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Assessment of Bio-Fuel Characteristics of Bio-Oil Produced From Sawdust of *Cordia Milenii and Nesogordonia Papaverifera* Wood Species

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ABSTRACT

The biomass conversion into fuels is a sustainable way to mitigate environmental issues such as global warming in parallel with an improvement of the energy security by reducing fossil fuels dependence. The study assessed the preparation and characterization of bio-oil produced from sawdust of selected wood species (Cordia milenii and Nesogordonia papaverifera) Sawdust samples of 200g each were collected from Forestry Research Institute of Nigeria sawmill at Ibadan and oven-dried at 103±2°C for 24 hours to 12% moisture content. Four replicates of bio-oil were produced at each temperature regime for each of the samples, two different temperature regimes were used (500°C and 600°C). The metallic container (pyrolytic chamber) was filled with 200 grams of the samples of each species and placed inside the Reactor which was connected to a condenser. Using standard test, physical properties, chemical and thermal characterization of bio oil and proximate analysis of the Bio-oil were assessed. Analysis of Variance (ANOVA) in Randomized Complete Block Design (RCBD) was used to ascertain significance difference in the oil yield produced at different temperature. The result shows that there was general increase in the volume of oil yield as the temperature increases. The volume of the oil ranged between 38.00cm^3 to 72.33 cm^3 and 52.93 cm^3 to 63.63 cm^3 respectively. The result of mean value for density (g/cm^3) of pyrolytic oil yield ranged respectively from 1.00 to 0.94, and 0.98 to 1.04 for Cordia milenii and Nesogordonia papaverifera. There was significant difference in the means of the volume of bio-oil obtained as pyrolysis temperature increased. The result of proximate analysis of bio-oil produced from selected sawmill wood residues shows the percentage fixed carbon values ranged from 23.33 to 58.33 in Cordia milenii and 28.33 to 56.67 in Nesogordonia papaverifera. The study revealed that pyrolysis is an efficient way to produce liquid fuels from biomass. The physical properties of the bio-oil obtained from sawmill wood residues falls within the acceptable range for fuel production. The selected wood species are therefore suitable for production of bio-oil with acceptable physical and chemical properties.

Keywords: *Bio-oil, Cordia milenii, Nesogordonia Papaverifera, Pyrolysis and Temperature*

INTRODUCTION

Renewable energy is of growing importance in satisfying environmental concerns over fossil fuel usage. Wood and other forms of biomass including energy crops, agricultural and forestry wastes are some of the major renewable energy resources available. These can provide the only source of renewable liquid, gaseous and solid fuels. Biomass is considered the renewable energy source with the highest potential to contribute to the energy needs of modern society for both the developed and developing economies world-wide (IEA, 2000). Energy from biomass based on short rotation forestry and other energy crops can contribute significantly towards reducing the green house gases emissions and to the problems related to climate change (IEA, 1998). Biomass is expected to be a major source of sustainable energy in the future as the World transitions from traditional carbon-based fuels such as coal, petroleum and natural gas to carbon-neutral fuels to combat global warming and fossil fuel depletion (Huber, 2008). Biomass-derived biofuels are the only current sustainable source of liquid hydrocarbons required for transportation. However, an economic way of making them has not yet been devised despite the fact that lignocellulosic biomass costs significantly less than crude oil (about $ 15 per barrel of oil energy equivalent). One of the promising conversion processes for liquid fuel production is fast pyrolysis. This involves heating biomass rapidly (high heating rate) at a high temperature in the absence of oxygen to produce the pyrolysis vapour. The evolved vapour is then cooled down to room temperature to obtain pyrolytic liquid product, which is called "bio-oil". The non-condensable gases and the solid residue bio-char are valuable by-products which can be used as a heating source. The process conditions of fast pyrolysis are normally selected in order to obtain the highest liquid yields. Apart from the process parameters, the characteristics of biomass feed stocks also play an important role on the pyrolysis end products. The production of bio-oils offers advantages over conventional biomass combustion and gasification. During pyrolysis the alkali and other mineral components of the biomass are predominately entrapped in the char residue. The resultant liquid bio-fuel can be fired at high efficiency in diesel engines or gas turbines (Czernik and Bridgewater, 2004). Also, the liquid state of this fuel can make feasible the physical separation between the pyrolysis plants (close to the biomass sources) and the power units (close to the electricity consumers). Biomass fuels and residues can be transformed to energy via thermal, biological and physical processes. In thermal conversion, combustion is already widely practiced; gasification attracts a high level of interest as it offers higher efficiencies compared to combustion; and fast pyrolysis is attractive as liquid is produced that offers advantages in storage and transport and flexibility in applications, although it is still at a relatively early stage of development. The products and applications of these thermal conversion processes are summarized in fig.1.

