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PRODUCTION OF BIOETHANOL FROM GROUNDNUT (*ARACHIS HYPOGEAE* L.) PEELS AND SHELLS

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Abstract-This research investigated the feasibility of groundnuts shells and peels for bio ethanol production. Proximate and fiber composition analysis conducted on the samples were also reported. Fourier Transform-Infrared Ray (FTIR), Refractometer and Scanning Electron Microscopy (SEM) were used to perform analytical investigation on the peels and shells to determine the functional groups and the surface morphology of the samples respectively. The chemical composition of peels and shells were: moisture content of 6.00±0.09 and 6.50±0.10, ash content of 2.72 ±0.09 and 8.00±0.11, lignin of 27.00±0.28 and 28.00±0.50, hemicellulose of 29.00±0.76 and 46.00±0.01 and α-cellulose of 37.00±0.58 and 34.00±0.28 respectively. The optimum acid concentration (H_2SO_4) used for the hydrolysis were (4% and 6% w/v respectively), the best reaction time and temperature were noted at (60 min, 100 ^oC) for peels and (90 min, 120 ^oC) for shells. About 7.89% and 3.94% of ethanol were recovered from 100 g of peels and shells respectively and the FT-IR spectral proved that the bio-liquid obtained from the samples was bioethanol. The SEM for pre-hydrolyzed biomass shows a well-organized and smooth surfaced structure while the post hydrolyzed biomass showed a ruptured surface that revealed effective hydrolysis during liquefaction process. This study showed that the biomass samples are promising feedstock for bio-refining process.

Keywords**: Groundnut peels, shells, lignin, fermentation, bioethanol.**

I. INTRODUCTION:

The Nigerian environment is highly polluted with enormous amounts of waste such as Agricultural waste, food waste, industrial waste, and animal waste, and these are a major problem in the country [1]. If properly processed and utilize, it can be a potential source of biomass energy in Nigeria [2]. It is estimated that approximately, Nigeria generates 74,428.85 tons of municipal waste daily (or approximately 27,166,530.25tons annually) which has a potential biogas generation of 2.04 million m^3 every day [3]. Groundnuts are species of legumes. Residues from groundnut pods are called SHELL and the residue from the roasted nut is called PEELS. The production of peanuts according to the Food and Agriculture Organization (FAO) statistical yearbook in 2013 was 43,982,066t, produced in 27,660,802 hectares [4]. Peanuts are grown mainly in Asia, with a global production rate of 65.3%, followed by Africa with 26.2%, the Americas with 8.4%, and Oceania with 0.1% .[4].

Only small part of the groundnut shell is used as compost and animal feed. Lately, groundnut shell has been used as a feedstock in oil production. In recent years (2018) the World has been experiencing a tremendous increase in the search for alternative energy sources to replace the conventional fossil fuels due to the finite nature of crude oil and other fossil fuels which must increase by 60% in 2050 [5]. One of the most attractive alternatives (fossil fuels) is bio-ethanol (alcohol) produced from agricultural crops and residue [6]. The production of ethanol from lignocellulosic wastes is dependent both on the availability in large quantities at low cost. Cellulose is the most abundant biopolymer in the world [7]. Cellulose is found in a wide range of species and present along with hemicelluloses, lignin, pectin, wax and resins [8]. It can be obtained from numerous resources, such as wood, eucalyptus, sisal, cotton, coconut fibers, and non-plant sources, including forms produced by bacteria and found in tunicates. The structure of cellulose is organized into fibrils, which are surrounded by a matrix of lignin, extractive inorganics and hemicellulose [9].

This makes renewable resource an attractive feedstock for the production of motor fuel alcohol [10-12].Biomass conversion to bio fuels involves two processes which are thermochemical and biochemical processes. In this study, biochemical conversion was used in production of fermentable sugars and their conversion into liquid fuels (ethanol, butanol) or gaseous compounds (methane) by use of specific microbial population [13] There are three methods of extracting sugars from biomass, which are concentrated acid hydrolysis, dilute acid hydrolysis and fermentation. Hydrolysis process is the breaking down of the cellulosic part of the biomass into sugar solutions that can then be fermented into ethanol, and yeast is added to the solution. The ethanol,

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which is produced from the fermentation process, still contains a significant quantity of water, which must be removed. This is achieved by using the fractional distillation process. The distillation process works by boiling the water and ethanol mixture. Since ethanol has a lower boiling point (78.3 ^{o}C) compared to that of water (100 ^{o}C), the ethanol vaporizes before water, which then condensed and recovered as distillates as described by Ogunsuyi and Badiru [14]. Bioethanol is far better than the conventional fuels. By encouraging bioethanol use, the rural economy would receive a boost from growing necessary crops. Bioethanol is biodegradable and far less toxic than fossil fuels. This study investigated the viability of the biomass as feedstock for the production of bio-ethanol as an alternative fuel to conventional fossil fuel.

