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Determination Of Proximate Analysis Of Bio-Mass In Selected Bio-Oil Ash Content

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ABSTRACT
The study looked at the proximate analysis of biomass in selected bio-oil ash content. The study used two research questions. The study employed the experimental research design. Proximate analysis is used to identify the physical properties of the biomass and bio-oil, which include moisture, ash, volatiles, and fixed carbon content on a dry basis. The fixed carbon, moisture, volatiles, and ash contents in EPFB biomass were determined by weighing a sample mass (W_s) of 3g in a Petri dish and drying it in an electric oven set at 105°C according to the standard method. To evaluate the biomass and bio-oil ash content, ASTM D-3175-01 technique was used in which 1.0g of EPFB biomass sample was heated to 700 °C in a muffle furnace and kept for 12 hours to burn off the carbon. After that, the sample was cooled and weighed again. This was determined by estimating the loss in weight resulting from heating the EPFB under rigidly controlled conditions in a platinum crucible with a closely fitting cover. The measured weight loss, corrected for moisture, establishes the volatile matter content. To eliminate air contact throughout the devolatilization process, the dried and powdered EPFB biomass particle sample was kept in a closed crucible and heated to 900°C for 7 minutes at a heating rate of 100°C/min. The crucible is then cooled and weighed. Findings obtained from the study showed that research question I, table 1, revealed that pH at EPFB and diesel is 2-3 and 0.00; Density (kg/m^3) at EPFB and diesel is 1300 and 800; Viscosity Pa's (40^{0}C) at EPFB and diesel is 0.04-0.01 and 0.004; and Moisture at EPFB and diesel is 26.5 and 0.006. Also, findings obtained from research question 2, table 2, revealed that pH at EPFB and heavy fuel oil is 2-3 and 5; Density (kg/m^3) at EPFB and heavy fuel oil is 1300 and 1000; Viscosity Pa's (40^{0}C) at EPFB and heavy fuel oil is 0.04-0.01 and 0.12; and Moisture at EPFB and heavy fuel oil is 27.8 and 1.6. Finally, it was recommended that fuel blend with biomass should be improved on by the application of optimization technology to enhance quality.
Keywords: Proximate Analysis, Bio-Mass, Bio-Oil, Ash Content

INTRODUCTION

The term biofuel refers to liquid, gas and solid fuels predominantly produced from biomass (Demirbas, 2006). Biomass can be defined as the biodegradable fraction of products, waste and residues from organic non-fossil material of biological origin that is readily available on recurring sustainable basis (Bridgewater, 1999). Biomass may be considered as the energy derived from plants, such as trees, grasses, agricultural crops/residues, organic fractions of municipal solid wastes, paper, cardboard, food waste, animal manure, green waste and other waste (Demirbas, 2009; Sambo, 2000). It is in abundance and stands as the third energy resource after oil and coal (Yaman, 2004; Radmanesh *et al*., 2006). The significant advantage of using biomass is that it can be converted to liquid, solid and gaseous fuels

(Yaman, 2004). It can also contribute to mitigating the effects of climate change as it will replace conventional fossil fuels (Radmanesh *et al*., 2006; Tsai *et al*., 2005).

Various routes exist by which biomass can be converted into bioenergy and other industrial products. Such routes include: biological, chemical and thermal processes. Biological method involves the use of fermentation (bacterial and fungal) and anaerobic digestion, chemical processes involve the transesterification of oil to produce biodiesel, while thermal conversion processes include direct combustion, gasification and pyrolysis. Out of all these processes, pyrolysis produces energy fuels with high fuelto-feed ratios, making it probably the most efficient process for biomass conversion and the method most capable of competing and eventually replacing non-renewable fossil fuel resources (Demirbas, 2006). The liquid product of the fast pyrolysis of biomass is called bio oil. This bio oil is a dark brownish viscous, free-flowing organic liquid that is made up of highly oxygenated compounds, which bear some resemblance to fossil crude oil (Czernik and Bridgwater, 2004). The synonyms for bio-oil include pyrolysis oils, pyrolysis liquids, bio crude oil (BCO), wood liquids, wood oil, liquid smoke, wood distillates, pyroligneous acid and liquid wood (Mohan *et al*., 2006). Bio oil is considered as relevant technologies for the following reasons: energy security, environmental concerns, foreign exchange savings, and socio economic issues related to the rural areas.

