

UNIVERSITY OF CAPE COAST

THE EFFECTS OF MOISTURE AND FERMENTATION PERIODS ON THE
PHYSICAL AND BIOCHEMICAL PROPERTIES OF 'AMELONADO' AND
'HYBRID' VARIETIES OF COCOA BEANS

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JULY, 2015

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‘HYBRID’ VARIETIES OF COCOA BEANS

BY

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THESIS SUBMITTED TO THE DEPARTMENT OF AGRICULTURAL
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TECHNOLOGY

JULY, 2015

DECLARATION

Candidate's Declaration

I hereby declare that this thesis is the result of my own original work and that no part of it has been presented for another degree in this University or elsewhere.

Candidate's Name: Elliot Kwaku Anyidoho

Signature:

Date:

Supervisors' Declaration

We hereby declare that the preparation and presentation of this thesis were supervised in accordance with the guidelines on supervision of thesis laid down by the University of Cape Coast.

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ABSTRACT

The effect of moisture content (5-24%) on some physical and compressive properties of the 'Amelonado' and 'Hybrid' varieties of cocoa beans were studied. Alongside, the effects of fermentation periods (0-8 days) on the biochemical profiles of the dried beans were studied in three morphological parts (whole bean, nib and shell). Four experiments were separately conducted as completely randomized, factorial designs.

Compared to the 'Amelonado' variety, the axial dimensions (*viz.* length, width and thickness) of the 'Hybrid' cocoa beans were significantly higher ($p < 0.05$). With increasing moisture content, the bean mass, particle density, porosity, angle of repose and the coefficient of friction increased linearly in both varieties while inversely, the bulk density decreased. Increasing the moisture content decreased the rupture force with lesser deformation. As the beans were compressed, there was *ca.* 2 to 3-fold higher fracture resistance in the horizontal orientation compared to the vertical orientation.

There were variable effects of fermentation period on phytochemicals including polyphenols, free fatty acid (FFA), titratable acidity, total soluble solids and pH in the spatial regions. Irrespective of fermentation period, the FFA content of the whole bean, nib and bean shell of both varieties remained within the acceptable range ($<1.75\%$). The ash and carbohydrate content in the respective spatial regions of both varieties increased ($P < 0.05$) with fermentation duration. However, as the fermentation period increased the protein content in all the different parts of the beans decreased, irrespective of the variety.

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DEDICATION

I dedicate this work to my loving and supportive wife, Mrs. Yvonne Ibiele Anyidoho and children, Eyram, Klenam and Kekeli.

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CHAPTER ONE

INTRODUCTION

General introduction

Cocoa (*Theobroma cacao*) labelled ‘the golden tree’ whose scientific name means “food of the gods” in Greek, is an ancient crop of the lowland tropical forest. It is believed to have originated from the Central and Southern America (Polly, 1963). The crop is now grown in more than 50 countries on 0.2 per cent of the world’s agricultural land. Today, cocoa is one of the most important agricultural export commodities in the world. For instance in 2012, 4.1 million metric tons of cocoa beans were produced for a total export value of US\$8.4 billion (FAO, 2013). This is even a small fraction of the total value of the chocolate market, estimated at more than US\$83 billion (MarketsandMarkets, 2013). Five countries alone accounted for 80% of the global production. Measured by volume, the top 5 producers are Côte d’Ivoire (36%), Ghana (22%), Indonesia (11%), Nigeria (6%), and Brazil (5%) (ICCO, 2013).

Currently, cocoa is the backbone of the economies of some West African countries including Ghana. The country is almost synonymous with the cocoa crop, with the slogan “Ghana, Cocoa! Cocoa, Ghana”! This is due to the pivotal role it plays in the nation’s economy. It is generally believed to have been introduced into Ghana by Tetteh Quarshie in 1879 from Fernando Po though some evidence in the

record of the Basel Mission in Accra showed that cocoa was growing in their compound long before that time (Sundiata, 1974). The cocoa crop is cultivated on about 1.5 million hectares of land by some 800,000 farming families in six out of the ten regions of Ghana (Afoakwa, 2010).

Three main groups of cultivated cocoa are recognized: ‘Criollo’, ‘Forastero’ and ‘Trinitario’ (Cocoa Manual, 2010). The ‘Criollo’ variety is reported to be very vulnerable to diseases, possesses bland flavour and pleasant aroma (Lefeber *et al.*, 2011). The ‘Forastero’ group is hardy and high yielding, and forms the bulk of commercial cocoa widely planted in plantations. The ‘Amelonado’ and Upper Amazon cocoa belong to this group. It possess 'harsh' flavour with bitter taste. The ‘Trinitario’ consists of very different heterogeneous types (Wood and Lass, 1985).

Table 1.1 simplifies the properties of the three main group of cocoa.

Table 1.1. Different varieties of cocoa and their characteristics

	‘Criollo’	‘Forastero’	‘Trinitario’
Pod Husk			
Texture	Soft	Hard	Mostly hard
Unripe fruit colour	Red/Green	Green	Red/Purple
Ripe fruit colour	Yellow/Orange	Yellow	Orange
Pod surface	Warty and conspicuously furrowed	Not warty and furrow is inconspicuous	Intermediate
Beans			
Average number per pod	20-30	30 or more	30 or more
Seeds	Plump	Flat	Intermediate

Source: Cocoa Manual, 2010

The 'Hybrid' cocoa are progeny crosses between selected Upper Amazon types ('Criollo' and 'Forastero' varieties). It is considered to be of better quality, early bearing and disease tolerant than the 'Amelonado' variety. The major cocoa types cultivated by Ghanaian farmers are Amazonia (34.4%), the 'Amelonado' (13.3%) and the 'Hybrid' (52.3%) (Afoakwa 2010). Plate 1.1 shows the shapes of the cocoa pods from different varieties.

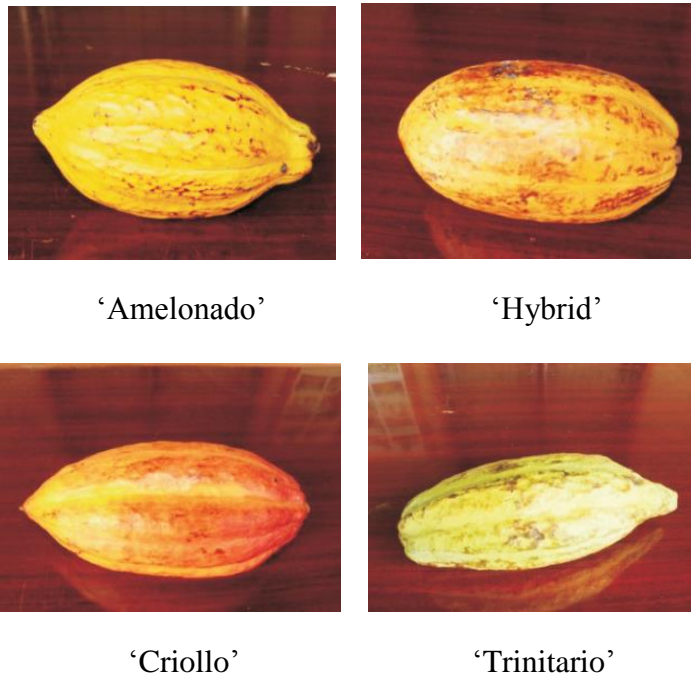


Plate 1.1: Pods of the different types of cocoa

Cocoa beans are usually processed into chocolate, cocoa powder, cocoa liquor, cocoa butter and cake. Rossini *et al.* (2011) reported that the cocoa powder is essentially used in flavouring biscuits, ice cream, dairy products, drinks and cakes and in the manufacture of coatings for confections and frozen desserts. Cocoa is also a popular raw material in the cosmetics and pharmaceutical industries. Studies show that the cocoa bean contains flavonoids with antioxidant properties that can

reduce blood clot and the risk of stroke and cardiovascular attacks (Cooper *et al.*, 2008). The crop is very low in cholesterol and a good source of protein, potassium, zinc, and dietary fibre. Currently, the pod husks and shells are used for the preparation of animal feed and fertilizer in Ghana (Ntiamoah and Afrane, 2008).

Postharvest operations for cocoa, as shown in Plate 1.2, generally consist of manual seeds extraction by breaking the pod and removing the seeds followed by fermentation, drying, cleaning, sorting and grading. Processing of cocoa beans into various cocoa and chocolate products starts with an on-farm fermentation of the beans followed by drying, and roasting during industrial processing. These postharvest processes are very crucial to the quality of the finished products as they initiate the formation of chocolate flavour precursors and the brown colour of cocoa products (Adeyeye *et al.*, 2010). The fermentation process breaks down the mucilaginous pulp surrounding the beans and causes cotyledon death (Afoakwa *et al.*, 2008).



Plate 1.2: Postharvest operations for cocoa

In Ghana these postharvest handling operations are often done manually and excellently by farmers on small-scale basis, leading to superior quality specifications. This explains why cocoa beans from Ghana have established a worldwide reputation as the ingredient of preference by quality oriented cocoa products manufacturers (Jonfia- Essien, 2004). According to the Quality Control

Division (QCD) of the Ghana Cocoa Board, cocoa beans are classified by size based on the number of beans weighing 100g. Table 1.2 shows the seven categories that are declared for the main harvesting season.