II. MATERIALS AND METHODS

Sample collection and preparation

Groundnut (*Arachis hypogeae L.*) peels and shells were collected from a nearby market (Plates 1a and 1b). Groundnut shells and peels were cleaned and air dried at room temperature for 3 days which led to the removal of dust and sand from the samples. Then, the materials were ground into particle sizes between 1 and 2mm using a milling machine.

Plate 1a: Groundnut peels

Plate 1b: Groundnut shells

Acid Hydrolysis of Peels and Shells

The Groundnut shells and peels were subjected to acid hydrolysis using H_2SO_4 of various concentrations (2%, 4%, 6%, 8%, and 10%) w/v. The hydrolysis was performed at varying reaction time between 30 min and 120 min) and temperature of 60^{o} C and 120 ^{o} C.

Fermentation Medium**:** The hydrolysate was allowed to cool, then filtered to remove the residue and the sugar level was checked using Refractometer. The hydrolysate was neutralized using 2M NaOH and adjusted to a pH of 5.5 using pH meter.

Process of fermentation

The yeast used was *sacchromyces cerevisiae* (20 g) and was activated by using warm water to dissolve it with constant shaking, it was then added to the hydrolysed biomass to ferment for 5 days, thereafter subjected to distillation (ethanol boils at 78^{o} C) and further redistilled with calcium oxide to get purified bio ethanol by using distillation setup consisting of Liebig condenser and fractionating column. The method adopt for the determination of the refractive index was as described by Josly [15], using a refractometer

Extractive Determination

The biomass was extracted according to TAPP1 T222 standard [16]. About 3g of the groundnut peels and shell were weighed inside a filter paper and wrapped with a thread, then placed in the extraction thimble of soxhlet extraction. The boiling flask contained 1:2 ethanol (95%) and toluene which was extracted for 8 h and the extraction was distilled to near dryness before evaporation on a heating mantle until the solution was completely evaporated. The flasks were oven dried at 105 ^{o}C. The outcome was placed in a desiccator and weighed repeatedly until a constant weight was obtained. The experiment was done in triplicate and the following formulas were used to obtain the extractives in equation 2.1.

$$\% \text{ Extractive} = \frac{Wa - Wb}{Wa} \times 100 \qquad 2.1$$

Where Wa = weight of initial dried samples. W_b = weight of final dried samples

Determination of Lignin Content

Lignin, expressed as Klason lignin was estimated directly [17] as follows:

About 1 g of the extracted sample was put in a 100 ml beaker and then treated with 15ml of 72% H_2SO_4, added to the sample drop by drop with constant stirring by a stirrer. After complete breakdown, the reaction was allowed to stand and the beaker was covered kept in water bath at 20^{o} C for 2 hours, the content was diluted with a volume of 575ml of distill water, It was then transferred to a 1 liter round bottom flask then heated for 4 hours and left over night at room temperature. The lignin was filtered on an ash less filter paper

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and washed with hot water and dried at constant weight of 105° C in oven. The lignin was calculated according equation 2.2

$$\text{Lignin (\%)} = \frac{final\ Weight}{initial\ Weight} \times 100 \quad \textbf{2.2}$$

Holocellulose estimation
Holocellulose, the total carbohydrate fraction (cellulose and hemicellulose) of the raw material was estimated [18] as follows:
About 1g extractive (which was extracted with ethanol – toluene mixture 1:2 for 8 h)

was suspended in 150 ml of 1M sodium acetate and boils for 5 h at 75°C and the solution was stirred mechanically then, 10 drops of glacial acetic acid and at every 1h (4 mls) 1.5 g sodium chlorite were added for 4 h and the reaction has been allowed to proceed under vigorous stirring. The solution was then cooled, filtered and washed with distilled water until free of acid, then with acetone and left to dry at room temperature. The holocellulose was then calculated according to equation 2.3.

