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RESEARCH PAPER

Compositional Analysis and Characterization of Lignocellulosic Biomass from Selected Agricultural Wastes

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Abstract

Agricultural wastes have been identified as a potential lignocellulosic biomass for bioethanol production. An accurate biomass characterization is needed to evaluate the new potential lignocelluloses biosource for biofuel production. This study evaluates the compositional analysis and characterization of three agricultural wastes (melon husk, moringa pod and mango endocarp). The samples were collected locally in Sheda Village, FCT, Abuja, Nigeria. The lignocellulose biomass composition of the samples was determined by using a proven economically viable gravimetric method and the samples were further characterized using the FTIR. The results showed that a significant amount of hemicelluloses content was found, from 19.38% to 27.74% and the highest amount was present in melon musk. The amount of cellulose ranging from 22.49% to 45.84% was found where the highest amount was found in mango endocarp. Lignin content was in the range of 22.62% to 29.87% and melon husk was shown to have the highest amount. The FTIR spectroscopic analysis showed a broad band at 3422.99 cm^{-1}, 3422.66 cm^{-1}, 3422.85 cm^{-1} (for mango endocarp, melon husk and moringa pod respectively) representing bonded –OH groups. The peak around 1637 cm^{-1} corresponds to C=C stretching of conjugated carboxylic acids. The aliphatic chains, $-CH_2-$ and $–CH_3$, which form the basic structure of cellulose material, were seen at 1205.72, 1204.50 and 1206.24 cm^{-1}. The signals at 1056.15, 1035.80 and 1055.86 cm^{-1} correspond to C-O-R (alcohols or esters) vibration. The results show that the samples contain significant quantity of lignocellulosic biomass. Thus, the agricultural wastes could be of valuable use in biofuel production.

Keywords: melon husk; mango endocarp; moringa pod; lignocellusic biomass; biofuel

INTRODUCTION

An agrarian country like Nigeria is rich in many agricultural by-products, among which are melon seed husk, mango endocarp, and moringa pod. Nigeria ranks 10th among the major producers of mango in the World (Rekhapriyadharshini, 2015). After the processing of mango fruit, around 35-60% of the mango fruit will turn into a waste (O'Shea et al., 2012). Also, every year more than one million tons of mango seeds was produced as wastes and at present was not utilized for any profitable purposes (Leanpolchareanchai et al., 2014). Ayotunde et al. (2011) reported that a normal-sized Moringa tree (15-20 feet in height) can produce thousands of seed pods which will resulted in uncountable amount of Moringa seeds. Most agro wastes, such as moringa pod, mango endocarp, and melon husk, do not have economically viable technologies their conversion. They are normally burned in the field. This habit pollutes the environment as well as cause other problems such as the air plane accident due to the smoke clouds in the sky (Li et al., 2008). Agricultural wastes have been acknowledged as one of the alternatives to grains for fuel or ethanol production without endangering food security. The abundance and renewability of agro wastes have made them a candidate of raw materials for the production of bioethanol commercially (Mtui, 2009). However, their recalcitrance to degradation and unique chemical composition were a challenge to be tackled before this become a reality (Himmel et al., 2007).

Lignocellulose has been recognized as a potential and major source for biofuels and other value-added products. Lignocellulose is a major component of municipal solid wastes, crop residues, forest residues and dedicated energy crops. Lignocelluloses produced from agricultural and forest residuals contributes to the major amount of the total biomass available in the world (Kusch and Morar, 2009). Lignocellulosic biomass comprises of all plants and plant-derived materials such as crops and trees, wood and wood and municipal residues (Ayeni et al., 2013). Lignocellulosic biomass is a non-edible plant material which consist of the polysaccharides cellulose and hemicellulose. The third major component is lignin. It is a phenolic polymer which needed for structural strength of the plant. These major components are bonded together through a covalent bonding, various intermolecular bridges and van der Waals' forces which resulted in their resistant to enzymatic hydrolysis and insoluble in water (O'Sullivan, 1997). The minor component in biomass is the extractives. The extractives are the components present outside the cell wall; they are composed of low or medium molecular weight and easily extracted by specific solvents such as acetone, toluene, alcohol and water (Silvério et al., 2006).Many have reported that the reduction or lowering of cellulose's crystallinity caused a higher rate of bioconversions for the lignocelluloses (Hall et al., 2010; Goshadrou et al., 2011; Jeihanipour et al., 2010b; Ostovareh et al., 2015).

