Effect of Alkaline Pretreatment on the Mophology of Biomass Prior To Anaerobic Digestion

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ABSTRACT

Anaerobic digestion using lignocellulosic materials as the substrate is a cost-effective strategy for biomethane production, which provides great potential to convert biomass into renewable energy and organic fertilizer. However, the recalcitrance of native lignocellulosic biomass makes it resistant to microbial hydrolysis, which reduces the bioconversion efficiency of organic matter into biogas. As a measure to alter the structure of lignocelluloses biomass to make the holocellulose suitable for bio conversion, this study uses 5% w/v NaOH solution to delignify groundnut shell and sugarcane bagasse to alter the morphology of the biomass prior tanaerobic digestion. The characteristics of the treated and untreated samples were analysed via FTIR and Thermogravimetric analyses. The findings of the study for all the essential parameters, using standard methods, before and after the alkalization process, showed that, pretreatment of groundnut shell and sugarcane bagasse with 5% wt/v NaOH can effectively reduce the lignin and hemicellulose content and increase the cellulose content. In conclusion, the de-lignified biomass have greater potential for biogas generation than the untreated samples. The study recommend the use of groundnut shell and sugarcane bagasse for biogas production as a worthwhile venture, considering the zero cost and the substrates are best efficient when pretreated with NaOH.

1. INTRODUCTION

In the last few decades, due to rapid industrialization and urbanization, there was enormous pressure to reduce utilization of fossil fuels as most of the countries depend on it for power generation and for transportation needs (Cai *et al.,* 2019). Petroleum–based fuels play a key role as a primary source of energy and its continuous usage leads to an increase in CO_2 content in the atmosphere and global warming (Cai *et al.,* 2019). In the light of this, less polluting alternative sources of energy need to be sourced and utilized at a maximum possible extent. However, it is important to replace energy from fossil fuel with renewable energy sources such as solar energy, wind energy, geothermal energy, hydroelectric energy,

biomass energy, ocean energy etc., in other to remedy environmental disasters (Oloko-Obba *et al.,* 2018).

Renewable resource is a resource that can be produced continuously by nature or by people. It is environment friendly, low-cost, clean and multipurpose fuels. Non-renewable resource is a resource that takes too long to replace or cannot be replaced at all. The renewable energy sources such as biomass, wind, solar energy etc. fulfill 14% of total world energy demand (Yavini *et al.,* 2014).

Also, an increase in waste generation through agricultural practices, as a result of population growth and urbanization, has led to massive garbage disposal and management problems and has necessitate waste management system, an integral part of resource management (Janke *et al.,* 2016).

Government and industries are constantly searching for advanced technologies that will allow for more eco-friendly and cost effective waste treatment/managements. The only technology that can successfully treat the organic fraction of wastes is anaerobic digestion (Janke *et al.,* 2016). Anaerobic digestion is applicable for a wide range of materials including municipal, agricultural and industrial wastes (Kinyua *et al.,* 2016). During anaerobic digestion, the main plant biomass components, proteins, polysaccharides and lipids are initially hydrolysed to more simple amino acids, monosaccharides and free long chain fatty acids and glycerol. The fermentable products are fermented by various bacteria either to volatile fatty acids or to a mixture of carbon dioxide and hydrogen. Acetotrophic and methanogenic bacteria then convert acetic acid and hydrogen into a mixture of methane and carbon dioxide. However, the amount of organic materials currently available for biogas production is limited and new substrates as well as new effective technologies are therefore needed to facilitate the production of the biogas industry all over the world (Sárvári *et.al.,* 2016).

Studies have shown that lignocellulose biomass is a promising substrate for biogas generation. According to Yu *et al.,*(2019), the main challenge is that, it is difficult to be degraded due to two critical chemical bonds, namely hydrogen bonds and ether ester bonds. The former exists between lignin and polysaccharides, and the later is present between hemicellulose and cellulose. The OH- produced by alkali can weaken or break those bonds, which leads to easier degradation of lignocellulose biomass (Yu *et al.,* 2019).

However, due to their complex hierarchical structure and recalcitrant nature, pretreatment steps present the most critical challenge to biomass utilization prior to conversion. The carbohydrate fraction of lignocelluloses biomass is degradable in anaerobic digestion, whereas the lignin fraction is generally considered difficult to degrade. Typically, the digestate collected from biogas digesters is rich in lignin due to the degradation of the other components (Theuretzbacher *et al.,* 2015).

Duc *et al.,* (2019), reported that groundnut shells are rich in many functional compounds and composed of cellulose, hemicellulose and lignin. This enables the shells to be used in different ways. Muhammad *et al.*, (2015) assessed the management of groundnut wastes and found that, some of the wastes were used as animal feed whilst others were disposed in landfills or simply burnt. The conversion of groundnut waste to bio fuel would be more lucrative than utilization in ways that affect the environment. Some of the bio fuels that can be obtained from groundnut shells as reported by Duc *et al.,* (2019) include biodiesel and bio ethanol. Also, Nyachaka *et al.,*(2013) and Olafimihan *et al.,*(2015) investigated the production of bio ethanol from groundnut shells. Oyelaran (2015) investigated the production of briquettes from groundnut shells with waste paper.