$$\text{Holocellulose} = \frac{Wa-Wb}{Wa} \times 100 \quad \textbf{2.3}$$

Wa = Final weight of the dried sample

Wb = Initial weight of sample

Alpha cellulose content
About 1g of holocellulose sample which does not dissolve in 17.5% sodium hydroxide solution was added into a 250 ml beaker was left to rise for 3min [19] . The beaker was then covered and left for 35 min at 20 °C. Distilled water (100 ml) was then added and the material was quickly filtered under suction using a funnel. The filtrate was then poured on the paste twice before washing with distilled water. After washing with distilled water till neutrality 100 ml of 10% acetic acid was added drop wise followed by distilled water. The temperature was kept constant at 20°C during the whole experiment. The alpha cellulose was then calculated (in equation 2.4) after drying at 105 °C to constant weight.

$$\text{Alpha cellulose (\%)} = \frac{final\ weight\ of\ oven\ dried\ sample}{intial\ weight\ of\ sample} \times 100 \quad 2.4$$

Hemicellulose Determination
The hemicellulose was determined by difference between holocellulose and $\boldsymbol{\alpha}$- cellulose contents as shown in equation 2.5

Hemicellulose (%) = Yield of Holocellulose (%) – Alpha cellulose (%) 2.5

III. RESULTS AND DISCUSSION

Chemical Composition of Groundnut Biomass
Table 1 shows the amount of moisture in the biomass which was (6.00±0.09, 6.50±0.10) for peels and shells respectively. The moisture content found in the shells was 5.79% as reported by Miguel [20]. The ash content of the groundnut peels and shells were 2.72±0.09, 8.00±0.01 respectively which were relatively higher compared to Annika [21].

The extractives for shells were (25.50^{d}±0.70) and peels (37.95^{c}±0.05) were compared. The lignin contents were 27.00±0.28 for peels and 28.00±0.50 for shells which is relatively low and good for the production of bio ethanol, the hemicellulose were 29.00±0.76 for peels and 46.00±0.01 for shells. The $\boldsymbol{\alpha}$- Cellulose for peels and shell were 37.00±0.58, 34.00±0.28 respectively.

Monomeric Sugar Content of the Groundnut Peels and Shells after Hydrolysis and Yeast Assay
The percentage yield of ethanol gotten from groundnut peels and shells were (31.56%, 52.30%) respectively which was similar to (0.5 mg/ml on Day 4.)[22]. Also after purification (with CaO), the crude ethanol yield drastically reduced to 7.89% of peels and 3.94% of shells. The results showed that the biomass contained a level of fermentable sugar which indicated alcoholic content of bioethanol liquor and that they are promising source of ethanol production**.**

Results of Peels and Shells Brix Level against Acid Concentration (H_2SO_4) with temperatures 60 °C, 80 °C and 120 °C
Figure 1 shows the effect of varying acid concentration on brix level in the hydrolysate. The result showed direct proportional increase of the acid concentration with brix. The trend continued and the optimum contact was not obtained at 30min until the experiment proceeded to a higher time above 30min**.** Figure 2 shows best hydrolysis at 4% acid, at a time from 60 min and above the optimum contact was attained at 60 min for peels and 90min for shell. This implies that quantitative recovery of monomeric sugar is not achievable at lower contact time for groundnut biomass. Figure 3 shows the optimum temperature at 120° C. The optimum sugar level for shell was attained at 6% w/v of acid concentration.

Properties of the derived bio ethanol
The refractive index for peels and shells were 1.348 and 1.350 respectively and the molecular weight is 46.7 with structural formula of C_2H_5OH.The derived bioethanol boils at 78 °C.

Characterization of Derived Bio ethanol of Groundnut Peels and Shells with FTIR
Figures (4 and 5) were the spectral for FTIR which show the functional groups. Figure 4 shows the spectrum of groundnut peels shows absorption in the following regions: 3426.00 cm^{-1} O-H stretch of alcohol, 1638.70 cm^{-1} C-H stretch of alkane

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and 1042.25 cm^{-1} C-O stretch of alcohol Figure 5 shows the spectrum of groundnut shells shows absorption in the following regions: 3427.00 cm^{-1} O-H stretch of alcohol, 1640.51 cm^{-1} C-H stretch of alkane and 1056.06 cm^{-1} C-O stretch of alcohol. In these spectra, the compound identified proved that samples are bioethanol produced.