Purpose of the Study

The study looked at determination of proximate analysis of bio-mass in selected bio-oil content. Specifically the study sought to:

1. Find out the variation of yield obtained from Bio-oil (EPFB) and diesel.
2. Find out the relative yield obtained from Bio-oil (EPFB) and Heavy fuel oil.

Research Questions

The following research questions were used as a guide for the study:

1. What is the variation of yield obtained from Bio-oil (EPFB) and diesel?
2. What is the relative yield obtained from Bio-oil (EPFB) and Heavy fuel oil?

Scope of the Study

The study is limited to proximate analysis of bio-mass in selected bio-oil ash content. It is also limited to laboratory analysis of yield obtained biomass, diesel and heavy duty oil.

LITERATURE REVIEW

Biomass Availability in Nigeria

Majority of the world poor live in sub-Saharan Africa. Nigeria is the most populous country in sub-Saharan Africa with nearly one quarter of sub-Sahara Africa's population and is one of the poorest countries in the world despite the huge resources from crude oil export (Etiosa *et al*., 2007). The current population of Nigeria stands at 167 million with an annual growth rate of 2.3 per cent (Zubem, 2012). Nigeria is located in West Africa, between latitudes 4 and 14o north of the equator and longitude 3 and 14o east of Greenwich, along the Gulf of Guinea (Sambo, 2009; Obioh, 2009). It borders the Gulf of Guinea, between Benin (773km) on the west and Cameroon (1, 690km) on the east (www.nationsencyclopedia.com, accessed on December 14, 2012). It also borders the Republic of Niger (1,497km), Chad (87km), and Atlantic Ocean (853km) at the north, north-east, and south, respectively. The land mass of the country extends from the Gulf of Guinea in the south to the Sahel (the shore of the Sahara Desert) in the north and this amounts to a total land area of 910, 768km^2 (www.nationsencyclopedia.com, accessed on December 14, 2012; Obioh, 2009). Approximately 33% or 300,550 km^2 of the total land area is arable, while 3.1% or 28,234 km^2 is under permanent crops and approximately 2, 820 km^2 or 0.31% is under irrigation (CIA, 2009). About 13,000 km^2 of the total compact area of 923,768 km^2 which Nigeria occupies is water and the terrain thus varies from coastal swamp and tropical forest in the south, to savannah and semi-desert in the north (Obioh, 2009). The availability of biomass resources follows the same pattern as the vegetation of the nation (Sambo, 2000). Thus, the rain forest in the south generates the highest quantity of woody biomass while the guinea savannah vegetation of the north central region generates more crop residues than the Sudan and Sahel

savannah zones. Global climate models predict increased precipitation in some areas in Nigeria and this should result in increased biomass availability (Obioh, 2009). However, countering the increased biomass availability will be the increased flooding in the south and drought in the North. As would be expected, the net effect of climate change on biomass availability will depend on the relative magnitudes of these changes. Biomass is the major energy source in Nigeria contributing nearly 78% of Nigeria primary energy supply (Edirin & Nosa 2012). In Nigeria, the following biomass resources are available; fuelwood, agricultural waste and crop residue, sawdust and wood shaving, animal dung/poultry droppings, industrial effluents/municipal.

