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Channeling Biomass Waste as An Alternative Industrial and Domestic Energy with Pollution Effects Mitigation in Nigeria: An Overview

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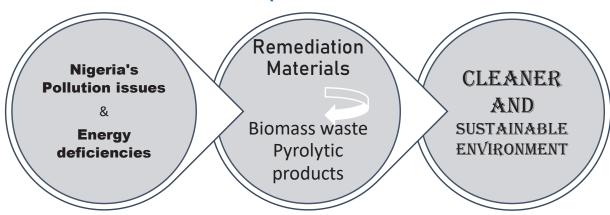
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Abstract

This write-up provides an in-depth analysis of major anthropogenic activities contributing to environmental pollution in Nigeria. It identifies and discusses environmental problems associated with fossil fuel (petroleum products, gases), heavy metal, dye, domestic and industrial wastes in Nigeria. It describes the world reserve of fossil fuel as being scarce, limited and non-renewable but provided a suitable alternative (biomass) as renewable material with potential of drastically reducing reliance on fossil fuel and removing environmental nuisance in Nigeria. It discusses the models and mechanisms of using biomass waste for environmental remediation. The common demerit of crude bio-oil is its low heating value that limit its use as engine fuel, the write-up discusses methods of upgrading crude bio-oil to be fit as engine fuel. This write-up proffers how one environmental problem (biomass waste) could be used as a cheaper and sustainable solutions for energy generation and pollution control in Nigeria.

Graphical Abstract



Highlight

- 1. Biomass concept and biomass waste in Nigeria
- 2. Sources of environmental pollution and consequences in Nigeria
- 3. Biomass wastes role in environmental remediation
- 4. Adsorption techniques and kinetics studies in using biomass waste as adsorbent for environmental remediation
- 5. Biomass waste as an alternative energy
- 6. Identified areas of application biochar for Nigeria's environment sustainability

Keywords: Biomass, Fossil Fuel, Adsorbent, Pyrolysis, Bio-Oil, Biochar

Introduction

Nigeria is a country in west Africa blessed with many varieties of biological resources (plant and animal). Biological resources are naturally existing substance, a free gift of nature found in natural habitation, botanical garden, zoological garden etc. Biomass is the total mass of biological resources in a geographical area. Biomass in this context will be limited to plant materials.

Plant exists as vascular and non-vascular. Examples are; grasses, herbs, shrubs, trees, perennial crops etc. Plants are indispensable and their uses seem unlimited in every area of our lives e.g. medicine, food, chemical, textile, bio-materials, agro-allied, rubber industries etc. Plant could be grown for food purposes or other industrial uses while nature also grow plant itself with or without economic importance. Plant materials useful in energy generation are termed lignocellulosic biomass and through their subjection to thermochemical modifications, biofuel is produced [1]. Their usefulness doesn't give room for over exploitation to preserve biodiversity else if being over-extracted in the absence of effective implementation of sustainable use measures; desertification, erosion and leaching could set in such area and this will have tremendous negative effects on the sustainability of such environment.

Plants are not totally consumable as food material; the unused parts are termed plant wastes. Wastes from plant could be in form of seed, seed shell, pod, residues etc. Nigeria is highly blessed with diverse species of food crops e.g. cocoa, rice, beans, sugar cane, trees, kolanut, palm tree, cassava, banana tree etc. with common practise whereby farmers and plant processors burn wastes generated from these plant materials. Combustion of plant wastes release carbon dioxide (CO₂) into the atmosphere, a well-known greenhouse gas that contributes to global warming but these largely generated agricultural wastes can be explored for the purposes of environmental sustainability and energy generation. They could be tapped as a source of biofuel to solve the envisage fossil fuel shortage and environmental degradation associated with continuous burning of fossil fuel in Nigeria.

Another useful property of biomass waste is bio-degradability. Biomass wastes have potential to be transformed into manure or compost since they are made up of biodegradable organic materials that can be mixed with some soil or kept in a pit to get rotten, after being rotten it can then be used as fertilizer thereby reducing the need for inorganic fertilizer that could be washed off by rain to nearby water source which consequently cause toxicity of the water body. Biomass wastes usage for fertilizer purposes will discourage the common practice in Nigeria which is throwing them into open places, burning, as land fill etc.

The world reserve of fossil fuel is scarce, limited and non-renewable there is a need for a suitable alternative which is also renewable. Biomass can be explored as suitable alternative fuel i.e. biofuel, depending on usage, they are classified as primary and secondary [1]. Wood, sawdust, plant pod, seed shell etc. are naturally existing organic materials that can be used in their unprocessed state as fuel hence termed primary biofuel. In their unprocessed state they can be used as biofuel for cooking and power generation in the industry. Thermochemical modification of primary fuel produces three major products belonging to the three states of matter useful as fuel and classified as secondary biofuel [1].