Table 1.2: Categories of cocoa in Ghana for the 2013/2014 cocoa season

Classification	Beans count/100g
Super Main (Category H)	0 – 90
Main Crop (Category A)	91 – 100
Super Light (Category L)	101 – 110
Light (Category F)	111 – 120
Small (Category P)	121 – 130
Type 4 Beans (Category V)	131 – 150
Remnants (Category R)	151 – 180

(Source: Quality Control Company, Ghana COCOBOD, 2013/2014)

Information on the physical, mechanical and biochemical properties of agricultural products is needed in the design of machines used during harvesting, sorting, cleaning, handling and storing of agricultural materials and converting them into food, feed and fodder. These properties are influenced by a number of factors such as the cultivar or variety, temperature, and moisture content (Shitanda *et al.*, 2002).

Physical properties are an important aspect of food quality and relate to food safety. The knowledge of a food's physical properties helps in predicting the behaviour of new raw materials. Aviara *et al.* (1999) stated that knowing the physical properties of sheanut, for example, is fundamental because it facilitates the design and development of equipment for harvesting, handling, cleaning, separation, storing, drying and processing. The hardness of grains is an important

feature of how they are processed for foods and feeds, and it imparts various properties such as particle size distribution and starch damage (Bhave and Morris, 2008). Behaviour under static or dynamic stresses governs the extent of potential mechanical injury (for example, during hopper storage or discharge) and can provide valuable information on the design of handling machinery.

On the other hand, the nutritional quality of cocoa products are determined largely by the chemical composition of the cocoa powder, which is dependent on the quantum of proteins, carbohydrates, fats, minerals and phytochemicals in the cocoa products (Adeyeye *et al.*, 2010). It is imperative to know the nutritional status of foodstuffs. Cocoa powder and chocolate are extremely rich sources of many essential nutrients and phytochemicals that can contribute to a healthy diet.

Statement of research problem and justification

The physical characteristics of agricultural materials affect how they are to be processed, handled, stored and consumed. Understanding of the physical characteristics facilitates proper design of machines and processes to harvest, handle and store agricultural materials and to convert these materials into food and feed. According to Mohsenin (1986), knowledge of these characteristics are important to engineers, processors and food scientists, plant breeders, and other scientists who may find new uses for them. These properties include size, shape, mass, density, deformation in response to applied static and dynamic forces, moisture adsorption and desorption characteristics (Stroshine and Hamann, 1995).

The study of these is one of the unique responsibilities and interests of Agricultural Engineers and Food Process Engineers.

The physical characteristics are also affected by parameters such as the variety, temperature and moisture content. These physical properties are important for the design of storage and processing equipment. Therefore, knowledge about the physical properties of the two varieties of cocoa beans at varying moisture contents is important in the design and construction of such equipment.

The physical, compressive and other engineering properties are important in many problems associated with the design of machines and the analysis of the behaviour of the product during unit operations such as drying, cleaning, sorting, crushing, and milling. The solutions to problems of these processes involve knowledge of the physical, compressive and other engineering properties (Akaaimo and Raji, 2006). Like any other food material, cocoa beans are hygroscopic and this nature affects its physical and mechanical properties. The engineering properties of cocoa beans are moisture-dependent.

It is essential to understand the physical and mechanical laws governing the response of the two varieties of cocoa beans 'Amelonado', and 'Hybrid' so that handling equipment can be designed for maximum efficiency. Some physical and compressive properties of category B cocoa beans have been determined. However, no work appears to have been done on the physical and mechanical properties of 'Amelonado' and 'Hybrid' cocoa beans. And since these properties are prerequisites for the design of equipment for cleaning, sorting, crushing, handling and other postharvest operations, it is essential to determine them. This research, as part

of its objectives, was designed to evaluate and compare some physical and mechanical properties of the ‘Amelonado’ and ‘Hybrid’ cocoa bean varieties at different moisture contents.

On the other hand, Ieggli *et al.* (2011) stated that nowadays, consumers are more concerned with the nutritional status of foodstuffs. Taking cognizance of this Jonfia-Essien and Navarro (2010) stated that the free fatty acids (FFA) content must be less than 1.0% to meet the acceptable level of 1.75% in cocoa butter extracted from the dry cocoa beans. And considering that cocoa powder and chocolate are extremely rich sources of many essential nutrients and phytochemicals that can contribute to a healthy diet, it is imperative to periodically research into the raw cocoa beans and its food products. Therefore, in this study, the effects of fermentation of the cocoa beans on the proximate and phytochemical compositions were also determined.

General objective of the thesis

The overall objective of this research was to examine and compare some selected physical and mechanical properties of ‘Amelonado’ and ‘Hybrid’ varieties of cocoa beans as affected by moisture content. The effects of fermentation periods on the spatial profiles of biochemical compositions in the whole cocoa bean, nib and the shell was investigated.

Specific objectives

More specifically the study:

- i. determined the effect of moisture content on physical properties such as the axial dimensions, bean mass, 1000-bean mass, particle density, bulk density, porosity, angle of repose and coefficient of static friction of 'Amelonado' and 'Hybrid' cocoa beans.
- ii. investigated fracture resistance of cocoa beans as affected by moisture content, variety and bean orientation.
- iii. examined the effects of fermentation period on three morphological parts (whole bean, nib and shell) of 'Amelonado' and 'Hybrid' varieties of cocoa beans in relation to:
 - a. the spatial distribution of phytochemicals such as polyphenol, free fatty acid (FFA), pH, total soluble solids (TSS) and titrable acidity.
 - b. the proximate compositions including crude protein, carbohydrate, fat, ash and moisture contents.

Organization of the remainder of the thesis

Chapter 2 presents the review of research related to the problem being investigated. The effect of moisture content on some selected physical properties of 'Amelonado' and 'Hybrid' cocoa beans is contained in chapter 3. The mathematical backgrounds relating to the physical characteristics of agricultural produce are included in this chapter. Chapter 4 outlines the mechanical properties

of both varieties as affected by moisture content and orientation to the direction of the applied force. The influence of moisture content and bean orientation on the rupture force, axial deformation, and energy absorbed for these cocoa varieties are presented in this chapter. Chapter 5 focuses specifically on the phytochemical compositions of the two varieties ‘Amelonado’ and ‘Hybrid’. The chapter investigated the impact of fermentation period of the cocoa beans on the concentration and spatial profiles of phytochemicals such as polyphenol, free fatty acid (FFA), pH, total soluble solids (TSS) and titrable acidity content in the nib, shell and dry cocoa bean of the two varieties. In Chapter 6, the proximate compositions of the two varieties of cocoa beans ‘Amelonado’ and ‘Hybrid’ has been presented. This chapter holistically deals with the impact of fermentation of cocoa beans on the proximate analysis involving crude protein, carbohydrate, fat, ash and moisture contents of dry cocoa nib, cocoa shell and raw cocoa bean. Finally, Chapter 7 gives the general discussion and Chapter 8 states conclusions and recommendations emanating from the entire study.

CHAPTER TWO

LITERATURE REVIEW

Introduction

The physical characteristics of agricultural materials including cocoa beans are affected by parameters such as the moisture content and drying time. Therefore, knowledge about the physical properties of cocoa beans at varying moisture contents is important in the design and construction of sorting, grading and cleaning equipment. Based on this, several researchers including Abano and Amoah (2011) and Baryeh (2001) have determined the physical properties of different agricultural products as a function of moisture content.

Postharvest operations for cocoa beans generally consist of cleaning, sorting and grading. In Ghana these operations are often done on small-scale and manually. These methods of handling beans are not only time and energy consuming, but also inefficient as they come with some chaff, unwholesome and non-uniform bean sizes. Lack of standard principles for sorting, grading, packaging and purchasing companies' preferences has led to problems in storage and marketing.

Moisture content

The entire component of food material is made up of moisture content and dry matter content, the two sum up to unity or 100%. The amount of water in a food is denoted by its moisture content. A food's storability is directly related to moisture content, along with temperature and oxygen availability. Moisture is present in foods in either solid form (ice), liquid (water), or vapor (humidity in air). Moisture content of agricultural material is described as the percentage equivalent of the ratio of weight of water to the weight of dry matter or total weight. Singh and Dennis (2009) stated that two bases are widely used to express moisture content; namely, moisture content wet basis and moisture content dry basis.

Moisture content on wet basis (MC_{wb}) is the amount of water per unit mass of moist (or wet) sample. On the other hand, moisture content on dry basis (MC_{db}) is the amount of water per unit mass of dry solids (bone dry) present in the sample. Mathematically, moisture content (MC) of grain can be expressed as a percentage on a wet basis (wb) or a dry basis (db) as:

$$MC_{wb} = \frac{W_i - W_d}{W_i} * 100 \quad (2.1)$$

$$MC_{wb} = \frac{W_i - W_d}{W_d} * 100 \quad (2.2)$$

Where: MC_{wb} is the moisture content (% wb), W_i is the initial mass of sample (g),

W_d = dried mass of sample (g).

The relationship is useful to calculate MC_{wb} when MC_{db} is known. Similarly, if MC_{wb} is known, then MC_{db} may be calculated from the following equation:

$$MC_{wb} = \frac{MC_{db}}{100+MC_{db}} * 100 \quad (2.3)$$

$$MC_{db} = \frac{MC_{wb}}{100 - MC_{wb}} * 100 \quad (2.4)$$

Humid air properties are known as the psychometric properties of the air. Psychometric properties are important in food storage, drying, and adsorption as well as human comfort. Moisture properties are of great economic importance to the food industry. Air with low relative humidity has a greater tendency to withdraw moisture from food materials. Foods in high humidity air will have less tendency to lose moisture to the air.