Sugarcane (*Saccharum officinarum*) is one of the most important crops globally as it provides 60% of the total global sugar requirement. In Nigeria, two types of sugarcane are grown, which are the industrial and soft, or chewing, cane (Zahir *et al.*, 2016). Sugarcane is, however, largely consumed domestically as the sugar industry is yet to be developed (Zahir *et al.*, 2016).

The residues from sugarcane are bagasse and leaves. Bagasse is obtained after sugarcane is crushed to obtain juice used for sugar and ethanol production. Bagasse is used in the production of industrial enzymes, organic acids, xylitol, and ethanol. The leaves are also called sugarcane trash and produces fly ash, severely damages soil microbial diversity and raises environmental concerns when burnt (Maryana *et al.*, 2014) and (Gonzalez *et al.*, 2014).

Alkaline pretreatment with sodium hydroxide is a viable, low-cost option for modifying the structure of lignocelluloses prior to hydrolysis and fermentation of the carbohydrate fractions. Modenbach and Nokes in 2012, reported that it can be performed using a wide range of operating conditions. For instance, reaction times can be as short as a few minutes or on the order of hours or days, with temperature ranging from ambient to 150°C.

2.MATERIALS AND METHODS

2.1 Materials

The agricultural wastes used as substrates in this research are: Substrate A (Groundnut shell), obtained from Argungu groundnut Sheller plant, Substrate B (Sugarcane bagasse), obtained from Argungu local sugarcane market. The chemical reagents used for this research are; Sodium Hydroxide, Detergents, Distilled Water, Tetraoxosulphate (vi) Acid, 6wt.% Potassium Hydroxide Solution, acidified aqueous sodium chlorite ($NaClO_2$) solution, 5 wt. % $NaClO_2$ solution, Selenium, Boric Acid, and Hydrochloric Acid. Measuring cylinders, plastic bowls, weighing balance, mercury-in glass thermometer (0-100^{0}C), digital pH meter (Hanna model 211), sieve with a mesh size of 32 microns, source of heat, and oven, Lenton Furnace, Porcelain Crucibles, Kjeldahl Flask, TGA51, FTIR Prestige 21.

2.2 Sample Preparation

The groundnut shell and sugarcane bagasse were gathered, in order to remove impurities, the groundnut shell and sugarcane bagasse samples were physically treated by sorting. It was then washed with detergent and heated water at 60°C, sun dried, pulverized to smaller sizes and sieved with a mesh size of 32 microns according to the method of (Chubuike *et al.*,2017) and (Pang *et al.*,2014).

2.3. Delignification of Substrate Using Aqueous Sodium-Hydroxide Solution

A 40g purified groundnut shell and sugarcane bagasse were each chemically treated by soaking in 5 wt. % aqueous sodium hydroxide solution. The pH of the solution was regulated until it reaches 9.1. The mixture was maintained at 25°C for 24hrs. The treated groundnut shell and sugarcane bagasse were each filtered and thoroughly washed with distilled water until a neutral pH was obtained (i.e. pH=7.10). Thereafter, the treated groundnut shell and sugarcane bagasse were oven-dried at 60°C for 48 hrs. The dried groundnut shell and sugarcane bagasse was stored in sealed plastic bags at 25°C for subsequent investigations in accordance with the previous methods (Birnin-Yauri *et al*., 2016.

2.3 Determination of Holocellulose of Treated and Un-treated Substrates

To determine the holocellulose i.e. cellulose and hemicellulose contents; sodium hydroxide treated and untreated groundnut shell and sugarcane bagasse were reacted with acidified aqueous sodium chlorite ($NaClO_2$) solution to delignify them. The $NaClO_2$ solution was acidified with a H_2SO_4 solution until a pH of 4 is reached. Thereafter, 1g each of the groundnut shell and sugarcane bagasse were soaked in 5 wt. % $NaClO_2$ solution at 70°C for 1 hr, at a weight ratio of 1:20 the groundnut shell and sugarcane bagasse to $NaClO_2$ solution. Once the treatment was complete, it was filtered and washed thoroughly with distilled water and oven-dried at 60°C until a constant weight was achieved (Birnin-Yauri *et al*.,2016).

2.4 Determination of Cellulose Content of Treated and Untreated Substrates

The cellulose content was determined by treating 1g holocellulose with 6wt.% potassium hydroxide solution at 25°C for 24 hr, the mixture was then filtered, and the solid residue obtained was washed thoroughly with distilled water and oven-dried at 60°C until a constant weight was obtained (Birnin-Yauri *et al*., 2020).

