



Harnessing the Thermal Potentials of Bitter Kola Tree Using Thermo-Gravimetric Analysis (TGA) Method

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Abstract:

This research focused on harnessing the thermal potentials of the bitter kola tree relying on the information determined by the Thermo-gravimetric Analyzer. Today the world is facing some critical problems such as: high fuel prices, climatic changes, and air pollution. Higher Heating Value (HHV) is one of the most important properties of fuels which explains the higher energy content and determines the efficient use of biomass and fossil fuels. This research work aimed to conduct thermo-gravimetric analysis on Bitter kola tree energy crop. The materials for the research was acquired from a nearby farmland and further dried under sunlight for a period of four

weeks before being dried further in the oven at regulated constant temperature, it was pulverized and further analyzed to determine the moisture content, ash content, crude fat, crude protein and crude fibre. From the experimental results, it was revealed that the moisture content of bitter kola tree particles was very high (44.37) compared to mangrove (22.75). The volatile matter was very low (43.47) compared to mangrove (55.65). These facts are responsible for the low combustion characteristics of bitter kola tree. This project work will educates anyone who chooses to venture into biomass generation of energy with energy crops to know the exact crop sample with the highest heating value for increased coefficient of performance and efficiency of the steam or turbine engines to be used for generating electricity

Keywords: *thermal potential, bitter kola, pulverized, moisture content, thermo-gravimetric analysis.*

Introduction

The need for energy sources with low greenhouse gas emissions and sustainable production encourages the search for alternative biomass sources. However, the use of biomass fuels faces the problem of storage, transport and lower energy densities. Low-density values can negatively affect energy density, leading to an increase in transportation and storage costs. Use

of pellets as alternative biomass source is a way to reduce the volume of biomass by densification, which improves their energy quality. They are produced by diverse biomass resources and mainly from crop plants. In all cases, it is important to evaluate the fuel characteristics, to determine their suitability on the heating system and handling properties. (Oyedepo, 2012)



Whenever wood biomass is used as a fuel it can be safely stored and preserved in the form of logs or chippings without any potential energy loss. The amount of energy that can be produced from wood biomass depends on the heat content of the material when it is dried. The storing of wood prior to its burning reduces its moisture content thereby increasing its heating value and efficiency. The higher temperatures gained from burning drier wood, the more heat per unit weight of raw wood fuel, and the higher the efficiency. Also wood fuel contains minimal amounts of sulphur and heavy metals and therefore, not a threat to acid rain pollution. The continuous increasing of the CO₂ emission into the atmosphere, mainly due to the combustion of fossil fuels, is leading to global warming.

The sources of biomass can be divided in two domains. The first consists is the use of the residual material from forestry and agriculture, such as wood and straw. The second domain is the growing of energy crops, meaning the cultivation of plants specifically for energetic use such as whole cereal plants, willows, and fodder grasses.

Currently, energy plantations have been in the focus of interest besides wastes of plant origin (Senelwa & Sims, 1999; Mészáros et al., 2004; Collura et al., 2005). Among the numerous tested energetic plants; Maize Cobs (MC), Sugar Cane (SC), Palm Kernel Shell (PKS) and Okanagan Wood (OW) seem to be especially, promising 'energy plant' and chemical feedstock due to their high production potential (Collura et al., 2005; González et al., 2006; Styles et al., 2007).

Moreover, gas emission analysis is becoming very important in the field of thermal analysis. Firstly, European standards are more stringent concerning the pollutants emissions. Therefore, CO, the total hydrocarbon content and dust emissions need to be analyzed during energy crops combustion (Taralas & Kontominas, 2004). Secondly, biomass pyrolysis allows the produce of fuels and could be able to supply hydrogen. The gas produced (H₂, CO, CO₂, CH₄, etc.) could be employed in internal combustion engines, gas turbine and other operating devices

(Williams & Besler, 1993). If gaseous emissions are well controlled, particles monitoring needs more improvement.

Fine particles are likely to pose a risk to environment and health because they can travel deeply into the respiratory tract. Particularly, very small particles (diameter below 1.1 μm) which largely dominate in number may be responsible for some adverse health effects associated to air-pollutant exposure. These ultra fine particles get deposited in the alveolar regions of the lung where the absorption efficiency for trace elements is up to 60–80% (Linlay et al., 1997; Becker et al., 2005). Therefore, in a context of environmental policy, it is useful to identify and characterize the sources of ultra fine particles. Cascade impactors are widely used for this purpose since they allow collecting particles and measuring the number size distribution. They can be used in many fields, e.g. particles emitted from diesel engines, ambient aerosols or other aerosols from combustion sources (Shi et al., 1999; Johansson et al., 2003; Lavta-Somppi et al., 1998; Wierzbicka et al., 2005; Hueglin et al., 1997).

