Pyrolysis of Groundnut Peels and Shells for Bio-Based Products (Bio- Oil and Bio-Char)

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***Abstract: -* This research aims at pyrolyzing groundnut biomass (shells and peels) for the production of bio oil. About 750 g of groundnutpeels and shells were subjected to slow pyrolysis at 450 ^{o}C in a fixed bed reactor. Gas Chromatography-Mass Spectrometry (GC-MS) was used to characterize both the bio oil and bio char obtained from the peels and shells. The peel was found to contain 16.3% and34.1 %, of bio oil and bio char respectively while the shell contained 11.7% and 44.5% of bio oil and bio char as well respectively. The GC-MS results of the derived bio oil from both fractions of the biomass revealed the presence of phenol, 2-methoxybenzene, alkanes, naphthalene-1, 6-dimethylhexadecanoic methyl esters, acetamide and methyl stearate which were being reported as the major components of wood preservatives. This study showed the potential ofthe biomass as viable feedstock for sustainable production of bio-based chemicals, in view of its availability.**

***Keywords:* Groundnut peels, Groundnut shells, Pyrolysis, Bio-oil and Bio-char.**

I. INTRODUCTION

Energy crops and agriculture residues in Nigeria is about 28.2 million hectares of arable land [1]. It is estimated that Nigeria generates approximately 74,428.85 tons of municipal waste daily (or approximately 27,166,530.25 tons annually) which has a potential to generate biogas of 2,040,000m^3 every day [2].Groundnut or peanut is notably called "poor man's nut" [3]**.** Today, it is an important oilseed and food crop globally [4]. This plant is one of the commonest crop in Nigeria and has never been found uncultivated. Groundnut shells have about 20% of the dried peanut pod by weight, that is, there is a significant amount of shell residual left over after groundnut processing [5]. Botanically, groundnut is known as *Arachishypogaea*L, which was being derived from two Greek words, *Arachis* meaning a legume and *hypogaea* (meaning harvested below ground) [6]. The main sources of groundnuts are in China, India, Nigeria, USA, Myanmar, Indonesia, Sudan, Vietnam and Thailand (FAO, 2013). Typically, groundnut is grown for consumption. Residues of groundnut pods are called shell and those from roasted groundnut are called Peels. Only small part of the groundnut shell is used as compost and animal feed, while significant proportion is grossly underutilized [7].

Pyrolysis is the thermo chemical breaking down of organic material at high temperature and in the absence of oxygen. Recently, pyrolysis is getting more relevance due to its ability to produce a combination of solid, liquid and gaseous products in different proportions.This is being achieved through the variation of operating parameters such as temperature or heating rate. This conversion method alsoprovides opportunity for transforming materials of low-energy density into bio-fuels of high-energy value, In addition, other high-value addedchemicals have been reported to be obtainable from the biomass [8-9]. One of the greatest advantages of this process is that different types of raw materials can be used - industrial and domestic residues. Different types of pyrolysis have been developed namely; flash, catalytic fast, intermediate, slow, vacuum pyrolysis.

Fast pyrolysis technology applied to groundnut shell for bio-oil production has both fuel value and environmental benefits in terms ofwaste management, mitigation of environmental pollution resulting from gas emission during fossil fuel processing [10]

Hitherto, in Africa, Nigeria in Particular, where groundnuts are being produced well above12376 Kg ha^{-1}annually,25% and 30% of the total weight of the legume, being eliminated as residues in the last stage of the processing of the groundnut, either for oil production or for direct consumption without shell [11;7].

Therefore, this present research endeavor focuses on the feasibility of utilizing the biomass resource as feedstock for the production of bio-oil and bio char. Bio-oil is essentially considered as based chemical for the production of wood preservative, energy generation while the bio-char can serve as bulk material for printing purposes., activated carbon for water purification and agro- materials for soil remediation [12].