2.5 Determination of Hemicellulose Content of Treated and Untreated Substrate

The observed difference between holocellulose and cellulose contents was recorded as the hemicellulose contents of the groundnut shell and sugarcane bagasse (Birnin-Yauri *et al*., 2020).

2.6 Determination of Lignin Content of Treated and Untreated Substrate

The lignin content was determined by submerging 1g of sodium hydroxide-treated and un-treated groundnut shell and sugarcane bagasse in 72 wt % H_2SO_4 at 30°C for 1hr, then the solution was diluted to 3% H_2SO_4 and refluxes for 2hr, the mixture was then filtered and the

insoluble solid residue obtained was washed thoroughly with distilled water and oven-dried at 60°C until a constant weight was obtained. All the above mentioned analyses were carried on average of triplicate (Birnin-Yauri *et al*.,2020).

2.7 Thermo Gravimetric Analysis

Thermo gravimetric analysis of the substrate was carried out using macro thermo gravimetric analyzer (TGA51). The TG experiment was performed under nitrogen atmosphere. A known amount of substrate was measured; the samples were heated from 48.70 ^{0}C to 800 ^{0}C. Thermo gravimetric weght loss curves for each substrate were plotted against temperature.

2.8 FTIR (Fourier Transform Infrared Spectroscopy)

The functional groups and chemical characteristics of treated and un-treated samples were obtained by Fourier Transform Infrared Spectroscopy (FTIR) (Prestige 21 Shimadzu, Japan) with a resolution of 4 cm–1 in a spectral range.

3.0 Results And Discussion

3.1 FTIR Spectra

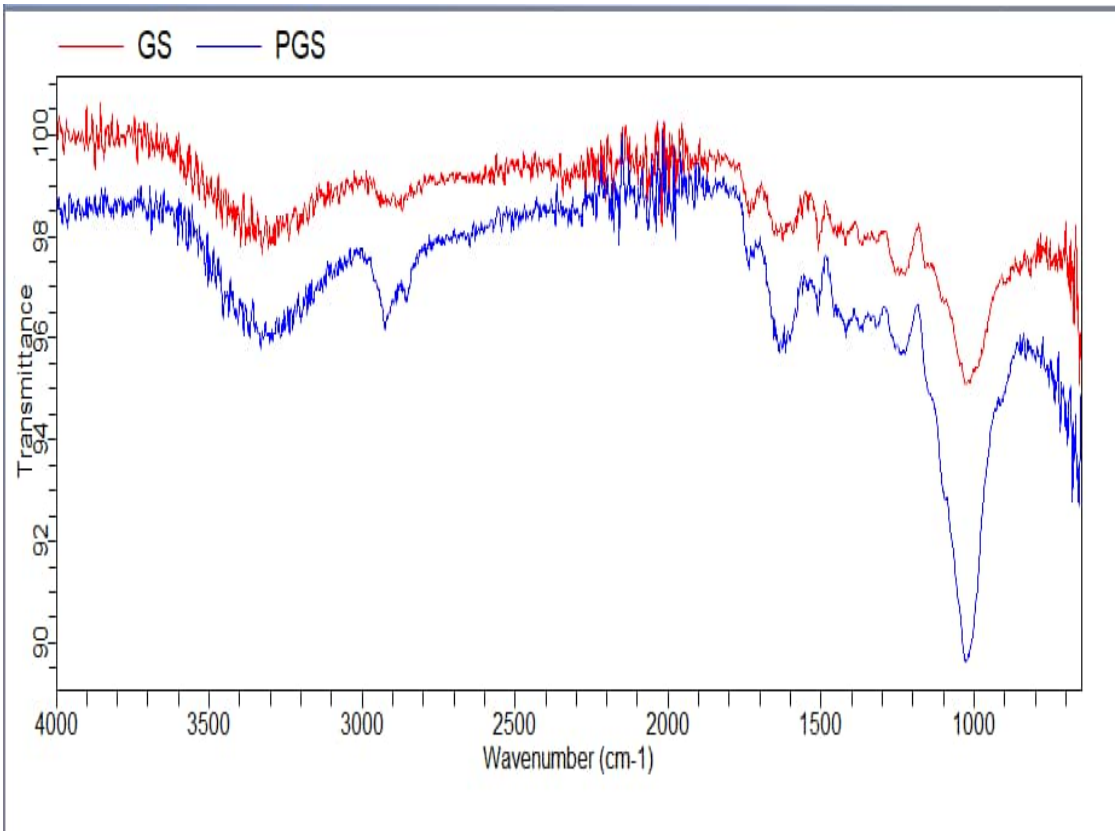

Figure 3.1a: Spectra of Treated Groundnut Shell (TGS) and Untreated Groundnut Shell (UGS)

Figure 3.1a shows the FTIR spectra of treated and untreated groundnut shell. PGS depicts treated groundnut shell and GS depicts untreated groundnut shell. The intensity of the treated sample is lower than that of the untreated sample.

