ANALYSIS OF COCOA POD AS A SUBSTITUTE FOR COMBUSTIBLE ENERGY COMPONENT OF EXPLOSIVE

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ABSTRACT

Explosives are found as chemical components, mechanical mixtures of solids or solids, and liquids capable of rapid and violent action under the effect of external impulses such as heat, fire, and spark producing large volumes of gas with great release of energy. This project aims to analyze some cocoa pods obtained from Idanre, Ondo state to determine whether they could serve as a substitute for combustible components of explosives. The experiment was carried out on cocoa pods picked from Ipogba, Odomu Alade Idanre in Ondo State, picking 10 fresh cocoa pods at two different locations (A1, B1) and 10 dried cocoa pods (A2, B2). The tested specimens include a series of proximate tests for both fresh-ripped and decay-dried cocoa pods which was based on the standard of the Association of Official Analytical Chemists and the American Standard Test Method. The calorific values were determined using the Oxygen Bomb Calorimeter. The results of the proximate tests on the fresh (A) and dried (B) cocoa pods respectively are: moisture content (8.67 %; 10.42 %), ash content (8.56 %; 3.16 %), protein content (4.94 %; 7.35 %), Fat content (12.9%; 14.96%), fiber (29.35 %; 29.18 %), CHO (29.9 %; 15.61 %) and calorific value 390.02 Kcal/kg -1 and 85.01Kcal/kg -1. If some additives were added to the cocoa pod it can be a source of substitute for explosive.

KEYWORDS: Cocoa pod; calorific value; explosive; proximate test

INTRODUCTION

The oldest type of explosive which was first known is black powder. In the 11th century, black powder was used for war purposes and its uses in the mining industry did not start until 1627 in an underground mine in Bulgaria (Harding, 1999; Gordon et al., 2013).

Generally, explosives are chemical compounds or mixtures ignited by heat, spark, impact, or friction, and upon ignition, they decompose very rapidly in a detonation. There occurs a rapid release of heat with high pressure and a large quantity of gases which expand rapidly with sufficient force to overcome confining forces (Isife & Adeloye, 1999). The power of an explosive to do work depends on the fact that a small volume is capable under certain conditions of charging into a high volume of gas at a high temperature. The charge takes place almost instantaneously resulting in the development of great expansive force at the moment of detonation.

Another oldest kind of explosive ever used is a mixture of sulphur, charcoal, and sodium or potassium Nitrate. This Nitrate supplies the oxygen for combustion of the sulphur and charcoal. As the manufacture advances, other types of explosives were discovered, which are different in components, an example is ANFO which is a mixture of Ammonium Nitrate and Fuel oil. The ratio of the mixture is 10 of Ammonium Nitrate and 1 of fuel oil, others are Nitroglycerine, Dynamite, Slurry explosive, and Water gel. (Liu, 2004; Grent, 2011)

With the growth of the chemistry of carbon compounds, comes the discovery of several new compounds that could be exploded: they included: gun cotton (cellulose Nitrate), Nitroglycerine, Mercury Fulminate, and a little TNT (trinitrotoluene).

As raw materials for these entire compounds, nitric acid and a source of carbon compound were needed. (Gordon, 2013).

As the number of explosives grew, it became possible to classify them in accordance with their function. Most explosives are used either as high explosives, propellants, or initiators. High explosives (e.g. TNT) provide the main filling for bombs and shells. They are required in small quantities and their function is to explode very rapidly. Propellant e.g. cordite is 963 (A mixture of gun-cotton and Nitroglycerine) and explodes relatively slowly and steadily so that it exerts a uniform thrust in all directions of the short hole. (Fiona, 2011).

To optimize blast design, the knowledge of the explosive energy is paramount and this is transferred into five principal components during blasting: fragmentation, heave, air blast, ground vibration, and heat (Sanchidrian et al., 2007). Calnan (2015) in his investigation discussed different types of energy involved in blasting and suggested ways to optimize it through an energy partition system. Also, sourcing a local substitute for the energy component of explosives is the major aim of this investigation and is very important to improve the national economy whereby wastes can be turned into an economically viable material.