Size and shape

Size of grain refers to the characteristics of the grain which in turn determine how much space it occupies. Within limits, size can be described in terms of length, width, and thickness. These axial dimensions of agricultural product determine the size while its volume determines the shape (Irtwange and Igbeka, 2002). The determination of length, width and thickness is useful in the design of bean metering devices, sorting sieves, pneumatic conveying systems and planters attached to combine harvesters. Length, width and thickness measurements are usually replicated several times due to their irregular nature. According to Shitanda *et al.* (2002), the dimensions of agricultural materials also vary widely with growing season, growing location and variety. Shape is used to describe unprocessed foods. It is connected with the geometrical form of the product (food). Example: carrots = cones. Differences in size and shape can be used to improve the

quality of grains by removing foreign materials and damaged particles. Seeds may be separated into size categories before being sold on the market. Dimensions are known to increase with increasing moisture content up to a certain point after which there is no more appreciable dimensional change. Most experiments are carried out between 5% and 25% moisture content.

Bean mass and 1000-bean mass

Bean mass is the quantity of matter that an individual grain contains. The 1000 grain mass refers to the mass of 1000 grains. It includes the dry matter and the moisture present within the grains. However, the moisture present is dependent on the water holding ability of the grain and void spaces.

The 1000 grain mass of cereal grains is a useful index to ‘milling outturn’ in measuring the relative amount of dockage or foreign material in a given lot of grain, and the amount of shriveled or immature kernels (Saiedirad *et al.*, 2008). The mass of 1000 grains has been found to increase linearly with an increase in moisture content for barley grains (Tavakoli *et al.*, 2009).

Particle density

The particle density is the mass of solid divided by the volume occupied by the solid excluding void spaces. It is also referred to as true density or particle density or specific density. Density of grains decreases linearly with increasing moisture content. It is determined using the toluene (C₇H₈) or methanol (CH₃OH) displacement method. Toluene is used instead of water because it is absorbed by

seeds to a lesser extent. The volume of toluene displaced is found by immersing a weighted quantity of seeds in the measured toluene (Tavakoli *et al.*, 2009). The true density increases nonlinearly from 0.75 to 1.21 g/mm³ as the seed moisture content increases from 5% to 25% for pigeon pea (Baryeh and Mangope, 2002). Linear increase of seed density as the seed moisture content increases has been found by Singh and Goswami (1996) for cumin seeds.

Bulk density

Bulk density is the mass of a group of individual particles divided by the volume of the space occupied by the entire mass, including the air space. It is expressed in metric units of gm cm⁻³ or kg m⁻³ (Stroshine & Hamann, 1995). The bulk density can be determined using a container of known volume. The container is weighed, filled with the seeds, striking off the top without being compacted and reweighed. The bulk density is calculated as the mass of seed divided by the container volume. Bulk density can also be determined with a weight per hectolitre tester, which is calibrated in kg per hectolitre. This has a predetermined volume and a measure of the weight easily enables the researcher to determine the bulk density. This method has been used by several researchers including Jain and Bal (1997) for pearl millet. According to Baryeh (2001), the bulk density decreases as the moisture content increases up to 25%, beyond which it does not change appreciably.

Porosity

Porosity is the percentage of the total container volume occupied by air spaces between the particles. Porosity depends on true and bulk densities and hence its magnitude of variation depends on these factors and is different for each seed or grain. It affects the resistance to airflow through bulk solids. Singh and Goswami (1996) and Baryeh and Mangope (2002) found the porosity of cumin and pigeon pea, respectively, to increase with increase in moisture content. However, Suthar and Das (1996) found porosity to decrease linearly with an increase in moisture content for pumpkin and karingda seeds, respectively. High porosity at high moisture content indicates that less number of beans can be stored at high moisture content than at low moisture content due to increase in inter-bean voids when the porosity is high for cocoa beans. Low porosity implies low percentage air space and more resistance to fluid flow, thus difficult to cool or heat. While, in high porosity of produce air flows easily through the bed, and cooling or heating is faster and hence power required by pumps and fans is low. Grain bed with low porosity will have greater resistance to water vapor escape during the drying process, due to the reduction in pore spaces. Hence in the design of postharvest drying equipment, knowledge of porosity of crops is essential when designing ventilation systems (Tavakoli *et al.*, 2009).

Sphericity

One commonly used technique for quantifying differences in shapes of grains, vegetables and fruits is to calculate sphericity. The sphericity can be

described by defining three characteristics dimensions; the major, intermediate and minor (Mohsenin, 1986). This according to Stroshine and Hamann, (1995) to is based on the assumption that the volume of a solid can be approximated by calculating the volume of a triaxial ellipsoid with diameters equal to the major, intermediate and minor diameters of the object. Data from sphericity is useful in sieve size determination and in selecting sieve separators.

Angle of repose

The angle of repose is the maximum angle of a stable slope determined by friction, cohesion and the shapes of the particles. It indicates the cohesion among bulk material. The higher the cohesion, the higher the angle of repose (Pradhan *et al.*, 2009). It is affected by the surface characteristics, shape and the moisture content of the grains. These angles are very useful for calculating the quantity of granular materials which can be placed in piles or flat storages. Angle of repose is very useful; it indicates the ability to flow, design of equipment for processing, storage and to size conveyor belt for transporting the material (Gharibzahedi *et al.*, 2010). A linear increase in angle of repose as the seed moisture content increases has been reported by Suthar and Das (1996) for karingda seeds, Bart-Plange and Baryeh (2002) for cocoa beans and Kabas *et al.* (2007) for cowpeas.

Coefficient of static friction

Coefficient of static friction is the ratio of the force required to slide the material over a surface divided by the normal force pressing the material against

the surface (Bahnasawy *et al.*, 2004). It is determined by the use of a tilting table and a lifting screw mechanism. It is calculated as the tangent inverse (\tan^{-1}) of the angle which the tilting table makes with the horizontal when grains just start moving along the table. An increase in the coefficient of static friction with moisture content has been observed by Kabas *et al.* (2007) for cowpeas using rubber, plywood and galvanized sheet. The coefficient of friction is important in the design of conveyors because friction is necessary to hold grains to the conveying surface without slipping or sliding backward (Tavakoli *et al.*, 2009).

Biochemical properties

Some phytochemical in cocoa beans

Cocoa contains about three hundred and eighty (380) known chemicals, ten (10) of which are psychoactive compounds. It is a rich source of dietary polyphenols. Cocoa polyphenols have been reported in many studies as bioactive compounds, with antioxidant properties (Lettieri-Barbato *et al.*, 2012). In their natural state, cocoa beans are virtually inedible because of their high concentration of polyphenols, which gives them an extremely bitter flavor. Cocoa beans are naturally tart and acidic. So, this powder, which is a very concentrated part of the cocoa bean, is acidic with a pH of about 5.5. Cocoa powder is a favorite of many pastry chefs because of its intense chocolate flavor. Cocoa powder's acidity is an advantage since it causes the proteins in baked goods to set rapidly (Rusconi and Conti, 2010). Fermentation of cocoa beans prior to drying affects the pH, titratable acidity and total polyphenols. The majority of wineries measure sugar as total

soluble solids (TSS) in degrees Brix and converted to Baume units. One unit of Baume is equivalent to 1.8 degrees Brix. TA indicates the total amount of organic acids in solution and the pH relates to the free hydrogen ions in solution indicating the alkaline/acidity balance (Taubert *et al.*, 2007).

Health benefits of cocoa phytochemicals

Cocoa contains a high level of flavonoids, specifically epicatechin, which is reported to have beneficial cardiovascular effects on health. Prolonged intake of raw cocoa has been linked to cardiovascular health benefits. It is believed also that the consumption of flavanol-rich cocoa improves blood flow and this may help to achieve health benefits in hearts and other organs. Foods rich in cocoa appear to also reduce blood pressure (Taubert *et al.*, 2007).

Proximate Compositions

Ash

Ash is what remains after the food is burned. It consists primarily of elements, including calcium, phosphorous, iron, zinc and selenium. Typically, ash content is in the range of 5 percent to 8 percent on a dry-matter basis. Though not really a nutrient as such, an entry for *ash* is sometimes found on nutrition labels. There have been some concerns that too much ash may contribute to feline urological syndrome in domestic cats.

Carbohydrate

Carbohydrates are a class of natural organic substances which includes sugars, starch and cellulose. Total sugars comprise of sucrose, fructose, glucose, mannitol and inositol (Asiedu, 1991). The sucrose concentration of the unfermented beans generally comprised about 90% of the total sugars (2.4-8.0%), whereas both fructose and glucose made up to 6%, other sugars were found to be less than 4%.

Fat

Cocoa is not fat free. Cocoa beans has a high fat content of about 45-55%. The variation in the fatty acid composition in cocoa beans may be caused by ambient temperatures at which cocoa beans are grown. Other factors that may affect the composition may include edaphic factors and shading. The fat from cocoa is particularly used in cosmetics, pharmaceutical industries (Asiedu, 1991).