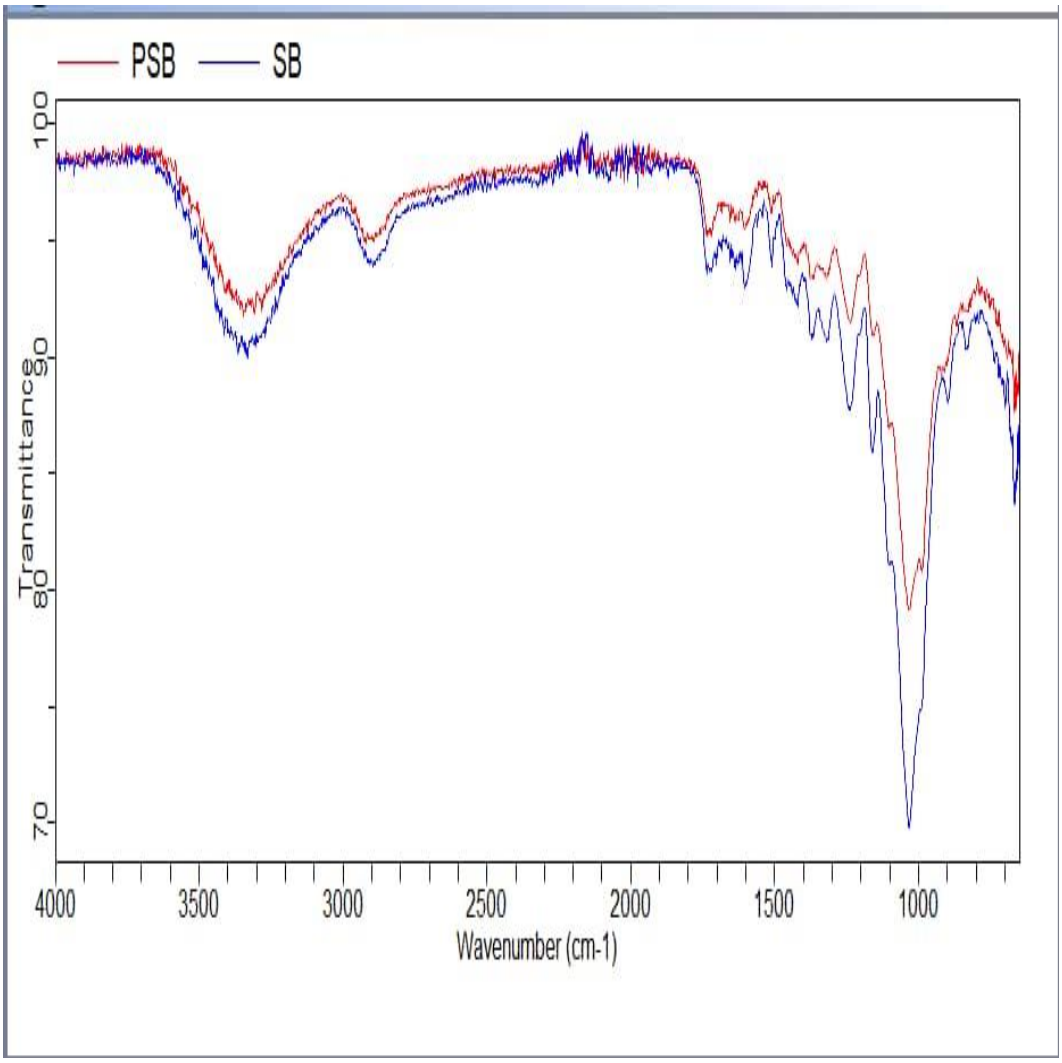

Figure 3.b: Spectra of Treated Sugarcane Bagasse (TSB) and Untreated Sugarcane Bagasse (USB).Figure 3.1b shows the FTIR spectra of treated and untreated sugarcane bagasse. SB depicts treated groundnut shell and PSB depicts untreated groundnut shell. The intensity of the treated sample is lower than that of the untreated sample.