X-ray diffraction (XRD), infrared (IR) spectroscopy, Fourier transform (FT)-IR spectroscopy (FTIR), Raman spectroscopy, terahertz-time domain spectroscopy (THz-TDS), and nuclear magnetic resonance (NMR) are commonly used methods for the evaluation of the crystallinity of a substrate (Park et al., 2010; Vieira and Pasquini, 2014). At present, FTIR, XRD, and NMR are the most employed among the methods (Ju et al., 2015). FTIR is the simplest method with easy sample preparation and does not require specific operation experience (Fan et al., 2012).

The production of ethanol from lignocellulose require four main steps: pretreatment, hydrolysis, fermentation, and product purification. Hydrolysis converts carbohydrate polymers into monomeric sugars which are then fermented to ethanol. The process of pretreatment is purposely for lysing the lignin seal and distrupting the crystalline part in cellulose so that it would be easier for the enzyme to convert carbohydrate polymers into fermentable sugars (Kusch and Morar, 2009). Accurate measurement of the content of lignocelluloses biomass very importance because it will determine the amount of ethanol yield (L/mg) (Sluiter et al., 2010). The determination of lignocellulose composition is the key component which determine the overall efficiency of processes designed to convert lignocellulosic biomass to ethanol. Study shows that not much work has been carried out to estimate the lignocelluloses biomass composition of melon husks, moringa pod, and mango endocarp. This research is, therefore, aimed at analyzing and characterizing the lignocelluloses biomass of the selected agricultural wastes to ascertain the morphological and chemical properties as well as their composition.

MATERIALS AND METHODS

All biomass materials will undergo compositional analysis using the gravimetric method reported by Ayeni et al. (2015).

Extractives: 2.5 g of each of the dried samples was extracted with 150 mL acetone using Soxhlet extractor set up. After the extraction process, the sample will be air dried at room temperature before being kept in a convection oven at 105 ^{o}C to get the constant weight. The (%w/w) of the extractives content was determined by calculating the difference in weight of the raw extractive-laden biomass and extractive-free biomass (Blasi et al., 1999; Li et al., 2004; Lin et al., 2010).

Hemicellulose: 150 mL of 0.5 M NaOH was added was added to 1 g of extractives free dried biomass in a 250 mL Erlenmeyer flask. The the mixture was boiled for 3.5 hours before being cooled, filtered and washed using distilled water to get neutral pH. The residue then dried in convection oven at 105 ^{o}C. Then, the hemicellulose content (%w/w) of dry biomass was calculated by finding the difference of the sample before and after the treatment. (Blasi et al., 1999; Li et al., 2004; Lin et al., 2010; Ayeni et al., 2013).

Lignin: 3 mL of 72 % H_2SO_4 was added to 0.3 g of dried extractive-free samples. Then the initial hydrolysis was initiated by keeping the sample at room temperature for 2 hour while shaking it at 30 minutes intervals. The second step of hydrolysis was carried out by adding 84 mL of distilled water and placed the mixture in an autoclave for 1 hour at 121 °C. The slurry was then cooled at room temperature. Hydrolysates were filtered using a vacuum filtration. The lignin content was calculated as the summation of acid insoluble lignin and acid soluble lignin (The acid soluble lignin and insoluble lignin were determined by UV-visible spectroscopy and gravimetric analysis, respectively) (Sluiter et al., 2008).

Cellulose: The cellulose content (%w/w) was calculated.

FT-IR Spectroscopy:

Fourier transform infrared (FTIR) spectroscopic analysis was used to study the surface chemistry of the waste samples. Dried waste samples were characterized using a Nicolet IS 5 Thermo Fisher Scientific, USA FTIR spectrophotometer. Each sample was scanned between the wavelength of 400 and 4000 cm^{-1}. FTIR spectra of the samples give information about the characteristic functional groups on the surface of melon husk, moringa pod and mango endocarp.

