction. After extraction, the wood was washed with extra clean water at pH 4. The final product (Cellulose) was dried in a muffle furnace at a constant temperature of 105^0C for 4 hours and weighed. The final product suspected to be cellulose was then subjected to a tri-iodide phosphoric acid confirmatory test.

*(v) Lignin Content (LC)***:** 72 % H_2SO_4 was used to dissolve all the carbohydrates in the extractive-free wood sample, leaving lignin as the insoluble residue. The residue was washed with 500 ml of hot water to remove the acid. Then, it was dried at 105 ^{0}C for 2 hours and was weighed as the weight of the Acid Insoluble Lignin. The percent weight of Lignin was found using Eq. (5),

$$\mathrm{L\,C} = (\text{ lignin weight}/\text{extractive free meal weight})100\% \quad (5)$$

2.5 Calorific value of DWSD

The combustion heat of fuel is the amount of heat produced when the fuel is burned completely. The two heating values (gross or high heating value and net or low heating value) are defined by Dulong's formula, equation (6) and respectively. The amounts of elements (C, H, O, N and Ash) were expressed in mass percentages as obtained from ultimate analyses. LHV was calculated using equation (7).

$$HHV(KJ|Kg) = 354.68\,C + 1376.29H - 15.92Ash - 124.69(O + N) + 71.26 \quad (6)$$

$$LHV(KJ|Kg) = HHV(KJ|Kg) - 218.13H(Wt\%) \quad (7)$$

3. Results and Discussion

3.1 DWSD Feedstock Analyses

The nature and the type of pyrolysis feedstock are central to the yield distribution of pyrolysis process. The results of proximate, ultimate, chemical composition analyses and the caloric values of the sample were presented in Table 1, while the interpretation of the FTIRS OF DWSD sample is presented in Table 2 clearly showing the functional groups and the classes of compounds contained in the sample.

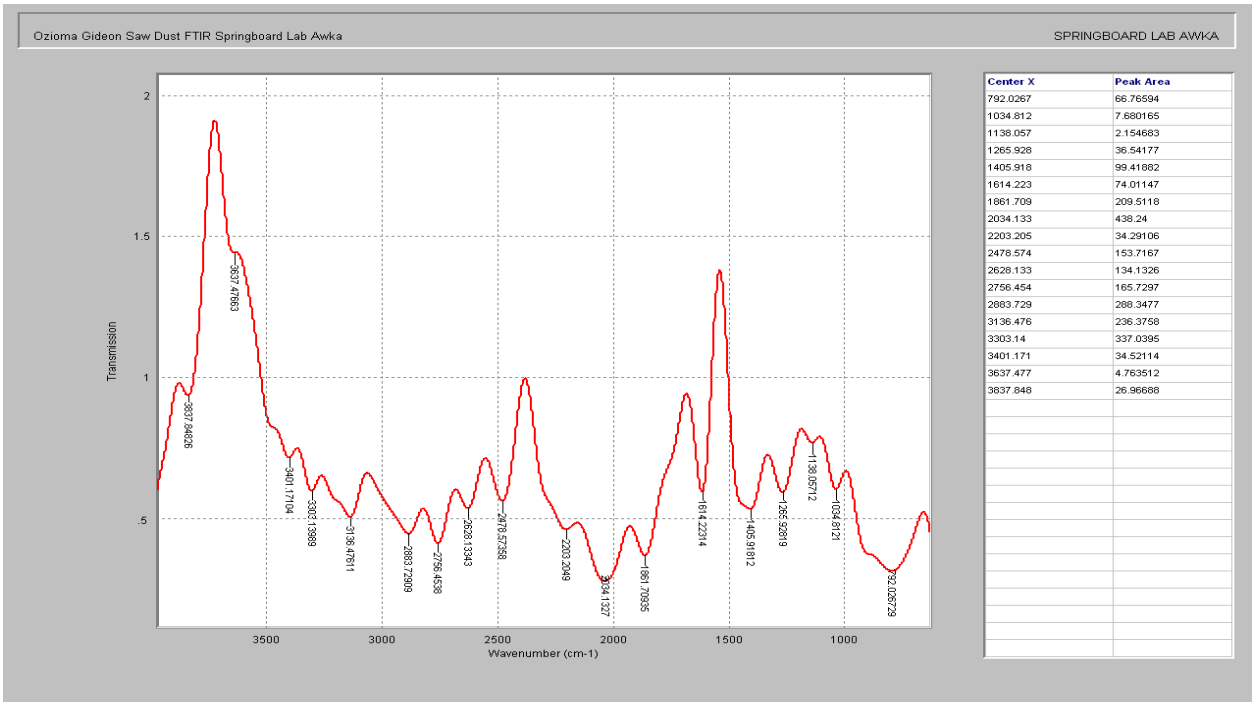
From Table1, the proximate analysis indicates high PVC (83.2 wt. %), low PMC (8.2 wt. %),) and low PAC (wt. %), while the chemical composition results show high cellulose plus hemicellulose contents, 56.60 wt. %, than lignin content, 41.00 wt. %. The high PVC and high cellulose and hemicellulose contents indicate high biomass potentials for pyrolysis oil production while low PFC and lignin contents indicate low yield of Char. The proximate and the chemical compositions analytical values are typical of hardwoods [5, 7, and 16].