Nigeria ranks as the third largest cocoa producer in Africa, accounting for approximately 12 % of global production, Currently, Nigeria's cocoa production capacity is around 340,000 metric tons. This places Nigeria as the fourth-highest cocoa producer globally, following the Ivory Coast, Indonesia, and Ghana (Afolayan, 2020; Nigerian Bureau of Statistics, 2013). In Indonesia, an investigation was carried out on how cocoa shells could be used as a source of fuel energy to supplement the domestic needs of the nation (David et al., 2022).

Syamsiro (2021) studied the combustion of Bio-Pellets from Indonesian Cocoa Pod husk and identified that Cocoa Pod Husk is of high potential as an alternative fuel for the combustion system. Comparing the calorific values of sawdust, switch grass, cocoa pod husk, and bagasse, Adeyanju (2022) shows that cocoa pod husk has the highest value in the production of synthesis gas. All those researchers who had discovered the usage of biomass to generate fuel only did it for domestic use and had not explored its employment in explosive manufacturing for mining activity.

MATERIALS AND METHOD

Cocoa pod samples were taken from Ipogba, Odomu Alade Idanre in Ondo State. Idanre is the largest cocoa-producing area in Nigeria located at a Longitude of 7º 36' 20", Latitude of 5º 26'34''E in elevation of 320 m.
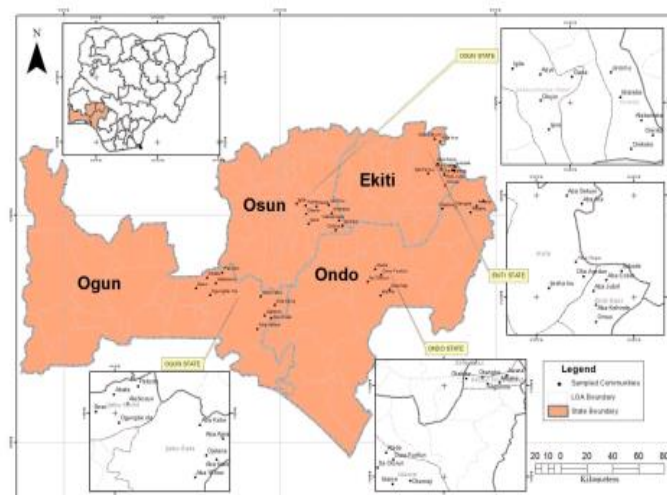

Figure 1: Regional map of the study area (Ojo, 2005)

Two types of samples: fresh and ripe (A1, B1) and decayed and dry (A2, B2) were collected from two different places, A and B, with sample bags at Ipogba and Odomu in Alade Idanre. Ten (10) ripe and fresh cocoa pods were taken and dried in the oven and ground into powder, while ten (10) decayed and dried cocoa pods were also picked and prepared by drying in the oven and ground into powder. The laboratory experiments were conducted to determine the moisture content, ash content, protein content, crude fibre content, fat content, carbohydrate content, and

calorific value of both samples. The following are the procedures for their determination.

Procedure for moisture content

The standard method of ASTM E871 – 82 (2013) was used to determine the moisture content. Clean Petri dishes with lids were labeled and dried in an oven at 100 ^{o}C for 30 minutes, cooled in a desiccator containing reignited CaO as a desiccant, and weighed to a constant weight (W1) using a Mettler balance scale. Five gramme (5 g) of each sample were weighed into respective Petri – dishes. The dishes and food samples were weighed again before drying (W2). The Petri – dishes and the samples were transferred into the oven (Galenkamp, size 3, hot box, London, UK) and maintained at 105 ℃ for 3 hours. The dishes with the content were removed and quickly transferred into a desiccator containing CaO as a desiccant to cool and re-weighed. The samples were returned to the oven and re-dried for a further one hour, cooled, and weighed. The procedure was repeated until a constant weight was attained (W3). Triplicate analyses were determined on each sample.