RESULTS AND DISCUSSION

Lignocellulose Biomass Composition

The basic lignocellulose biomass composition of the melon husk, moringa pod, and mango endocarp is shown in Table 1. The basic lignocellulose biomass composition of the melon husk, moringa pod, and mango endocarp is shown to contain the highest amount of cellulose (45.84%) while hemicellulose was found to be highest in Moringa pod. There is no significant difference in the amount of lignin from the samples. Generally, the composition of lignocellulosic biomass feedstock consists of cellulose, hemicelluloses, lignin, extractives and ash are as shown in Figure 1. Results from this study are comparable to those reported in the literature (Table 2).

Table 1. Compositional analysis of raw lignocelluloses of samples (% w/w).

Sample	Extractive	Ash	Hemicellulose	Lignin	Cellulose	Hemicellulose/lignin
Melon husk	19.03	0.87	27.74	29.87	22.49	0.93
Moringa pod	12.53	0.62	39.94	22.62	24.29	1.77
Mango endocarp	5.34	0.57	19.38	28.87	45.84	0.67

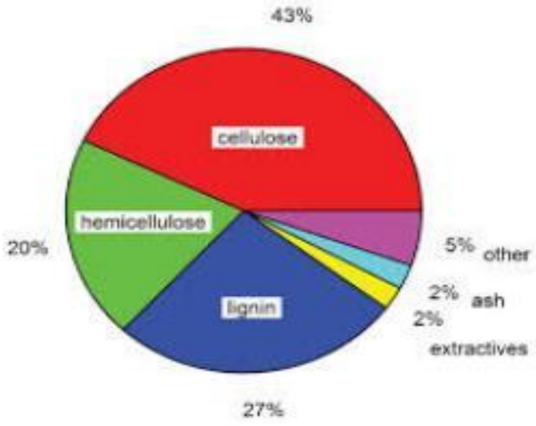

Figure 1. Composition of lignocellulosic biomass (Ali and Jamaludin, 2015).

Table 2. Reported compositional analysis of raw lignocelluloses of sugarcane bagasse, siamweed, and Rice straw (%w/w).

Sample	Cellulose	Hemicellulose	Lignin	Ash	Extractives	References
Sugarcane bagasse	35-49	16-33	11-25	4-9	2	Bon (2007); Mesa et al. (2010); Ayeni et al. (2015)
Siam weed	4.8±0.9	40.2±2.3	29.9±0.7	23.2±5.3	0.9±3.1	Ayeni et al. (2015)
Rice straw	32-47	19-27	5-24	12.4		Karimi et al. (2006); Sarkar et al. (2012)

The quantity of the various lignocelluloses components of biomass affects their availability and the ease of their usage in the production of biofuel. Literature has shown that the cellulose component of biomass is the most abundant renewable organic resource followed by the hemicellulose component (Chen, 2014; Ali and Jamaludin, 2015). The high cellulose component of the mango endocarp and the high hemicelluloses component of moringa pod from this study is a reflection of their potentials of being of valuable use in biofuel production as a sizeable quantity of simple sugars for the onward production of biofuel will be obtainable from them.

The structure of the plant cell wall is compact. There is different bonding among cellulose, hemicellulose, and lignin. Cellulose and hemicellulose or lignin molecules are mainly coupled with a hydrogen bond. In addition to the hydrogen bond, there is the chemical bonding between hemicellulose and lignin, which results in the lignin, isolated from natural lignocelluloses, always contains a small number of carbohydrates (Chen, 2014). The hemicelluloses/lignin interaction will, therefore, affect the release of simple sugars from the biomass during hydrolysis. Mango endocarp sample, from this study, displayed the lowest hemicellulose to lignin ratio (0.67) followed by melon husk (0.93) while moringa pod displayed the highest hemicelluloses to lignin ratio (1.77). Considering the extra bond strength imparted on the biomass by the hemicelluloses and lignin interaction, the ease of hydrolysis of the samples in this study would be in the order: Mango endocarp>Melon seed husk>Moringa pod

FT-IR Spectroscopy

Fourier transform infrared spectroscopy is widely used to identify functional groups in the complex organic mixture and to compare similarities between substances. In this study, FT-IR was used to demonstrate the physical structure and functional groups of lignocelluloses materials of mango endocarp, melon husk, and moringa pod. The FT-IR spectra of the components of the dried waste samples are shown in Figures 2-4. The characteristic/prominent peaks for samples are provided in Table 3.