Scanning Electron Microscopy
Plate 2a, 2b and 3a, 3b shows the scanning electron microscope of Pre and Post hydrolysed groundnut biomass. SEM analysis was carried out on Pre and Post hydrolysed groundnut shells. Plate 2a and 3a showed a smooth surface and a compacts structure that is well organized while plate 2b and 3b showed a ruptured surface which means it was effective because it had opened the pore space.

Percentage yield of bio ethanol
Weight of biomass =100g, weight of derived bio ethanol=31.56g

$=\frac{31.56}{100}$ x 100 =31.56%

Bio ethanol yield after purification = 7.89%

For shells: weight of derived bio ethanol= 52.3g

$\frac{52.3}{100}$ x 100 = 52.3%

Bio ethanol yield after purification = 3.94%

Table 1: Proximate and Fiber Composition of Groundnut Biomass

Serial number	Fiber components	Peels (%)	Shells (%)
1	Moisture	6.50^{a}±0.10	6.50^{b}±0.01
2	Ash	2.72^{a}±0.09	8.00^{a}±0.01
3	Extractive	37.95^{c}±0.05	25.50^{d}±0.70
4	***α***- Cellulose	37.00^{e}±0.58	34.00^{f}±0.28
5	Hemicellulose	29.00^{e}±0.76	46.00^{f}±0.01
6	Lignin	27.00^{g}±0.28	28.00^{h}±0.50