Lignocellulosic biomass is largely available, renewable and have ease of growth with wide spread distribution across areas cover with soil and water. The abundance, availability, cheap sources, eco- friendly nature of plant wastes make them a good alternative energy to curtail the negative and environmental damaging effects of fossil fuel [2]. This eco-friendliness makes lignocellulosic biomass a source of renewable energy with potential to solve world energy crisis [3]. Its pyrolytic products are; liquid(pyro-oil), gas and solid(biochar) with great potential as bio-fuels. Thermochemical degradation of biomass can produce liquid fuel (ethanol, methanol and biodiesel) and gaseous fuel e.g. (light hydrocarbon, methane) etc. [1]. The reasonable low content of sulphur in a biomass and its pyrolytic products favours non-alteration of the concentration of CO₂ in the atmosphere when thermochemically converted to generate energy. Hence, biofuel from this source had emerged as a promising fuel to limit greenhouse gas emissions, thereby will lead to a cleaner environment, reduction in environmental degradation and economic sustainability in Nigeria if being adopted.

Sources of Environmental Pollution and Consequences in Nigeria

Human activities spill crude oil into the environment [4]. Its spillage result into the release of crude oil components; trace metals, sulphur, colour, floating particles, mineral oils, aromatic compound $(C_6H_6, CH_3C_5H_6, (CH_3)_2C_6H_4, polycyclic aromatic hydrocarbons),$ C₆H₅OH, salt, ammonia, saturated and unsaturated hydrocarbons, etc. into the ecosystem [5]. Heavy metal, dyes, suspended particles, chemicals associated with (paper, pharmaceutical, cement, textile, chemical industries effluent) are pollutants if being discharge into water bodies (groundwater, lakes, rivers, seas, oceans, lagoon), air and land in untreated or partially treated form which then constitute a potential danger to the environment. Burning of fossil fuel releases greenhouse gases which are major cause of climatic change. Climatic change has created worrisome situation due to its negative impact on the environment and its demography, which will likely displace millions of people in developing countries and cause social unrest in a very near future [6]. Industrial production supported by burning of fossil fuel is largely done in the developed countries hence they are the major contributor to changes in climatic condition but have developed technologies, policies and rich economic status so that they will be least affected [7]. Assessment of the impact on large number of developing countries showed climate change has an aggregate effect on biomass and alters the balanced state of our ecosystem. In recent times, some sectors supporting the economy growth of Nigeria appear to have been hit by the adverse effects of climate change. These impacts have been recorded in agricultural, mining, health (medicine and

pharmaceuticals), species of plant and animal, socio-economic, manufacturing industries and power generation. Food and livestock production have been hampered in Yobe due to sand dunes and desert encroachment that has gulped ~30,000 hectares of land [8]. There are noticeable evidences that climate change is affecting our lives in the negative direction with the existing cases of diseases outbreak, drastic decline in agricultural produce and heat waves increase. Desertification is on a continuous increase due to rainfall reduction in the Northern Nigeria with an insignificant effect on Nigeria major food producer (Benue state). The sudden rise in water had affected Nigerians living in the coastal by halting fishing activities. Temperature and rainfall have significant effects on disease pathogen, these two factors could enhance the easier distribution of pathogens responsible for malaria, typhoid, and diarrheal [9]. Harsh climatic condition such as high intensity of sunlight in the Northern Nigeria, excessive rainfall in the Sothern Nigeria etc. could cause illness, injury/accident and death.

The Nigeria country rely on hydroelectricity for her power supply, climate change trend is expected to negatively affect meagre electricity supply used in the country through service interruptions to be likely caused by the damage of power lines and power generation equipment impacted by water level rise in sea, heavy/intense floods and harsh weather condition [10]. Manufacturing sectors that relied on agricultural produce in Nigeria e.g. sugar, flour, brewery etc. as inputs might likely suffer losses from reduced potentials output. Oil production wells in the Niger delta regions will be likely submerged by a sharp rise in sea level (1-3 meters) cutting large revenue sources from Nigeria.

Oil mining and exploration activities are common in the Niger Delta, South-South, Nigeria. These had resulted into a lot of spillage which has adverse effects on the quality of water, soil and aquatic organisms. In Nigeria, common causes of oil spills are; leakage of pipeline due to corrosion, sabotage by oil bunkering activities, uncoordinated oil well drills, faulty machines, poor technical skill in handling transportation logistics of oil vessels etc. Hundreds to millions barrel of crude oil had been spilled over years e.g. about 300,000 barrels due to GOCON's Escravos spill, Texaco Funiwa-5 caused 400,000 barrels lost, SPDC's Forcados Terminal storage issues wasted 580,000 barrels, Funiwa-5 caused about 37.0 million litres lost [11]. These spilled oils find their ways into the Atlantic Ocean and causing serious damages to plants and animal in the mangrove swamp [11]. Health issues are associated with oil spill on land or water due to the present of organic, inorganic and heavy metal present in crude oil [12]. Soluble contaminants get dissolved and become oxidized in aquatic environment, bacterial conversion is also common and then contaminant eventually sink to the bottom of the aquatic environment due to their higher density. The contaminants in the soil have pronounced impacts on the terrestrial life and had caused a drastic reduction in farming activities due to poor harvest yield. Action of heat or sunlight evaporates the volatile constituent of the spilled oil which negatively affect aerial life while the less volatile component undergoes emulsification

with water and pose a great danger to the aquatic life [13]. Cancer, tumour, rashes, respiratory diseases, intestinal infectious etc. are common health issues associated to feeding/consumption of plant, water or animal contaminated with oil spill [14]. Ingesting large amounts of chromium from this spilled oil can cause peeling of the walls of stomach and results into ulcers and stomach trouble and also likely responsible for kidney and liver diseases [12].

