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Investigation of Ultimate and Proximate Properties of Cashew Pulp Substrate in South West Nigeria for Bioethanol Production

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Abstract: *Cashew apples are used in the industry for the production of juice, ethanol, wine and syrup but the pulp has been underutilized, this reason triggered the ultimate and proximate analysis properties of cashew pulp to be investigated for the production of alternative fuel mainly bioethanol. The cashew pulp powdered substrate was prepared by extracting the juice, dry (sun dried and air dried) and pulverized for easy properties analysis. The ultimate analysis properties for the sun dried and air dried substrate samples were done by Flash Smart V CHNS Elementar analyzer and the result obtained as followed; 1.14 and 1.12% for sulphur, 1.57 and 1.49% for hydrogen, 39.90 and 39.98% for oxygen, 2.53 and 2.72% for nitrogen and finally 54.86 and 54.69% for carbon respectively, while the proximate analysis properties for the sun dried and air-dried substrates obtained as; 13.22 and 9.78% for moisture, 2.04 and 2.58% for volatile matter, 1.75 and 2.52% for Ash and lastly 82.99 and 85.12% for fixed carbon. The results of the conducted study were compared with other biofuel reported in the past literature and the results appears to correlate with the ultimate analysis range of the other feedstocks which are used as a raw material for biofuel. With the results obtained from proximate and ultimate properties in each substrate indicate that cashew pulp can be used as a feedstock for the production of biofuel and this will increase the feedstocks data bank.*

Keywords: *Substrate, biofuel, cashew pulp, pulverized, ultimate, proximate.*

1. INTRODUCTION

A lot of cashew apples are left wasted in the plantation farm after the nut separation causing environmental pollution, while it can be transformed into biofuel mainly bioethanol by fermenting it with microorganism. Cashew apples are majorly consumed as a fruit in western region of Nigeria because is highly nutritious form of food which provides substantial amount of energy. Cashew pulp is the leftover of cashew apples after the juice might have been extracted, the cashew pulps has been wasted in the cashew plantation farm due to lack of technical conversion of cashew pulp to a useful biofuel. Many studies and research were later put in place to examined and discovered that cashew apples have some essential minerals, vitamins and sugars such as glucose, fructose and sucrose [1] and some amino acids [2] which are present in the water juice, whereas the leftover pulp is a reservoir of cellulose, hemicellulose, pectin and protein which are good attribute of biofuel [1]. The abundance of cashew apples wasted in the farmland and the amount of cashew nuts exported in Nigeria annually make it clear that cashew pulp can be a very good substrate to research on. Nigeria energy sector is still heavily dependent on non-renewable fuel such as fossil fuel and natural gas as a source of energy without preparing the replacement due to depletion and harmful effect of the fossil fuel towards nature.

Nigeria dependency on fossil fuel can be lessened by substituting them with other renewable energies, such as thermal, hydro, hydrogen, solar, wind and biofuel. In term of biofuel as a renewable energy can be sourced from many wasted fruits a biodegradable agricultural wastes such as water melon, rotten banana, cashew apple, orange and many more which are not been properly and wisely managed in Nigeria range from farmland to market area due to lack of storage. Biofuel has been in used in energy sectors as alternative energy source all over the world due to some factors such as low emissions, government initiatives for renewable energy technologies and a substantial untapped biofuel potential [3].

Nigeria needs to focus on the development of renewable energy, green technology and energy conservation for the future in order to sustainably feed the rapid growth energy demands for end-use sectors, as well as to face the challenge of global climate change [4].

Since there is few or no research on converting cashew pulp into useful energy in south west Nigeria, the aim of this study is to investigate the characteristics properties of cashew pulp and its potential to become a feedstock for alternative biofuel. In this article, the details on sample collection, preparation and analysis conducted were described for the potential of the cashew pulp to become a feedstock of alternative biofuel.