Calculation

The moisture content of each sample was calculated as the difference in weights before and after drying to constant weights. Values were expressed as percentage moisture.

$$\text{Moisture content (\%)} = \frac{W2 - W3}{W2 - W1} \times 100 \dots\dots\dots\dots. \text{Eq. 1}$$

Procedure for the determination of ash content

The ash content was determined using the official method of the ASTM D1102 – 84 (2013). Two gramme of each sample were weighed into a weighed crucible and incinerated in a muffle furnace at 600 ℃ for about 6 hours. Then the crucible was removed and cooled in a desiccator and reweighed and the following equation was used for its percentage calculation.

$$\text{Ash content} = \frac{(\text{Weight of crucible} + \text{Ash}) - (\text{Weight of crucible})}{\text{Weight of sample}} \times 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. \text{Eq. 2}$$

% organic matter = 100 - % Ash

W1 = wt of the crucible or can
W2 = wt. of sample + can
W3 = wt. of sample + crucible from furnace

Procedure for protein content determination

Protein was determined by the automated micro-Kjeldahl method described by AOAC (1995). One gramme of each sample was weighed into the micro-Kjeldahl flask and 20ml concentrated H_2SO_4, 2g Na_2SO_4, 0.5 $CuSO_4$ (as a catalyst), and 0.1g, selenium was added to the flask. The mixture was boiled on a digester until the black solution became clear after which it was made up to 100ml with distilled water. About 5 ml samples were drawn from the solution and subjected to steam, boric acid, blue methyl, and red methyl. The end product was titrated against 0.01N HCL. The percentage of nitrogen was determined from the following formula:

$$\text{\% Nitrogen} = \frac{\text{Titre x N x DF xMWN x 100}}{\text{Weight of sample in Mg.}} \dots\dots\dots\dots\dots\dots\dots. \text{Eq. 2}$$

Titre = Final burette reading -initial burette reading
N = Normality of acid
DF = Dilution factor
MWN =Molecular weight of nitrogen.
Percentage protein = % Nitrogen x 6.25 (conversion factor).

Procedure for crude fibre determination

According to AOAC (2005) standard, 0.5g of the sample was weighed into a 1-liter conical flask (W1), followed by the addition of 200 ml of boiling 25 % H_2SO_4. The solution was boiled gently for 30 minutes. Using cooling fingers to maintain a constant volume. The solution was then filtered through muslin cloth, stretched over a 9 cm butchner funnel, and rinsed with hot distilled water. The residue was scrapped back into the flask with a spatula and 200ml of boiling 1.25 % NaOH was added and the solution was allowed to boil gently for 30 minutes with boiling fingers used to maintain a constant volume. This was washed thoroughly again with hot distilled water and it was rinsed once with 10 % HCl and twice with industrial methylated spirit. The residue was rinsed finally three times with petroleum ether (40 - 600 ℃ boiling range) and will be allowed to drain, dried, and

scrapped into a crucible. The residue is dried overnight at 105 ℃ in the oven (Galenkamp, size 3, hotbox, London, UK), cooled in a desiccator, and then weighed (W2). Ashed at 550 ℃ for 90 minutes in a muffle furnace and then cooled in a desiccator and reweighed (W3).

$$\% \text{ Crude Fibre} = \frac{W_2 - W_3}{W_1} \times 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. \text{Eq. 4}$$

Procedure for fat determination
The fat content of the sample was determined by the Soxhlet extraction method (AOAC, 1995). The extraction flask was weighed; two gramme of each sample was weighed into a filter paper and introduced into the extraction thimble. The thimble was placed into the Soxhlet extractor; some quantity of petroleum ether was placed into the flask and connected to the Soxhlet apparatus. The extraction lasted for about 6 hours at 40-60 ℃ after which the solvent (petroleum ether) was recovered leaving only the extract in the flask. The extract was dried at 100 ℃ to expel the remaining solvent, then cooled in the desiccator and weighed.