Biomass Wastes Role in Environmental Remediation

Many countries of the world including Nigeria intervened in agriculture by providing improved seedlings and fertilizers to boost local production of food but this has a separate environmental concern. There is an increase in annual production and consumption of agricultural produce and consequently, large quantity of wastes will be generated from these plants which are often burnt as wastes while the rest constitute environmental nuisance especially in Nigeria with poor or inadequate waste management facilities. This write-up is a critical collection of areas in which these wastes can be explored and used as adsorbent that can remove pollutants and soluble petroleum fractions from oil spill affected water with the added value of using one environmental problem to eliminate another. Although there are existing techniques applicable to recover oil spill from different surfaces which include: booms; skimmers; sorbents; dispersants; insitu burning; bioremediation and magnetic nanocomposites [15]. But from Analytical Hierarchy Process (AHP) method, preference is given by the experts for the use of sorbents.

The preferable sorbent for the removal of oil spillage are those which are cheap, affordable and readily available, low H2O pick-up, large pores size to attain high oil sorption capacity (oleophilicity or lipophilicity) with efficient holding potential during material transfer, significant absorbate regaining, excellent adsorbent physical and chemical stability for reuse, ability to resist deformation by chemical attack and UV-degradation.

Inorganic adsorbents and organic (synthetic and natural) adsorbents have been used for adsorption of oil but organic synthetic adsorbents cannot/hardly decompose by soil microorganism e.g. bacteria and hard to degrade due to synthetic nature, also exfoliated graphite and silica aero gel which are mineral products showed exceptional oil sorbents capacity but are expensive [17]. The expensive/hazardous chemical treatment methods have called for the need of an alternative materials, especially biodegradable ones e.g. biomass waste. Biomass wastes had shown appreciable adsorption capacity for spilled oil and its component e.g. rice straw[18]; sun flower, grasses [19]; grasses and cotton waste, peat moss, maize cob[20]; coconut shell, wood Aqua Nuchar[21]; plant barks, fibre plants (kenaf &kapok) [22]. Activated carbons from coconut shell, bituminous coal, lignite, wood Aqua Nuchar and Mead Wetvaco showed good adsorption capacity for 2-phenylphenol, biphenyl, and phenanthrene [21]. Agricultural wastes generated from sun flower, rice, maize, grasses, leaves and straw are useful adsorbents [19]. They have unique properties (can be regained after use, unaltered chemical state, excellent mechanical strength, pores for adsorption after being pyrolysed etc.) make them choice adsorbents. Carbonized rice husks obtained from pyrolytic process at 700° C K_F of 16~g/g for heavy crude oil removal [19].

Slow biomass waste pyrolysis produces large amount of biochar. Biochar are porous, promising and environmentally friendly adsorbent. A study pyrolyzed rice husk activated with KOH in CO₂ environment via one and two steps to obtain char. More pores developed in the one step pyrolysis are responsible for higher adsorption capacity of the biochar for phenol [23].

Agricultural waste generated in large quantity can be processed to be used as adsorbent since this remove waste form the environment. In their raw form, pores for adsorption are limited, but if carbonized, the obtained activated carbon performs better as an adsorbent. These wastes can also be pretreated or modified for the removal of industrial specific pollutant [24-25]. Modification are done with reagent or condition that enhance higher adsorption capacity of the adsorbent e.g. using H3PO4 can effectively decrease soluble ash, providing an alternative route during pyrolysis and thereby create more pores due to increased volatile materials and reduced unwanted substance in bio-char [26]. The high content of carbon and silica may favour sorption e.g. rice husk [27].

Toxicity of heavy metal is a major challenge to the ecosystem, agriculture, animal and human health hence pollution by heavy metals has received continuous attention in the past few decays. The use of rice husks to remove pollutants from industrial wastewaters has been widely reported as shown in Table 1. to remove heavy metal that might have been generated from exploration, drilling, paint, agrochemicals, dyeing, battery industries and discharge as effluent to surface water.

Table 1: Rice Husk as An Adsorbent

Industries	Some Common pollutants in Effluent	Application to remove named pollutant
Cement, Oil Refinery, Battery Industries	Pb	[28-29]
Battery Industries	Cd	[24, 30]
Steel Industry	Cu	[28, 31]
Steel Industry	Zn	[32]
Pharmaceuticals	Se	[24, 32]
Dye and tie industries	Reactive (blue, orange and yellow)	[33]
Agrochemicals	Paraquat	[34-35]
Agrochemicals	2,4-dichlorophenol	[36]

pH, initial concentration, agitation rate, sorbent dosage, different treatment conditions with varying modifier concentration, duration, and temperature were investigated parameters that determine the adsorption capacity of an adsorbent [28, 37, 38].