2. MATERIALS AND METHODS

2.1 Material Preparation

The cashew apples used in this study were collected at cashew plantation farm Ode Ekiti High School, Ode Ekiti, located at latitude 7° 47' 21.27"N and longitude 5° 42' 56.20"E Gbonyin Local Government, Ekiti State, South West of Nigeria. Yellow cashew species were used for this research, the cashew nut was removed because it is the target of the farmers and the cashew apple is seen as a waste product. 5 kg of wet cashew apples were collected from the lumps in the farm land, the wasted cashew apple was thoroughly washed and allowed to drain before the juice extraction. The juice was extracted manually [5]. The pulp was divided into two equal parts, the first portion was sun dried for two weeks and the second portion was air dry in the room for four weeks, each sample was pulverized manually using mortar and pestle purposely because the powdered (substrate) samples will be pure and free from extra substance or deposit. The samples properties were done at Prof. Julius Okojie Central Research Laboratory in the Federal University of Technology Akure, Ondo State, Nigeria.

2.2 Methods

2.2.1. **Determination of Proximate Analysis of Cashew Pulp Substrate.**

Proximate analysis indicates the percentage by weight of the fixed carbon, volatile matters, moisture content and ash.

1. **Determination of Moisture Content.**

Fifty grams of each sun dried and air-dried cashew pulp powder were kept in a different silica crucible, heated in a furnace at one hundred and ten degree Celsius for one hour. Each crucible was taken out, then cooled in a desiccator and weighed, the process was taken and repeated for two times, at the first and second time the constant weight of anhydrous are achieved.

$$\text{Moisture content of the samples} = \frac{\text{Loss in weight of the substrates}}{\text{Weight of the initially taken}} \times 100 \qquad 1$$

2. **Determination of Volatile Content.**

Again, the free substrate moisture content sample of fifty grams of each sample (sun dried and air dried) was taken, heated in a different crucible fitted with cover in a furnace at higher temperature of nine hundred and fifty degrees celsius for seven minutes then weighed and recorded, then the results were compared with the sample (moisture free substrate content), the loss in weight of moisture free substrate is volatile matter [6]. Equation 2 shows the percentage of volatile matters given by:

$$\text{Volatile Matter} = \frac{\text{Loss in weight of moisture free substrate}}{\text{Weight of moisture free substrate}} \times 100. \qquad 2$$

3. **Determination of Ash Content**

Also, another sample of sun dried and air-dried cashew pulp substrate of fifty grams each respectively was kept in an open silica crucible, heated at seven hundred and fifty degrees Celsius in a furnace for a period of five minutes, then weighed and recorded according to Nwaokobia [6], this process was done on each substrate for two times and constant weight was achieved, the weight of residue obtained after burning gives the ash content.

$$\text{Ash in the substrates} = \frac{\text{Weight of residue ash formed}}{\text{Weight of the substrates taken}} \times 100 \qquad 3$$

4. **Determination of Fixed Carbon**

With these the fixed carbon for sun dried and air-dried samples respectively was calculated and determined by adding the total percentage of moisture content, volatile matter and ash content in each dry cashew pulp powdered, then the sum was deducted from one hundred [6].

$$\text{Fixed Carbon} = 100 - (\text{\% of moisture content} + \text{\% of volatile matter} + \text{\% of Ash content}) \qquad 4$$

2.2.2 Determination of Ultimate Analysis Properties of Cashew Pulp Substrate

The Ultimate analysis in various elemental chemical constituents such as carbon, hydrogen, oxygen, sulphur was determined by using Flash Smart V CHNS Elementar analyzer based on the principle of Dumas method. Ultimate analysis is very useful in determining the quantity of air required for combustion, the volume and the composition of the combustion gases.

1. **Determination of Carbon and Hydrogen**

Fifty grams of each sample sun dried and air-dried cashew pulp substrate was burnt in a current of dry oxygen thereby converting carbon and hydrogen of the substrate into carbon dioxide ($C + O_2 = CO_2$) and water ($H_2 + 1/2O_2 = H_2O$). The product of combustion of each sample are passed over weighed tubes of 1 mL of anhydrous calcium chloride ($CaCl_2$) and 1 mL of potassium hydroxide (KOH) respectively which absorb water and carbon dioxide. The increase in the weight of calcium chloride tube represents the weight of water formed and the increase weight of potassium hydroxide (KOH) tube represent the weight of carbon dioxide formed according to Nwaokobia [6].