Protein

There are two types of proteins in cocoa, namely, albumin and globulin and these are usually classified according to their solubility and electrophoretic mobility. Proteins are a significant component of cocoa beans, both in quantity and they play a role in the development of flavour precursors (Wright *et al.*, 1982).

Fermentation

At the end of pod breaking fermentation begins. Fermentation is done the same day the pods are broken. It is normally done in six days. The importance of cocoa fermentation is to develop chocolate precursors in the bean. The cocoa bean itself does not undergo fermentation but the pulp surrounding it (Wood and Lass, 1985). Cocoa fermentation is a spontaneous process and occurs in two stages.

Anaerobic phase (Stage 1)

This occurs within the first two days when the pulp does not allow air circulation. Yeast and lactic acid bacteria fermentations occur in this phase. Yeast fermentation transforms pulp sugar into alcohol and lactic acid resulting in an increase in temperature. The pulp then breaks down, drains away and air penetrates the beans.

Aerobic phase (Stage 2)

This occurs from day three onwards and aeration allows strong growth of acetobacteria which transform alcohol to acetic acid. Temperature then increases up to 50 °C. Acetic acid penetrates into the bean causing the formation of chocolate flavour precursors. At the end of fermentation the temperature reduces causing the growth of putrefaction bacteria and prolonged fermentation will result in the development of hammy, off-flavour typical of over-fermented cocoa.

Drying of Cocoa

At the end of fermentation, drying begins. Drying is done the same day fermentation ends. Drying is the reduction of moisture in fermented beans from about 55% to 7%. After fermentation, the beans are carried to the drying area and spread thinly on raised mats. The beans are stirred frequently to pick out germinated, flat and black beans, placenta and foreign materials, There are two methods of drying – sun drying and mechanical drying. Sun drying is best for good quality beans. There is also the oxidation (browning) of polyphenols resulting in the reduction of astringency and bitterness. The beans are dry when they produce a 'cracking' sound after pressing them lightly in the fist. Drying is not stop until the beans are well dried. The minimum period of drying is 7 days. Well fermented and well dried beans are brown in colour (CRIG, 2010).

Whole cocoa bean

The most useful and valuable part of the crop is the bean. Cocoa beans are the seeds of the tree *Theobroma cacao*. Each seed consists of two cotyledons (the nib) and a small embryo, all enclosed in a skin (the shell). The food store consists of fat, known as cocoa butter, which amounts to about half the weight of the dry seed. The quantity of fat depends on the variety of cocoa and the environmental conditions.

Cocoa nib

The nib of the cocoa bean is the seed part of the bean which is free from cocoa bean shell. Cocoa processing is basically a means of converting the cocoa

beans into nib. The cocoa bean has chocolate smell. Typical analytical data ranges for chemical components of cocoa nib are: fat content of 48 to 57%; theobromine content of 0.8 to 1.3%; caffeine content of 0.1 to 0.7%; ash content of 2.6 to 4.2%; and water content of 2.3 to 3.2% (Aregheore, 2002).

Cocoa bean shell

The cocoa bean shell is a dry, crisp, slightly fibrous brown husk with a pleasant odour resembling that of chocolate. The fibre content is equivalent to medium quality grass hay in feeding value. When the shell is removed, it may contain 2-3% of an unseparated cocoa nib. The shell that covers the cocoa bean is used as mulching material on the farm in some countries. After conventional drying, the shell of the bean comprises about 12 to 15% of the weight of the bean, while the nib and residual moisture amounts to approximately 85 to 88%. Studies showed cocoa shell to be a useful ingredient in cattle feeding (Aregheore, 2002).

Plate 2.1 depicts the three morphological regions of the cocoa bean.



Plate 2.1: Morphological parts of the cocoa bean

CHAPTER THREE

EFFECTS OF MOISTURE CONTENT ON SOME PHYSICAL PROPERTIES OF TWO VARIETIES OF COCOA BEANS

Introduction

Physical properties are characteristics of a food material which are independent of the observer, measurable and define the state of the material. Singh *et al.* (2004) stated that data on physical properties are important in the design of a specific machine or analysis of the behaviour of products in order to perform various post-harvest operations.

It has been reported that knowledge of physical properties and their dependence on the moisture content are useful for the design and development of methods and equipment (Aviara *et al.*, 1999). The authors further noted that the optimum performance of machines could be achieved at a specific range of moisture content. Moisture content has a great influence in threshing, separation, cleaning and grading operations.

Principal axial dimensions of barley grain are useful in selecting sieve separators and in calculating grinding power during size reduction. They can also be used to calculate surface area and volume of grains, which are important during modelling of grain drying, aeration, heating, and cooling. Particle density, bulk

density, and porosity play an important role in the design of silos and storage bins, separation from undesirable materials, sorting and grading (Tavakoli *et al.*, 2009).

It is indicated that the major moisture-dependent physical properties of biological materials are size and shape, mass, crushing strength, bulk density, porosity, filling and emptying angle of repose and coefficient of friction (Visvanathan *et al.*, 1996). These properties have been investigated for jack bean seeds (Eke *et al.*, 2007). Bart-Plange and Baryeh (2003) also investigated some of these properties of category B cocoa beans.

Despite the increasing interest in cocoa little is known on the basic physical characteristics of the ‘Amelonado’ and ‘Hybrid’ cocoa varieties. However, some physical properties of category B cocoa beans have determined by Bart-Plange and Baryeh (2002). In order to design post-harvest handling such as categorization of the cocoa beans and processing machines for these varieties of cocoa, it is necessary to determine the effect of moisture content variation on their physical characteristics. Therefore, this research was designed to evaluate and compare some selected physical properties of two varieties of cocoa beans ‘Amelonado’ and ‘Hybrid’ at different moisture contents. The two varieties of cocoa beans were carefully selected due to the preference of the ‘Tafo Hybrid’ to the obsolete ‘Amelonado’ variety. These properties include size and shape, bean mass, 1000 bean mass, sphericity, particle density, bulk density, porosity, angle of repose and coefficient of static friction.

Materials and methods

In Ghana, there are three different types of cocoa grown. They include the ‘Amazonia’, ‘Amelonado’ and ‘Hybrid’ cocoa. The ‘Hybrid’ cocoa is the most important type that is grown and consumed. The ‘Hybrid’ pods from which the cocoa seeds are obtained for nursing is highly recommended by the Cocoa Research Institute of Ghana (CRIG). The ‘Hybrid’ pods are crosses between parent clones of desirable qualities made on a commercial scale in specially prepared fields called seed gardens under the upkeep of the Seed Production Unit (SPU). In this study the ‘Amelonado’ and ‘Tafo Hybrid’ cocoa bean types were used.

Raw materials and experimental location

The ‘Hybrid’ cocoa pods were obtained from the seed gardens of SPU located at Saamang while the ‘Amelonado’ types were harvested from Aiyinasi both towns in the Western Region of Ghana. After storage for two days the pods were taken to a central point at Kejebil-Takoradi for fermentation and drying. The dried beans were taken to the Quality Control Division of the Ghana Cocoa Board at Kejebil-Takoradi for grading into various categories. Both ‘Amelonado’ and ‘Hybrid’ cocoa beans used for this research fell in Category H also known as Super Main Crop. Sample selection was randomized all through the study. After the categorization the beans were taken to the laboratory situated at Technology Village of the School of Agriculture, University of Cape Coast for the investigations.

Determination of moisture content

Having followed the procedure detailed by ASAE, (1999) initial moisture contents of 5.6 and 6.8 % (wb) for ‘Amelonado’ and ‘Hybrid’ varieties were arrived at, respectively. Three bean samples each weighing 5 g from each variety were oven dried at 105 °C for 24 hours. The samples were cooled in a desiccator, reweighed and the weight loss of samples was recorded. The average moisture content on wet basis was calculated using Eq.2.1. In order to attain the desired moisture levels for the study, samples were conditioned by drying or rewetting with a calculated amount of distilled water. The desired moisture contents for lesser values were obtained by drying to attain a sample mass given by the expression:

$$M_f = M_i \left[\frac{100 - m_i}{100 - m_f} \right] \quad (3.0.1)$$

Those of higher moisture levels were prepared by adding distilled water as calculated from the following equation:

$$M_w = M_i \left[\frac{m_f - m_i}{100 - m_f} \right] \quad (3.0.2)$$

Where: M_f is the mass of water added in g; M_i is the initial mass of the sample in g; m_i is the initial moisture content of the sample in % wb; m_f is the final moisture content in % wb and M_w is the mass of water removed.

The samples were then poured into separate zip lock bags which were tightly sealed. The samples were kept at 5°C in a refrigerator for a week to enable the moisture to distribute uniformly throughout the sample. Before starting a test, the required quantity of the bean was taken out of the refrigerator and allowed to equilibrate to the room temperature for 2 h (Singh and Goswami, 1996; Coskun *et*

al. 2006). All the physical properties of the beans were determined at four moisture levels in the range of 6.0%, 12.0%, 18.0% and 24.0% (wb) with four replications at each moisture content.

Experimental procedures

The experiment to determine the physical properties of the varieties of cocoa beans were conducted using a completely randomized design at four moisture levels. The following methods were used in the determination of some selected physical properties of the cocoa bean.