The worldwide increase of urbanization and industrialization obviously leads to huge environmental contaminations, especially in surface and groundwater resources. To reduce environmental contaminants, activated carbons (ACs) which are solid materials, black in color and highly porous in nature, are well-established good adsorbents. It has been clearly shown that their high adsorbent capacity is due to their micro-porosity, mesoporosity, high surface area, large pore volume, greater extent of surface reactivity (Das, et al., 2015) and variable characteristics of surface chemistry, low ash content, relatively high mechanical strength, and their amorphous nature.

ACs is the final product of activation process of carbonaceous materials from different sources and with carbon content in the range 70- 90% (Danish, et. al.; 2013). Porous structures and adsorption properties can be obtained in carbonaceous materials via either chemical or physical activation. In recent years, ACs are being produced from a large number of easily

available low-cost materials and carbonaceous materials such as coal, or fossil-based raw materials have high carbon with low inorganic content and are relatively expensive which limits the extensive use (Ozdemir, et al., 2014).

Alternatives are, for example, agricultural products like rice and coffee husks (Tchuifon TDR.; 2015), reedy grass leaves (Xua et al., 2014) and fox nut shell (Arvind et al.; 2016). Activated carbon preparation is performed either by a physical or a chemical activation (Arvind et al.; 2016). Physical activation is performed in two steps; one step is pyrolysis or carbonization of the precursor in an inert atmosphere and at a temperature range from 400 to 500°C. The second step is an activation process of the resulting char in the presence of steam, CO₂, nitrogen or air, where the char is placed under a heat treatment at high temperature from 700 to 1100°C in the presence of oxidizing agents, such as CO₂, water steam, nitrogen or air (Arvind et al., 2016).

In chemical activation, the precursor is mixed with a certain amount of active agents such as KOH (Ndi, et al., 2014), H₃PO₄ (Ndi, et al., 2014), ZnCl₂ (Ndi, et al., 2014) (Das, et al., 2015), NaOH, HNO₃, CaCl₂, or K₂CO₃. In the chemical activation method, the process is carried out at lower temperature (400-700°C). The activating agent act as dehydrating agent that inhibit the formation of tar as well as reject

volatile substances during the process, which helps to enhance the yield of the activated carbons and to decrease the carbonization temperature compared to physical activation method.

The production of AC from agricultural by-products has both economic and environmental effects, as it converts unwanted, low-value agricultural waste to useful high-value adsorbent (Ekpete, et al., 2011). Finally, it reduces the importation of activated carbon. In the present work, ACs were prepared from carbonaceous agriculture waste, bitter kola wood by using chemical activating agents phosphoric acid, potassium hydroxide and zinc chloride at different temperatures and impregnation ratios.

Garcinia kola, a flowering plant (Clusiaceae family) also known as “bitter kola” is an economic tree growing in humid forestlands of West and Central Africa with a long history of use in traditional medicine and traditional events. Cameroonians greatly consume it, particularly in the West region. The preparation of activated carbons from bitter kola wood appears to be an alternative method to valorize it, and thus reduce environmental pollution. To the best of our knowledge, no study has been reported on the preparation of ACs from bitter kola nut shell.



Figure 1. Bitter kola plantation, Fruits and Seeds

The present study has been motivated by the fact that bitter kola wood possibly has a low value of

ash content and a high volatile matter percentage. It is thus a potential new precursor

for the production of ACs. The aim of the present work was to study the characteristics of chemically activated carbons (with H₃PO₄, KOH and ZnCl₂ as activating agents) obtained from bitter kola nut shells. The changes in structural morphology, chemical and physical properties of raw material and its obtained ACs have also been investigated.

Garcinia kola Heckel belongs to the Family *Guttiferae*, it is a medium size tree that grows up to 12 m high and found in moist forest throughout West and Central Africa (Isawumi, 1993). In the Eastern and South-western parts of Nigeria, *G. kola* plays a vital role in the socioeconomic and medicinal profile of the people. The level of exploitation of *G. kola* from the wild has increased over time due to the global high demand for direct consumption, confectioneries and pharmaceutical industries (Yakubu et al., 2014).

Bitter kola otherwise known as (*Garcinia kola*) is an important medicinal crop of the tropics. It regarded as one of the most important crops used in treating purgative, anti-parasitic, antimicrobial, treatment of bronchitis, throat infections and prevention of relieve colic, cure head or chest colds and relieve cough in the continent of Africa. For bitter kola nut and shell, whose medicinal and economic potential are increases growing fast, there is much need to develop appropriate technology and equipment for various unit operations and to minimize the drudgery and improve sanitation of the processing operations. This required the knowledge of physical properties of the crop.