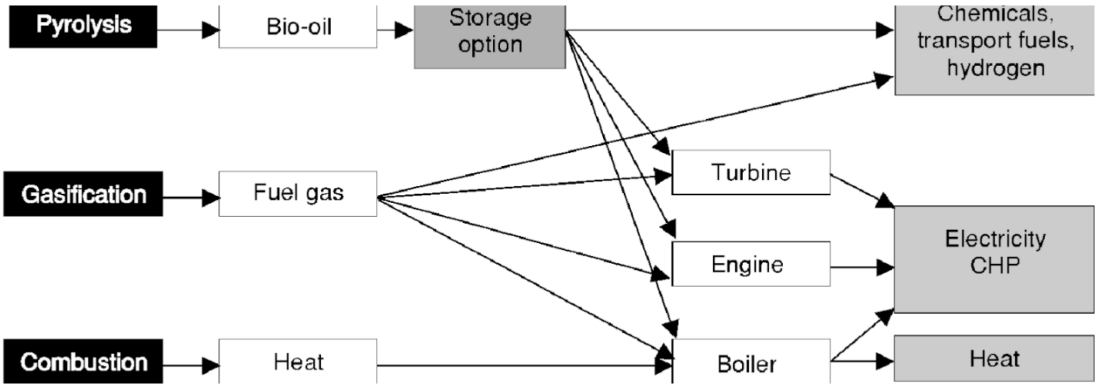


Fig1. *Products from thermal biomass conversion*

Source: *Bridgewater, (2003)*

Pyrolysis is the thermal destruction of biomass into fuel liquids, gases, and char (solid residue) in the absence of oxygen. It is usually understood to be anhydrous (without water). Pyrolytic products can be used as fuels, with or without prior upgrading, or they can be utilized as feedstock for chemical or material industries. Because of the nature of the process, yield of useful products is high compared to the other processes. In general, pyrolytic yield are more refined and therefore can be used with greater efficiency. Materials suitable for pyrolysis processing include coal, animal and human waste, food scraps, paper, cardboard, plastics, rubber and biomass (Adegoke 2017). Pyrolysis is publicise to be one of the most promising thermo chemical technologies with the potential to convert cheap, local, and abundant lignocellulosic biomass such as grasses and trees into a useful form (Mohan, et al. 2006, Lu, et al.2010), and commercial scale plants. Thermal technologies include direct combustion, gasification, liquefaction, and pyrolysis, all of which have the benefit of using lignocellulosic materials. Only pyrolysis and liquefaction produce a liquid product, and although recent work on liquefaction has shown promising results (Soria, et al. 2008a, Soria, et al. 2008b, Adegoke 2017), it is currently a nascent technology with high capital costs due to the high pressures required. Pyrolysis has the advantage of low capital investment and a liquid final product that can be transported and converted via catalysis to fuels and valuable products such as food flavorings, fertilizers, resins, and other specialty chemicals that are fully compatible with existing petroleum infrastructure. This provides significant economic advantages over ethanol that requires parallel infrastructures. Furthermore, all pyrolysis products can be utilized in the pyrolysis system. The alaming poor energy supply and distribution has necessitated renewed research into alternative source of energy. Although, Nigeria is an oil producing country, but it concentrated on exporting of crude oil and import refined petroleum products since refineries in the country operate below 10% production capacity.(Fuwape 2007). The high prices of oil which has a disproportionate impact on the country economy requires diversification of the energy sector and improve economic power of individuals through the use of biofuel as an alternative energy source. Also, there are serious environmental pollution problems associated with the use of fossil fuel. There is therefore need to identifying the sustainable energy options for energy production without polluting the environment.

MATERIALS AND METHODS

Sample Collection and Preparation

Sawdust samples of Nesogordonia papaverifera and Cordia millenii (200 gramms each) were collected from Forestry Research Institute on Nigeria sawmill, the sawdust were oven-dried at 103±20C for 24 hours to 12% moisture content. Four replicates of bio-oil were produced at each temperature regime for each of the samples.

Bio Oil Production

The (pyrolytic chamber) was filled with 200 grammes of the samples of each species and placed inside the Reactor which was connected to a condenser. Two different temperature regimes were used i.e. 500°C and 600°C. The evolving gas was distilled in the condenser to form bio-oil which was collected inside a conical flask.

Fabricated Pyrolysis Reactor

- Feedstock (sawdust)
- Pyrolytic chamber (Reactor)
- Furnace
- Chamber rod (Liquid passage)
- Condenser
- Cold water inlet
- Cold water outlet
- Emitted gas
- Pyrolytic oil and tar
- Conical flask

Fuel Characterization Examination

To characterize the bio oil and char, the following tests were performed using standard test.

Physical Properties Characterization of Bio Oil

PH Determination

The pH of the condensate was determined with the use of MICROFIED SM-3H pH meter which has an electrode that was calibrated with two buffer solutions.

Density Determination

The density of a material is defined as mass per unit volume of sample. Electronic weighing balance was used to weigh the samples while measuring cylinder was used to determine the volume.

$$\text{Density (g/cm}^3\text{)}\ \frac{\text{Mass}}{\text{Volume}}$$

Where: M = mass of the bio-oil obtained (g), V = volume of bio-oil obtained (cm^3)

Proximate Analysis of the Bio-Char

Proximate analysis was carried out to determine the following:

- Percentage Ash Content
- Percentage Volatile Matter
- Percentage fixed Carbon
- Heating Value

Percentage Ash Content

Two grams of oven dried sample was kept in furnace at temperature of 5500C for three hours and was weighed after cooling. The percentage ash content was calculated thus:

$$\%Ash = \frac{D}{B} \times 100$$

Where: % A = Percentage ash, D = Weight of ash, B = weight of oven dried sample

Percentage Fixed Carbon

The percentage fixed carbon was calculated by subtracting the value of percentage volatile matter and ash content from 100%. It was calculated according to the formula below:

$$\%\ fixed\ carbon = 100-(\%V+\%A)$$

Where %V = Percentage Volatile Matter

% A = Percentage Ash Content

Percentage Volatile Matter

Two grams of pulverized sample was weighed into crucible before transferred into muffle furnace at 550°C. This was left for 10minutes; the content was later cooled in dessicator and weighed to determine the percentage volatile matter with the formula below:

$$Volatile\ Matter\ (\%) = \frac{B-C}{B} \times 100$$

Where B = Weight of oven dried samples, C = Weight of sample after 10minutes in the furnace at 550°C

Heating Value

The heating value or calorific value of a substance, usually a fuel or food is the amount of heat energy released during the combustion of a specified amount of sample. The calorific value is a characteristic for each substance. It is measured in unit of the substance, usually mass, such as Kcal/kg, KJ/kg, J/mol, and Bt/m3. Heating value is usually determined by the use of a bomb calorimeter but due to in availability of bomb calorimeter estimation method was used. Heating value was calculated using the formula below:

$$HV = 2.326\ (147.6C + 144V)\ Kj/kg$$

Where HV = Heating Value, C = Percentage fixed Carbon, V = Percentage Volatile Matter

Chemical and Thermal Characterization of Oil

Determination of acid value

This was done according to Pearson (1976). Two grams of oil was weighed into a dried 250ml Erlenmeyer flask. Thirty millilitres of a solution made of equal volumes of 95% ethanol and diethyl ether was added to dissolve the oil. The sample solution was then titrated with 0.1N methanolic potassium hydroxide solution with the addition of 0.5ml phenolphthalein solution until a slight pink colour persisted for 15 seconds. Blank titration without oil was also carried out under the same condition.

$$ACID\ VALUE = \frac{Titration\ (ml\ x\ 5.61)}{Wt\ of\ sample\ used}\ mg\ KOH/g\ oil.$$

Pour Point

The temperature at which the oil pour was determined by putting samples inside test tube, then placed in a freezer and the lowest temperature at which the pouring occur was recorded as the pour point.