Husk of many plant crops have been extensively used for heavy metal adsorption either in modified or activated form. Locust beans husk was used in [37] being activated by H_3PO_4 to remove metal ion pollutants (Pb²⁺ and Ni²⁺) from aqueous solution. In [37] parameters varied were initial time, adsorbate concentration and adsorbent dosage. Maximum adsorption capacities of Activated LBH were 19.85mg/g (79.4%) for Pb²⁺ and 11.10mg/g (57.1%) for Ni²⁺ at a duration of 2h with initial metal dosage of 100ppm. Rice bran is relatively affordable, available and has high adsorption capacities which was demonstrated in [38] in modified form to remove Pb²⁺ from aqueous solutions with maximum adsorption capacity ~70.8 mg Pb²⁺/g rice bran at room temperature and at the initial Pb²⁺ concentration of 400 mg/L and neutral pH.

One of the major ingredient in textile industry is dye e.g. Congo red, its discharge into water body poses a great challenge to marine organisms and also renders such water unfit for drinking but this can be remediated by using hydrothermal liquefaction of

combined wastes from rice and animal excrete which produced char useful in removing considerable amount of Congo dye [39]. Removal efficiencies were 66.8–96.9% and 68.9–98.8% for RH and CD respectively.

The use of dye in textile, wood and pulp industries is very essential to have a good and appealing finished product. These dyes when released into the environment could contaminate both surface and underground water and are likely to cause high toxicity and genetic mutation [40]. Methylene blue and methyl red are aromatic hydrocarbons that find application in these industries as dyes but exposure to these dyes can cause irritation of the skin, eyes and the alimentary tract if consumed [41]. Modification of raw agricultural waste such as rice husk using modifying agent NaOH has good removal efficiency for reactive yellow dye from aqueous solution [42].

Nitrogen oxides are pollutants with source majorly from fossil fuel combustion. NO₂ is a toxic gas which pose a serious and damaging threat to plant and animal. NO₂ has been reported to cause leaves withering and death in plant, lung damage and cancerous diseases [43]. A study reported the carbonization of agricultural wastes to produce activated carbon for organic dyes (methylene blue and

methyl red) removal in aqueous solution and toxic gases (NO₂) [44]. Activated bio-carbon of raspberries showed highest adsorption capacity. The researcher used cost effective waste materials (nettle, green tea, blackcurrant and raspberries) to achieve environmental sustainability [44].

Hydrogen sulfide (H₂S) is another toxic gas that pose a great challenge to the normal state of health with major source from industrial processes involving fossil fuel [45]. It is not only toxic but also attack and damage materials made of steel across its path [46] and when it escapes to the upper atmosphere, it combines with rain water leading to the formation of acid rains [47]. In a study prepared a composite of copper and activated carbon from peanut shell being activated by KOH which successfully adsorbed H₂S[48]. Experimental data obtained fit into Langmuir isotherm models and well defined by kinetics of the pseudo first order and adsorption of adsorbate into pores was well defined by intraparticle and film diffusion. Adsorbent used can be successfully regenerated, and reused [48].

Rice husk is a major waste obtained during the milling of rice. It is very rich in cellulose with large surface area but the nano-size cellulose obtained from rice husk has larger surface area that absorbed up to 92.99% Cr (VI) [49]. The process for Cr (VI) adsorption on the nano-cellulose fibre was endothermic and spontaneous with reference to $-\text{ve }\Delta G^{\circ}$ and +ve [49]. Yasodha and Sasirekha, used coffee husk a low-cost adsorbent for Zn^{2+} adsorption from electroplating industrial effluent as an alternative to existing techniques but expensive methods of Zn^{2+} removal. Zn^{2+} was effectively removed by activated coffee bean husk from this effluent at varied parameters of pH, adsorbent dosage and agitation time [50].

Contamination of terrestrial and aquatic regions as a result of industrial and agricultural activities in Nigeria is an increasing environmental concern. Cases of values above permissible limits of World Health Organization (WHO) for Pb, Ni, Cr, Cd, Mn, Cd and Fe were recorded in a water body near Larfarge cement, Ewekoro, Nigeria [51]. A recent study reported untreated effluent from aquacultural, urban, agricultural and industrial zones were responsible for heavy metal (Fe, Co, Cd, Pb, Ni and Zn) pollution of Lake Asejire in Nigeria [52]. A study revealed CO and SO₂ concentrations in Zaria metropolis were above the locally and globally stipulated air quality indices [53]. A study analysed the heavy metal concentration in four major vegetables, fish and water samples around industrial area of Challawa in Kano State, Nigeria. The revealed concentrations of Cd and Cr in water, fish and these vegetables (spinach, onion, tomato and lettuce) were above the permissible limits of WHO and if consume may pose potential health risk to human [54].

There are wide range of pharmaceutical, chemical, oil and gas, cement industries etc. that these adsorbents will be greatly useful as pollutant removal in Nigeria. So, exploration of these adsorbents can solve problems associated with heavy metal pollution reported in cases above.