The knowledge of engineering properties of bitter kola nut and shell like any other biomaterial is fundamental because it facilitates the design and development of equipment for harvesting, handling, conveying cleaning, delivering, separation, packing, storing, drying, mechanical oil extraction and processing of agricultural products, their physical properties have to be known (Aviara et al., 2005; Davies, 2011).

Presently, the equipment used in processing bitter kola nut and shell have been generally design without taken into cognizant the physical

properties of bitter kola nut and shell which include the size, mass, bulk density, true density, sphericity, porosity, coefficient of static friction and angle of repose and resultant systems leads to reduction in working efficiency and increased product losses (Manuwa & Afuye, 2004; Razari et al., 2007).

The engineering properties have been studied for various agricultural products by other researchers such as almond nut and kernel (Aydin, 2003), soybean (Manuwa & Afuye, 2004 Davies & El-Okene, 2009), African nutmeg (Burubai et al., 2007), caper fruit (Sessiz et al., 2005) cocoa bean (Bart-plange and Baryeh, 2002), jatropha seed and karanja kernel (Pradhan et al., 2008), gbafilo fruit and kernel and cowpea (Davies & Zibokere, 2011), pigeon pea (Shepherd & Bhardwaj, 1986), locust bean seed (Ogunjimi et al., 2002), wheat (Tabatabaefa, 2003) and pistachio nut and its kernel (Razari et al., 2007) and groundnut grain (Davies, 2009).

Investigation was therefore carried out to determine the engineering properties of bitter kola nut and shell such as axial dimension, geometric and arithmetic mean diameter, sphericity, surface area, unit mass, 1000 grain mass, true volume, true and bulk densities, porosity, angle of repose and static coefficient of friction of bitter kola nut and shell in order to develop appropriate equipment that will alleviate laborious nature experience in processing the crop.

Garcinia kola, a flowering plant (*Clusiaceae* family) also known as “bitter kola” is an economic tree growing in humid forestlands of West and Central Africa with a long history of use in traditional medicine and traditional events. Nigerians greatly consume it, particularly in the West region. After bitter kola are removed most of its nut shells are discarded as solid waste or burned off in stacks or used as a mulch, which suppresses weeds, and other vegetable growth. In turn, the shell of bitter kola becomes a residue, which has no commercial value and causes environmental pollution and degradation.

Therefore, the preparation of activated carbons from bitter kola wood appears to be an alternative method to valorize it, and thus reduce

environmental pollution. To the best of our knowledge, no study has been reported on the preparation of ACs from bitter kola wood. The present study has been motivated by the fact that bitter kola wood has a low value of ash content and a high volatile matter percentage. It is thus a potential new precursor for the production of ACs.

Materials and Methodology

Preparation of *Garcinia kola* wood absorbents

Garcinia kola nut shells were collected from the field in Ado-Ekiti local government, Ekiti state of Nigeria. The raw materials were carefully washed with tap water and rinsed with distilled water to eliminate impurities. It was then dried under sunlight for four weeks and dried in an oven at 105°C for 72 hours to remove excess or residual water. The dried raw materials were crushed using the pulverizer and sieved to obtain particle size.

Preparation of Activated Carbons

The preparation of activated carbons from *Garcinia kola* wood was performed through a one-step chemical activation process. The impregnation ratio (IR) was determined as the ratio of the weight of activating agents (W) to the weight of the dried bitter kola wood (W_{raw}).

$$IR = \frac{W}{W_{raw}} \quad (1)$$

200 g of dried *Garcinia kola* wood was impregnated with different solutions of activating agents (H_3PO_4 , KOH and $ZnCl_2$) at 0.20 M, with impregnation ratios 1:1 and 2:1. Each mixture, maintained at room temperature, was shaken manually for 20 minutes. The impregnated *Garcinia kola* wood was dried at 105°C for 48 hours in an oven for any water present in the sample to be completely evaporated. The dried mixtures of impregnated *Garcinia kola* wood were then cooled for 45 minutes at room temperature and the dry mass

recorded. Then, the impregnated *Garcinia kola* wood was placed into porcelain crucibles with lids and introduced in an electric furnace, which has an automatic regulation, and a temperature programmer coupled to it. The samples have been carbonized and activated in one step for 1 hour at different temperatures 400°C, 450°C and 500°C, at the heating rate of 5°C per minute in the absence of CO_2 , H_2O , O_2 , and N_2 gases. The weights of the activated sample were further measured and recorded.