$$\% \text{ fat} = \frac{(\text{weight of flask} + \text{oil }) - (\text{weight of flask})}{\text{Weight of sample}} \times 100 \dots.. \text{Eq. 5}$$

Procedure for the determination of carbohydrates
A 0.2, 0.4, 0.6, 0.8, and 1ml of working standard (with 0.1mg/ml conc.) of glucose was taken in boiling tubes and the final volumes of each tube were made 1ml by adding distilled water. 1 ml of 5% Phenol and 5 ml of 96 % Sulphuric acid were added one by one in each tube and shaken well so that the Phenol and Sulphuric acid were mixed thoroughly with working standard. After 10 minutes all the tubes were placed in a water bath at 25 – 30 ℃ for 15 minutes. Blank was set with 1ml of distilled water and absorbance of each tube will be taken at 490 nm with the help of spectrophotometer. Then the whole process following the Phenol and Sulphuric acid method was repeated with 0.2 ml of the processed samples and the Absorbance of sample solutions were taken. Preparation of sample: 100 mg of the sample will be weighed and taken in a boiling tube. Boiling tubes were kept in a water bath for 3 hrs. and then removed

from the water bath and cooled to room temperature. After cooling it was neutralized by adding solid sodium carbonate until effervescence ceases. The final volume was made to 100 ml by adding distilled water and centrifuged. The supernatant was used as a sample in further process.

Procedure for the determination of calorific value
The calorific value of the samples is the number of heat units that are evolved when a unit mass of the samples or unit volume of gas is completely burnt and the combustion products cooled to 298 k (25%). The calorific value of the sample is considered to be the most important parameter needed before the sample can be used efficiently in combustion and furnace plants. The cocoa pod sample (sample A&B) in pulverized form was explosively detonated by electrical ignition in a stainless steel bomb containing a known weight of samples in oxygen at a pressure of about 2500 km/m^3. The bomb was immersed in a known mass of water in a calorimeter so that the heat released on combustion was transferred to the water. The temperature of the water measured (which is a function of time) so that the acted rise in temperature due to the burning of the samples could be interpolated thereby allowing for heat loss from the calorimeter.

$$\text{Calorific Value} = \frac{(\text{Final Reading} - \text{Initial Reading})}{\text{Weight of samples}} \times 100 \dots.. \text{Eq. 6}$$

It is measured in Kcal/kg and to determine the calorific value (GE: Gross Energy) for each sample, equation (7) was employed.

$$\text{Gross Energy (GE)} = (4xCHo) + (9xFat) + (4xProtein) \dots.. \text{Eq. 7}$$

Nitrogen-free extract (NFE) consists of carbohydrates, sugars, starches, and a major portion of materials classed as hemicellulose. When crude protein, fat, ash, and fiber are added and the sum is subtracted from 100 the difference is NFE.

Then the NFE was calculated by equation (8)

$$\text{NFE} = 100 - (\%\text{Ash} + \%\text{Crude Protein } + \text{Fat } + \text{Fibre}) \dots.. \text{Eq. 8}$$

