Full Length Research Paper

Conversion of lignocellulose from palm (*Elaeis guineensis*) fruit fibre and physic (*Jatropha curcas*) nut shell into bio-oil

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Harmful gases are released into the atmosphere through burning of residues which is commonly practiced in Nigeria and can be attributed to climate change issues. Agricultural residues have the potentials to be used as energy and chemical source and meet its deficit in the country. This paper focuses on utilization of lignocellulosic materials obtained from two agricultural residues through renewable technology to produce bio-energy and chemical feedstock. The lignocellulosic materials were extracted from palm fruit (*Elaeis guineensis*) fibre and physic nut (*Jatropha curcas*) shell, and pyrolyzed under low temperature and pressure at various particle sizes. The main properties of solid (lignocellulosic) materials were tested and the bio-oil produced was analyzed using GC-MS. Results show proximate analyses (volatile, ash and fixed carbon contents) and ultimate analysis (carbon, oxygen, nitrogen, magnesium, phosphorus and zinc). The pH value of the bio-oil from both residues increased with increase in temperatures. The density, viscosity and calorific value of the palm and physic residue oil are 831.99 and 947.5 kg/m^3, 0.695 and 1.58 cPa at room temperature, 22.33 and 14.169 kJ/g, respectively. Aromatics and other compounds are major dominant compounds in the palm fruit fibre oil which is characterized for bio-fuel production. Physic nut shell oil contains aromatic ethers, cyclic ethers, secondary amides and organic halogen compound which are important chemical feedstock. Conversion of these residues to useful products will alleviate the energy supply deficit, improve social and economic development, promote clean and healthy atmosphere of the nation and significantly contribute to global climate change mitigation.

Key words: Palm fruit fibre, physic nut shell, lignocellulose, pyrolysis, bio-energy, climate change.

INTRODUCTION

Climate change can be described as a change in the statistical properties of the climate system when considered over long periods of time, regardless of cause (GCC, 2001). Climate change could be caused by human activity, as opposed to changes in climate that may have resulted as part of Earth's natural processes (NASA, 2011) and fluctuations over periods shorter than a few decades. In the context of environmental policy, the term *climate change* has become synonymous with anthropogenic global warming. Global warming is stated

as gradual increase in the average temperature of earth's surface and its ocean (Idowu et al., 2011) while climate change includes global warming and everything else that will be affected by increasing greenhouse gas levels (UNFCCC, 1994). Climate change also refers to a change of climate which is directly or indirectly attributed to human activity that affects the composition of the global atmosphere and which is in addition to natural climate variability observed over comparable time periods. Improper disposal and burning of agricultural residue are commonly practiced in rural areas of Southwest Nigeria and these are examples of the human activities that can contribute to climate change; extreme temperature and heat waves from burning activities release greenhouse gas emission into the atmosphere which can attribute to the global warming resulting to climate change. Therefore, it is profitable if these residues are converted to bioenergy and biochemical from affordable and surplus biomaterials to alleviate the climatic problem and hence the positive outcome can be resulted to policy making on environmental protection.

Biomass in general, can displace most of other fuel or source of energy, from the fact that biomass fuels have a very significant part to play in meeting our energy needs. It is a unique part with the realization of the finite limitation of the fossil resources, a sense of urgency has developed in the exploration of alternative energy and feedstock sources. Bioenergy technology could be defined as the conversion of biomass energy into other useful forms of energy for industrial and domestic purposes (FAO, 2015; Elum et al., 2016). Other forms of renewable energy that are predominantly used are from water and coal for generation of power, heating, cooling and transport fuels due to advanced technologies. Ackom and Ertel (2005) reported that about 60% of total energy consumed in Africa comes from biomass and by its projection in 2030; about 823 million people in Africa will depend on biomass. It is observed that more than 70% of the people living in the rural areas in Nigeria are using fuel wood, and the country uses more than 50 million tonnes of fuel wood annually (Oyedepo, 2014). This is due to insufficient and high prices of conventional fuel and this situation has led to both deforestation and desertification that are going on at the rate of 350,000 ha/annum while reforestation is only about 10% (Amigun et al., 2008) due to negligence attitude of people and weak policy in the country (Elum et al., 2016).

Agricultural residues can be transformed into various forms of biofuels and biogas. Bio-energy are produced from biomass and could be in the form of liquid, gaseous or solid state which can be used for cooking, heating, electricity generation, as fuels for transport and to replenish farm soil (FAO, 2015). Generally, biofuels and biogas are produced from biomass through biochemical (fermentation and anaerobic digestion) or thermochemical processes such as gasification, pyrolysis and liquefaction (Amigun et al., 2008). Biofuels can be made from the use of energy crops that have been cultivated exclusively for their production or from crop and forestry residues. These biofuels are wood-based methanol and biodiesel from soy, rapeseed oil and switch grass, also from corn and sugarcane-based ethanol known as bioethanol derived from fermentation of organic, sugar-rich substrates into alcohol through microbial degradation (Adebayo et al., 2013; Nehrenheim, 2014) for use in vehicles, machinery and generators (Oniya and Bamigboye, 2012). Biodiesel is basically a type of biofuels having about 38% higher energy than ethanol that could be made from oil crops such as canola, palm, rapeseed, sunflower, coconut and soybean (Fekete, 2013) and non-food energy crop such as physic nut (*Jatropha curcas* and *Eucalyptus* spp.) was discussed by Jatropha World Team (JWT, 2010). Biodiesel is meant for diesel engines and the demand for biodiesel in Nigeria has been projected to increase to 900 million litres in 2020 from the 480 million litres demanded as of 2007 (Samuel and Adekomaya, 2012). Biogas is formed when organic materials are degraded in the absence of oxygen (Itodo et al., 2007). It is a mixture of methane (60 to 70%), carbon dioxide (30 to 40%) and traces of hydrogen sulphide, ammonia, and carbon monoxide (Ngumah et al., 2013; Usman and Ekwenchi, 2013). Biogas technology is anaerobic digestion of organic materials which has been in existence since 1850s, and the main products are biogas (energy) and char (biofertilizer) which is the residual effluent (Ngumah et al., 2013; Usman and Ekwenchi, 2013). The black solid product, obtained after pyrolysis process known as char, has potential soil-quality benefits which include an increase in organic matter and soil carbon (Bello et al., 2009).