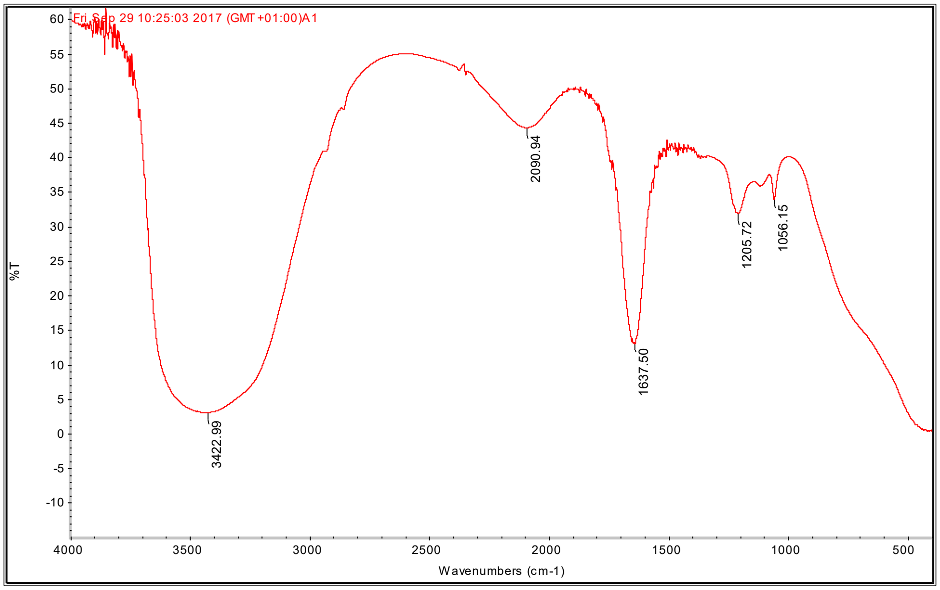

Figure 2. FT-IR Spectrum for Mango endocarp.

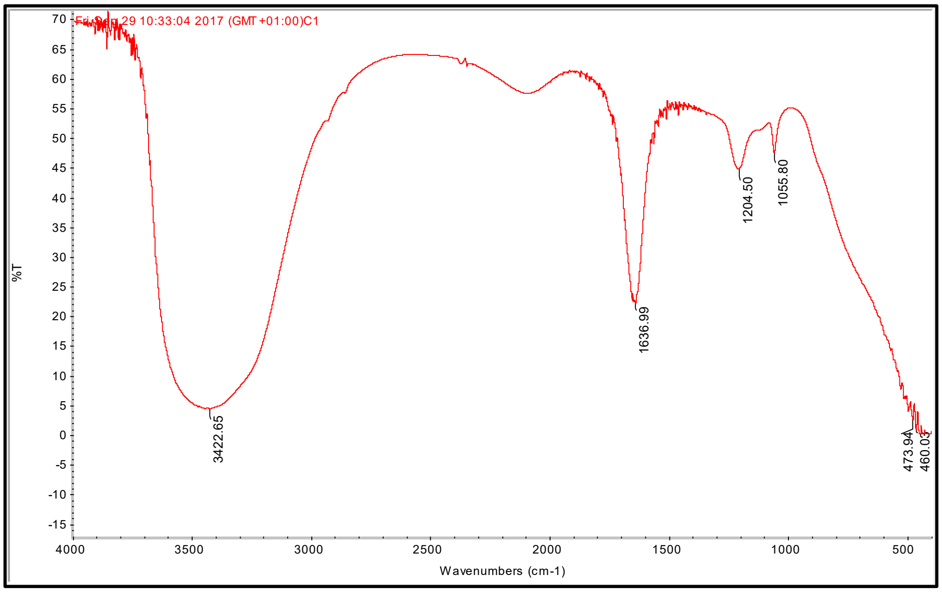

Figure 3. FT-IR Spectrum for Melon husk.