RESULTS AND DISCUSSION
Proximate analyses of the samples
Table 1 shows the results obtained from the test carried out on a fresh Cocoa pod (sample A1). The

average value for moisture content, crude protein, ash content, fat, crude fibre, and carbohydrate are respectively 8.14 %, 9.07 %, 3.07%, 25.33 %, 25.4 %, and 31.4 %. On the other hand, the results in Table 2 are from dried and decayed Cocoa pod (sample A2) with an average value of moisture (12.46%), crude protein (8.06 %), ash content (3.17 %), fat (26.41 %), crude fibre (25.36 %) and carbohydrate (30.1 %). The results of the parameters analyzed in both samples A1 and A2 are almost the same except for moisture content where a major difference was observed; this could be a result of the absorption capacity of the decayed cocoa pod. The proximate analysis carried out in this study provides information needed for volatile matter, moisture, ash, and fixed carbon content of samples which are important features necessary for the thermal conversion of any biomass into energy (Tanger et al., 2013; David et al., 2022). The nutrient composition of the cocoa samples was determined using the standard procedures of the Association of Official Analytical Chemists (AOAC, 1999, 2005) and the American Standard Test Method (2013).

Table 1: Proximate analysis of fresh cocoa pod (SAMPLE A1)

Sample	Moisture (%)	Crude protein (%)	Ash (%)	Fat (%)	Crude Fiber (%)	CHO (%)
A1	8.14	9.07	3.07	25.33	25.38	31.00
A1	8.14	9.07	3.07	25.38	25.38	31.00
A1	8.14	9.07	3.07	25.33	25.38	32.00
Average Value	8.14	9.07	3.07	25.33	25.4	31.4

Table 2: Proximate analysis of dried and decayed cocoa pod (SAMPLE A2)

Sample	Moisture (%)	Crude protein (%)	Ash (%)	Fat (%)	Crude Fibre (%)	CHO (%)
A2	12.46	8.06	3.17	26.43	25.36	30.00
A2	12.47	8.06	3.17	26.43	25.36	30.00
A2	12.46	8.06	3.18	26.43	25.36	31.00
Average Value	12.46	8.06	3.17	26.41	25.36	30.1

Furthermore, the results from the samples taken from the second location, B1 for fresh Cocoa pod (Table 3), are moisture content (9.24 %), crude protein (0.8 %), ash content (14.04 %), fat (0.5 %), crude fibre (33.3 %) and carbohydrate (28.4 %) and the B2 for dry pod (Table 4) showed the following average values: moisture content (8.37 %), crude protein (6.63 %), ash content (3.14 %), fat (3.51 %), crude fibre (33 %) and carbohydrate (1.12 %).

Table 3: Proximate Analysis of fresh cocoa pod (SAMPLE B1)

Sample	Moisture (%)	Crude protein (%)	Ash (%)	Fat (%)	Crude Fibre (%)	CHO (%)
B1	9.24	0.66	10.33	0.55	33.44	29.01
B1	9.24	0.73	15.35	0.55	33.30	26.02
B1	9.24	0.85	16.43	0.57	33.22	30.00
Average Value	9.24	0.8	14.04	0.5	33.3	28.4

Table 4: Proximate Analysis of dried and decayed cocoa pod (Sample B2)

Sample	Moisture (%)	Crude protein (%)	Ash (%)	Fat (%)	Crude Fibre (%)	CHO (%)
B2	8.36	6.62	3.10	3.63	33.78	1.04
B2	8.45	6.65	3.16	3.51	32.66	1.12
B2	8.31	6.63	3.16	3.40	32.56	1.11
Average Value	8.37	6.63	3.14	3.51	33.00	1.12

As observed from Table 5, the value of the Gross Energy as determined by equation (7) for Sample A is 390.02 Kcal/kg-1 and that of Sample B is 85.01 Kcal/kg-1. Also, the Nitrogen Free Extract value in Sample A is 38.22 % and for Sample B is 52.54 %.