Elemental Analysis of Bio-Oil

Ultimate analysis is performed to determine the elemental composition of the materials. It was carried out using a LECO CHNS 932 elemental analyzer which provides carbon, hydrogen, nitrogen, sulphur percentage composition of the selected samples. When the summation of these compositions is subtracted from 100, it gives oxygen percentage composition.

Compositional Analysis (FT-IR)

Spectroscopic analysis using photo spectrometer was performed using PERKIN ELMER 1600 series model to know the functional group present in the bio-oil.

Data Analysis

Analysis of Variance (ANOVA) in Randomized Complete Block Design (RCBD) was used to ascertain significance difference in the oil yield produced at different temperature. The statistical model is as stated below:

$$Yij = \mu + Bi + Tj + eij$$

Yij = Individual Observation

μ =Overall mean

Bi = Effect of ith Block (Temperature)

Tj = Effect of ith Treatment (Wood Specie)

eij= Random error term

Duncan Multiple Range Test (DMRT) was used for any variables (temperature and wood Specie) that are significant at 5% level of probability as follow-up test.

Ten Chemical properties were assessed for each species.

RESULT AND DISCUSSION

Results

Physical Properties of Pyrolytic Oil

The physical properties of pyrolytic oil of the two selected wood species (Cordia milenii and Nesogordonia papaverifera) at two different temperature regimes (500°C and 600°C) was shown in Fig 1-5. The physical properties which include bio-oil yield (g/cm3), pH, Acidic value, pour point and Density (g/cm3) of the pyrolytic oil were assessed.

Pyrolytic oil yield

There was general increase in the volume of oil yield as the temperature increases. The volume of the oil ranged between 38.00cm3 to 72.33 cm3 and 52.93 cm3 to 63.63 cm3 for Cordia milenii and Nesogordonia papaverifera respectively (Fig 1). There was significant difference in the means of the volume of bio-oil obtained as pyrolysis temperture increases. This further shows that the two selected sawmill wood residues differs significantly at P □ 0.05 within the two temperature regime used (Table 1).

PH value of bio-oil yield

The result of pH value reveals that high mean pH of 3.57 was recorded at 600°C while

3.53 was recorded at 500°C in Cordia milenii. while in Nesogordonia papaverifera high pH of 3.73 was again recorded at 600°C and 3.640C at 500°C (Fig 2) There is significant difference in the pH of bio-oil liquid produced at 500°C and 600°C for the selected sawmill wood residues at P □ 0.05 level of significance (Table 1).

Acidic value of bio-oil yield

The highest and lowest mean value for acidic value of liquid produced from Cordia milenii and Nesogodonia papaverifera ranged from 5.79 to 7.62 and 1.37 to 2.54 respectively (Fig 3). The analysis of variance showed that there was significant difference in the acidic value of the pyrolytic liquid at temperature of 500°C and 600°C (Table 1).

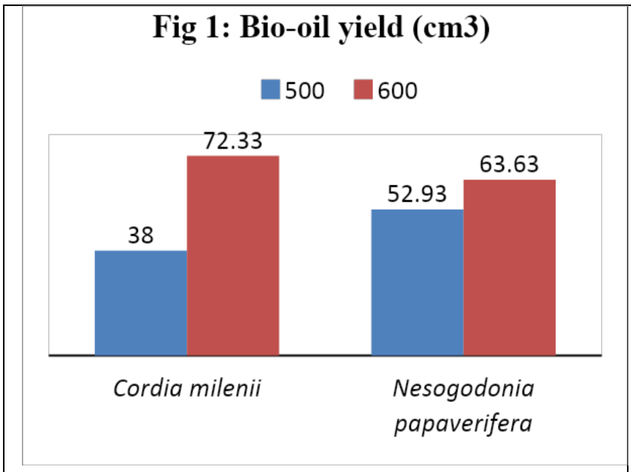


Fig 1: Bio-oil yield (cm3)