The elemental composition of a biomass indicates the calorific values and the pollution emission index of biomass. The HHV= 20.61MJ/kg, falls within typical biomass caloric values, while the nitrogen content indicates negligible emission of nitrogen oxide in the environment from the biomass and by extension, the products [5, 7]. In Table 2, it can be seen that the sample contains many hydrocarbon functional groups which belong to the organic compound classes: alkanes, alkenes, aromatics, ketones, alcohol, ether, aldehydes, carboxylic acids, etc) qualifying the biomass a good candidate for bio-oil production. In conclusion, the feedstock characterization results show that DWSD sample has great potentials for use in production of pyrolysis oil.

Table 1: The Results of the DWSD Pyrolysis Feedstock Characterization

Test No	Characterization	Values
1	Percentage Moisture Content, PMC (%)	8.20
2	Percentage Volatile Content, PVC (%)	83.20
3	Percentage Ash Content, PAC (%)	0.40
4	Percentage Fixed-carbon, PFC (%)	8.20
5	Carbon, C (%)	50.50
6	Hydrogen, H (%)	5.82
7	Nitrogen, N (%)	0.03
8	Oxygen, O (%)	43.05

9	Cellulose Contents (%)	41.00
10	Lignin Contents (%)	26.60
11	Hemicellulose Contents (%)	30.00
12	Extractives Contents (%)	2.40
13	Higher Caloric Value, HCV (MJ/Kg)	20.61
14	Lower Caloric Value, LCV (MJ/Kg)	19.34
15	Bulk Density (kg/m^3)	230



Center X	Peak Area
792.0267	66.76594
1034.812	7.680165
1138.057	2.154683
1265.928	36.54177
1405.918	99.41882
1614.223	74.01147
1861.709	209.5118
2034.133	438.24
2203.205	34.29106
2478.574	153.7167
2628.133	134.1326
2756.454	165.7297
2883.729	288.3477
3136.476	236.3758
3303.14	337.0395
3401.171	34.52114
3637.477	4.763512
3837.848	26.96688

Figure 1 FTIR of DWSD Feed Sample

Table 2: The DWSD FTIR Spectra Interpretation

S/N	Peak Centre (cm^{-1})	Transmission Range (cm^{-1})	Peak Area (%)	Functional Group	Compound Class
1	792.027	840 – 740	3.28	C = C Bending	Tri-subst. Alkenes
2	1034.891	1070 – 1030	0.38	S = O Stretching	Sulphur oxide
3	1138.070	1150 – 1085	0.11	C – O Stretching	Ether
4	1265.928	1275 – 1200	1.80	C – O Stretching	Alkyl aryl Ether
5	1405.918	1440 – 1395	4.89	O – H Bending	Carboxylic acid
6	1614.223	1620 – 1610	3.64	C = C Stretching	, -unsaturated Ketone
7	1861.709	2000 – 1650	10.30	C = C Bending	Aromatic Compound
8	2034.133	2140 – 1990	21.45	N= C = S Stretch	Isothiocyanate
9	2203.205	2260 – 2190	1.69	C≡≡≡≡C Stretching	Alkynes di-subst.
10	2756.454	2830 – 2695	8.15	C – H Stretching	Aldehydes
11	2883.729	3000 – 2840	14.18	C – H Stretching	Alkynes
12	3138.476	3200 – 2700	11.62	O – H Stretching	Alcohol
13	3303.140	3333 – 3200	16.57	C – H Stretching	Alkynes
14	3401.176	3550 – 3200	1.70	O – H Stretching	Alcohol (molecular Bond)
15	3637.477	3700 – 3584	0.23	O – H Stretching	Alcohol (Free)

4. Conclusions

The present research verified the suitability of DWSD pyrolysis for pyrolysis oil production. DWSD feedstock characterization had been successfully carried out via proximate, ultimate, chemical compositions, fuel characteristics and FTIRS analyses. The following major results were obtained.

- *Proximate analysis result:* Percentage Moisture Content, PMC; Percentage Volatile Content, PVC; Percentage Ash Content, PAC and Percentage Fixed Carbon Content, PFC are 8.20, 83.20, 0.40 and 8.20% respectively.
- *Ultimate analysis result*: C, H, N, and O are 50.50, 5.82, 0.03 and 43.05% respectively.
- *Fuel Characteristic* results showed the HCV and LCV = 20.61MJ/Kg and 19.34MJ/Kg respectively.
- *Chemical compositions* results indicated the percentage contents of Cellulose, Lignin, Hemicellulose and Extractives as 41.00, 26.60, 30.00 and 2.40 respectively.
- *FTIRS* results indicated the presence of hydrocarbons, majorly.

It can easily be seen that the high percentage volatile contents and high cellulose, hemicellulose contents indicate high biomass potentials for pyrolysis oil production while low percentage fixed carbon contents and lignin contents indicate low yield of Char. Ultimately the low ash and high carbon contents present the sample of DWSD with excellent caloric values, while its low nitrogen content indicates very insignificant environmental hazards in relative to fossil fuels. In conclusion this present study verified the suitability of the DWSD sample for the production of pyrolysis oil.

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