Environmental Remediation Properties of Biochar

Biochar is a promising replenishing agent for lost nutrient in soil and also with promising potential to remove or reduce damaging effect associated with greenhouse gases [55]. An acidic soil can be amended by the application of biochar since its increases soil pH thereby reducing soil toxicity associated with acid content in the soil. Biomass wastes have varied component of ash and volatile matter, hence biochar that result from its pyrolysis will definitely have varied ash and volatile content which significantly have effect on the biochar application [56]. Biochar are solid products obtained from pyrolysis of biomass waste. They have pores that can capture CO₂ from the atmosphere and reduce greenhouse gases [2009] [57]. This process creates an unaltered carbon percentage in the ecosystem [58]. FTIR of biochar showed it contains C=C of aromatic hydrocarbons and it does not easily loose its carbon [53]

Adsorption Techniques and Kinetics Studies in Using Biomass Waste as Adsorbent for Environmental Remediation

Table 2: Summary of Adsorption Techniques and Kinetic Studies in Using Biomass Waste as An Adsorbent for Environmental Remediation.

Model/Isotherm/ Kinetics	Equation	Parameter Definition and Other	Reference
Freundlich isotherm	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	C_e = equilibrium concentration in (mg/L), q_e = amount adsorbed (mg/g) and K_F = adsorption capacity, n = adsorption intensity	(Abbas et al., [60] More- no-Piraján and Giral- do,[61]
		Defined range for favourable adsorption = $0.1 < 1/n < 1.0$	
Langmuir isotherm	$\frac{C_{\rm e}}{q_{\rm e}} = \frac{C_{\rm e}}{q_{\rm m}} + \frac{1}{q_{\rm m}b}$	$\begin{aligned} \textbf{q}_e &= \text{equilibrium adsorption capacity of adsorbent, } \textbf{q}_m &= \text{saturated monolayer sorption capacity, } \textbf{b} &= \text{free energy of adsorption,} \\ \textbf{C}_e &= \text{equilibrium concentration} \\ \textbf{Plots of C}_e / \textbf{q}_e \text{ vs C}_e \text{ to obtain parameters of the Langmuir isotherm.} \end{aligned}$	

First order and Pseudo first order	$\frac{1}{q_t} = \frac{1}{q_e} + \frac{k_1}{q_e t}$ $In (q_e - q_t) = In q_e - k_1 t$	q_e = equilibrium quantity of adsorbate in (mg/g) , q_t = quantity of oil adsorbed at time t in (mg/g) , k_1 = first order rate constant expressed in (\min^{-1}) and t = time expressed in (\min) . Hence, a straight line between parameters $1/q_t$ vs $1/t$ and In $(q_e - q_t)$ vs t usually for both first order and pseudo first order kinetics. The values of k_1 and q_e can be estimated from the slope and intercept. The q_e & R ² values provide useful data whether the adsorption fits to pseudo first order kinetics. Kinetic models help in designing and optimization process of using adsorbent for pollutant treatment.	
Second order and Pseudo second – order	$\frac{1}{C_e} = k_2 t + \frac{1}{C_o}$ $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	k_2 = second order rate constant in (mg/g). A plot between parameters $1/C_e$ vs t and t/q_i vs t usually for second order or pseudo-second order. The values of q_e and k_2 can be calculated from the slopes and intercepts of these plots respectively.	
Elovich model	$q_t = \frac{1}{b}\ln(ab) - \frac{1}{b}\ln t$	'a' is the initial adsorption rate in (mg/g/min) and 'b' is related to the extent of surface coverage and the activation energy for chemisorption (g/mg). A plot of q _t vs ln t will give a straight line with a slope of 1/b and an intercept of 1/b ln (ab) with good correlation coefficients if the adsorption follows Elovich model. It has practical application in chemisorption process and valid for heterogeneous adsorbent surface.	
Intra particle diffusion	$q_t = k_i t^{\frac{1}{2}}$	k_i = rate constant of intra-particle diffusion and obtained from the slope in a linear plot of q_i vs $t^{1/2}$. Initial adsorbate adsorption takes place on the surface of the adsorbent. There are cases where the adsorbate also diffuses into the interior pores of the adsorbent.	
Thermodynamic Studies	$\Delta G^{\circ} = -RT Ink$ $\ln(K) = -\frac{\Delta H^{o}}{RT} + \frac{\Delta S^{o}}{R}$	R = global gas constant (8.314 Jmol-1K-1), T = Temperature (K), K = Distribution co-efficient = Q_e/C_e which may be obtained from Langmuir adsorption isotherm at different temperatures), ΔG° = Change in Gibbs free energy (J/mol), ΔS° = Change in Entropy (J/mol.K), ΔH° = Change in Enthalpy (J/mol). ΔH° and ΔS° will be determined from the slope and intercept of the plot between ln K and 1/T respectively.	

Biomass Waste as An Alternative Energy

Biomass wastes are new and the future energy sources with valuable potential as a good alternative to fossil fuel. It has wide acceptance as it performs better than fossil fuel in reduction of emission of greenhouse gases e.g. CO₂, and are largely renewable.