3.2a Thermogram of the Samples

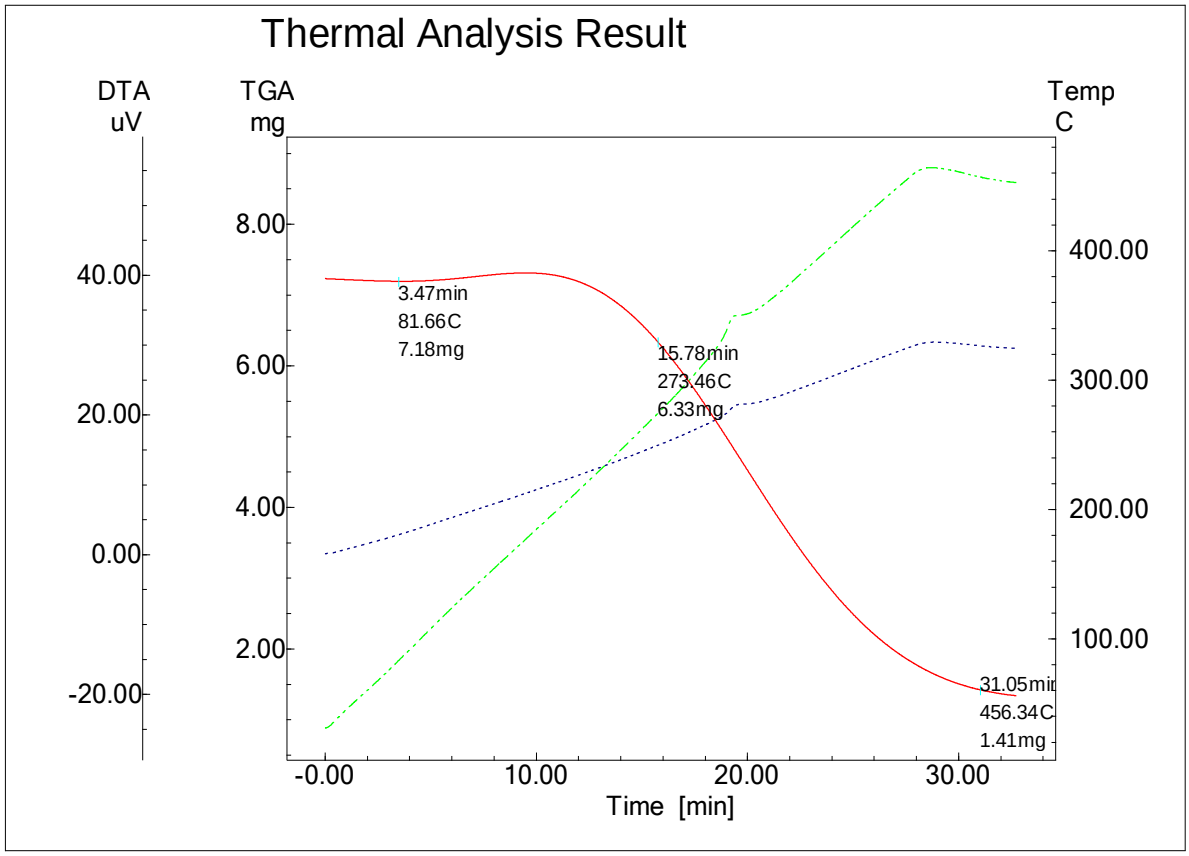

Figure 3.2a: Thermogram of Untreated Groundnut Shell (UGS)

The thermogram shows that the initial temperature of degradation was 81.66 ^{0}C, occurs after 3.47 minutes and corresponds to 7.18mg mass loss. The second temperature of degradation was 273.46^{0}C, occurs after 15.78 minutes and corresponds to 6.33mg mass loss. The maximum temperature of degradation was 456.34 ^{0}C, occurs after 31.05 minutes and corresponds to 1.41mg mass loss.