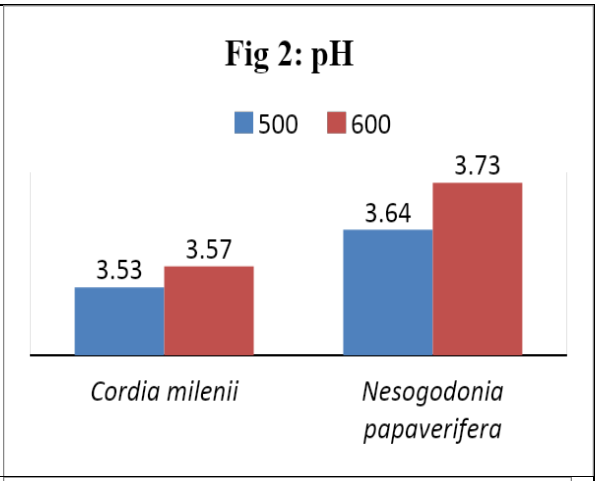


Fig 2: pH

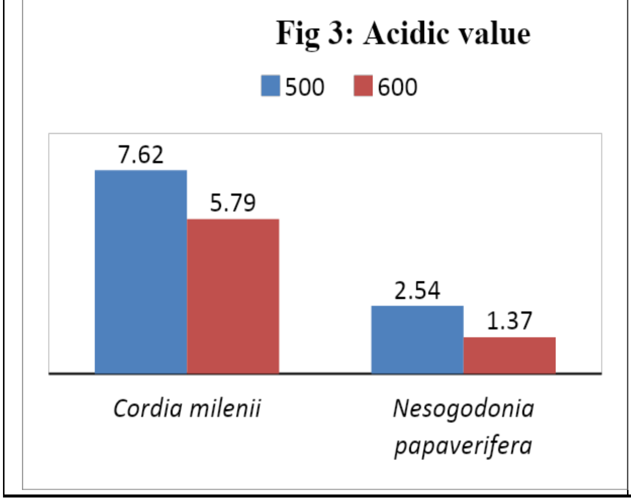


Fig 3: Acidic value

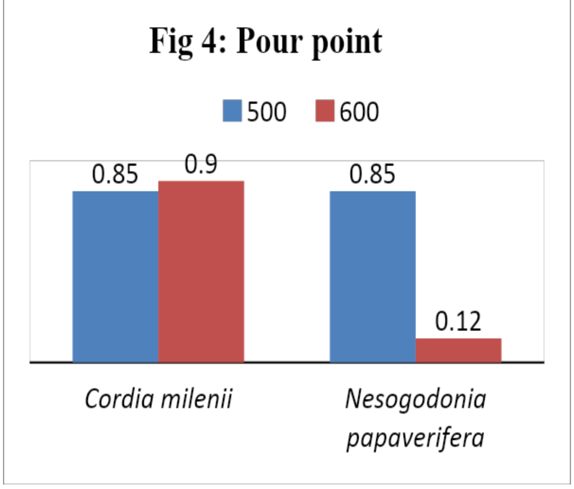
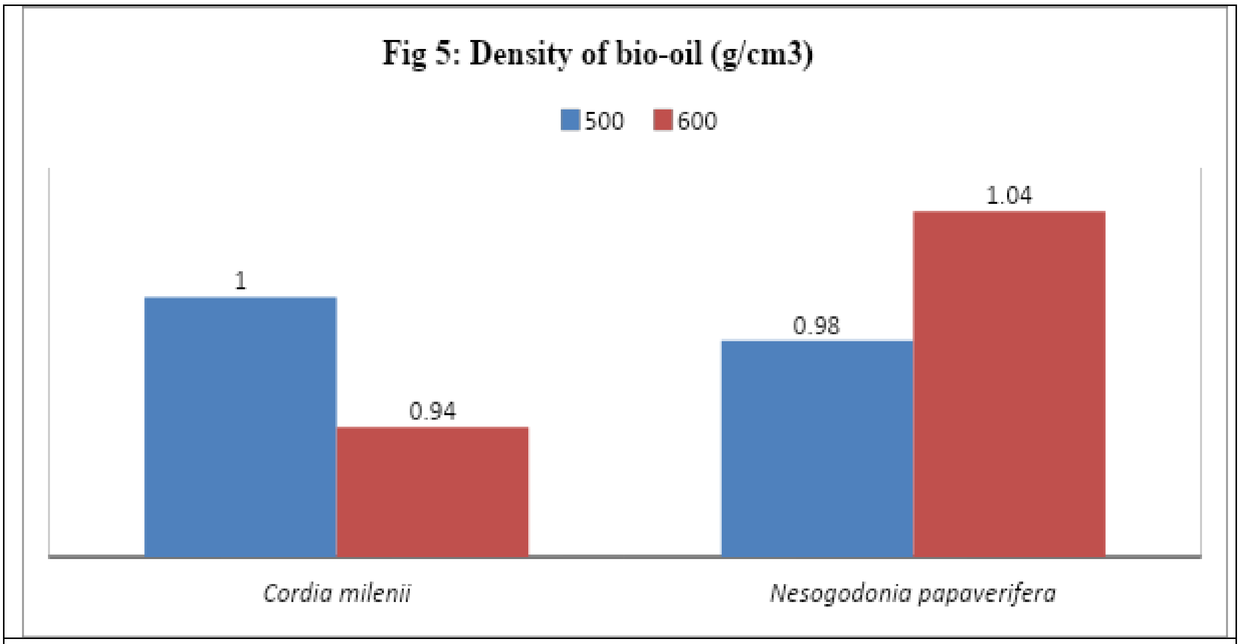


Fig 4: Pour point



The blue cones represent temperature application at 500°C while the red cones represents 600°C

Fig1-6. *Physical properties of pyrolytic oil produced from the selected wood species*

Pour Point of Bio-Oil Yield

The result also revealed that there is significant difference in the pour point of bio-oil yield at the two temperature regimes adopted for pyrolysis (Fig 4). The result presented in Table 1 revealed the highest and lowest mean values for the pour point of liquid produced which ranged from -0.85 to -0.90 and -0.85 to -0.12 for Cordia milenii and Nesogordonia papaverifera respectively (Table 1).

Density of Bio oil yield

The result presented in Fig 5 shows the highest and least mean value for density (g/cm3) of pyrolytic oil yield which ranged respectively from 1.00 to 0.94, and 0.98 to 1.04 for Cordia milenii and Nesogordonia papaverifera.

Table1. *ANOVA for Physical properties of pyrolytic oil produced from the selected wood species*

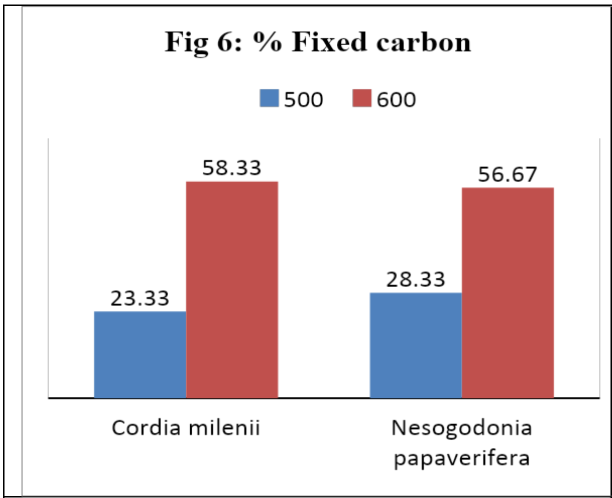
SV	Df	SS	MS	F-cal	Remark
Bio-oil yield					
Treatment	2	821.56	410.78	39.54	*
Temperature	1	1705.28	1705.28	164.14	*
Trt*Temp	2	502.62	251.31	24.19	*
Error	12	124.67	10.39		
Total	17	3157.13			
pH					
Treatment	2	0.086	0.043	61.43	*
Error	15	0.005	0.0007		
Total	17	0.091			
Acidic value					
Treatment	2	68.183	34.091	4.005	*
Error	15	127.677	8.512		
Total	17	195.86			
Pour point					
Treatment	2	0.506	0.253	281.11	*
Error	15	0.013	0.0009		
Total	17	0.519			
Density					
Treatment	2	0.024	0.012	4.00	*
Error	15	0.043	0.003		
Total	17	0.067			