Percentage of Carbon in the dry cashew pulp = $\frac{12Z \times 100}{44X}$ 5

Percentage of hydrogen in the dry cashew pulp =$\frac{2Y \times 100}{18}$ 6

Where, X = weight of cashew pulp sample taken
Z = increase in the weight of potassium hydroxide (KOH) tube.
Y = increase in the weight of calcium chloride ($CaCl_2$)

2. Determination of Nitrogen

Another fifty grams of each dried cashew pulp substrate sample was heated in a furnace with 1 mL of concentrated sulphuric acid respectively in the presence of potassium sulphate and copper sulphate in a long neck flask according to the Kjeldahl method. Thereby converting nitrogen of cashew pulp substrate to ammonium sulphate. When clear solution was obtained, this clear solution shows that the whole nitrogen has converted into ammonium sulphate, each result was treated with fifty percent sodium hydroxide (NaOH) solution. The ammonium formed is distilled over and absorbed in a known quantity of standard sulphuric acid solution. The volume of unused sulphuric acid is then determined by titrating against standard sodium hydroxide (NaOH) solution.

Equation 7 is used for calculating the percentage of nitrogen;

$$\% \text{ of N} = \frac{V \times P \times 1.4}{W} \quad 7$$

Since, $(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2NH_4OH$

One liter of (N/10) H_2SO_4 consumed is equivalent to 0.1 gm mole of ammonia or 1.4 gm of nitrogen.

V = V1 – V2 8

Where: % of N = Percentage of Nitrogen (N) in cashew pulp sample
V = Volume of acid used
V1 = Volume of H_2SO_4 neutralized in the blank.
V2 = Volume of H_2SO_4 neutralized in determination.
P = Normality
W = Weight of dry cashew pulp taken

3. Determination of Sulphur

Fifty grams of each sample of sun dried and air-dried cashew pulp substrate was burnt completely in a bomb calorimeter in a current of oxygen respectively according to Nwaokobia method [6]. The Ash obtained contains sulphur of the cashew pulp substrate as a sulphate which was extracted with 1ml of dilute hydrochloric acid and the acid extracted was treated with 1ml of barium chloride solution to precipitate the sulphate as barium sulphate.

$S + 2O_2 = SO_4$
$SO_4 = BaSO_4$

The precipitate of barium sulphate is fitted, washed, dried and weighed from which the sulphur in cashew pulp substrate is computed.

Percentage of Sulphur in cashew pulp = $\frac{0.1374Y \times 100}{X}$ 9

32 grams sulphur in the dry cashew pulp substrate will give 233 grams $BaSO_4$
Where; X = weight of cashew pulp sample taken
Y = weight of BaSO4 precipitate formed
Then, the amounts of sulphur in cashew pulps are: $\frac{32Y}{233} = 0.1374Y$ 10

3. RESULTS AND DISCUSSION

Proximate and ultimate analysis properties of the cashew pulp were done for the two samples, the sun dried and air dried substrate sample and results were presented in Table 1. Proximate analysis is the analysis that indicates the percentage by weight of the fixed carbon, volatile matter, ash and moisture content in the dry cashew pulp.

Table 1: The proximate analysis result of the cashew pulps powder

S/N	Moisture %	Volatile matter %	Ash %	Fixed Carbon %
Sun Dry	13.22	2.04	1.75	82.99
Air Dry	9.78	2.58	2.52	85.12

Ultimate analysis is the analysis which was done to determine the various constituents of a liquid fuel. The analysis gives the percentage content by mass of the liquid in terms of chemical elements such as oxygen, sulphur, hydrogen, carbon and nitrogen.
Table 2 shows the ultimate analysis properties result obtained from sun dry and air-dry pulp substrates.

Table 2: The ultimate analysis result of the cashew pulps substrate

S/N	Sulphur %	Hydrogen %	Oxygen %	Carbon %	Nitrogen %
Sun Dry	1.14	1.57	39.90	54.86	2.53
Air Dry	1.12	1.49	39.98	54.69	2.72