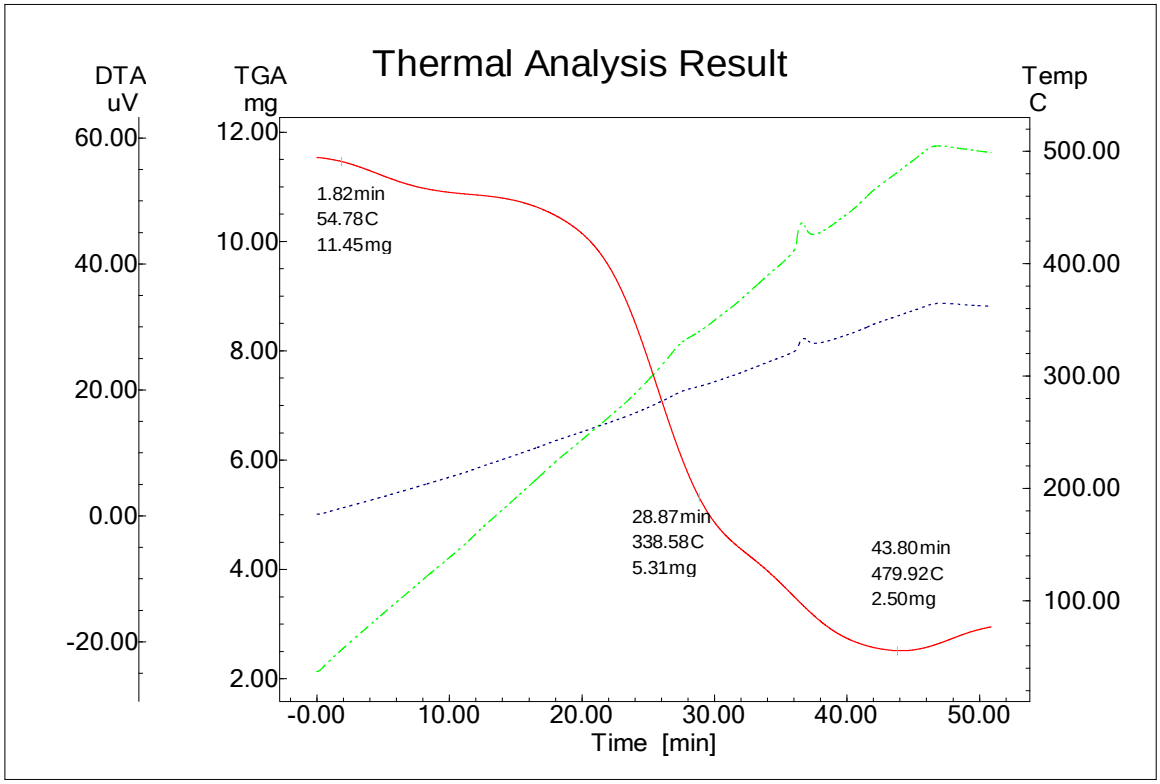

Figure 3.2b: Thermogram of Untreated Sugarcane Baggasse (USB)

The thermogram shows that the initial temperature of degradation was 54.78^{0}C, occurs after 1.82 minutes and corresponds to 11.45 mg mass loss. The second temperature of degradation was 338.58^{0}C, occurs after 28.87 minutes and corresponds to 5.31mg mass loss. The maximum temperature of degradation was 479.92 ^{0}C, occurs after 43.80 minutes and corresponds to 2.50mg mass loss.

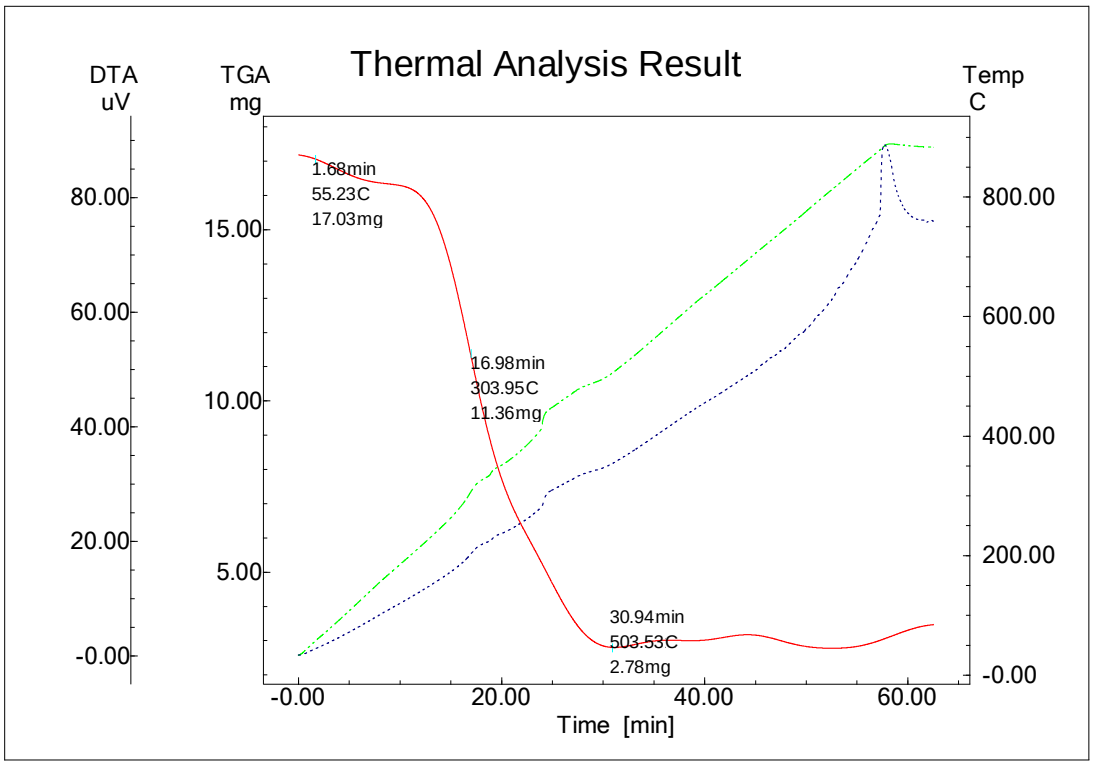

Figure 3.2c: Thermogram of Treated Groundnut Shell (TGS)

The thermogram shows that the initial temperature of degradation was 55.23^{0}C, occurs after 1.68 minutes and corresponds to 17.03 mg mass loss. The second temperature of degradation was 303.95^{0}C, occurs after 16.98 minutes and corresponds to 11.36 mg mass loss. The maximum temperature of degradation was 503.53 ^{0}C, occurs after 30.94 minutes and corresponds to 2.78 mg mass loss.