To generate energy from biomass, they are usually subjected to thermochemical conversions in the presence of O₂ (combustion and gasification) or absent of O₂ (pyrolysis). In pyrolysis, carbon-based materials are usually heated in temperature range (300–1000 °C) in a chamber filled with inert gas to obtain char, bio-oil and gas. Different types of pyrolysis exist which differed by heating rate, chamber temperature and vapour & solid residence time in pyrolytic chamber. Oxygen or Air support biomass combustion and gasification to generate heat, steam and electricity at temperature range of (800–1200 °C). Gasification is designed to obtain majorly gases from biomass. Biomass wastes can be converted to petroleum after series of chemical reactions through the process called liquefaction. Products of these thermochemical processes could be any of gas, liquid and char with potential of being used as fuel. Of the four major thermochemical conversion methods, pyrolysis and liquefaction can be used to produce bio-oil.

Biochar as An Alternative Energy

The solid product of lignocellulosic biomass waste is biochar with wide application as fuel, adsorbent, soil remediation etc. X-ray fluorescence analysis of biochar reveals it contains metals in oxide form. and due its metal content, it finds application in metallurgy acting as a potential alternative for coke that is conventionally gotten from pollutant inherent fossil fuels [62,63]. Biochar has been developed extensively as sources of bioenergy through (e.g. pyrolysis, combustion); biomaterials through (e.g. activated carbon, adsorbents and specialty materials) production; chemical reactions (e.g. catalyst and catalyst support); agriculture (e.g. water retention and plant nutrition); depleted environmental recovery through (e.g. carbon sequestration and removal of heavy metal, other pollutants); and pharmaceutical effluent removal [58]. Biochar will significantly fit into most of the listed applications above base on its carbon content, surface area, pore size distribution, alkalinity, ion-exchange capacity and elemental composition [64,65].

Bio-Oil

Cracking of heavier or higher molecular weight fraction of crudeoil e.g. naphtha, light diesel, or heavier hydrocarbons produces lighter hydrocarbons and aromatic compounds which are the basic materials in the gas, petroleum and chemical industries. A supportive source for the raw material needs of these industries is bio-oil since it contains some olefins and aromatics, and their contents can be significantly increased by catalytic upgrading [66]. Bi-oil can be used as alternative energy in fuel engines, thermal/heat production and a good chemical substitute for phenols in wood resins.

Fast pyrolysis has been largely developed to produce bio-oil from biomass in which 60-70 wt % pyrolytic liquid can be achieved but

largely depends on the type of feedstock (Rowland et al.,2002).

A wide temperature range between 300-900 °C degrade the major components of lignocellulosic biomass to produce a dark brown organic bio-oil with almost the same chemical component as its source biomass [67]. Bio-oil are complex chemicals that can be used as fuel in kilns, boilers, furnaces, diesel engines and heat turbines. They are used as chemical addictives in food flavours, resins, pesticide, fertilisers, emissions control agents etc.

There is limitation to direct use of pyrolytic oil as biofuel in engines because it is highly rich in oxygenated compounds such as RCOOH, RCHO, ArOH, ROH, ROR, organic polymers, low amount of hydrocarbon, not chemically stable and high water causing low heating value. Therefore, there is need to upgrade biooil to improve properties that make bio-oil suit as fuel in engine [68].

To date, various upgrading techniques have been developed to upgrade and improve bio-oil quality;

Emulsification

Bio-oil from biomass and crude oil from fossil fuel have different densities and polarities hence are not miscible with each other. To achieve smooth combination of these fuel, stirring needs to be done in the presence of surfactants e.g. octanol, n-butanol etc. Ultrasonic emulsification technique achieves higher miscibility [69,70]. Miscibility of these fuel can be achieved by higher mixing intensity and a moderate mixing time to avoid separation of surfactant from the fuels which could cause lower emulsion stability [71]. Emulsification is a promising technique to improve properties of bio-oil that make it fit as fuel, it is a rapid and easy technique for the production of stable emulsion fuel. Expensive nature of commonly used surfactants and rigorous additional treatment pose great limitations with this technique. And also, emulsification is ineffective to reduce oxygen content and water content of biocrude oil responsible for its acidity and corrosion [71].

Esterification

The ease of flow of bio crude oil termed 'viscosity' and its stored value of chemical energy i.e. calorific value (CV) are two major properties that make bio-oil find application as a lubricant and fuel respectively and which can easily be adjusted and improve by the addition of polar solvents e.g. C_2H_5OH , CH_3OH , $C_5H_4O_2$ etc. a process called solvent esterification. The higher heating value of the added organic solvent shift the emulsion to higher caloric value. Viscosity improvement may be associated to bio-oil dilution, modified microstructure of bio-oil, and/or inhibition of chain growth [72]. Bio-oil stability is also a major property that affect bio-oil performance as fuel but direct addition of solvent could also improve it. However, catalytic esterification has proven to be better in bio- oil upgrading by producing bio-oil of higher quality since it reduces associated acidity and corrosiveness. This is achieved by converting oxygen related functional groups into their correspond-

ing stable esters [73]. Esterification is achieved in the presence ROH compound such as C₂H₅OH, CH₃OH, an acid and catalyst application e.g. zeolites catalyst, silicas catalyst, carbon-based solid acid catalysts etc. [73, 74]. Produce ester in the mixture can easily be separated by fact that it has lower boiling points as compare to their corresponding acids and thereby allowing separation of unreacted alcohols, water, and volatile esters from the mixture.