Pyrolysis is a process of the thermo-chemical conversion of biomass to char, bio-oil and gas, in the absence of oxygen and other reactants (Balat et al., 2009; Goyal et al., 2006). It is a non-equilibrium process where the biomass undergoes multistage decomposition resulting in large changes in specific volume. In this conversion process, combustion and gasification occur where complete or partial oxidation is allowed to proceed. The reaction rate, order and product yields depend on parameters such as temperature, heating rate, pre-treatment, catalytic effects, particle size etc (Bridgewater and Peacookie, 2000) and these parameters influence the optimum value in a fast pyrolysis process (Faisal et al., 2011). Moreso, Tsai et al. (2006) reported that fast pyrolysis is the most suitable process route to maximize

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the yield of liquid product. It is on this note that the paper emphasizes the importance of pyrolysis on the extract lignocellulosic content of two agricultural residues to simultaneously respond to bioenergy and chemical production.

Lignocellulosics are three-dimensional, naturally occurring, polymeric composites primarily made up of cellulose, hemicelluloses, lignin, and small amounts of extractives and ash (Rowell, 1992). Cellulose is the focus of much research because it is the dominant lignocellulosic compound and "next generation fuels" mostly based on cellulose (Kullander, 2010; Valentine et al., 2012). Some sources of lignocellulosics include agricultural residues, water plants, grasses, wood, and other plant substances (Limayem and Ricke, 2012; Sanchez and Cardona, 2008). In addition, Bello et al. (2009) stated that cellulosic material is recognized as a possible supplement for long term requirement as abundant renewable resources in organic materials obtained from plants. Lignocellulosic materials have also been called photomass because they are a result of photosynthesis. Wood and other lignocellulosics have been used as "engineering materials" because they are economical, low in processing energy, renewable and strong (Rowell, 1992). Lignocellulosic can decompose because it is organic in nature and burn under high temperature. However, a key factor affecting the efficiency of bioethanol production is the complex composition of lignocellulosic materials during the conversion processes (Jordan et al., 2012; Himmel et al., 2007; Dixon, 2013). The plant cell walls consist of cellulose, hemicellulose, and lignin as the major components that comprise around 90% of its dry biomass (Gibson, 2012; Harris and Stone, 2008; Pauly and Keegstra, 2008). Lignocellulosics can also be combined in an inorganic matrix to produce composites and also be combined with plastic in several ways. One example of this technology is reinforced thermoplastic composites, which are lighter in weight, have improved acoustical, impact and heat reformability properties, and cost less than comparable products made from plastic alone. The concept of combining lignocellulosics with other materials provides a strategy for producing advanced composites to achieve enhanced properties of all types of materials. These advantages make possible the exploration of new processing techniques, new applications, and new markets (Rowell, 1992).

This work focus on alleviating and coping with the negative effects that emanates from fossil fuel-based energy sources, renewable energy utilization plays a vital role in meeting current and future energy demands. At different processing sites visited in the study community, it is observed that the selected agricultural residues (palm fruit fibre and physic nut shell) used in this work are improperly disposed and leads to land and water pollution. Sometimes, the residues are burnt which causes air pollution by releasing greenhouse gas into the

Figure 1. Fresh physic nuts (*Jatropha curcas*).

atmosphere which can attribute to the problem of climate change and global warming. This study employed renewable technology for purpose of converting waste to energy and greatly contribute to global climate change mitigation. The detrimental effects of climate change require that alternative forms of energy such as biogas be utilized to avoid environmental catastrophes. The renewable technology activities can improve social development and economy identity and strength of the villages and cities and it also has beneficial and better environmental implications on the nation.

MATERIALS AND METHODS

Material and sample preparation

Physic nut shell is an agricultural residue obtained, after dehusking process of physic nut fruit (*Jatropha curcas*), which is left in the farm unused but decomposed over a long period. Palm fruit fibre is a waste material of African palm kernel fruits (*Elaeis guineensis*) after oil extraction process is done. Heap of this waste is formed at the processing site but this residue is not easily decomposed because of oil reminant in it and this has disrupted the landscapes, soil percolation and water infiltration are difficult resulted to low cultivation of other arable crops in the surrounding. The two residues (palm fruit fibre and physic nut shell) used for this research were collected from small scale processing centres in nearby villages via Ogbomoso town (8°07' N, 4°16'E), Nigeria. Figures 1 to 4 show the fresh fruits and the residues.

The samples used were sun dried and ground into fine particle size. The samples were then screened to give various fractions using different wire mesh sizes. The diameter of the particle size of the residues used ranged from 0.250 to 0.550 mm in form of 0.250, 300, 0.425 and 0.550 mm. Each sample was mixed with sodium anhydrous in order to make it dried and remove totally the moisture in it. The extraction, pyrolysis and proximate analyses of the samples were carried out at the laboratory of the Department of Chemistry, University of Nairobi, Kenya while the samples were taken to Kenya Agricultural and Livestock Research Organization Laboratory for ultimate analyses. Proximate composition was investigated to determine the fuel property of the solid sample residue and this was carried out in the Department of Physics,

Figure 2. Physic nut shell (residues).

Fruit fibre

Figure 3. Fresh palm kernel fruits (*Elaeis guineensis*).

Figure 4. Palm fruit fibre (residue).

University of Nairobi, Kenya. The samples were analyzed for the volatile matter, ash and fixed carbon contents to determine the composition of residues (Faisal et al., 2011).

Experimental procedure

Extraction of the lignocellulosic material from the samples

Lignocellulose was prepared from physic nut shell and palm fruit fibre according to the methods reported by Bello et al. (2009). Fifty (50) grammes of the raw ground sample residues were weighed using an electronic weighing balance Mettla Toledo, with an accuracy of 0.01 g, the sample was put in a 500 ml round bottom flask. Then, 200 ml of ethanol and distilled water was measured (1:1 v/v) using a 100 ml measuring cylinder, and poured into the sample. The flask containing the sample was put on an electric heating mantle set at 70°C and allowed to boil for 30 min. Each purification process was maintained for all particle sizes. After the final decantation of the final supernatant, the resultant material (purified sample) was drained and dried in an oven at 105 for 48 h and cooled in an air tight dessicator with dessicant. Extraction or purification process of the sample was achieved to obtain lignocellulosic contents from the samples.