Size and shape

The axial dimensions such as length (L), width (W) and thickness (T) of the beans which are shown in Plate 3.1 and Fig. 3.0.1 were determined using a digital micrometer screw gauge with 0.001mm sensitivity. Ten beans each were randomly selected from 10 sub-samples, each containing 100-beans. Bean size was determined by measuring the principal dimensions of the selected beans labeled 1 to 100. The digital micrometer was controlled when it made contact with a seed in order to minimize compression. Several researchers including Galedar *et al.* (2008) and Milani *et al.* (2007) have measured these dimensions for other grains and seeds in a similar manner.



Plate 3.1.: Axial dimensions of a cocoa bean

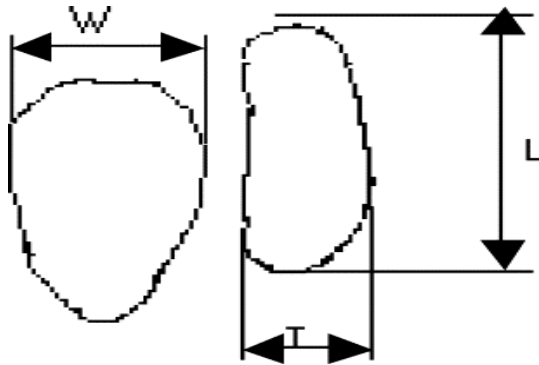


Fig. 3.0.1. Axial dimensions of cocoa beans

From the average of the axial dimensions the geometric mean diameter D_g , arithmetic mean diameter D_a , radii of curvature R , sphericity \emptyset and surface area S , were determined by using the following mathematical expressions:

The geometric mean diameter, D_g was determined using the relation given by Sharma *et al.* (1985) as:

$$D_g = (WTL)^{0.333} \quad (3.0.3)$$

Where L , W and T are the major (length), intermediate (width) and minor (thickness) diameters of the bean, respectively.

The arithmetic mean diameter, D_a was calculated based on the equation given by Mohsenin (1986):

$$D_a = \frac{(W + T + L)}{3} \quad (3.0.4)$$

The degree of sphericity, \emptyset was calculated according to the relation established by Mohsenin (1978) stated below:

$$\emptyset = \frac{(WTL)^{0.333}}{L} \quad (3.0.5)$$

On the other hand, the formula given by Jain and Bal (1997) was adopted in determining the sphericity, \emptyset :

$$\emptyset = \left[\frac{B(2L - B)}{L^2} \right]^{0.333} \quad (3.0.6)$$

Therefore, deducing from Eq. 3.0.3 and 3.0.5 the following relation was arrived at and also used in establishing sphericity, \emptyset :

$$\emptyset = \frac{D_g}{L} \quad (3.0.7)$$

The surface area, S as stated by Jain and Bal (1997) was determined from the following expression:

$$S = \frac{\pi BL^2}{(2L - B)} \quad (3.0.8)$$

Where $B = \sqrt{(WT)}$

The surface area, S was also found by using the McCabe, Smith and Harriott (1986) relation stated below:

$$S = \pi D_g^2 \quad (3.0.9)$$

Bean mass and 1000-bean mass

Five samples each of 1000-beans which were at the moisture content of 6%, 12%, 18% and 24% wb, were randomly selected and weighed on an electronic

balance having accuracy of 0.001g. The total mass obtained at each moisture content was divided by 1000 to obtain the bean mass.

The mass of 1000-beans for each variety of same category was obtained by counting 1000 beans for the desired moisture content, weighed on an electronic balance and replicated four times. The weights were averaged to obtain the 1000-bean mass. Other researchers have used similar methods including Gharibzahedi *et al.* (2010) and Tavakoli *et al.* (2009).

Particle and bulk densities

For the particle density, 100 beans were picked at random from each variety sample and the mass determined. Methanol was poured into a measuring cylinder and the volume recorded. The beans were then immersed to displace methanol in the measuring cylinder. The particle density was found as an average of the ratio of the mass of beans to the volume of methanol displaced by the beans. Methanol is preferred to water because it is absorbed by the beans to a lesser extent. Its surface tension is low so that it fills even shallow dips in a bean and its dissolution power is low. This method has been used by Abano and Amoah (2012) for tiger nut.

Bulk density is the ratio of the mass of beans sample to its total volume. The bulk density was determined by using the standard test weight procedure. This was achieved by filling a predefined container of 1000 ml with cocoa beans from the height 0.15m at a constant rate and the top leveled. No separate or additional manual compaction was done. Weighing of the empty 1000 ml volume container with electronic balance preceded the filling of the container with beans. The total

weight of beans and container was recorded. The bulk density was determined as the ratio of the measured mass of the beans only to the volume occupied by the beans (volume of container) at each moisture level. Four (4) replications were done and the average was taken. Several researchers used similar procedure including Bart-Plange and Baryeh (2002) for category B cocoa beans.

Porosity

The porosity is the proportion of air or void space in the beans which is not occupied by the bean, usually expressed in percentage. The porosity of the beans was calculated from the values of the particle and bulk densities obtained by the following equation according to Mohsenin (1978).

$$\varepsilon = \left[\frac{\rho_p - \rho_b}{\rho_p} \right] 100 \quad (3.1.0)$$

Where; ε is the porosity, ρ_p is the particle density, and ρ_b the bulk density.

Angle of repose

The filling or static angle of repose is the angle formed with horizontal surface at which the beans will stand when piled. To determine the filling angle of repose, a cardboard measuring 200mm in diameter (placed on a horizontal surface as depicted in Fig. 3.0.2) was used and the beans were allowed to fall from a height of 150mm to form a natural heap. The angle of repose was taken to be the arctangent of the ratio of height of the conical heap to the diameter of the cone.

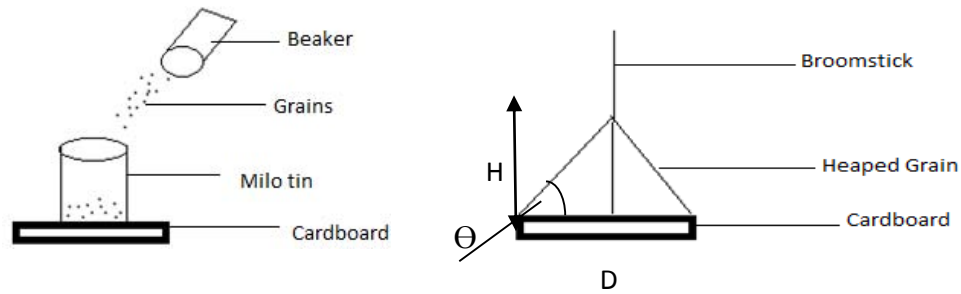


Fig. 3.0.2. Apparatus and experimental set up for determining angle of repose

The height and diameter of the heap were measured and the angle of repose was calculated as:

$$\theta = \tan^{-1} \frac{2H}{D} \quad (3.1.1)$$

Where; H is the height of the conical heap (mm), D is the diameter of plywood (mm) and θ is the angle of repose.

Coefficient of static friction

The coefficient of static friction was obtained by filling a PVC cylinder of 100mm diameter and 50mm height with the beans and placed on the friction surface. The cylinder was pulled up slightly (3mm) to avoid contact between it and the friction surface. The friction surface was part of a special construction, which is hinged at one end so that it can be lifted gradually at the unhinged end by means of a bolt and nut arrangement. The angle at which the beans just began to slide down was recorded as the static angle of friction between the beans and the friction surface. Abano and Amoah (2012) and Dutta *et al.*, (1988) have used this method for other grains. The coefficient of static friction was subsequently found as:

$$\mu = \tan \theta \quad (3.1.2)$$

Where μ = coefficient of static friction θ = angle of tilt of table

Results and discussion

Table 3.1 shows the summarized results of the physical properties of ‘Hybrid’ and ‘Amelonado’ cocoa beans. The mean values for the length, width, thickness, arithmetic mean diameter and geometric mean diameter were determined as 22.065 mm, 12.482 mm, and 8.510 mm, 14.353 mm and 13.176, and 21.834 mm, 12.415 mm, 8.345 mm, 14.198 mm and 12.026 mm for ‘Hybrid’ and ‘Amelonado’ cocoa beans, respectively. The results that the bean shape and size of ‘Hybrid’ cocoa are larger than those of ‘Amelonado’ cocoa bean. The mean particle density and bulk density of ‘Amelonado’ cocoa beans were 920.748 kg/m³ and 611.313 kg/m³, respectively. The mean particle density and bulk density of ‘Hybrid’ cocoa beans were 987.515 kg/m³ and 646.633 kg/m³, respectively.