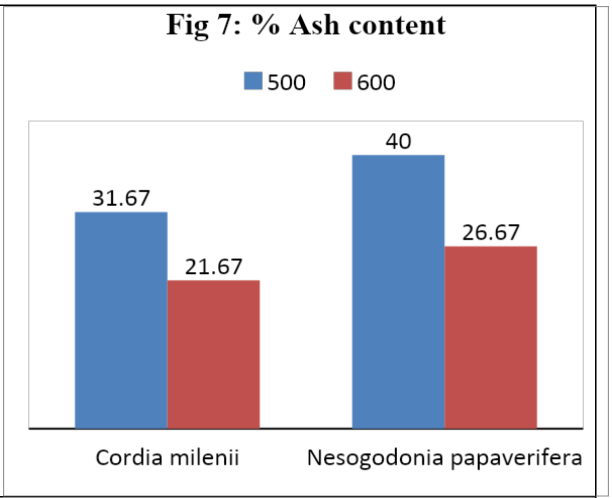
** Significant at 5% level of probability*

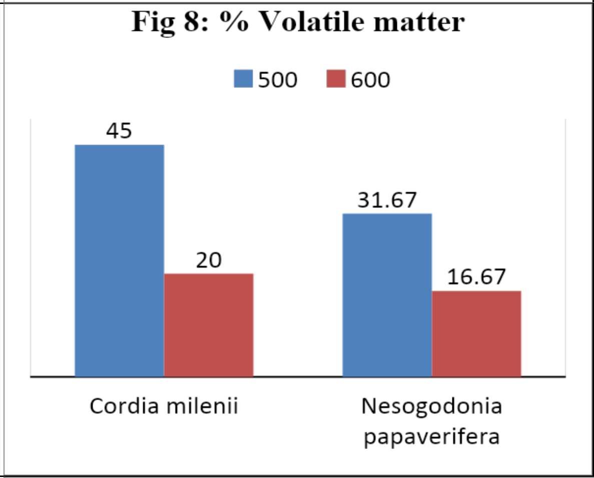
Proximate Analysis of Bio-Char Produced From Selected Sawmill Wood Residues

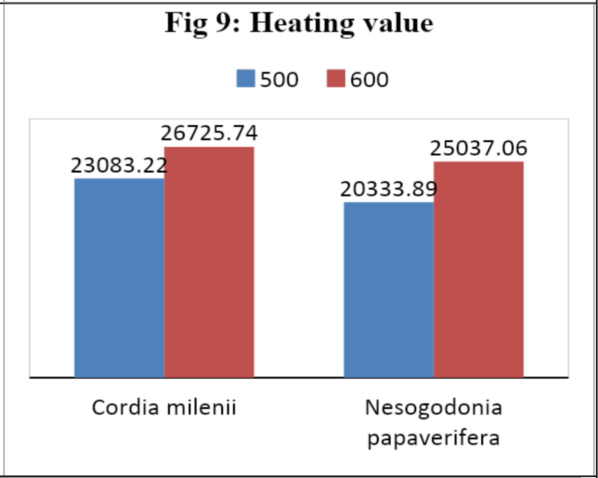
Percentage Fixed Carbon

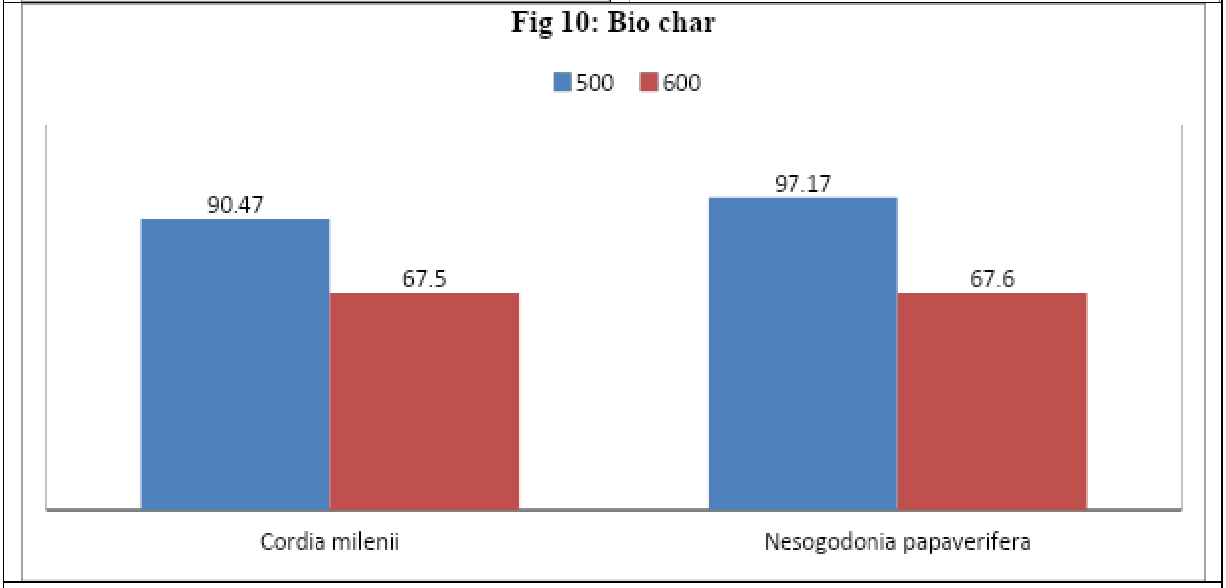
The result of mean percentage fixed carbon is presented in Table 2. The result from analysis of variance shows that there is no significant difference between the selected sawmills wood residues used at different temperature range (Table 2). The percentage fixed carbon values ranged from 23.33 ± 5.77 to 58.33 ± 7.64 and 28.33 ± 2.89 to 56.67 ± 15.28 for Cordia milenii and Nesogordonia papaverifera and this is further illustrated in Fig. 6











The blue cones represent temperature application at 500°C while the red cones represents 600°C

Fig 6-10. *Proximate analysis of pyrolytic oil produced from the selected wood species*