Pyrolysis process

The lignocellulosic (purified) samples were pyrolysed in batch-type reactors in which the reactors are the ampoule and tubular systems. One end-opened narrow cylindrical pyrex tubes of about 3 cm diameter and 15 cm long was used with a tight lid. The pyrex ampoules was made by joining bulbs of 5 cm diameter with the cylindrical tubes. 2 g of lignocellulose was measured in each case and introduced into the reactor by means of narrow plastic funnel. In order to ensure quantitative transfer of the charge, a small Teflon rubber tubing about 2 cm long was used in the joining of the funnel and reactor outlet, and by gently tapping and varying the amount of the charging materials until the exact weight of 2 g as required was introduced into the reactor. Then, 0.2 g of glass wool was placed at the constriction level of the reactor. The wool was held fixed at the constriction point above the reactor so as to prevent discharge of gas during the evacuation period. High vacuum pump was used for the evacuation and the glass was sealed with a hand torch burner when the pressure reaches 0.1 mmHg as was measured with a pirant vacuum gauge. The duration of the evacuation was 5 to 30 min for the tubular and ampoule reactors. A thermostat oven furnace was required as shown in Figure 5; the isothermal temperature was allowed to run for ten minutes before introducing reactor and was maintained throughout the run. Each pyrolysis reaction lasted for 120 min at each temperature selected ranging from 200 to 400°C. To terminate a run, the reactor was removed from the furnace and placed in a dessicator and allowed to cool to ambient temperature level. The gas produced was collected through the tight fitted tap joined to the upper part of the reactor, with a small teflon rubber tubing inserted for easier discharge into an air tight gas bag. The weight of the gas produced was obtained by subtracting the final weight of the glass reactor after gas discharge from the initial weight before heating in a furnace. The pyrolysed sample (solid) was collected from the reactor for further process so that liquid extract can be produced using soxhlet extraction as shown in Figure 6; the extraction was carried out for 72 h.

   2 g of the pyrolysed sample were measured and put into dried thimble container and introduced into soxhlet extractor. Then 100 ml of methanol and dichloromethane solvent, (1:1 v/v) each was poured into a round bottom (250 ml) flask and placed on the electric heating mantle set at 20°C for 24 h. Then, the extracted
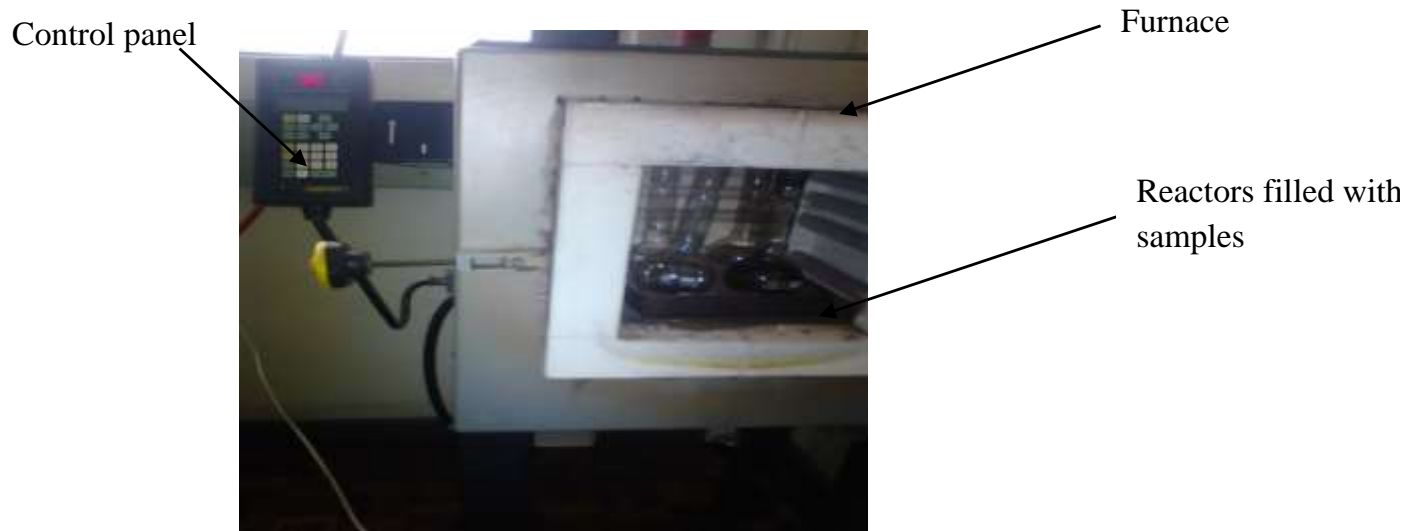
Control panel

Furnace

Reactors filled with samples

Figure 5. Pyrolysed samples inside the furnace**.**

Figure 6. Soxhlet extraction experiment for the residues.

sample was taken out of the thimble and put into crucible and dried in an oven for 48 h at a temperature of 105°C. The extracted solvent in the round bottom flask was then concentrated using the vacuum pump set. The concentrated extract was cleaned using a glass column (10 cm) filled with sodium sulphate to remove water or impurities. The clean sample filled into 0.2 ml chromatograph vials and then introduced to GC/MS for analysis.

Experimental design

The response surface methodology (RSM) was employed in this study and this is necessary to evaluate the performance of variables in pyrolysis system in other to optimize the bio-oil and biogas in the samples (physic nut shell and palm fruit fibre).The effects of tested parameters such as temperatures and particle sizes on the pyrolysis efficiency were determined to identify optimal bio-oil and gas conditions. RSM helps proper design of experimental work and optimization can either be minimum or maximum variables of design parameters. Design expert 6.0.8 software was used to analyze the

tested parameters and response. This was obtained by the response surface regression procedure using the following second-order polynomial equation (Yunardi et al., 2011; Gratuito et al., 2008; Faisal et al., 2011).

The temperatures chosen were 200, 250, 300, 350 and 400°C while the particle sizes were 0.25, 0.300, 0.425 and 0.55 mm and each experiment was replicated three times. The reaction time and product yield are the responses. The model used for predicting is generally a quadratic equation or second order model. The model equation can be expressed as follows:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum \sum_{i<j=1}^{k-1} \beta_{ij} x_i x_j \qquad 1$$

Where, y is the predicted response (Y_{char}, Y_{gas} and Y_{oil}); x_i and x_j are the coded independent variables corresponding to temperature and particle size and β_0, β_i, β_{ii}, and β_{ij} are intercept, linear, quadratic and interaction constant coefficients respectively. RSM package was also used for regression analysis and analysis of variance (ANOVA). Response surfaces, normal probability and plots were developed using the fitted quadratic polynomial equation obtained from regression, holding one of the independent variables at a constant value corresponding to the stationary point and changing the other variable. The independent variables being studied were temperature and particle size. The dependent variables were the retention time, yields of oil, gas and char. The design of three levels low, medium and high are coded as -1, 0 and +1 was applied to this study. Another step is checking the adequacy of the model. To achieve this aim is testing of the lack-of-fit which is defined as a measure of a model failure in representing data in the experimental domain (Faisal et al., 2011).