3.1 Summary of physical properties of Hybrid and Amelonado cocoa beans

Variety	Property	N	Mean	S.D.	Min. Value	Max. Value	
Hybrid	Length	100	22.065	± 0.143	21.773	22.414	
	Width	100	12.482	± 0.040	12.377	12.571	
	Thickness	100	8.510	± 0.071	8.383	8.710	
	AMD	100	14.353	± 0.082	14.196	14.565	
	GMD	100	13.176	± 0.076	13.044	13.377	
	Bean mass	4	1.297	± 0.013	1.270	1.332	
	1000-Bean mass	4	1290.46	± 22.62	1242.05	1345.34	
	Porosity	4	34.33	± 3.578	26.3	41.4	
	Angle of repose	4	30.4	± 2.121	25.2	34.6	
	Particle density	4	987.515	± 17.84	946.21	1028.31	
	Bulk density	4	646.633	± 23.73	602.37	697.11	
	<i>Coefficient of static friction on various surface</i>						
		Plywood	4	0.841	± 0.128	0.577	1.111
		Steel	4	0.744	± 0.130	0.488	1.000
	Glass	4	0.672	± 0.145	0.364	0.966	
	Rubber	4	0.302	± 0.033	0.231	0.384	
Amelonado	Length	100	21.834	± 0.111	21.636	22.073	
	Width	100	12.415	± 0.017	12.236	12.536	

Thickness	100	8.345	± 0.117	8.004	8.533
AMD	100	14.198	± 0.062	14.086	14.375
GMD	100	12.026	± 0.068	12.906	13.216
Bean mass	4	1.189	± 0.028	1.139	1.257
1000-Bean mass	4	1188.37	± 27.96	1133.236	1261.41
Porosity	4	33.175	± 4.336	21.8	42.1
Angle of repose	4	32.275	± 1.912	27.9	36.5
Particle density	4	920.748	± 31.27	831.30	974.15
Bulk density	4	611.313	± 19.11	563.90	649.86
<i>Coefficient of static friction on various surface</i>					
Plywood	4	0.884	± 0.100	0.675	1.150
Steel	4	0.756	± 0.110	0.577	1.072
Glass	4	0.697	± 0.110	0.488	1.000
Rubber	4	0.346	± 0.036	0.268	0.424

Where: N is the number of samples, S.D. is the standard deviation, Min. is minimum Max. is maximum value, AMD is the arithmetic mean diameter and GMD is the geometric mean diameter.

Size and shape

Table 3.2 display the mean values of the principal dimensions, arithmetic and geometric mean diameters, and bean and 1000-bean masses of the ‘Hybrid’ and ‘Amelonado’ cocoa beans (category H) obtained in the study. ANOVA results showed that the difference among moisture levels were statistically significant at the 5% level of probability for the three principal dimensions of each variety. Generally, the ‘Hybrid’ had the longest average bean length of 22.172 mm and width of 12.593 mm, while ‘Amelonado’ recorded the longest average bean thickness of 9.096 mm. Fig. 3.0.3 shows the effects of moisture content on the dimensional ratios. The ratio of length to thickness, L/T, shows the highest ratio, followed by the length to width, L/W for both varieties. The ratios did not seem to have appreciable increase with increase in moisture content. Similar characteristics were observed by Bart-Plange and Baryeh (2002) for category B cocoa beans.

Table 3.2: Some physical properties of ‘Hybrid’ and ‘Amelonado’ cocoa beans

Variety	MC (% wb)	L (mm)	W (mm)	T (mm)	D _g (mm)	D _a (mm)	Bean Mass (g)	1000-Bean Mass (g)
‘Hybrid’	6.1	21.901	12.488	8.383	13.152	14.257	1.270	1242.046
	12.1	22.204	12.571	8.710	13.412	14.495	1.286	1267.646
	18.1	21.773	12.377	8.438	13.116	14.196	1.299	1306.630
	24.1	22.172	12.593	8.510	13.310	14.425	1.332	1345.342
‘Amelonado’	6.1	21.636	12.236	8.386	13.012	14.086	1.139	1133.236
	12.1	21.655	12.366	9.096	13.420	14.372	1.145	1158.880
	18.1	22.073	12.520	8.533	13.276	14.375	1.215	1199.962
	24.1	21.971	12.536	8.004	12.981	14.170	1.257	1261.406

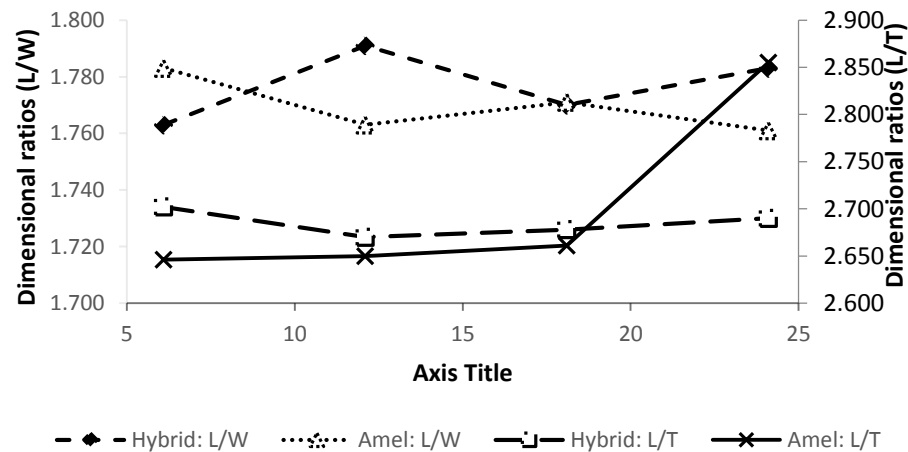


Fig. 3.0.3. Effect of moisture content on dimensional ratios

Bean mass

The effect of bean mass of ‘Hybrid’ (category H) and ‘Amelonado’ (category H) cocoa beans is graphically depicted in Fig. 3.0.4. The bean mass increased significantly at 5% level of probability from average values of 1.270g to 1.332g and 1.139g to 1.257g for ‘Hybrid’ and ‘Amelonado’ cocoa beans respectively within corresponding moisture content range of 6.1 to 24.1% (wb). Similarly, the difference between the bean mass values of the two varieties were statistically significant at the level of 0.05. The following linear regression equations describe the relationship between the bean mass (B_m) and moisture content wet basis percent (m) for each variety, and the regression coefficient of the best fit:

$$B_m = 0.0033m + 1.2467 \quad (\text{‘Hybrid’}: R^2 = 0.9525)$$
$$B_m = 0.0071m + 1.0823 \quad (\text{‘Amelonado’}: R^2 = 0.9233)$$

The ‘Hybrid’ cocoa beans had higher values than the ‘Amelonado’ cocoa beans and this may be due to the higher moisture absorbing capacity of the ‘Hybrid’ cocoa beans. Both varieties exhibited linear relationship with increasing moisture variation. It has also been found by the following researchers that there exist linear relations: Tavakoli *et al.* (2009) for barley grains and Gharibzahedi *et al.* (2010) for black cumin. The bigger dimensions of ‘Hybrid’ as compared to those of ‘Amelonado’ confirm the predominance of ‘Hybrid’ in cocoa industry of Ghana.

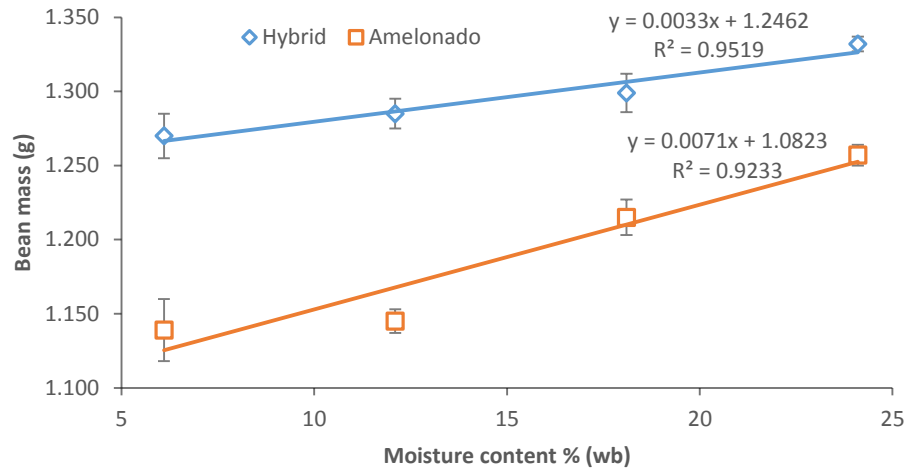


Fig. 3.0.4. Effect of moisture content on bean mass for both varieties

1000-bean mass

The effect of moisture content on 1000-bean mass is shown in Fig. 3.0.5. The 1000-bean mass increased linearly with the moisture content in all the varieties under investigation. The 1000-bean mass increased linearly with the moisture content in all the varieties under investigation. Generally, the 1000-bean mass of ‘Hybrid’ changed in the range between 1242.046 to 1345.342 g at a moisture content range of 6.1 to 24.1% (wb). On the other hand, the 1000-bean mass of ‘Amelonado’ ranged from 1133.236 to 1261.406 g at a moisture content range of 6.1 to 24.1% (wb). The difference among the bean mass values of the two varieties were statistically significant at the level of 0.01. The 1000-bean mass of bambara groundnuts, coffee, and sunflower showed similar linearly increasing variation with moisture content as found by Baryeh (2001); Chandrasekar *et al.* (1999), and Gupta

and Das (1997). The variation of 1000-bean mass with moisture content for ‘Hybrid’ and ‘Amelonado’ can be expressed, respectively as follows:

$$1000_m = 5.8145m + 1202.6 \quad (R^2 = 0.9657)$$

$$1000_m = 7.0932m + 1081.3 \quad (R^2 = 0.9657)$$

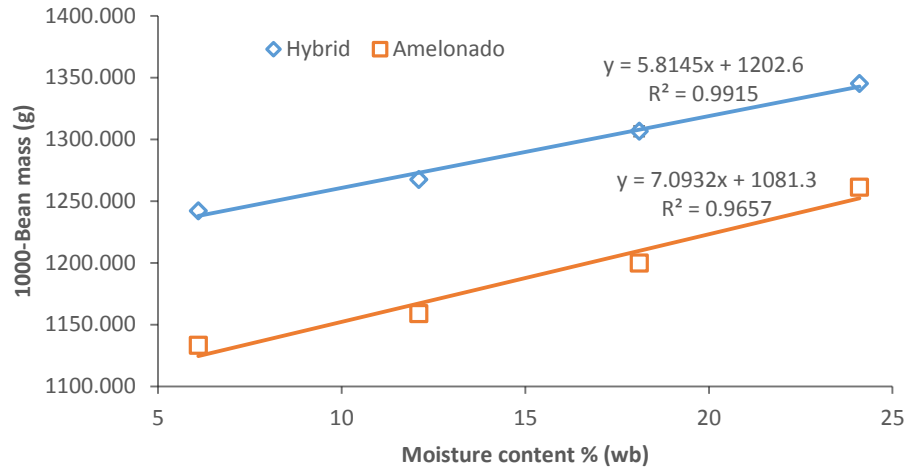


Fig. 3.0.5. Effect of moisture content on 1000-bean mass.