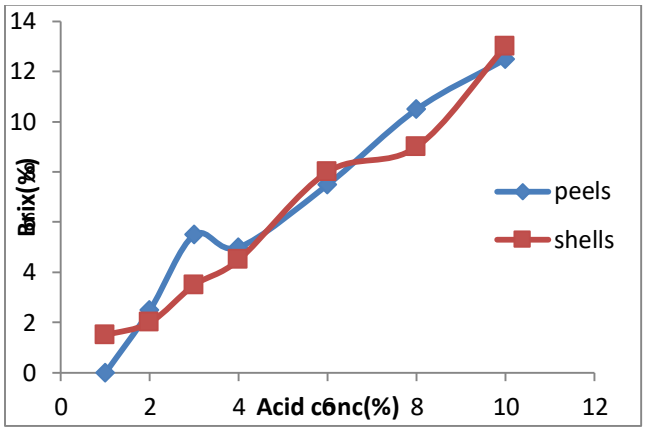

Figure 1: Effect of Acid Concentration against Brix at 30min, 80 °C

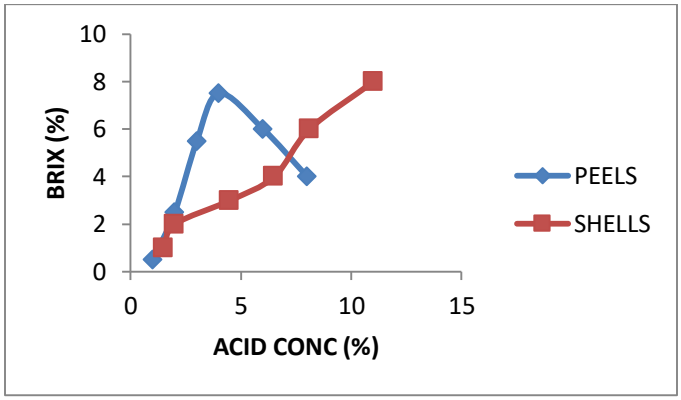

Figure 2: Effect of Acid Concentration against Brix at 60 minutes, 100 °C

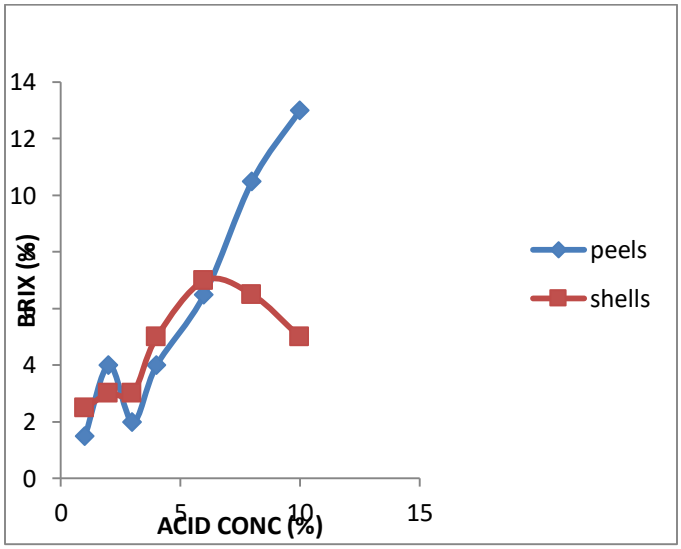

Figure 3: Effect of Acid Concentration against Brix at 90 min, 120 °C

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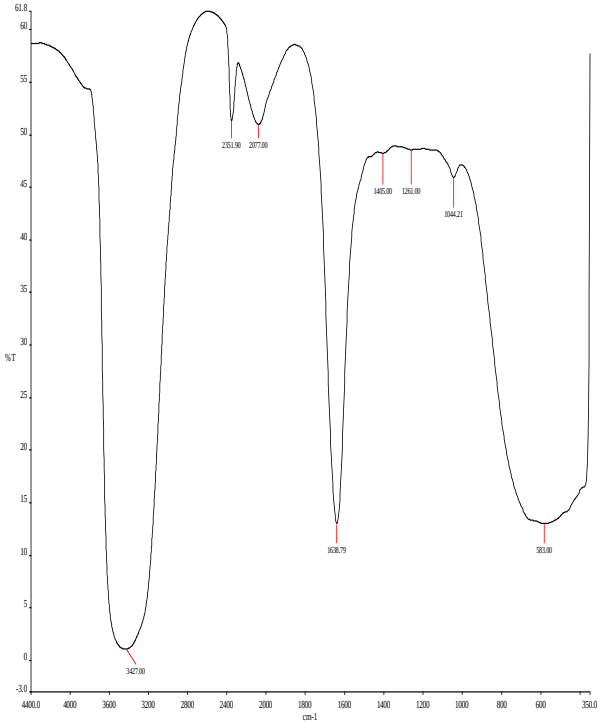

Figure 4: FTIR Spectrum for Derived Bio Ethanol Groundnut Peels

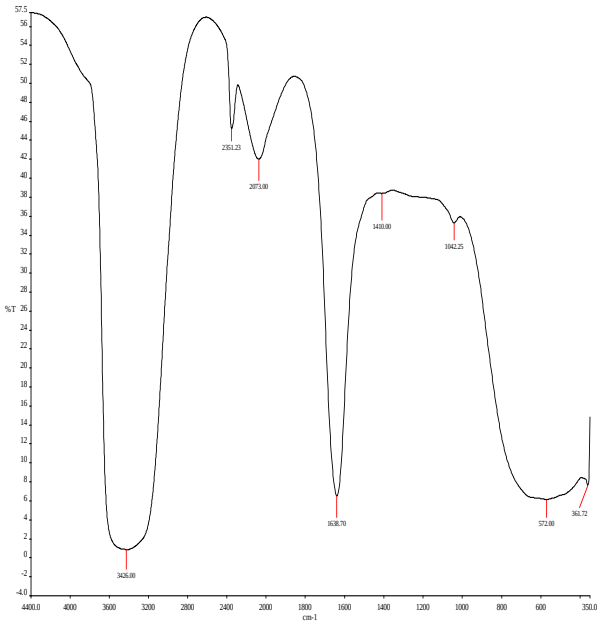

Figure 5: FTIR Spectrum for Derived Bio Ethanol Groundnut Shells

Plate 2a: Pre –hydrolyzed groundnut peels

Scanning Electron Microscopy: Plates (2a, 2b) and (3a, 3b) show the SEM micrographs of the Pre and Post hydrolyzed groundnut biomass. SEM analysis was carried out on Pre and Post hydrolysed groundnut shells. Plate 2a and 3a show smooth surface with a compacts structure that was well organized while plate 2b and 3b show a ruptured surface which signified effective hydrolysis that opened up the pores space on the biomass