Following cooling at room temperature, the calculated samples were ground in a pulverizer and washed several times with distilled water to remove the residual chemical agents until a pH value of the resulting water was neutral. The various activated carbons thus obtained (CBH, CBK, CBZ) were dried for 24 hours in an oven set at 105°C. The resulting products were crushed into powder and well-kept for further tests. The ACs obtained was characterized by the determination of their iodine number for optimal impregnation ratio and optimal temperature of H_3PO_4 , KOH and $ZnCl_2$ activation. The proximate analysis of the *Garcinia kola* wood was determined according to standard techniques ASTM D2866-94.

Activated Carbon Yield and Burn-off

The activated carbons (ACs) yield and burn-off were calculated using the formulae:

$$Yield = \frac{W_{carbon}}{W_0} \times 100 \quad (2)$$

$$Burn - Off = W_0 - \frac{W_{carbon}}{W_0} \times 100 \quad (3)$$

where,

W_0 = weight of raw material impregnated (g)

W_{carbon} = weight of activated carbon obtained after calcination (g)

Determination of moisture content

Moisture content was determined using the air oven method. Crucibles were washed and dried in an oven. They were allowed to cool in the desiccator and weight was noted. 1.0g of the sample was then transferred into the crucibles and dried at a temperature between 103-105°C. The dry samples were cooled in a desiccator and the weight noted. They were later returned to the oven and the process continued until constant weights were obtained. Moisture content was calculated using the formula:

$$\% \text{ Moisture content} = \frac{\text{weight of loss (g)}}{\text{Weight of sample(g)}} \times 100 \quad (4)$$

Determination of Ash Content

Ash content was determined by weighing of finely ground sample into clean, dried previously weighed crucible with lid (W_1). The sample was ignited over a low flame to char the organic matter with lid removed. The crucible was then placed in muffle furnace at 600°C for 6h until it ashes completely. It was then transferred directly to desiccators, cooled and weighed immediately (W_2).

$$\% \text{ Ash content} = \frac{\text{weight of loss (g)}}{\text{Weight of sample(g)}} \times 100 \quad (5)$$



a) Electric Oven



b) Sample of the Bitter kola wood



c) Perkin Elmer Thermogravimetric Analyzer



d) Pulverizer



e) Pulverized bitter kola wood



f) Muffle Furnace

Figure 2. Materials and Equipment Used in the Process of Thermo-Gravimetric Analysis of Bitter Kola

Volatile matter and fixed carbon content

With the aim to determining volatile matter, 1.0 g of sample was put into a crucible pre-heated in the furnace to about 500°C for 1h and of known weight. The crucible and its content were then placed in a furnace regulated at 500°C for 2 h. After heating, the crucible is quickly covered, cooled in desiccator to ambient temperature and weighed. The percentage of volatile matter was calculated as indicated in equation (6):

$$\text{Volatile matter (\%)} = \frac{\text{weight of volatile component(g)}}{\text{Oven dry weight(g)}} \times 100 \quad (6)$$

The fixed carbon content of the activated carbon samples was calculated using equation 7.

$$\text{Fixed carbon (\%)} = 100 - [(\% \text{ volatile matter}) + (\% \text{ moisture content}) + (\% \text{ Ash content})] \quad (7)$$

Results and Discussion

The physiochemical properties of raw materials; bitter kola wood sample and the results gotten online for the mangrove wood are reported in Table above. The 12.16% ash content obtained in this study, which is lower than the norm (10%) and that of mangrove (21.61%) shows that the bitter kola wood does not burn completely but rather burn really slowly and little.

Table 1. The Physicochemical Characterization

S/N	Proximate Parameters	Composition(Bitter kola Wood Sample)	Composition(Mangrove Wood)
1	Moisture Content (%)	44.37	22.75
2	Ash Content (%)	12.16	21.61
3	Volatile Matter (%)	43.47	55.65

In addition, the volatile matter of the bitter kola wood which is 43.47% compared to that of the mangrove which is 55.65% also confirms that the bitter kola wood combusts slowly.

The moisture content of the bitter kola wood (44.37%) reveals that *Garcinia kola* wood is not entirely suitable for propagation and use as a reliable source of biomass. The mangrove wood has less moisture content (22.75%) and thus is more reliable compared to the bitter cola wood.

Conclusion

Chemical activation is one of the appropriate methods to obtain new ACs. In the present study, ACs with developed pore structure were prepared from *Garcinia kola* wood by chemical activation with phosphoric acid, potassium hydroxide and zinc chloride.

The research was successful and it was deduced that the bitterkola wood has the potential to be harnessed for use as an efficient biomass but the

presence of higher moisture content making combustion slower, as well as high ash content and low volatile matter.

It is thus recommended that any other available and more volatile wood be used as a source of biomass and the bitter kola wood should only be considered for use if there are little to no other more efficient options to be used and harnessed.

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