II. MATERIALS AND METHOD

Sample Preparation

Groundnut (*Arachishypogeae L.*) peels and shells were collected from a nearby market (plates 1a and 1b). The samples were air dried at room temperature for 3 days which lead to the removal of moisture in the samples. Then, the materials were grounded by a milling machine into particle sizes between 1 and 2mm. All glass wears were properly washed, rinsed with distilled water and dried in the oven to avoid error. Lastly, the samples were kept in a foil paper for further uses.

Preliminary Fiber Analysis (Lignin, Hemicellulose, and Cellulose)

Samples	Lignin	Hemicellulose	Cellulose
Peels	27.00±0.28	29.00±0.76	37.00±0.58
Shells	28.0±0.50	46.00±0.01	34.00±0.28

Plate 1a: Groundnut shells

Plate 1b: Groundnut peels

Pyrolysis Process: The pyrolytic experiment was conducted in a fixed bed reactor. About 750 g of groundnut peels and shells were weighed into the thimble of the pyrolyser and covered to exclude air from thepyrolyzer. The pyrolyzer was connected to an electric power source and Liebig condenser. A cooling system made up of a bucket filled with ice block was provided to cool the pyrolytic fuel evolving from the hot narrow tube attached to the reactor. The pyrolysis proceeded for 3 h at a temperature of 450 $^{\circ}$C. The bio-oil and bio char were recovered from the process after the completion of the reaction. The bio-oil mixed with pyrolytic fluid was separated by the use of a separating funnel. The lighter fraction was obtained first and the heavier one was recovered later and covered to avoidair.

Percentage yield of bio oil: The percentage yield was calculated as follows inequation 2.1

$$\% \text{ yield} = \frac{weig \quad of\ bio\ oil}{weigh \quad of\ biomass} x100 \text{.....................eqn2.1}$$

GC–MS characterization of bio oil:

Characterization of the pyrolytic oil was performed using GC–MS (Agilent technologies Model 2014) analyser to determine the chemical compounds present in the oil. Helium gas (carrier gas) was used at a constant flow rate of 1 ml\min and at intermediate polar capillary column of 30 m length, 0.33 mm internal diameter and 0.25 υm thicknesses. Injection was done in split less mode, injection temperature was 250 ^{o}C. The oven temperature was programmed from 90 ^{o}C for 10 min to 180 ^{o}C. Identification was done by comparing their mass spectral with a reference GC-MS spectral from NIST and WIELY library.

III. RESULTS AND DISCUSSION

The yields of the derived bio oil are shown in Figure 1. The Figure shows the percentage yields of bio-oil,bio-char and gas evolved in the course of the pyrolysis experiment. The bio oil content of the shell was found to be 16.3% compared with 11.7% recorded for the peels. The bio-char of the peels was found to be 44.5% which was higher than34.1% in the shells The results obtained from the lignin constituent of the biomass confirmed the percentage yield of the pyrolytic products as described by Annika *et al.,* (2016)[13].The lignin composition of the biomass was inversely proportion to the bio-oil contents of the biomass - peels was 11.7% while lignin was27.00±0.28, therefore, the obersevation was in reverse order.

In the case of shells, the bio-oil was found to be 16.3% while the lignin was 28.00±0.50.This trend was consistent with the finding of Annila *et al.,*(2016) with the report that a biomass with high lignin content will give a lower bio oil yield while a biomass with low lignin will yield a higher percentage of bio-oil.

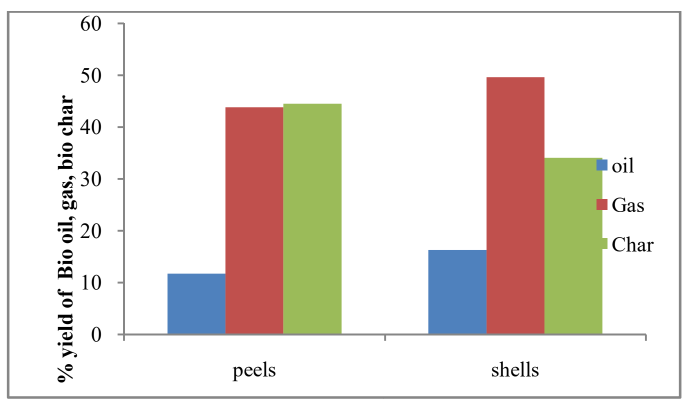

Figure 1: Groundnut Peels and ShellsPyrolysis % Yields in GramsGas chromatograph-Mass Spectrometry(GC-MS) Characterization