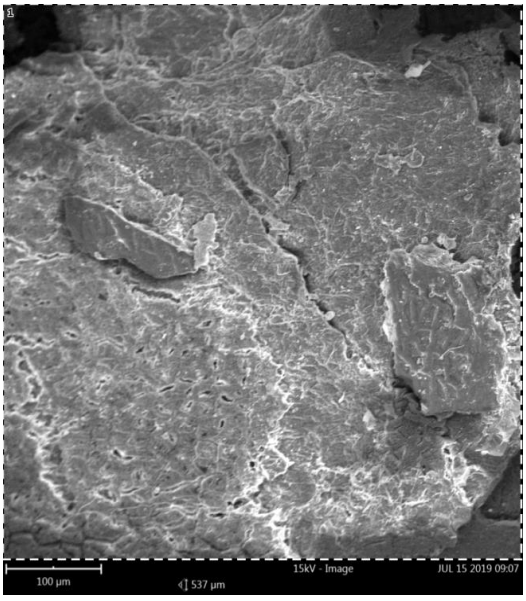

Plate 2b: Post- hydrolysed groundnut shells

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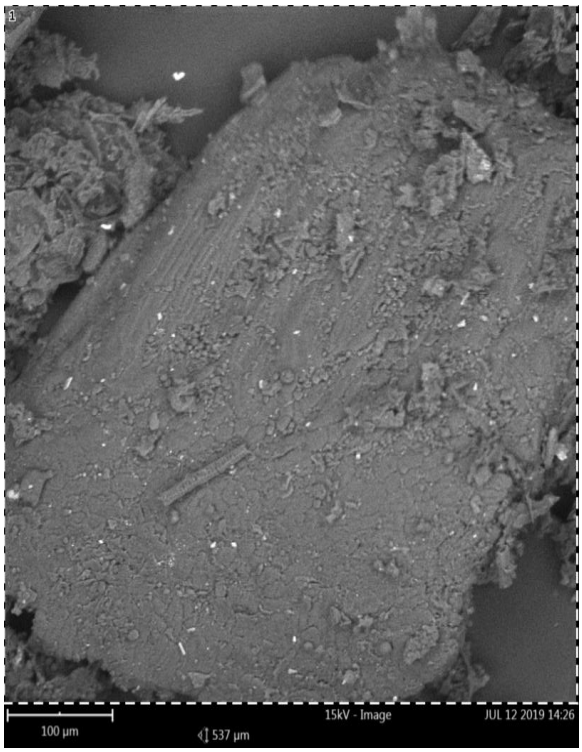

Plate 3a: Pre hydrolysed Groundnut shells

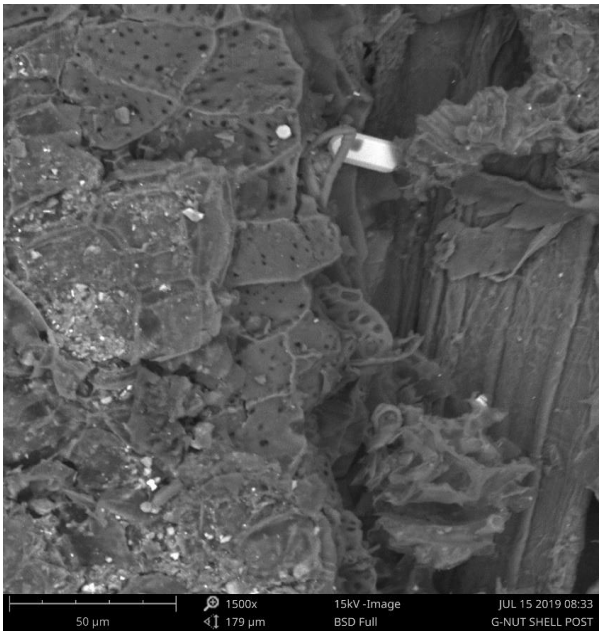

Plate 3b: **Post hydrolysed Groundnut shell**

IV. CONCLUSION

The moisture content of the biomass was low which implies no need for drying pretreatment in production of bio fuel. The ash of the groundnut peels and shells can be used for soil remediation.

The optimum acid concentration for the release of sugar for groundnut peel and shell were 4% w/v, 6% w/v of acid respectively. Also, reaction time was (60 min, 100 ^{o}C, and 90 min, 120^{o}C) for peels and shells.

Groundnut peels and shells are promising feedstock as a result of high amount of cellulose, lignin, and hemicellulose. The yeast used was *Saccharomyces cerevisiae* for the fermentation which took 5 days to ferment.

Bioethanol from groundnut peels and shells can be used as an alternative to synthetic ethanol and can be used as source of fuel and preservatives in confectionaries.

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