Characterization of bio-oil

The bio oil obtained, from lignocellulose of physic nut shell and palm fibre, was used for characterization. Litmus papers blue and red were used to check its acidity and alkalinity. A microprocessor pH meter (HANNA pH 211) was used to measure the pH of the oil. Analysis was done at room temperature; the meter was calibrated by measuring pH of buffer solution to be 7.03 at 23.6°C. The density of oil was conducted at room temperature of 23.6°C. The density is defined as sample mass divided by a fixed empty volume

Table 1. Main properties of the physic nut shell and palm fruit fibre.

Property	Values		Unit
Lignocellulosic analysis	Pns	Pff	
Cellulose	74.89±0.0128	28.99 ±0.029	%
Hemi cellulose	78.66±0.0148	38.96±0.0897	%
Lignin	50.92±0.005	60.36±0.41	%
Proximate analysis			
Moisture	4.61	5.93	%
Dry matter	95.24	94.09	%
Fat	84.37±10.12	20.13±0.12	%
Ash	13.60± 0.83	61.30±1.15	%
Volatile	56.01±11.15	49.89±3.12	%
Fixed carbon	25.79±0.83	38.70 ±1.15	%
Ultimate analysis			
Nitrogen	1.40	1.05	%
Phosphorus	0.43	0.24	%
Potassium	6.57	0.29	%
Calcium	6.48	3.22	%
Magnesium	0.59	0.08	%
Iron	96.02	20.17	wt%
Copper	0.834	2.17	wt%
Manganese	7.67	4.33	wt%
Zinc	15.67	1.83	wt%

pns, Physic nut shell: *pff*, palm fruit fibre.

of pycnometer. Then a 2 ml pycnometer was used to determine the density, the bio-oil was filled into the flask and weighed the mass. Viscosity of bio-oil was measured using Ostwald Viscometer (a U shape glass viscometer). All experiments were carried out three times and average readings were recorded.

Also, GC-MS was used to identify the chemical compositions of the bio-oil. The analysis was performed with Angilent HP 6890 (version 4.10) N gas chromatograph equipped with Agilent HP 5075 mass-selective detector (mass spectrometer), using a 30 m by 0.25 mm DB-5 ms capillary column (0.25 μm film thickness) with temperature capacity of -60 to 325°C. The GC oven was heated to 30°C for 3 min then to 290°C at a rate of 3.5°C /min while injection port and detector were set at 300°C. The carrier gas was helium with flow rate of 28 cm³/min and the effluent was monitored using a flame ionization detector (FID). Nitrogen was the makeup gas while hydrogen and compressed air are the lightning flame for FID.

A separate constituent of the pyrolysis mixture together with helium carrier gas goes to the flame ionization detector. It was at this zone that the separated organic compounds ionized at a high temperature in contact with hydrogen or air flame. A polarized electric grid captures the resultant ions which generates a current that will be recorded as a chromatogram. Peak areas of individual gases were measured and the abundance was determined from the prepared calibration. The calibration which is an external standardization has a technique involving essentially, the injection of known amounts of pure compounds as reference substance at the same conditions with that of the sample (pyrolytic products). The sample peak was compared with that of the standard. Also, individual compound was identified by matching their elution times along the base line with that of the standard. So, different components in the liquid solvent and their retention time displayed on the screen of the GC-MS monitor.

RESULTS AND DISCUSSION

Main properties of palm fibre

The results of the main properties of the agricultural residues used (physic nut shell and palm fruit fibre) are presented in Table 1. The proximate analyses are the physical characteristics such as moisture, volatile, ash and fixed carbon contents. The ultimate analysis is the composition of the materials in weight percentage such as carbon, oxygen, nitrogen, magnesium, phosphorus and zinc while the lignocellulosic values are based on the hemicellulose, lignin and cellulose of the materials.

Table 1 presents the main composition of the sample which includes the estimated value for cellulose, lignin and hemicellulose contents. The results revealed that the cellulose, lignin and hemicellulose values of physic nut shell and palm fibre are 28.99, 60.36 and 38.96% and 74.89, 78.66 and 50.92%, respectively. The values of latter residue are higher than the former; this might be because lignocelluloses in palm fibre do not decompose easily and next generation fuels are based on cellulose (Kullander, 2010; Valentine et al., 2012). From previous findings, cellulose is the strongest component of lignocellulose because it is polymer in nature. It also has fiber which is the smallest unit that can be used to produce high-yielding lignocellulosic composites (Rowell,
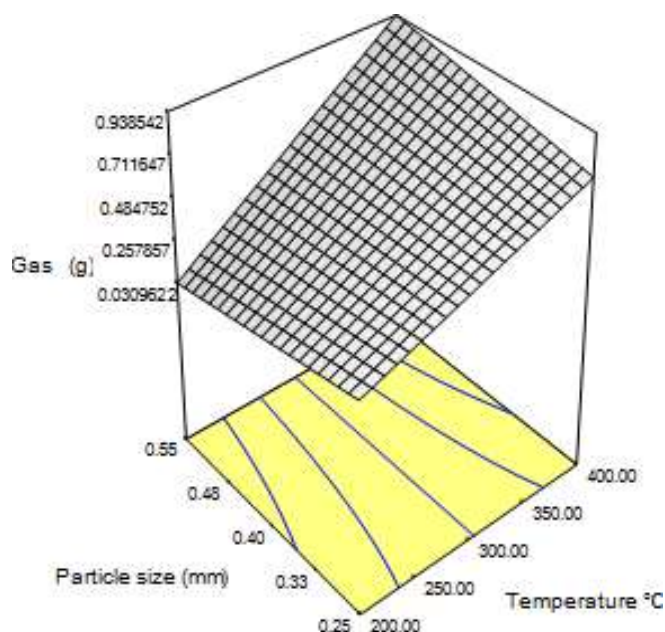
Figure 7. Effect of temperature and particle size on gas yield from physic nut shell.