Table2. *ANOVA For % fixed carbon*

SV	df	SS	MS	F-cal	Remark
% fixed carbon					
Treatment	2	19.444	9.722	0.175	Ns
Error	15	833.333	55.556		
Total	17	852.777			
% Ash content					
Treatment	2	158.333	79.167	33.934	*
Error	15	350.000	2.333		
Total	17	508.333			
% volatile matter					
Treatment	2	277.778	138.889	5.952	*
Error	15	350.000	23.333		
Total	17	627.778			
Heating value					
Treatment	2	17483899.60	8741949.79	3.15	Ns
Error	15	41661313.30	2777420.89		
Total	17	59145212.90			
Bio char					
Treatment	2	705.95	352.97	2.04	Ns
Error	15	2594.86	172.99		
Total	17	3300.81			

** Significant at 5% level of probability, Ns = Not significant at 5% level of probability*

Percentage Ash Content

The result of percentage ash content is presented in Fig 7. For both temperature regimes N. papaverifera has the highest mean percentage ash content while Cordia milenii has the less mean percentage ash content which ranged from 31.67 to 21.67 and 40.00 to 26.67 for Cordia milenii and Nesogordonia papaverifera respectively. The result from analysis of variance shows that there is significant difference between the selected feedstocks at different temperature (Table 2).

Percentage Volatile Matter

Cordia milenii has the highest mean percentage volatile matter at 500°C while Nesogordonia papaverifera at 600°C has the least mean percentage volatile matter (Fig 8). The result indicated that there is significant difference in the percentage volatile matter between the different sawmill wood residues at different temperature. The mean value for percentage volatile matter ranged from 45.00 to 20.00, and 31.67 to16.67 which indicated that Cordia milenii has the highest mean percentage volatile matter at 500°C while Nesogordonia papaverifera at 600°C has the least mean percentage volatile matter. (Fig. 8)

Heating Value of the Bio-Char

The result presented in Fig 9 revealed the high and less mean for the heating value of the bio char which ranged from 23083.22 to 26725.74, and 20333.89 to 25037.06 (Kj/kg) for Cordia milenii and Nesogordonia papaverifera respectively. The result of analysis of variance indicated that there was no significant difference in the heating values of the bio char (Table 2).

Bio char yield component

The result of the proximate analysis presented in Fig 10 reveals the highest and least mean bio char recovery after pyrolysis process which ranged from 90.47±10.05 to 67.50 and 97.17 to 67.60 for the selected wood species (Cordia milenii and Nesogordonia papaverifera) respectively. The result of analysis of variance indicated that there is no significant difference between the left over char as the pyrolytic temperature increases from 5000C to 6000C between the selected wood species (Table 2)

Table3. *Elemental components of pyrolytic oil*

Parameter (%)	*Cordia milenii*		*Nesogordonia papaverifera*	
	500°C	600°C	500°C	600°C
Carbon	47.39	47.02	49.9	50.02
Hydrogen	6.24	5.95	6.85	6.76
Nitrogen	< 0.1	< 0.1	< 0.1	< 0.1

Sulphur	0.02	-	-	-
Oxygen	46.25	46.93	43.15	43.22

Elemental Analysis of the Bio-oil

The results of the elemental composition of the pyrolytic oil are presented in Table 3. This revealed the carbon, hydrogen, nitrogen, surphur and oxygen content of the selected sawmill wood residues.

Compositional Analysis of the Bio-Oil

The graphical representations of FT-IR spectrum of the liquid obtained from pyrolysis of Cordia milenii and Nesogordonia papaverifera wood residues from sawmill at different temperature range are shown in Fig 11 - 14 while Table 4 and 5 indicated the functional groups of the two selected sawmill wood residues with their corresponding frequencies (cm-1) that were identified from FT-IR spectrum.

Table4. *Functional group present in sawmill wood residue of Cordia milenii as determined by FT-IR analysis*

Temperature (^{0}C)	Frequency (cm-^{1})	Functional Groups	Class of compounds
500	3600-3200	O−H stretch N−H stretch	Phenol,sec. Alcohol Primary amine
	3200-2500	O−H stretch	Carboxylic acid
	2500-2000	C≡N	Benzo-nitrile
	1775-1680	C=O	Carboxylic acid, ketones, aldehyde, esthers
	1650-1575	C=C stretch	Alkenes
	1590-1515	N−H bend C−H bend	Secondary amide Alkanes
	1490-1325	O−H bend O−H bend	Alcohol, phenols
	1300-950	C−H stretch	Alcohols, phenols Alcohols
	640-600	≡C−H	Alkynes, aromatics
600	3600-3200	O−H stretch N−H stretch	Phenol, sec. Alcohol Primary amine, water impurities
	2500-2000	C≡N	benzo-nitrile
	1775-1650	C=O	carboxylic acid, ketones, aldehydes, esthers
	1650-1575	C−H bend O−H bend	alkanes alcohols, phenols
	1490-1325	O−H bend C−O stretch	alcohols, phenols alcohols
	1300-950	C=C strech	Alkenes
	640-600	≡C−H bend	Alkynes aromatics

Table5. *Functional group present in sawmill wood residue of Nesogodonia papaverifera as determined by FT-IR analysis*

Temperature (^{0}C)	Frequency (cm^{-1})	Functional Groups	Class of compound
500	3600-3200	O−H stretch N−H stretch	Phenol, sec. Alcohol,water impurities Primary amine
	2500-2000	C≡N	Benzo-nitrile
	1775-1650	C□ O stretch	Carboxylic acid, ketones, aldehyde, esters
	1650-1575	C□ C stretch C−H bend	Alkenes Alkane
	1490-1325	O−H bend	Alcohols, phenols
	1300-950	O−H bend	Alcohols, phenols
	900-650	≡C−H bend C□ C	Alkynes Aromatic compunds, alkenes
600	3600-3200	O−H stretch N−H stretch	Phenols, sec. Alcohol Primary amine Water impurities
	2500-2000	C≡N	Benzo-nitrile
	1650-1575	C□ C stretch	Alkenes

	1490-1325	O−H bend C−H bend	Alcohols, phenols Alkanes
	1300-950	O−H bend C−O stretch	Alcohols, phenols Alcohols
	900-650	≡C−H bend	Alkynes,and aromatic compounds