Catalytic Upgrading

Processes to involve hydrogenation and catalytic cracking are applicable to obtain improved bio oil from crude bio oil for automobile use. Hydrogenation process improves crude bio oil properties by separating out its impurities or saturated carbon-carbon bonds. In the process, a hydrogen bond is being established with elements present in the crude bio oil and the removal of N₂, S, O₂, metal content and conversion of aromatics to naphthenes to enhance fuel properties e.g. cetane number, density and smoke point of the biooil [75]. Hydro-processing is of two major types i.e. hydrotreating and hydrocracking. Hydrotreating increases heating values of biooil by removing heteroatoms and saturated carbon-carbon. Bio-oil obtained may be subjected to further processing or blending before use. Bio-oil H/C that doesn't exceed the range of 1.5–2.0 is a good alternative for petroleum [76]. Bio-oil quality could also be improved by decreasing its sulfur content (hydro-desulfurization). Hydro-deoxygenation upgrade bio-oil quality through oxygen removal as H₂O and saturation of carbon-carbon bonds to produce rich aromatic hydrocarbons in the presence of catalyst such as HZSM-5 [77]. In contrast, catalytic cracking has proven to be more useful because it could remove oxygen and also enhance the esterification of alcohol and acidic compounds in bio-oil bringing about a reduced viscosity and acidity [71]. The very important application of catalytic cracking is to improve the yield of hydrocarbon fuel and increase its cetane number. Solar pyrolysis technique also worked like a catalyzed process since it has the advantage of leaching out of metallic species and drastically reducing oxygen content making bio-oil high heating value to increase and inhibit the generation of acids but favours formation of phenols and anhydrosugars [78]. A recent study obtained bio-oil from fast pyrolysis of pine wood dust in a fluidized-bed boiler at 550°C which was subjected to co-catalytic cracking process over HZSM-5. Acidity of the organic bio-oil decreased significantly after upgrading due to decrease in oxygen content [79].

An innovative but simplified technique for bio-oil quality was developed in a process that involve catalytic esterification and alkylation with azeotropic water removal using solvents such as n-C₄H₉OH and 2-methylfuran [80]. The H₂O content in the bio-oil decreased significantly by 24.61%, and acid number was reduced by 34.95 mg NaOH/g. Caloric Value (CV) of upgraded bio-oil was more than 2 times higher than crude bio-oil [80].

A study worked on fast pyrolysis of pinewood using a co-precipitated Ni–Co/Al–Mg catalyst. The ultimate parameters increased by 37%, 171% and decreased by 69% for C, H and O respectively.

The CV of the upgraded bio-oil increased by 15 MJ/kg, i.e. an 89% increase [81].

Ashutosh et al., used series of catalyst in their study but of all, the zeolites used HZSM5-375 was found to be the best catalyst for bio-oil upgrading due to its small crystal size and significantly large very-strong acid site content [82]. Upon bio-oil upgrading, the HHV value of the stock bio-oil increased from 27.03 MJ/Kg to 30.85 MJ/Kg over HZSM5-375 zeolite. In (Haowei et al.,2019) 97% cyclohexanol was achieved by 15% Ni/MgO-850 catalyst for both light and heavy lignin bio-oils.

Gases

Synthetic gases are obtained during pyrolysis of biomass wastes and which provides supportive heat energy to the process. The gases are mainly; H₂, CO₂, CO, light molecular weight compounds of general formular that corresponds to C.H. [83-84]. Goutam et al., pyrolyzed teak sawdust to obtain Non-condesable gases (H₂, CH₄, CO and CO₂) [65]. Studies Goyal et al.,[85] & Wei, [86] revealed that pyrolysis conditions and feedstocks type are factors that determine gases being generated and low molecular weight compound that correspond to general formular CxHy (where x and y are positive integer within the range ≤ 5 and ≤ 12 respectively) [84] are majorly from the reforming and cracking process of heavier molecular weight hydrocarbon and tar during pyrolysis [66]. This process can produce paraffin of large range (C₁-C₅₀), laboratory solvents, lubricants, synthetic gas (H2) etc. [87]. Sharara and Sadaka, worked on algae gasification at varied temperature and obtained an increased value for CO and H₂ concentrations in the producer gas (CO: 12.8% -16.9% and H₂:4.7% -11.4%) at 760 °C and 960 °C respectively [88]. Vladimirs and Aivars, reported that fuel moisture growth has an upward effect on the volume of hydrogen and methane in the syngas, but a significant decrease in carbon monoxide volume as moisture increases [89].