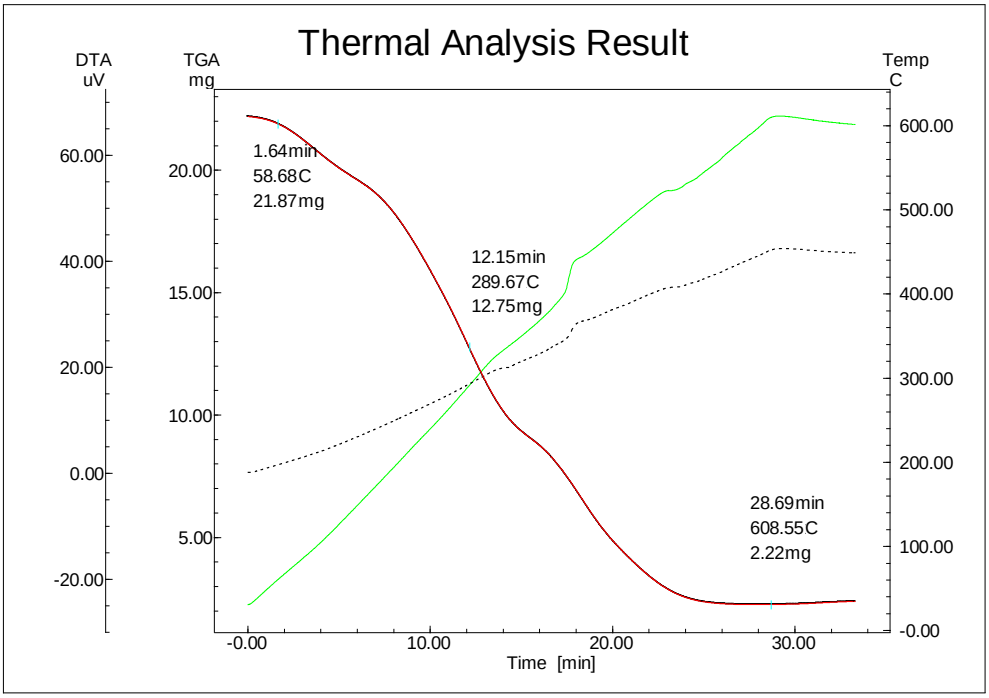

Figure 3.2d: Thermogram of Treated Sugarcane Baggasse (TSB)

The thermogram shows that the initial temperature of degradation was 58.68^{0}C, occurs after 1.64 minutes and corresponds to 21.87 mg mass loss. The second temperature of degradation was 289.67^{0}C, occurs after 12.15 minutes and corresponds to 12.75 mg mass loss. The maximum temperature of degradation was 608.55 ^{0}C, occurs after 28.69 minutes and corresponds to 2.22 mg mass loss.

As shown in figure 4.1a and 4.1b, the qualitative and quantitative changes in the chemical compositions of both the treated and untreated groundnut shell and sugarcane bagasse i.e. cellulose, hemicelluloses and lignin were analyzed using Fourier Transform Infra Red spectroscopy (FTIR). The spectra were recorded over a frequency range from 400 cm-^{1} to 4000 cm-^{1}. The most degraded sample had smallest absorbance and the least degraded sample showed highest absorbance, this was in line with the report of Pandey and Kim, (2011). The sharp peaks were detected in untreated groundnut shell and untreated sugarcane bagasse. These peaks disappeared or reduced after the treatment. Similar observation was reported by Birnin Yauri *et al.*, (2019).

The characteristic peaks of lignin and carbohydrates were found in the range of 1800 cm^{-1} - 700 cm^{-1}. Major signifying peaks of the lignin in untreated groundnut shell and untreated sugarcane bagasse were present in the range 1558 cm-^{1} - 1514.74 cm-^{1} and 1540 cm-^{1} - 1455cm^{-1} respectively, due to raised aromatic skeletal vibration (C=C) of the lignin. The peaks at 1260 cm^{-1} – 1270 cm^{-1} and 1330 cm^{-1} – 1375 cm^{-1} showed the existence of guaiacyl and syringyl groups in lignin for untreated groundnut shell and untreated sugarcane bagasse

respectively . The gradual disappearance of these peak bands indicated the degradation of syringyl and guaiacyl groups.

From the FTIR spectra in Figure 4.1a and Figure 4.1b, the broad and intense peak for untreated groundnut shell and untreated sugarcane bagasse at 3337 cm-^{1} and 3330 cm-^{1} respectively, were due to the OH stretching for hydroxyl group, this corresponded with the range previously reported by Alavudeen *et al*., (2015). There was a decrease in the O-H stretching in the region after the alkaline treatment. This decrease could be attributed to the removal of hemicelluloses and lignin as a result of the alkali pretreatment of the sample.