Tables 1.0 and 2.0, show the chemical constituents of the bio-oil derived through the pyrolytic conversion of the biomass. From the results, the most abundant compoundsare notably hexadecanoic,naphthalene-1,6-dimethyl,pentadecane, methyl stearate, and acid methyl ester which are commonly used as based chemicals for the production of lubricant [14].The chemical compounds identified in the biomass were consistent with the findings of [15] for groundnut shell. The other compounds also identified in the biomasswere phenol, 2-methoxybenzene, ethanamine, acetamide, naphthalene-1,6-dimethyl and squalene. The predominant compounds in the biomass are of alkanes groups which enhance the ability of the bio-oil to generate energy**.** The results confirmed that the shells of the groundnut biomass can potentially serve as wood preservative since, it was found to contain the basic chemical component of wood preservative chemicals. Bio- refinary process of the waste from the production of bio-based product will provide an alternative to many petroleum based chemicals,which are mostly toxic and non degradable in the environment.

Table 1: Chemical Compositions of the Groundnut Peels-Derived Bio oil

Retention time(min)	**Compound names**	**Peak area %**
7.244	Tetradecane	1.13
7.792	Naphthalene1,6dimethyl	1.49
8.553	Pentadecane	1.64
9.796	Hexadecane	3.89
10.96	Heptadecane	1.87
11.025	Pentadecane	1.09
11.268	Methyl tetradecanoate	1.31
12.073	Octadecane	2.17
12.163	Dodecane	1.14
13.125	Nonadecane	1.54
13.192	Hexadecenoic acid methyl ester	0.92
13.520	Hexadecanoic acid, methyl ester	33.31
14.130	Eicosane	1.72
15.149	Octadecadienoi acid methyl ester	21.38
15.220	11-Octadecenoic acid, methyl ester	18.80
15.392	Methyl stearate	3.28
16.00	Heptadecane	0.74
23.025	Squalene	2.57

Table 2: Chemical Compositions of the Groundnut Shell-Derived Bio oil

Retention time(min)	**Compound names**	**Peak area (%)**
3.220	Phenol, 2-methoxy	1.44
5.820	Phenol, 4-ethyl-2-methoxy	1.15
8.573	Pentadecane	2.57
9.801	Benzene ethanamine, 4-methoxy-. acetamide	1.02
10.701	8-Heptadecene	2.10
10.777	Heptadecane	2.41
10.958	Nonadecane	1.89
13.120	Octadecanamide	1.33
13.211	Hexadecanoic methyl ester	1.44
13.420	Propenamide	16.92
14.063	Octadecanamine	3.77
15.054	Hexadecanoic acid, methyl ester	4.72
15.106	9,12-Octadecadienoic acid methyl ester	24.09
15.173	Methyl stearate	15.03
15.358	Pyridine methanamine	9.27
15.587	Octadec-9-enoic acid ,oleic acid	1.01
15.744	Hexadecanoic acid methyl ester	4.97
18.930	Docosanoic acid, methyl ester	

IV. CONCLUSION

The lower lignin component of the groundnut biomass compared with other lignocellulose waste makes it an attractive feedstock for bio-oil production. The chemical composition of the derived bio-oilof the biomass confirmed the suitability of the waste for the production of bio-based chemicals that can find use in the production of wood preservative.

Conclusively, the use of agricultural waste such as groundnut peels and shells is cost effective, eco-friendly and sustainable in view of its unlimited availability. The biomass can serve as a dependable alternative source of energy and chemicals often derived from conventional sources such as fossil fuels if well harnessed. In addition, development of biomass conversion technology for the biomass will provide rural job opportunities through mass cultivation of the crop and valuable application of its post-harvest wastes.

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