3.1. Discussion

The percentage of moisture content of the dry cashew pulp substrate in the sun dry was higher than the result obtained from the air-dry pulp substrate, the difference occurs due to drying method adopted. Moisture content in air dried cashew pulp substrate correlate with result obtained from Digilla pulp and Sukur pulp reported by Nwaokobia [6]. The effect of moisture content decreases the heat content per kilogram and increase the heat loss due to evaporation and superheating of vapor. Volatile matters content helps in easy ignition of fuel because it contains methane, hydrocarbons, hydrogen, carbon monoxide and incombustible gases like carbon dioxide and nitrogen. Percentage of volatile matter of the samples (air dried and sun-dried cashew pulp substrate) agreed with Nwaokobia result on Krikiri date palm pulp [6] but far better compared to that of Digilla pulp and Sukur pulp. The effect of volatile matters is to increase the flame length and set minimum limit on the furnace height and volume. It is considering high calorific value which has the potential to become an alternative biofuel feedstock. Moreover, percentage of fixed carbon in the sun dry pulp substrate was lesser than the result obtained for the air-dry substrate. Both samples have better fixed carbon compared result reported by Nwaokobiaon Digilla pulp, Sukur pulp and Krikiri date palm pulp [6]and high fixed carbon is advantageous in ethanol production because it gives a rough estimate of heating value and determine the level of sugar concentration. With the result shows inTable 1, the two substrates can be a good source of biofuel production.

Ash is an impurity that will not burn, while the percentage of ash content in the sun dry pulp substrate was lesser than the result obtained from air dry substrate, both results significantly better compare to ash in Digilla pulp and Sukur pulp [6]. The ash is related to the inorganic material such as sodium, vanadium, calcium, magnesium, silicon, aluminum and so on that present in the fuel oil, there are impurities that will not burn which would affect the combustion efficiency. All the results obtained from the proximate analysis in the air-dry cashew pulp substrate was higher than the result obtained from the sun dry pulp substrate except the percentage of moisture content. With the analysis properties result obtained in Table 1 it shows that both air dry and sun-dried cashew pulp are best for the production of biofuel such as bioethanol. The percentage of sulphur from the sun dry pulp substrate was higher than the result obtained from air dry pulp substrate, the low sulpur contents in the substrates are welcomed development as there will be the minimal release of sulphur oxides into the atmosphere and since the percentage of sulphur content in sun dried and air dried are lower respectively that is an indication that the burning of biofuel in any of the substrate examined in this work will not pollute the environment [7]. While percentage of hydrogen obtained from sun dried pulp substrate was higher compared to air dry pulp substrate, the amount of hydrogen in both sun-dried and air-dried cashew pulp would contribute significantly to the combustibility of the biofuel.

The percentage of oxygen obtained from sundry pulp substrate was significantly lower than the result obtained from air dry pulp substrate. Oxygen is known as a constituent that promotes the production of unsaturated fatty acids and sterols, which allows the yeast to protect against osmotic pressure and increase ethanol and thus improve cell viability during fermentation [8]. Oxygen helps in breaking down cellulose and solubilized lignin and hemicellulose because the amount of fixed carbon present in the substrate gives a rough estimate of heating value in the fuel oil in the presence of catalyst by some percentage of H_2O_2 for a certain hour and temperature [9, 10]. Then, the percentage of carbon present in the sun dry pulp substrate was slightly higher than the result obtained from air dry pulp powdered. The presence of carbon in cashew will help in the formulation of carboric acid which improves the rate of chemical reactions during hydrolysis. When carbon reacts with oxygen to form carbon dioxide during hydrolysis, the exposure will reduce the pressure to atmospheric pressure [11].

The percentage of Nitrogen in the sun dry pulp substrate was lower than the result obtained from air dry pulp substrate. Low Nitrogen Contents in the sun-dried substrate will give the minimal release of Nitrogen oxides into the atmosphere and since the low percentage of nitrogen content in sun dried and air dried respectively that is an indication that the burning of biofuel in any of the substrate examined in this work will not pollute the environment [7].

4. CONCLUSION

With the results obtained, conclusion can be made from the study that, ultimate and proximate analysis of both cashew pulp substrates were compared with others biomass that has been used as the feedstock for biofuel production. Cashew pulp substrate either sun dried or air dried are feedstock that can be effectively used for the production of biofuel mainly bioethanol with its properties, its bioethanol can work effectively and efficiently due to high percentage of oxygen and carbon present in the substrates, With these, it is clear that cashew pulp is not a waste material and likewise it can increases farmers profit, create hundreds of employment for the people if it considered and can serve as source of income to the country at large if it can be used as feedstock for the production of bioethanol.

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