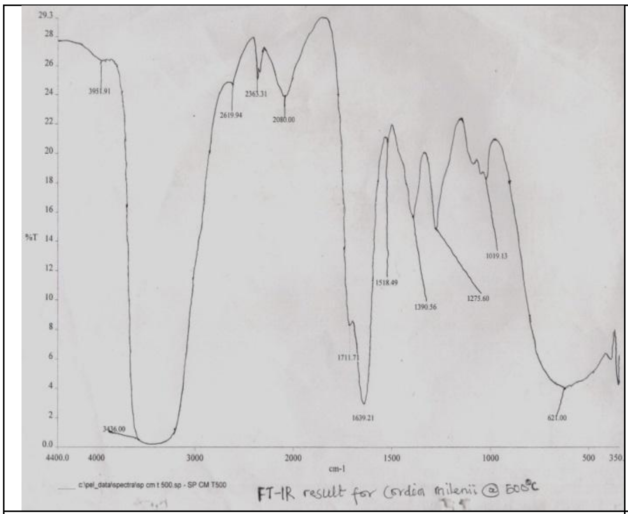


Fig11: FT –IR result for *Cordia milenii* at 500 °C

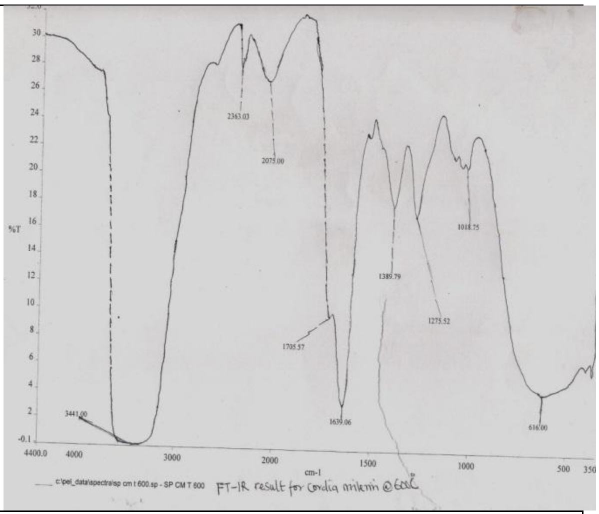


Fig 12: FT-IR result for *Cordia milenii* at 600 °C

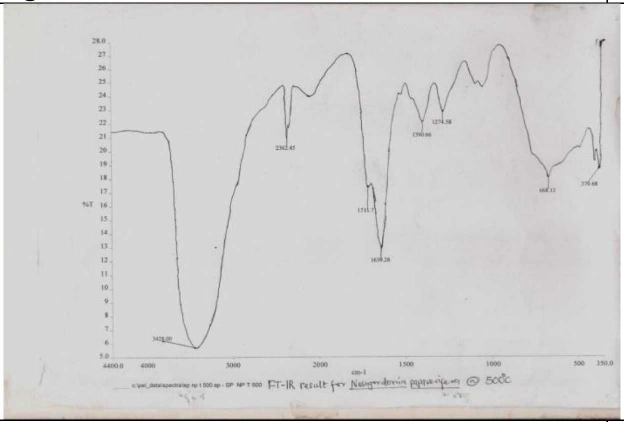


Fig 13: FT-IR result for *Nesogordonia papaverifera* at 500 °C

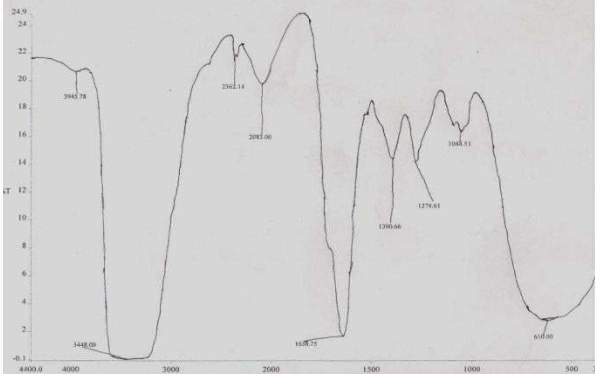


Fig 14: FT-IR result for *Nesogordonia papaverifera* at 600 °C

Fig11-14. *Graphical representations of FT-IR spectrum of the liquid obtained from pyrolysis of wood residues at different temperature range*

DISCUSSIONS

Physical Properties of Pyrolytic Oil

The study revealed that the bio-oil yield was higher at 600°C for Cordia milenii pyrolysis. At this condition the mean yield of Cordia milenii was 72.33g/cm3 compare to the yield of Nesogordonia papaverifera (63.63g/cm3). There was general increase in the volume of oil yield as the temperature increases. According to Solantaust et al. (2003) the bio-oil derived were not standardized products and can exhibit a wide range of properties and composition according to the feedstock and pyrolysis technique employed. Considerable experimental evidence suggested that there is increase in yield between liquid and gas and reduction in carbon solids (char) during wood pyrolysis which depends on the heating conditions (Park et al., 2010). Keown et al. (2005) reported that the cell structure may affect the pyrolysis behavior of biomass. The liquid yield was high showing the potential of reconversion liquid hydrocarbon from the fast pyrolysis of biomass. The liquid appeared brownish dark with a strong acidic smell. Heavy condensate or tar was also formed and adhered to the inner wall of condenser, liquid collectors and connecting pipes. At the initial stage, biomass is decomposed and depolymerized to small compounds by dehydration, dehydrogenation, deoxygenation and decarboxylation and these compounds may rearrange through condensation, cyclization and polymerization to form new compounds.

The characteristics of the oils derived from these two species were very similar to the characteristics of other biomass pyrolytic oils. The most prominent characteristic is the nature of the oil due to high oxygen content as agreed with Biotherm, (1999). A low pH range value of 3.52 - 3.73 is a common feature in the sampled species derived liquid and they are therefore very corrosive. The result of the density presented in Fig 5 revealed that there is significant difference in the values obtained for C. milenii and N. papaverifera with N. papaverifera having the highest density value of 1.04 g/cm3 which was high when compared with report of Solantausta et al; (1993) with approximated value of 1.2 g/cm3. Upon pyrolysis in the temperature range of 500°C - 600°C, the bio-oil yield of wood samples was higher. Its maximum value was reached at a higher temperature. Upon pyrolysis at 600°C, the formation of new, thermally more stable bonds occurs. This result agrees with Chirkova et al. (2006), whose results also reported higher yield of the char residue and increase in the amount of non-condensing gases upon pyrolysis of the samples. The result of the pour point revealed that C. milenii has the highest pour point value of -0.90 at temperature of 600°C which will not cause any trouble in most of the tropical regions but in colder regions with sub zero climate it may have freezing problems.