METHODS

Proximate analysis

Proximate analysis is used to identify the physical properties of the biomass and bio-oil, which include moisture, ash, volatiles, and fixed carbon content on a dry basis. Moisture content was determined using ASTM D4442 standard method (Naqvi *et al*., 2014). The fixed carbon, moisture, volatiles, and ash contents in EPFB biomass were determined by weighing a sample mass (W_s) of 3g in a Petri dish and drying it in an electric oven set at 105°C according to the standard method. The results are given as weight percent expressed on a dry basis. After drying to get the total dry mass (W_d), we use equation 1 to calculate the moisture content (MC) as:

The sample was weighed every hour for 24 hours until a constant weight was reached.

$$Moisture\ Content\ (MC) = \frac{w_s - w_d}{w_s} \times 100 \quad (1)$$

To evaluate the biomass and bio-oil ash content, ASTM D-3175-01 technique (Naqvi *et al*.,2014) was used in which 1.0g of EPFB biomass sample was heated to 700°C in a muffle furnace and kept for 12 hours to burn off the carbon. After that, the sample was cooled and weighed again. The weight differential accounts for the ash in the biomass sample. The ASTM E-872 method was used to calculate the volatile matter (Auta *et al*., 2014). This was determined by estimating the loss in weight resulting from heating the EPFB under rigidly controlled conditions in a platinum crucible with a closely fitting cover. The measured weight loss, corrected for moisture, establishes the volatile matter content. To eliminate air contact throughout the devolatilization process, the dried and powdered EPFB biomass particle sample was kept in a closed crucible and heated to 900°C for 7 minutes at a heating rate of 100°C/min. The crucible is then cooled and weighed. Equation 3.2 is used to calculate the biomass's fixed carbon content on a dry basis:

$$Fixed\ Carbon(wt\%) = 100 - MC(wt\%) - VM(wt\%) - AC(wt\%) \quad (2)$$

Where MC=moisture content, VM=volatile matter, and AC= ash content.

Ultimate Analysis of Biomass

The ultimate and proximate analyses of the biomass and bio-oil obtained with a CHNOS analyzer were performed using the modified Pregl and Dumas technique (ASTM D5373). The biomass was combusted in a high-temperature oxygen stream using the CHNS/O analyzer (Perkin Elmer PE2400 elemental analyzer, Spectrum II) to determine the C, H, O, N, and S contents of the EPFB. The sample oxygen composition was determined by subtracting the percentages of carbon, hydrogen, nitrogen, and sulphur present in the sample from 100 (Wildschut *et al*., 2009). The oxides (CO_2, H_2O, and N_2) of the elements concerned are separated using helium as the carrier gas in the detector. Thermal conductivity is used to analyze combustion products in pure oxygen. The sample's elemental composition was then determined using the combustion products of their oxides, and the oxygen content was calculated by difference from 100 (Wildschut *et al*., 2009). According to Naqvi *et al*. (2014), the EPFB bio-oil was also characterized for total carbon, total hydrogen, and total nitrogen using ASTM D5291 method applicable to samples such as crude oil, fuel oil, and residues. Using the Murata *et al*. (2012) (ASTM E711-87) method in an oxygen bomb calorimeter, the calorific value of EPFB was calculated.

Gas Chromatography/Mass Spectroscopy (GC/MS)

The elemental chemical composition and functionality of the groups present in the bio-oil samples were detected using a combination of GC and MS (Shimadzu QP2010 Kyoto, Japan) to analyze the crude and upgraded bio-oil samples. The groups are identified using the standard I.R. spectra for hydrocarbons. The column was a Supelco SPBTM-1 Sulfur fused silica capillary column with a film thickness of 30m x 0.32mm x 4.0m and was connected to an FID detector on the instrument. The GC/MS shown in Figure 1 was utilized to undertake a qualitative and quantitative study of the bio-oil volatiles. In 5ml of acetone, 200 mg of cracked bio-oils were dissolved. The groups are identified using the standard I.R. spectra for hydrocarbons. The carrier gas was helium, and the flow rate remained constant at 1 ml min^{-1}. According to Charon *et al*. (2015) temperature program, 1 µl of bio-oil sample diluted in pure acetone was injected straight into the heated split injector (split ratio 20:1) at 250°C. For the work in the GC oven, the temperature ramps were as follows: the oven was kept at 50°C for 2 minutes, then heated to 90°C at a rate of 10°C/min for 20 minutes. A 2.8-minute solvent separation time was chosen to eliminate the solvent effect. After that, the instrument's spectroscopic software was used to identify the sample functional groups by comparing their characteristic absorption bands to the conventional I.R. spectra of hydrocarbons.