1992). Similar findings are reported from other materials, such that mango pod had 22.96, 50.59 and 26.45% (Olaleye, 2013), wheat straw had 38, 15 and 29% (Hongzhang and Liying, 2007) while palm shell contained 27.7, 44 and 21.6%, respectively (Faisal et al., 2011).

From Table 1, the moisture content (dry base) and dry matter of physic nut shell and palm fruit fibre are 4.61 and 95.24%, and 5.93 and 94.09%, respectively. Agricultural residues have different values like that of mango pod is 7.31% (Hongzhang and Liying, 2007) and coconut shell has 6.0% (Ojha and Michael, 2006). Several works had been done on proximate analysis of agricultural materials; the value of ash content for mango pod is 2.1% (Hongzhang and Liying, 2007); coconut has 0.6% (Sundaram and Natarajan, 2009) rice straw contains 7.56% (Ahamed et al., 2013), palm shell has 2.1% (Faisal et al., 2011). In this study, the higher ash content value of *pff* (61.30%) than that obtained from pns (13.60 %) and other materials and it might be because palm fibre is a product of oil crop and high ash content indicates quality energy source and high fuel property.

Moreover, the results of volatile content of pns and pff gave 56.01and 49.90%, respectively while other reports gave 66.89% for volatile content of rice straw (Ahamed et al., 2013); while palm shell had 67.2% (Faisal et al., 2011). This indicates that the particles of others are less dense than the former which makes its component to escape into the air. The fixed carbon content of 25.79 and 38.70% are for *pns* and *pff*. The values reported by other researchers were lower; rice straw contained 14.56% by Ahamed et al. (2013) and palm shell had 19.7% (Faisal et al., 2011). There is higher value of fixed carbon content of physic nut shell, 86.40%. From previous research, it was illustrated that fresh physic nut could absorb more carbon content from the atmosphere that is more carbon can be emitted with fresh fruits (Onifade and Jekayinfa, 2015) but burning its residues can do more harm to human because of its high volatility and ability to release gases into the atmosphere. This is one of the most promising solutions for tackling the growing carbon emissions from atmosphere (JWT, 2010), hence reducing the problem of ozone layer. This implies that physic nut has greater potential to absorb carbon emission, thereby making the atmosphere carbon neutral. This factor can be a strategy for climate change adaptation or mitigation, if more cultivation practice of physic nut is established or encouraged in different countries of the world.

Effects of process parameters on product yield

Figures 7 to 13 present the effect of temperature and particle size on gas, char and liquid yields from physic nut shell and palm fibre. It is observed from Figures 7 and 11 that gas yield increased with increase in temperature and particle sizes. The increase in temperature leads to formation of more gaseous molecules released, the higher the temperature the higher the gases released to the atmosphere. This means if the residues are burnt in an open space, some is inhaled by human and the remaining affects the climate.

As reported from previous research, the burning of wood emits obnoxious GHGs that are harmful to the
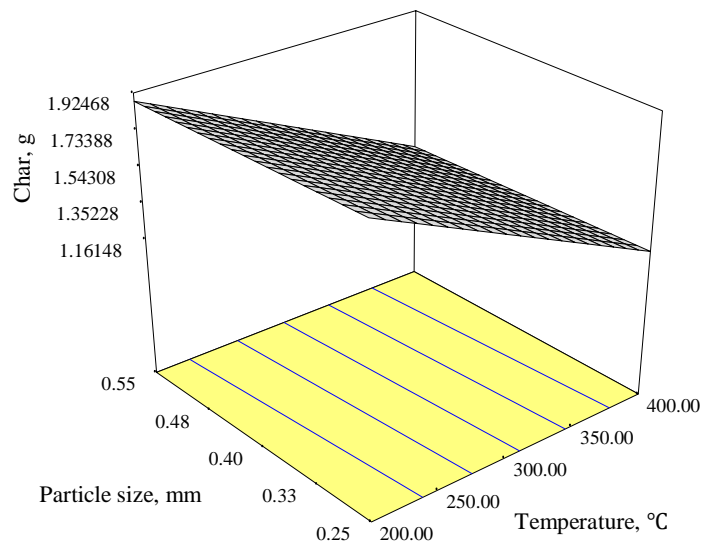
Figure 8. Effect of temperature and particle size on char yield from physic nut shell.
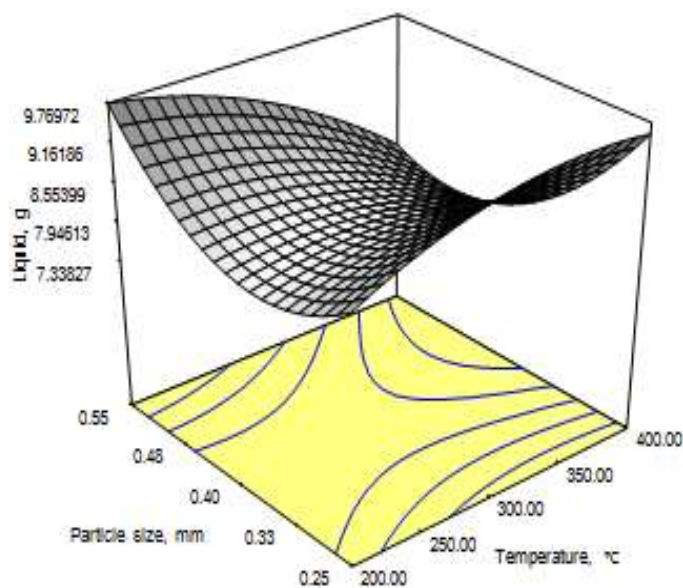

Figure 9. Effect of temperature and particle size on liquid yield physic nut shell.

environment (Pimentel et al., 1994; OECD/IEA, 2007; Davidsdottir, 2013).

Figures 8 and 12 depicted the effect of process parameters on the char yield. It was observed that increased in temperature and particle sizes lead to decrease in quantity of char produced. Figure 10 presented the char produced after pyrolysis. The char has potential soil-quality benefits for farming activities when it is incorporated into the soil. Application of residue char into the soil improves physical and chemical

properties of farm land (UNL, 2016). From Table 1, the results of ultimate analysis indicate that the residues have traces of Nitrogen, Phosphorus and Potassium which are good compounds to enrich the soil if the char is impoverished into the farm soil.