Proximate Analysis of Bio-Char Produced from Selected Sawmill Wood Residues

Proximate analysis is the quickest and simplest way of investigating the fuel quality of solid materials. After pyrolysis the volatile matter content of the selected sawmill wood species reduces between the different samples at different temperature with C. milenii having the highest volatile matter content of 45%, which indicates higher biomass to liquid fuels from this species. The result of the percentage ash content presented in Fig 7 indicated that N. papaverifera has the highest ash content (26.67) when compared with Cordia milenii (21.67) and this may be due to its chemical composition and presence of high extraneous materials. Percentage ash content, fixed carbon and volatile matter were the required prerequisite for the determination of heating value of the samples. As shown in (Table 2) there was no significant difference in the percentage fixed carbon between the species and differed significantly for percentage ash content and volatile matter between the species used.

Ash is an impurity that will not burn which reduces handling and burning capacity, it increases handling cost and affects combustion efficiency causes clinkering and slagging. The heating value range for the bio-char produced from C. milenii and N. papaverifera were obtained as 23083.22 - 26725.74 and 20333.89 - 25037.06 (Kj/kg) respectively. It was further shown that significant variations are not found among selected sawmill residues. This denotes high heating values as good combustion characteristics for energy generation and to acquire alternative source of bio- briquette for domestic and industrial application (Adegoke and Fuwape, 2008). Hence, any of these species can be used to meet the need of industrial combustion.

Compositional Analysis of the Bio-Oil

The elemental analysis of the oil is an important criterion for the design of a combustion plant utilizing the oil. The ultimate analysis showed the variations in the elemental composition of the selected sawmill wood residues (Table 3). The analysis showed significant variation in carbon and oxygen content whereas there were slight variations in hydrogen, nitrogen and sulphur content. Some of the oxygen in the original feedstock is thought to have turned into H2O, CO and CO2. The high oxygen content results in a low energy density of the bio oils. It was observed that changing the temperature causes a slight change in the elemental content of the bio-oil samples. However, no particular trends in the elemental composition were found within the range of reaction temperatures used.

Chemical Properties of Pyrolytic Liquid (FT-IR Analysis)

The FT-IR analysis suggested that the functional groups like alcohols, ketones, carboxylic acids, esters, alkanes, alkenes, alkynes, amide, nitriles, nitro compounds, ethers, aromatic rings were present in the bio-oil from C. milenii and N. papaverifera. The FT-IR spectra of bio-oil samples obtained from different temperatures exhibited the same peaks but these spectra differed in the relative intensity of some bands. It has to be confirmed with gas chromatography results. The functional groups of the two and various class of compounds that were identified from the FT-IR spectrum are presented in Table

4 and 5. The FT-IR spectra were recorded in the transmission mode between 3600 and 600 cm-1 for all samples. All the residues have similar aromatic and aliphatic functional groups but with different vibrating frequencies (cm-1).

At 5000C, the O−H stretching vibrating frequency between 3600 and 3200 indicated the presence of phenols and alcohols (−OH in alcohols and phenols). The group and class −NH2 in aromatic amines, primary amines and amides indicate the NH stretching vibrations. The absorbance between 2500 and 2000 represent the presence of benzo-nitrile with C≡H. The C=O deformation vibration between 1775 and 1650 cm-1 indicates the presence of carboxylic acid, ketones, aldehyde, esters and benzene derivatives. The absorption between 1680 and 1575 cm-1 indicated the presence of alkanes. The absorbance peaks between 1575 and 650 represent N−H bend, C−H bend, ≡C−H bend and C=C which further indicated the presence of alkanes, acohols, aromatic compounds and alkynes. The rise in these bands suggests an increase in aromatic structures, nitrogeous compounds and alkanes. The weaker bands suggest a decrease in carbonly groups (COOH, Ketones and aldehydes) as well as aliphatic groups.

Russell et al. (1983) recognized the formation of aromatic compounds, when cellulose was thermo-chemically converted in an alkali solution. They suggested that these aromtic were formed by condensation or cycliation of unstable intermediate fragments, which were generated by degradation of the cellulose. These changes observed by FT-IR indicate that bio oil possess both the aliphatic structures and aromatic components. The changes of intensity of the bands indicated the decrease in aliphatic structure and increase in aromatic components with increaseing reaction temperature. At 6000C similar functional groups were observed in the FT-IR spectrum in all the selected wood species without any effect of temperature regimes used during pyrolysis. Meier et al. (1997) and Bramer et al., (2004) reported that high oxygenated compounds present in biomass pyrolysis oil is responsible for differences in the properties and behaviour of bio-oil. Hence, it is important to deoxygenate the liquid by some upgrading technology.

CONCLUSION

Conclusion

Pyrolysis is a proficient way to produce liquid fuels from biomass. The quality of raw bio-oil produced has to be improved before it can be used as a traffic fuel or combusted in boilers. During pyrolysis process the solid content in the bio-oil can be reduced by efficient char removal. The bio-oil obtained showed comparable fuel properties and can be regarded as moderate grade commercial fuels. In order to utilize it as commercial transportation fuel certain improvement in properties like density and corrosiveness have to be stabilize. The bio-oil obtained contains chemical compounds of varying carbon chain length from C4 - C27 and functional groups such as alkanes, alkenes, alkynes, alcohols, ketones, aldehyde, aromatic rings, amides and nitrile compounds. Bio-char (charcoal) obtained has good calorific value, thus can be used as alternative fuel (briquette production). The physical properties of the bio-oil obtained from sawmill wood residues falls within the acceptable range for fuel production. The selected wood species are therefore suitable for production of bio-oil with acceptable physical and chemical properties. The thermal degradation processes (pyrolysis), may help to reduce environmental pollution, deforestation at the same time providing greater amounts of desirable, renewable fuel and chemical source thereby creating wealth from waste.

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