Figure 1: Gas chromatograph used for samples analysis

Fourier Transform Infra-Red (FTIR) Spectroscopy

The functional groups in the EPFB feedstock and bio-oil were obtained using a Perkin Elmer Spectrum 65 FTIR Spectrometer equipped with an infrared source and a potassium bromide beam splitter to access their characteristics. The EPFB biomass was combined with a proprietary powder and a sample preparation solvent to make a paste and compressed into pellets, following the process defined in the instrument manual for powdered samples before being placed into the instrument mold. Before scanning the samples, the bio-oil and biomass were prepared through KBr pretreatment. A small amount of the bio-oil was mounted on a potassium bromide (KBr) disc previously scanned as a background. The sample spectra were obtained using a resolution of 4cm^{-1} with 128 successive scans and a wavenumber region of 400-4000 cm^{-1} in the transmission mode to determine the vibration (stretching and bending) and rotation modes of chemical bonds. The absorption frequency spectra were recorded and plotted. Then, using the instrument's spectroscopic software, the sample functional groups were identified by comparing their characteristic absorption bands to the conventional I.R. spectra of hydrocarbons.

DATA ANALYSIS

Research Question 1: *What is the variation of yield obtained from Bio-oil (EPFB) and diesel?*

Table 1: Variation of yield obtained from Bio-oil (EPFB) and diesel.

S/N	Property	Bio-oil (EPFB)	Diesel
1	pH	2-3	0.00
2	Density (kg/m^3)	1300	800
3	Viscosity Pa.s (40^{o}C)	0.04-0.01	0.004
4	Moisture	26.5	0.006

Findings obtained from research question I, table 1, revealed that pH at EPFB and diesel is 2-3 and 0.00; Density (kg/m^3) at EPFB and diesel is 1300 and 800; Viscosity Pa's (40^{0}C) at EPFB and diesel is 0.04-0.01 and 0.004; and Moisture at EPFB and diesel is 26.5 and 0.006.

Research Question 2: *What is the relative yield obtained from Bio-oil (EPFB) and Heavy fuel oil?*

Table 2: Relative yield obtained from Bio-oil (EPFB) and Heavy fuel oil.

S/N	Property	Bio-oil (EPFB)	Heavy fuel oil
1	pH	2-3	5
2	Density (kg/m^3)	1300	1000
3	Viscosity Pa.s (40^{o}C)	0.04-0.01	0.12
4	Moisture	27.8	1.6

Findings obtained from research question2, table 2, revealed that pH at EPFB and heavy fuel oil is 2-3 and 5; Density (kg/m^3) at EPFB and heavy fuel oil is 1300 and 1000; Viscosity Pa's (40^{0}C) at EPFB and heavy fuel oil is 0.04-0.01 and 0.12; and Moisture at EPFB and heavy fuel oil is 27.8 and 1.6.

Summary of Findings

Below is the summary of findings:

1. Findings obtained from research question I, table 1, revealed that pH at EPFB and diesel is 2-3 and 0.00; Density (kg/m^3) at EPFB and diesel is 1300 and 800; Viscosity Pa's (40^{0}C) at EPFB and diesel is 0.04-0.01 and 0.004; and Moisture at EPFB and diesel is 26.5 and 0.006.
2. Findings obtained from research question2, table 2, revealed that pH at EPFB and heavy fuel oil is 2-3 and 5; Density (kg/m^3) at EPFB and heavy fuel oil is 1300 and 1000; Viscosity Pa's (40^{0}C) at EPFB and heavy fuel oil is 0.04-0.01 and 0.12; and Moisture at EPFB and heavy fuel oil is 27.8 and 1.6.

CONCLUSION

The findings revealed that the variation in density viscosity, pH and moisture on diesel and heavy fuel oil are different. This implies that fuel quality is determined by the standard of blend used at different conditions.

RECOMMENDATION

Finally, it was recommended that fuel blend with biomass should be improved on by the application of optimization technology to enhance quality.

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