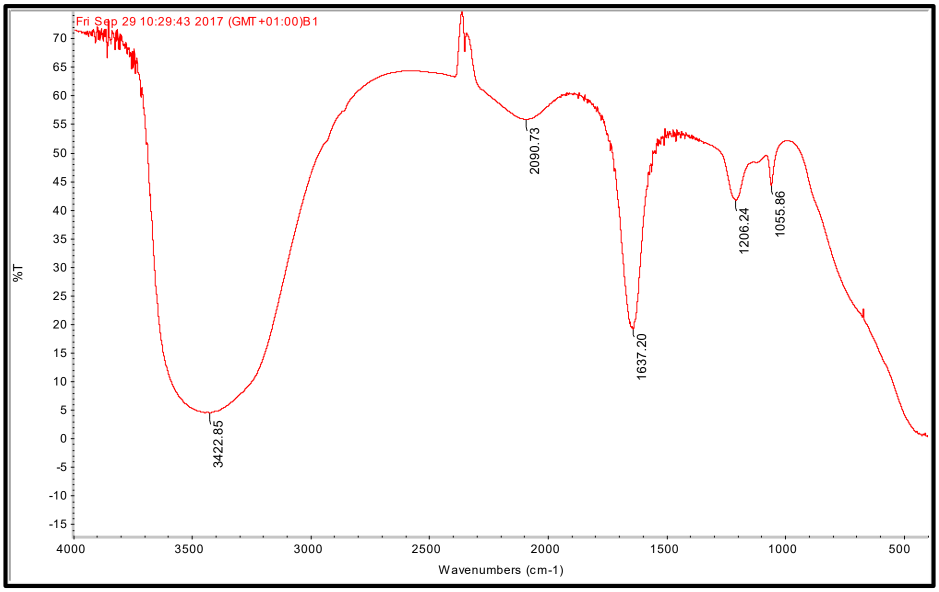

Figure 4. FT-IR Spectrum for Moringa pod.

As shown in Figures 2-4 and Table 3, the FTIR spectroscopic analysis indicated broadband at 3422.99 cm^{-1}, 3422.66 cm^{-1}, 3422.85 cm^{-1} (for mango endocarp, melon husk, and moringa pod respectively) representing bonded –OH groups. The peak around 1637 cm^{-1} corresponds to a C=C stretching of conjugated carboxylic acids. The vibrations of the aliphatic chains, $-CH_2-$ and $–CH_3-$, which form the basic structure of cellulose material, are seen at 1205.72, 1204.50 and 1206.24 cm^{-1}. The signals at 1056.15, 1035.80 and 1055.86 cm^{-1} can be attributed to C-O-R or C-O-R (alcohols or esters) vibration (Champagne and Li, 2009; Zapata, 2009). The observation in this study is in agreement with that reported by Sanchez et al. (2014) and Bello et al. (2017). These bands are therefore common to those observed in cellulose, hemicelluloses and lignin FT-IR spectra (Bodirlau et al., 2008; Xu et al., 2013).

Table 3. FTIR of Acid Hydrolysis of Extractive Free Mango Endocarp, Melon Husk and Moringa Seed.

Functional groups	**Mango endocarp**	**Melon husk**	**Moringa pod**
O-H stretch	3422.99	3422.66	3422.85
C=C stretch	1637.50	1636.99	1637.20
-CH_2- and –CH_3- vibration	1205.72	1204.50	1206.24
C-O-R (ester)	1056.15	1035.80	1055.86

CONCLUSIONS

The results of the samples analyzed in this study indicate that the agricultural wastes could be of valuable use in biofuel production as a sizeable quantity of simple sugars for the onward production of biofuel may be obtainable from them. This is shown in the quantity of lignocellulosic biomass, especially cellulose and hemicellulose, obtained from them. Thus, rather than been allowed to constitute environmental pollutants, they (melon husk, mango endocarp, and moringa pod) can be used as an alternative source of biofuel.

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