Particle and bulk densities

The particle density of beans of different varieties under different levels of moisture content is shown graphically in Fig. 3.0.6. It was seen that the particle density of the beans from both varieties increased with moisture content. The particle density at 6.1 to 24.1% (wb) of both ‘Hybrid’ and ‘Amelonado’ beans linearly increased (probability < 0.05) from 946.21 to 1028.31 kg/m³ and 831.30 to 974.15 kg/m³, respectively. The ‘Hybrid’ beans displayed a higher particle density than the ‘Amelonado’ cocoa beans. A similar trend was observed by Bart-Plange and Baryeh (2002) for category B cocoa beans. It could be deduced from the results

that the beans are likely to have high terminal velocities making pneumatic separation from lighter particles very feasible. A relationship between the particle density of the varieties and the moisture content can be represented by the following equations:

$$\rho_p = 4.605m + 917.98 \quad (\text{'Hybrid': } R^2 = 0.9991)$$

$$\rho_p = 7.4988m + 807.52 \quad (\text{'Amelonado': } R^2 = 0.8628)$$

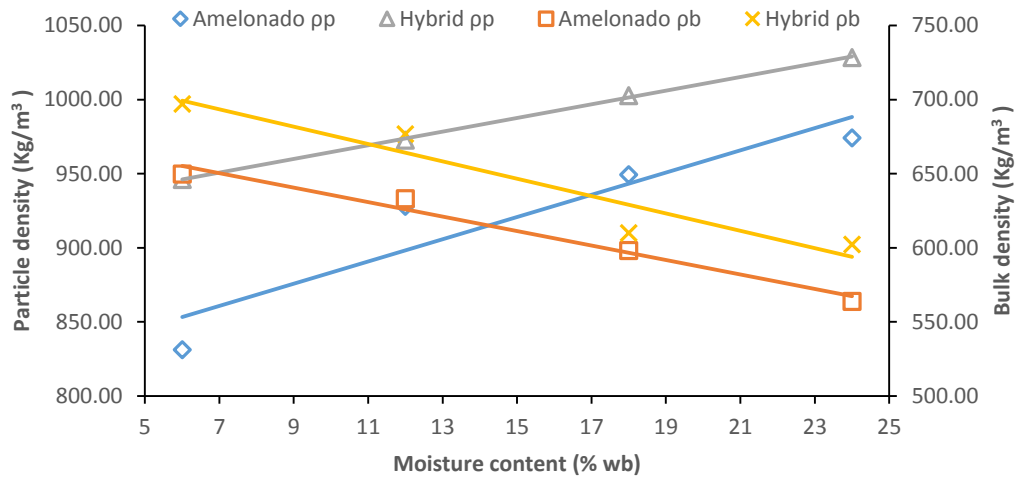


Fig. 3.0.6. Effect of moisture content on particle and bulk densities.

Fig. 3.0.6 also shows the variation of bulk density with bean moisture content. The average values of the bulk density for ‘Hybrid’ and ‘Amelonado’ beans decreased linearly from 697.11 to 602.37kg/m³ and 649.86 kg/m³ to 563.90 kg/m³ respectively, with an increase in moisture content from 6.1 to 24.1% (wb). The values were significantly different at the 5% level of probability. This can be attributed to the fact that an increase in mass owing to moisture gain in the bean sample was lower than the accompanying volumetric expansion of the bulk. A

relationship between the bulk density of bean and the moisture content was developed and is provided below. It is seen that the bulk density has a negative linear relationship with moisture content. A correlation coefficient for the proposed model ('Hybrid': R^2 value = 0.9119 and 'Amelonado': R^2 value = 0.978) indicates that the model has good fit.

$$\rho_b = -5.8495m + 734.96 : \text{'Hybrid'}$$

$$\rho_b = -4.8805m + 685.01 : \text{'Amelonado'}$$

A similar decreasing trend in bulk density has been reported by Bart-Plange and Baryeh (2002) for category B cocoa beans, and Tunde-Akintunde and Akintunde (2007) for beniseed. These observed discrepancies could be due to the cell structure, volume and mass increase characteristics of the grains and seeds as moisture content increases. The implication may be that the shells absorptivity of moisture is high and it has a reducing effect on the bulk density.

Sphericity

The variation of sphericity with bean moisture content is displayed in Fig. 3.0.7. From the graph, Eq. 3.0.6 gives higher values of bean sphericity than Eq. 3.0.5 for both varieties. This may be probably due to the shape assumption for the two equations. The bean sphericity ranges from 0.895 to 0.897 using Eq. 3.0.6, and 0.599 to 0.604 using Eq. 3.0.5 in the moisture content range of 6.1 to 24.1% (wb). Similarly, the bean sphericity ranges from 0.890 to 0.904 using Eq. 3.0.6, and 0.591 to 0.620 using Eq. 3.0.5 in the moisture content range of 6.1 to 24.1% (wb). The

moisture content did not have significant effect on the sphericity of both varieties. Both showed the same performance under Eq. 3.0.5 and same performance using Eq. 3.0.6. The shape of the bean is more close to Eq. 3.0.6 than Eq. 3.0.7 because this equation is for grains which are elongated like an ellipse, while Eq. 3.0.6 is for non-elongated grains. The mean sphericity for both varieties indicated that the bean shape ('Hybrid': 0.601 ± 0.001 , 'Amelonado': 0.600 ± 0.003) is quite far from the shape of a sphere and that the moisture content does not significantly affect the bean sphericity. This, therefore, means that a sieving or separating machine with circular holes will not easily let beans through. This shows that the bean will always not roll when it is on a particular orientation. This property is useful in the design of hoppers and de-hulling equipment for the beans.

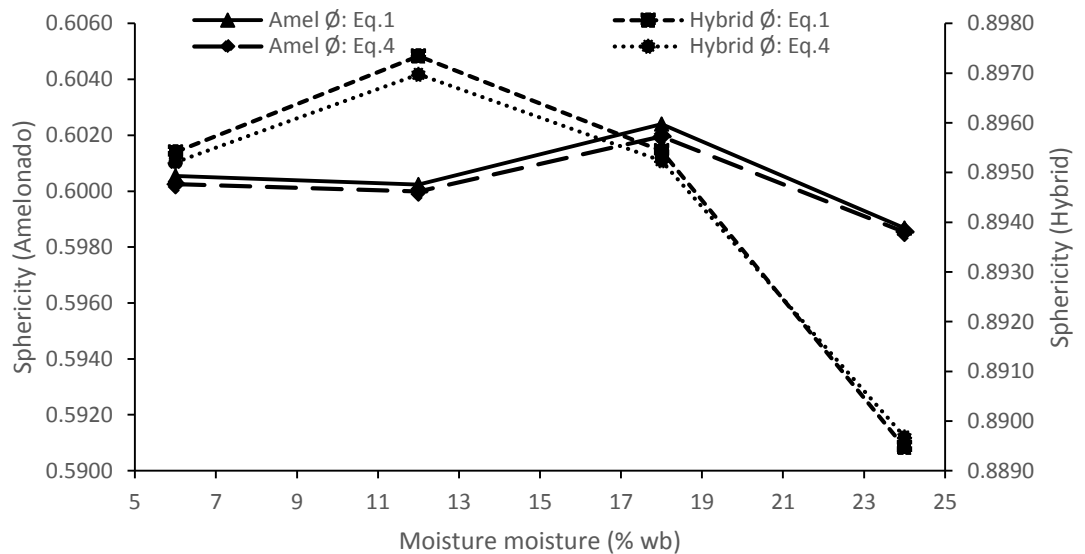


Fig. 3.0.7. Variation of sphericity with moisture content

Porosity

The porosity of cocoa beans of different varieties under different levels of moisture content is shown graphically in Fig. 3.0.8. This property is required for the flow of air and heat in agricultural material. This shows how easily a stream of heated air blown to dry a substance will pass through a pack of material and therefore affect the rate of drying of the material. The bean with low porosity will dry very slowly. From the graph it was seen that the porosity of the bean increased linearly with increase in moisture content for both varieties. The porosity increased significantly at 1% level of probability from 26.3 to 41.4 % and 21.8 to 42.1 % for ‘Hybrid’ and ‘Amelonado’ varieties respectively as the moisture content increased from 6% to 24% wb. (Fig. 3.0.8). The increase could be due to a decrease in the cohesion of the cell structure of the beans as a result of an increase in moisture content. The variation of porosity with moisture content for ‘Hybrid’ and ‘Amelonado’ can be expressed, respectively as follows:

$$\varepsilon = 0.9017m + 20.71 \quad (\text{Hybrid: } R^2 = 0.9526)$$

$$\varepsilon = 1.1017m + 16.54 \quad (\text{Amelonado: } R^2 = 0.9685)$$

Bart-Plange and Baryeh (2002) reported similar results for category B cocoa beans. However, this observation was contrary to Tunde-Akintunde and Akintunde (2007) who reported decrease in porosity with increase in moisture content for beniseed. Less number of beans can be stored at high moisture content than low moisture content when porosity is high at high moisture content due to increase in inter-bean voids when the porosity is high. In general, ‘Hybrid’ cocoa beans recorded higher average values of porosity as compared to the ‘Amelonado’ beans.