From Figures 9 and 13, it was observed that as temperature and particle sizes increased, increase in liquid yield occurred but liquid yield decreased as temperature increased. The increase in temperature aids formation of newer pores and an opening of the existing
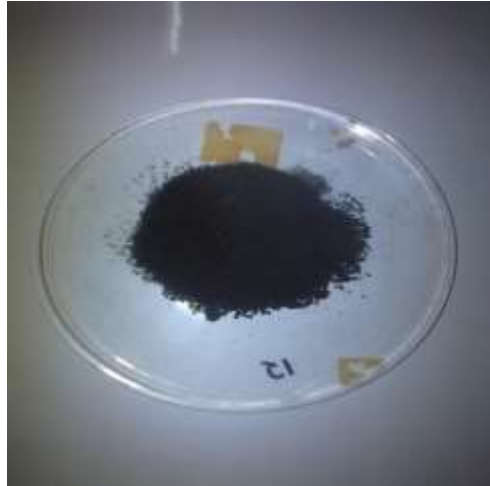
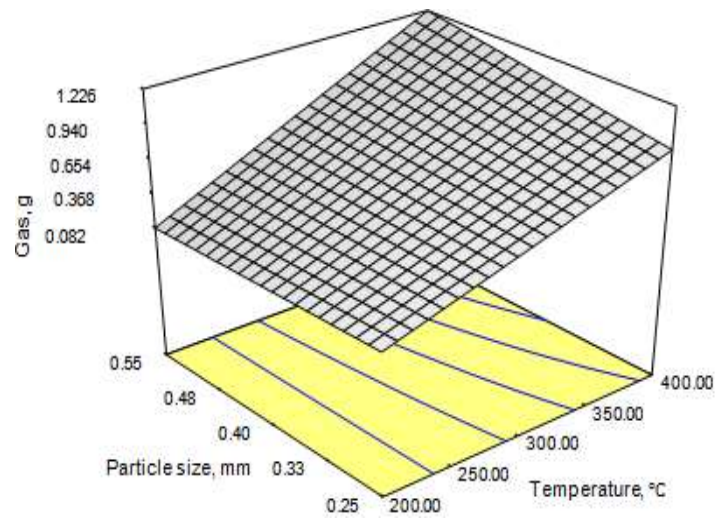**Figure 10.** The char produced after pyrolysis.

Figure 11. Effect of temperature and particle size on gas yield from palm fibre.
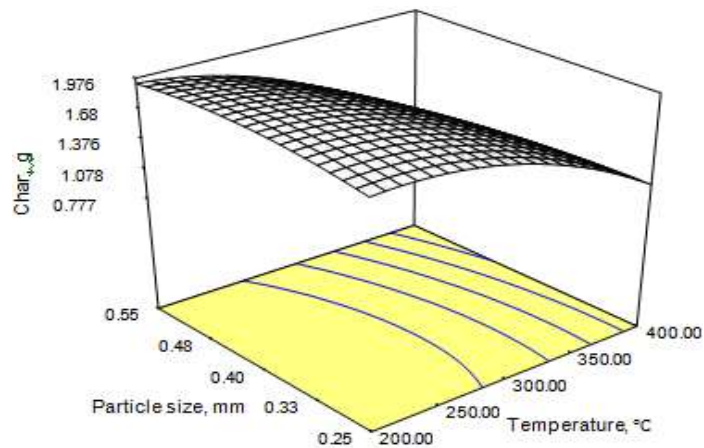

Figure 12. Effect of temperature and particle size on char yield from palm fibre.
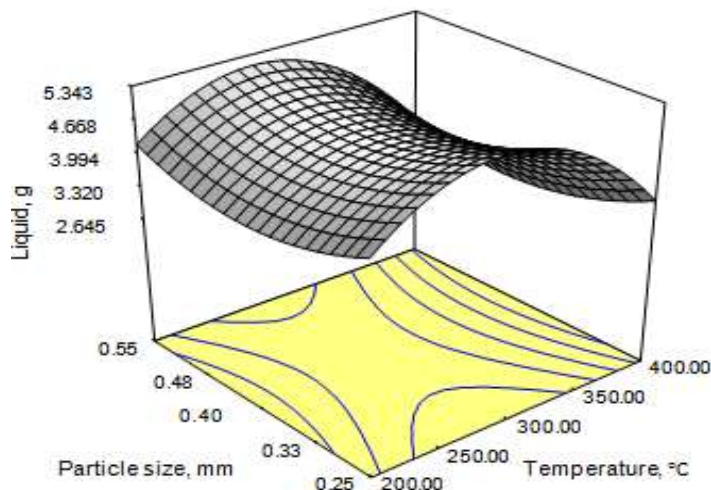
Figure 13. Effect of temperature and particle size on liquid yield from palm fibre.
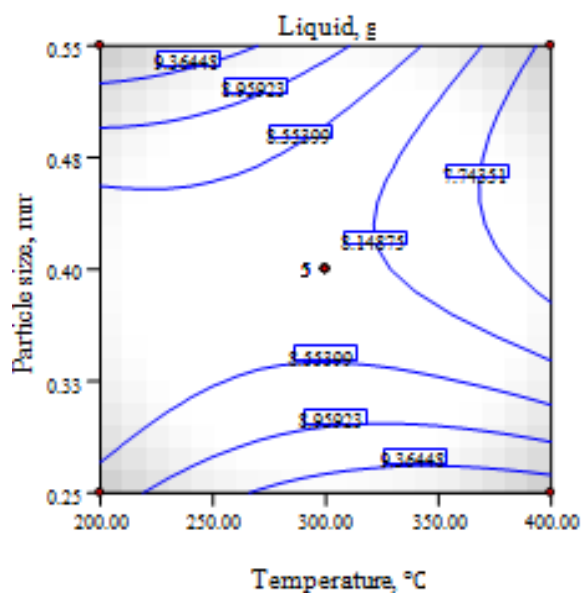

Figure 14. Effect of temperature and particle size on liquid yield from palm fibre.

pores for the liquid extract which leads to more liquid yield. If temperature is increased further, the pore wall of the materials could be collapsed; due to thinning porosity of the particle size as the surface area is reduced (Azargohar and Dalai, 2005) not only this but also increased ash content which offered a resistance to the diffusion of activating agent (Dutta et al., 2011).

Figure 14 shows the 3D surface plots obtained from numerical optimization of pyrolysis process where the optimum values of two process parameters for response product were found. It can be seen that the optimum values of process parameters varied slightly in each case. Therefore, application of numerical optimization was used to optimize the process where two process parameters were considered at a time. The desired objective of optimization was to maximize the temperature, particle size and product yield (liquid, gas and char). The optimum values of temperature and particle size predicted by the model were 300°C and 0.55 mm.