A, the peaks at 1627 cm^{-1} and 1509 cm^{-1} (Fig. 3.1a & 3.1b) in untreated groundnut shell and untreated sugarcane bagasse respectively; were due to the presence of hemicelluloses and can be assigned to the C=O stretching. Following the sodium hydroxide treatment, this peak absorbance intensity decreases as a result of partial removal of hemicelluloses from the sample. This is in line with the previous findings reported by Sahari, and Sapuan (2011) as well as Schwarzova (2016).

The 1751 cm^{-1} and 1723 cm^{-1} for untreated groundnut shell and untreated sugarcane bagasse respectively is the characteristic stretching vibration of an unconjugated C=O group in the acetyl group in hemicelluloses, this peak has decreased in intensity after the treatment with sodium hydroxide, which also indicates the partial removal of the hemicelluloses and lignin that are present in the samples.

Moreso, the bands at 1423 cm^{-1} and 1366 cm^{-1} in untreated groundnut shell and untreated sugarcane bagasse reveals the presence of methylene bending vibration, which implies that the substrate is a potential source of methane. This peak appeared weak in sodium hydroxide treated groundnut shell which also indicates partial removal of lignin. These FTIR findings corroborated with the results of proximate analysis of the treated and the untreated groundnut shell and sugarcane bagasse earlier reported.

The thermal stabilities of both the alkali-treated and untreated groundnut shell and sugarcane bagasse were analyzed using Thermo Gravimetric Analysis (TGA). The thermograms were presented in Figure 3.2a, 3.2b, 3.2c and 3.2d respectively for UGS, USB, TGS, and TSB. The TGA measured the reduction in weight percentage due to decomposition or degradation of the sample with respect to time and temperature.

The reduction in weight versus increase in temperature plot for both the treated and untreated groundnut shell and sugarcane bagasse were investigated. The treated samples showed higher initial degradation temperatures (Tonset), as well as maximum temperature of degradation (Tmax) than the untreated samples. This suggests that, the treated samples have higher thermal stability than the untreated samples. This could be due to the alkaline treatment which removed lignin, hemicellulose and other impurities from the treated samples, thereby enhancing its thermal stability.

During the initial thermal decomposition stage, around 81.66°C and 54.78^{0}C respectively for the untreated groundnut shell and untreated sugarcane bagasse. The samples mainly

undergo evaporation of moisture. The second step at temperature around 273.4°C and 338.58°C, which correspond to 6.33mg and 5.31mg mass loss respectively, for untreated groundnut shell and untreated sugarcane bagasse respectively was due to the decomposition of hemicelluloses and cellulose which usually take place around 200°C to 400°C as reported by Jonoobi *et al.,* (2009). However, the temperature around 456.34°C and 479.92^{0}C, which corresponds to 1.41 mg and 2.50 mg mass loss respectively for untreated groundnut shell and untreated sugarcane bagasse may be due to the decomposition of lignin which is believed to have wide range of temperature ranging from 200 °C to 700°C as reported by Narkpiban (2019).

The first decomposition rate with respect to temperature (Tonset) in treated groundnut shell and treated sugarcane bagasse occurred at 55.23 °C and 58.68 ^{0}C, which corresponds to 17.03 mg and 21.87 mg mass loss respectively, was due to evaporation of moisture.

The second step at temperature around 303.95 °C and 289.67°C, which correspond to 11.36 mg and 12.75 mg mass loss, for treated groundnut shell and treated sugarcane bagasse respectively was due to the decomposition of hemicelluloses and celluloses which usually occur around 200 °C to 400°C as reported by Jonoobi *et al.,* (2009). It may also be as a result of breakdown of molecular structure (Alvin *et al*., 2017 & Tan *et al*., 2017). However, the temperature around 503.53 °C and 608.55 ^{0}C, which corresponds to 2.7 mg and 2.22 mg mass loss respectively for treated groundnut shell and treated sugarcane bagasse was due to the decomposition of lignin which is believed to have wide range of temperature ranging from 200 °C to 700 °C as reported by Narkpiban (2019). It may also be connected to the improvement after alkali treatment in which the hydrophilic group (hydroxyl group) of lignocellulose was replaced by the alkaoxide group, which brings about an increased surface area and subsequent improvement in the thermal behaviours of the sample, this is in line with the earlier report of Chung *et al*., (2018). These results show that thermal stability of groundnut shell and sugarcane bagasse have increased due to chemical treatment with 5 wt% NaOH.

CONCLUSION

This study investigated and compared the effect of alkali pretreatment on the mophology of the biomass of groundnut shell and sugarcane bagasse. The findings of the study for all the essential parameters showed that pretreatment of groundnut shell and sugarcane bagasse with 5% wt/v NaOH can effectively reduce the lignin and hemicellulose content and increase the cellulose content. In conclusion, the treated (delignified) biomass has greater potential for biogas generation than the untreated biomass. The study revealed that the use of groundnut shell and sugarcane bagasse for biogas production is a worthwhile venture, considering the zero cost.

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