Table 5: Average values of proximate tests for fresh (A) and dried (B) cocoa pods

Sample	Mc (%)	C.p (%)	Ash (%)	Fat (%)	Fibre (%)	CHO (%)	GE (kcal/kg)	NFE (%)
A	8.67	4.94	8.56	12.9	29.35	29.9	390.02	38.22
B	10.42	7.35	3.16	14.96	29.18	15.61	85.01	52.53

The analysis carried out on fresh Cocoa pod at zone A1 and B1 (Tables 1 and 3) shows that the moisture content varies between 8.14 % and 9.24 %, the crude protein is between 0.66 % and 9.07 %, the ash content is from 3.07 % to 16.43 %, for the fat, it is between 0.55 % to 25.38 %, the fibre is from 25.38 % to 33.44 % and carbohydrate content is between 26.02 % and 32.00 %. On the other hand, the following are the variations that occur in the sample test of the decayed and dried cocoa pod (Tables 2 and 4): moisture content (8.31 % - 12.47 %), the crude protein (6.62 % - 8.06 %), the ash content (3.10 %-3.18 %), for the fat (3.40 % - 26.43 %), the fibre (25.36 % - 33.78 %) and the carbohydrate content is (1.04 % - 31.00 %).

Increases in moisture content usually require larger explosion ignition energies and reduce explosion severities. However, with some metal dust such as aluminum dust, increasing moisture may lead to a more explosion in hydrogen production (Abu El-Rub et al., 2004; Marques et al., 2010). The protein combustion process can analyze both liquid and dry fertilizer samples in the protein combustion process, all forms of protein are connected to Nitrogen gas by incineration and it causes a decrease in the body weight of the explosive (Falls, 2005).

Ash is a residue from combustion that cannot be burned or can no longer produce heat. The main content of ash is silica which has an unfavorable effect on the calorific value produced. The percentage of ash from the combustion of cocoa shells of 6.93038/gram still meets the standard of SNI 01-6235-2000, which is < 8 %, so the amount of ash produced from the combustion of cocoa shells (David et al., 2022)

Comparison of the Calorific Value of Cocoa Pod with the Currently used Explosive (ANFO)

The calorific value of a substance is the quantity of energy released by the substance during combustion. The calorific value is measured in Kcal/kg-1. An explosive must have a very high calorific value because it will use a great amount of energy to explode. It is the energy content that will determine those efficacies of the explosive and we can also take it as the strength of the explosive (Atlagic, 2020).

ANFO, Ammonium nitrate fuel oil, the reigning explosive, has the following calorific value as analyzed by Hartman (2009). The oxygen-balanced ANFO with 94.5 % of Ammonium nitrate and 5.5 % fuel oil respectively, has a calorific value of 930Kcal/kg-1. A positive oxygen-balanced ANFO having 96.6 % of Ammonium nitrate and 3.4% fuel oil has a calorific value of 600Kcal/kg-1 and the negatively oxygen-balanced ANFO having 92% of Ammonium nitrate and 8.0 % fuel oil has a calorific value of 810 Kcal/kg-1.

As observed by Hartman (2009) where the increase in the addition of the fuel oil affected the level of calorific value of the explosive positively, it will be of great economic importance, if the energy component of the explosive is substituted by the gross energy (390.02 Kcal/kg-1) from fresh cocoa (Sample A1, B1) and the 85.01 Kcal/kg-1 obtained from the decayed and dried pod (Sample A2, B2) with 38.22 % and 52.54 % of Nitrogen Free Extract value respectively.

CONCLUSIONS AND RECOMMENDATIONS

This research work showed that Nigeria is one of the world's foremost cocoa-producing nations which implies that Cocoa pods have been a waste material that is turned into raw material in mining Industries. The calorific value obtained from the proximate test done on the fresh-ripped cocoa pod is 390.02 Kcal/kg-1 with 38.22 % of Nitrogen Free Extract value and the gross energy result from the decayed dried pod is 85.01 Kcal/kg-1 with 52.54 % of Nitrogen Free Extract value. This implied that there is a substantial energy content in a cocoa pod that can serve as a local substitute for the imported energy component of explosives in the mining Industry.

It is recommended that more research be done on the energy content of Cocoa pods to carry out its impact assessment to design a cocoa pod plant for a large-scale production of cocoa pod powder that will help to harness the economic value of the vast pod that is being wasted it is presently.

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