Physical characterization of bio-oil

The physical properties of bio-oil produced from the two

Table 2. Physical properties of bio-oil.

Properties	Pns	Pff	Unit
Viscosity	1.58	0.695	cP
pH	6.94-7.72	4.64 - 6.43	Acidic
Density at 23.6°C	947.5	831.99	kg/m^3
Calorific value	14.169	22.33	kJ/g
Water content	4.6	5.39	%
C	60.73	65.24	%
H	6.88	5.07	%
N	0.98	1.10	%
O	17.81	28.60	%

residues (physic nut shell and palm fibre) investigated are presented in Table 2. The liquid extracts of *pns* were neutral because it has little or no effect on litmus paper because the oil pH values ranged from 6.94 to 7.72 at 22.8°C. The liquid extracts of *pff* were acidic in nature because it turned blue litmus paper to red, the pH values ranged from 4.64 to 6.43. The pH of the bio-oil increased with increase in temperatures, this meant that oil obtained at high temperatures are slightly acidic while oil obtained at low pyrolitic temperatures indicate low pH readings which is more acidic.

The density of the oil from *pns* and *pff* is 831.99 and 947.5 kg/m^3, respectively at 23.6°C. It was observed that all density values at different temperatures and particle sizes gave similar readings. The density and viscosity are related to phenomenon of liquid floatation which can have significant effect on fluid atomizers. The respective viscous values of bio-oil produced in this study gave 1.58 and 0.695 cPa at room temperature; this value was less than that of water (0.9107) used as standard. This indicated that the viscous period of bio-oil is less than that of water. Hence, this could be due to low level of water content (5.93%) in the samples which caused it to be less viscous. The presence of water content in bio-oil shows the presence of lignin in the raw material of *pns* and *pff* which is 50.92 and 60.36%. It has been reported that lignins are not crystalline, but highly branched and their structure and chemical composition is a function of their source. Lignins play a role in the natural decay resistance of the lignocellulosic substance and are associated with the hemicelluose (Rowell, 1990).

The calorific values of the bio-oil of *pns* and *pff* are 14.169 and 22.33 kJ/g as shown in Table 2, this shows the amount of energy produced by the complete combustion of 0.291 g of the oil. The calorific value is an important factor to determine the energy content of the fuel. Compared to other common fuel, gasoline (47 kJ/g), diesel (45 kJ/g), ethanol (29.7 kJ/g), wood (15 kJ/g) coal (15 kJ/g) and natural gas (54 kJ/g) (NIST), this indicates that bio-oil from palm fruit fibre is a potential source of energy and can be upgrade first before using it as fuel.

Chemical characterization of bio-oil

GC-MS was used to analyze and identify the chemical components in the liquid (bio-oil). Table 3 presents the details results of GC-MS analysis of bio-oil of physic nut shell. The most abundant products and highest peak area achieved by hexadecanoic (82.2%). Other prominent products are pentadecanoic acid (12-48.9%), octadecanoic (4.16-35.5%), eicosanoic (1.55-3.53%), linoleic acid (3.72-18.4), octanamine (2.71-12.3), ethynefluoro (8.75) and 2-hexanamine (15.13). It was observed that different values were obtained at various temperature and particle sizes. This shows effect of experimental parameters (temperature and particles sizes) on the chemical compounds produced from physic nut shell. For instance, highest peak of hexadecanoic (82.2%) was obtained at 300°C, 0.25 mm, pentadecanoic acid was high (38.5%), at 200, 0.55 mm; eicosanoic had value of 3.53% at 200°C, 0.55 mm, heptadecanoic has highest peak of 26.5% at 400°C and 0.42 mm. Only 200°C, at 0.42 mm produced amine compounds. Table 4 presents the details results of GC-MS analysis of bio-oil of palm fibre, GC-MS was used to analyze and identify the chemical components in the liquid. The most abundant products and highest peak area was achieved by hexadecanoic (81.3%).

Other prominent products are pentadecanoic acid (1.47-14.5%), octadecanoic (2.6-70.1%), eicosanoic (3.5-11.3%), 2-2-hydroxyethoxy (2.71-12.3%), ascorbic 2, 6-dihexadecanoic (7.1-14.3) and isopropyl palmitate (7.31-41.0). It was observed that different values were obtained at various temperature and particle sizes. This shows effect of experimental parameters (temperature and particles sizes) on the chemical compounds produced from palm fruit fibre. For instance, highest peak of methyl-hexadecanoic (81.3%) was obtained at 158.8°C, 0.42 mm, methyl-pentadecanoic acid was high (14.5%) at 441.42°C, 0.42 mm, eicosanoic had value of 11.3% at 300°C, 0.25 mm. Hepta decanoic has highest peak at 200°C, 0.55 mm. Only 300°C, 0.25 mm and 400°C, 0.25 mm contained ascorbic 2,6-dihexadecanoic.

Summarily, there are a great number of other compounds but their peak areas are low, so this study did not examine them further. The dominant compounds presented in Tables 3 and 4 are classified as aromatic oxygenated and hydrocarbon compounds found from lignocellulose bio-oil of both in physic nut shell and palm fibre. Oxygenated content is favorable to be used for fuels. Other compounds found in palm fibre show the potentiality to be used as polymer. Amines and organic halogen compounds are highly present in the physic nut shell oil which can be useful as chemical feedstock for further productions. The results obtained in this study showed different level of concentration of each compound and the values are higher than those obtained from palm kernel shell by Faisal et al. (2011). Evidently, from previous research, it was stated that lignocellulosic

Table 3. Identification and analysis of chemical compounds in bio-oil of physic nut shell by GC-MS.