Improving Pyrolytic Products Fuel Properties

Bio-oil reactivity relies largely on some ratios of its proximate and ultimate properties. For a crude bio-oil to serve as a good alternative to distillation product of crude oil, an H/C that doesn't exceed the range of 1.5–2.0 and also O/C < 0.6 is desirable [76]. Bio-oil having values that doesn't align with this range for the ratios needs further treatment and modification to serve as an alternative to these distillation products in automobile engines. In [76], H/C and O/C ratios of the condensable products lie within that of petroleum making it useful as good alternative in fuel engine. In a recent study reported H/C ratio of biomass waste (kusum seed char) to fall within range of petroleum which is responsible for its higher value of stored chemical energy [90]. Aromatic nature and extent of stability of solid residue obtained during the pyrolysis of biomass wastes can be given inferred from H/C ratio. A report [91], compared some selected biomass wastes based on evaluated VM/ FC ratio, the selected parts used in Karanja were of higher value in terms of VM/FC ratio when compared to Jatropha and also better than some common biomass wastes e.g. palm residues. Biomass

wastes with significant low moisture contents (<30%) and high C/N ratios (i.e., C/N ratios exceeding the value of 30) are good for thermochemical conversion. Study in [92], compared bio-oil products of non-catalytic and catalytic fast pyrolysis of corncob. O/C ratio reduction can be effected with increase in temperature which favours decrease in polarity of the bio-oil, the research on using HZSM-5 as catalyst significantly reduced the ratio from 0.582-0.149, leading to a significant increase of the product HHV from 18.8- 34.6 MJ/Kg [92]. Biomass wastes fuel of low percentage of nitrogen (<2.0%) and sulfur (<0.2%) is desirable as substitute for petroleum product because it will pose little or insignificant risk associated with the emission of their toxic oxides respectively during pyrolysis or combustion [93]. The C/H ratio is directly related to the amount of oxides of carbon released during the pyrolysis of biomass wastes, its higher percentage tend to higher residue of carbon in the exhaust of an engine that uses such fuel.

Practices That Could Encourage Availability of Biomass Waste to Point of Use in Nigeria:

- 1. Creation of waste collection centres nearest to farmland
- 2. Biomass wastes exchange for money
- Enacting laws that prohibits indiscriminate dump of biomass waste
- 4. Biomass waste exchange for fertilizer
- 5. Widespread sensitization of large biomass waste generator
- 6. Planting of energy crops
- 7. Enacting laws to discourage indiscriminate felling of trees for heating purposes

The large availability of biomass waste in Nigeria can be explored by industries that uses direct heating method e.g. the use of coal in cement industries can be replaced by firing palm kernel shell which reduces emission of greenhouse gases. Promising techniques for the conversion of biomass waste to useful material which could be adopted by industries in Nigeria include; Pyrolysis, Torrefaction, Gasification etc.

Conclusion and Recommendation

Biomass is a source of renewable energy which had become widely accepted as biofuels and biomaterials due to its ecofriendly nature and ease of growth. Products of thermochemical conversion of biomass could be any of gas, liquid and char with potential of being used as fuel having pyrolysis temperature and heating rates as the determining factors of volume/mass of products formed.

Two major challenges faced by Nigeria today have to do with energy and waste management. Biomass wastes can be explored as a suitable alternative energy and complementing energy to the dwindling, scarce and non-renewable fossil fuel and also use as an adsorbent to solve environmental pollution. The review had identified common environmental problems in Nigeria and discussed the mechanism of using biomass wastes for environmental remediation. Some concise and precise methods of upgrading crude biooil to be fit as engine fuel were discussed. The review proffers a

cheaper and sustainable solutions for energy generation and pollution control. The study described how one environmental problem (biomass waste) can be used to solve two major challenges faced by Nigeria and the rest of the world at large.

Recommendation:

Identified areas of application biochar for Nigeria environment sustainability.

The totality of the solid residue obtained from pyrolysis of biomass is biochar. Slow pyrolysis favours increased biochar production. Suggested areas of applications include [94-97];

- Heating biomass in an oxygen deprived environment under controlled temperature produced carbon which can be activated to increase its surface area by the use of chemicals or other physical methods to produce activated carbon. Activated carbon larger surface area than its source makes it find applications in polluted air and water remediation, removal of heavy metals in form of toxins etc. Activated carbon should be explored for these purposes and further research on its use as adsorbent can be investigated
- 2. Biochar is useful in fuel cell catalysis
- 3. The northern part of the country which has once being the food basket of the nation has been faced with desert encroachment and erosion in recent times thereby making it difficult for the soil to support plant growth but this can be corrected by using biochar because it enhances bioavailability of H2O, major and minor nutrients, avenue for increase soil
- 4. Biochar can be explored as soil conditioner and fertilizer because it improves cation-exchange capacity, water retention ability and works effectively in sequestering toxic heavy metals.
- 5. Areas in the nation experiencing soil acidity can be salvage by using biochar as a neutralizing agent since it is alkaline in nature
- Continuous availability of fixed carbon in the soil can be achieved by using biochar which is richer in fixed carbon when compared with others uncharred biomass

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