Chemical compounds	Molecular formula	Molecular weight (g/mol)	Peak probabilty (%)
9-octadecenoic	$C_{21}H_{40}O_2$	356	6.7- 35.3
Hexadecanoic acid	$C_{18}H_{34}O_2$	284	4.0 -82.2
n-propyl 11-octadecenoate	$C_{21}H_{40}O_2$	324	7.27
14-methylPentadecanoic acid	$C_{17}H_{34}O_2$	270	48.9
Linoleic acid	$C_{17}H_{34}O_2$	308	3.72-18.4
Ethyl Oleate	$C_{20}H_{38}O_2$	310	6.53
Eicosanoic acid	$C_{22}H_{44}O_2$	340	1.55-3.53
Butyl 9-octadecanoate	$C_{22}H_{42}O_2$	338	2.53-4.46
Trans -13-octadecanoic	$C_{19}H_{36}O_2$	296	4.16-5.99
Pentadecanoic acid	$C_{17}H_{34}O_2$	289	12-38.5
Methyl10-trans12-cis-octadecadienoate	$C_{19}H_{34}O_2$	294	2.57-8.65
Ethyl 9-cris, 11 trans-octadecadienoate	$C_{20}H_{36}O_2$	308	28.4-33.8
n-propyl 9, 12-octadecenoate	$C_{21}H_{38}O_2$	322	2.91-5.36
EthyneFluoro	C_2HF	44	8.74
2-Aminoheptane	$C_7H_{17}N$	115	6.69
2-hexanamine	$C_7H_{17}N$	115	15.13
Octanamine	$C_9H_{21}N$	143	2.71-12.3
Benzene thanamine	$C_9H_{11}F_2NO_3$	219	2.56-3.82
Dodecylmethylamine	$C_{13}H_{29}N$	199	2.77-3.0
Octodrine	$C_8H_{19}N$	129	2.36
Cyclopropanebutanoic	$C_{25}H_{42}O_2$	374	2.83
Ethyl iso-allocholate	$C_{26}H_{44}O_5$	436	4.72
14-methyl-hexadecanoate	$C_{19}H_{38}O_2$	298	3.43
3,9-Epoxypregnane	$C_{25}H_{41}NO_2$	435	1.89
Diethylene glycolmonolaurate	$C_{16}H_{32}O_4$	288	1.82
Tridecanoic	$C_{17}H_{34}O_2$	270	0.9-5.41
Docosanoic	$C_{24}H_{48}O_2$	368	0.37-3.7
Undecanoic	$C_{14}H_{28}O_2$	228	2.68
Oleic acid	$C_{18}H_{34}O_2$	282	2.29
Heptadecanoic	$C_{20}H_{40}O_2$	312	1.61-81.3
Bromodecanoic	$C_{12}H_{23}BrO_2$	278	0.73
Octadecadienoyl Chloride	$C_{18}H_{31}ClO$	298	2.80
Cyclopentanetridecanoic	$C_{19}H_{36}O_2$	296	1.07
Octadecanoic	$C_{20}H_{40}O_2$	312	35.3

Table 4. Identification and analysis of chemical compounds in bio-oil of palm fibre by GC-MS.

Chemical compounds	Molecular formula	Molecular weight (g/mol)	Peak probability (%)
3-methyl pentadecanoic acid	$C_{16}H_{32}O_2$	256	1.47-2.85
2,16-methyl hexadecanoic acid	$C_{18}H_{34}O_2$	284	1.30-10.15
Methyl hexadecanoic acid	$C_{17}H_{34}O_2$	270	81.3
14-Methyl pentadecanoic acid	$C_{17}H_{34}O_2$	270	9.92-28.7
Tridecanoic acid	$C_{17}H_{34}O_2$	270	2.58
Ethyl pentadecanoic acid	$C_{17}H_{34}O_2$	270	6.53
Ethyl eicosanoic acid	$C_{22}H_{44}O_2$	340	3.53-11.3
Ethyl hexadecanoic acid	$C_{19}H_{38}O_2$	298	2.84
Ethyl tridecanoate	$C_{15}H_{30}O_2$	242	1.46
Methyl octadecanoic	$C_{19}H_{38}O_2$	298	4.04-66.6
16-methyl heptadecanoate	$C_{19}H_{38}O_2$	298	10.5

Table 4. Contd.

Ethyl octadecanoic acid	$C_{20}H_{40}O_2$	312	60.7
Nonadecanoic acid	$C_{21}H_{42}O_2$	326	0.93
Cyclop1ropanepentanoic	$C_{20}H_{38}O_2$	310	3.73
Tetradecanoic	$C_{16}H_{32}O_2$	256	2.7- 4.63
Ethyl heptadecanoic	$C_{19}H_{38}O_2$	298	5.48
2-2-hydroxyethoxy	$C_{22}H_{44}O_4$	372	2.71-12.3
Hexadecanoic acid	$C_{18}H_{36}O_2$	284	49.4
Isopropyl palmitate	$C_{19}H_{38}O_2$	298	7.31-41.0
Ascorbic 2,6-dihexadecanoic	$C_{38}H_{68}O_8$	652	7.1-14.3
Ascorbic acid, 6-octadecanoate	$C_{24}H_{42}O_7$	442	2.8

fibers can be combined in an inorganic matrix to produce composites which are dimensionally and thermally stable, and majorly used as substitutes for asbestos composites (Rowell, 1992). It allows the scientist to design materials based on end-use requirements within the framework of cost, availability, renewability, recyclability, energy use, and environmental considerations.

Conclusion

This research was set up to explore and study the lignocellulosic characteristics of two agricultural residues as a provider of renewable energy and chemicals in Nigeria. The residues were pyrolyzed considering these experimental factors; temperature and particle size. The optimum process condition of bio-oil was produced at 300°C and 0.55 mm. It further examined the impact and advantage of biotechnology on farm residues studied to produce biogas, biochar and bio-oil and positive effects on climate change. This paper also revealed and identified the bioenergy and biochemical from lignocellulosic materials in physic nut shell and palm fibre which can be used for further processing in small and large scale industries. Aromatic oxygenated and hydrocarbon compounds present in lignocellulose bio-oil of physic nut shell and palm fibre are favorable to be used for fuels. Other compounds found in palm fibre show the potentiality to be used as polymer. Amines and organic halogen compounds are highly present in the physic nut shell oil which can be useful as chemical feedstock for further productions. The work analyses the use of lignocellulosic content of the residues studied as a great opportunity for bioenergy in its efficient forms and such engagement will enhance economic development and improve social wellbeing of the nation. It will promote innovation and imagination of the youth and means of empowering them. This showed possible ways that bioenergy would enhance Nigeria's economic diversification, reduce dependence on crude and export products. However, climate change has become one of the major challenges for mankind and the natural environment. It is reflected from these findings that both residues studied contained a lot of useful products that can be processed further, and if such biofuel and chemicals are burnt consistently will enhance gas emissions released into the atmosphere and rapidly growing volumes are recognized to be responsible for this climate change. It is profitable and highly beneficial that farm residues are rather used for energy and chemicals production than burning them that enhance less pollution and a cleaner environment. Thereby, this study is recommended for policy making on environmental protection in the nation.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

ACKNOWLEDGEMENTS

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