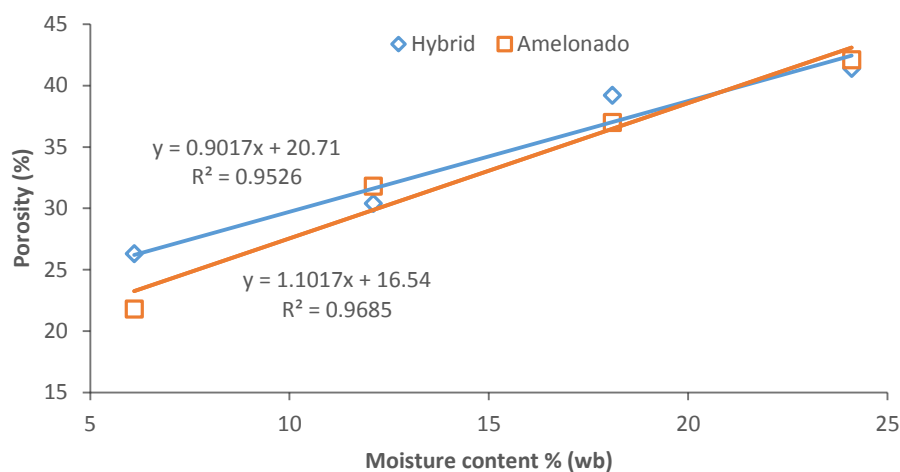


Fig. 3.0.8. Variation of porosity with moisture content.

Angle of repose

Fig. 3.0.9 shows how the filling angle of repose varies with moisture content. The angle of repose increased linearly with the moisture content in all the varieties under investigation. It revealed a significant difference ($p < 0.05$) between the average value of ‘Hybrid’ and ‘Amelonado’ varieties. Between moisture content of 6.1 to 24.1% (wb), the filling angle of repose increased significantly at the 1% level of probability for ‘Hybrid’ beans with values ranging from 25.2° to 34.6° . As moisture content increased from 6 to 24% (wb) for ‘Amelonado’ beans a linear increment at 1% level of probability was observed from 27.9° to 36.5° . Amin *et al.* (2004) and Razari *et al.* (2007) recorded increase in the angle of repose for lentil seeds and for wild pistachio nut and its kernel respectively, as moisture content increased. This property is needed in determining the minimum slope of

flow in self emptying bin or hoppers. ‘Amelonado’ cocoa bean exhibits higher values than that of ‘Hybrid’ cocoa beans, which may be due to the differences in the sizes since smaller sizes can interlock more to cause a higher heap formation than relatively bigger sizes. The relationship between the moisture content and the filling angle of repose may be expressed as:

$$\theta_f = 0.54m + 22.246 \quad (\text{‘Hybrid’}: R^2 = 0.972)$$

$$\theta_f = 0.4917m + 24.851 \quad (\text{‘Amelonado’}: R^2 = 0.9924)$$

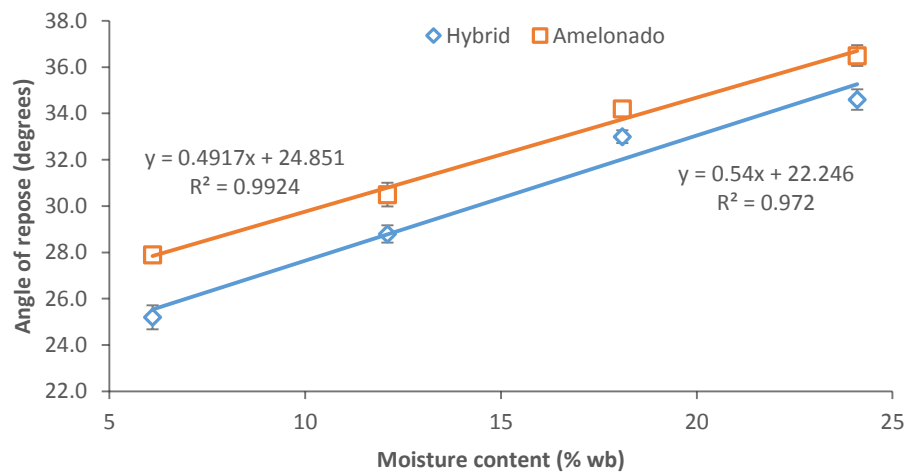


Fig. 3.0.9. Effect of moisture content on angle of repose.

Coefficient of static friction

Plywood

The variation of frictional co-efficient against moisture content for plywood surface is given in Fig. 3.1.0 for both ‘Hybrid’ and ‘Amelonado’ cocoa beans. The co-efficient of static friction increased linearly (probability < 0.05) from 0.577 to

1.111 and 0.675 to 1.150 for ‘Hybrid’ and ‘Amelonado’ cocoa beans respectively as moisture content increased from 6.1 to 24.1% wet basis correspondingly. It also revealed a significant difference ($p < 0.05$) between the average value of ‘Hybrid’ and ‘Amelonado’ varieties. The co-efficient of static friction showed a positive linear correlation with moisture content for both varieties with the relation:

$$\mu_{plywood} = 0.0321m + 0.3558 \quad (\text{‘Hybrid’}: R^2 = 0.9500)$$

$$\mu_{plywood} = 0.0253m + 0.5025 \quad (\text{‘Amelonado’}: R^2 = 0.9550)$$

It was observed that the friction offered was less for ‘Hybrid’ cocoa beans than for ‘Amelonado’ cocoa beans at all moisture content but for 12.1% (wb) moisture content. The reason for the increases in friction co-efficient on a plywood surface at higher moisture content may be due to the water present in the bean that causes the beans to become rougher offering a cohesive force on the surface of contact in both cases. The difference in sizes as well as rougher surface development could also account for the reason why ‘Amelonado’ cocoa beans show higher frictional values than ‘Hybrid’ cocoa beans. This was similar to the co-efficient of friction on plywood which also increased linearly for coffee and black cumin grains as moisture content increased as reported by Chandrasekar et al. (1999) and Gharibzahedi et al. (2010).

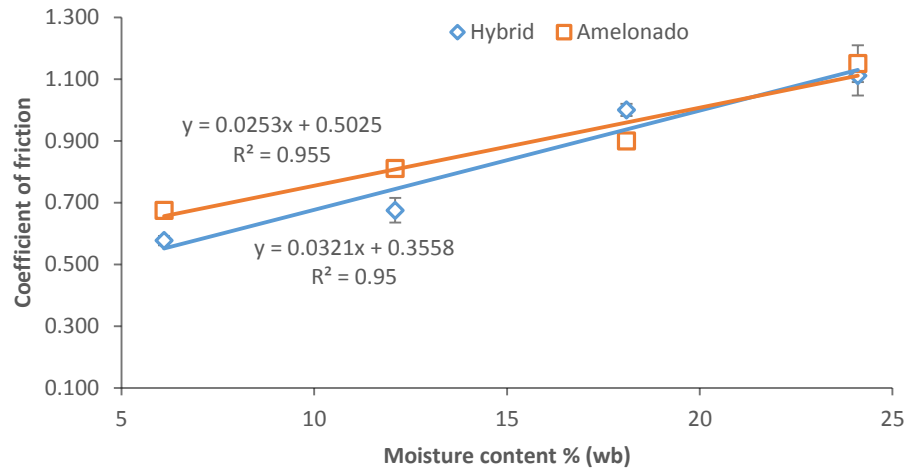


Fig. 3.1.0. Effect of moisture content on coefficient of friction on plywood.

Steel

The values of the co-efficient of static friction observed for mild steel between a moisture content of 6.1 to 24.1% (wb) for ‘Hybrid’ cocoa bean was 0.488 to 0.1.000 ($p < 0.05$) while that of ‘Amelonado’ cocoa bean was 0.577 to 0.1072 ($p < 0.05$). This is depicted graphically in Fig. 3.1.1 where both varieties show an increase in their frictional coefficient, linearly, on mild steel with increasing moisture content. However, ‘Amelonado’ cocoa bean possesses higher frictional co-efficient of static frictions than ‘Hybrid’ cocoa bean. The co-efficient of static friction of cocoa beans (‘Hybrid’ and ‘Amelonado’) may be represented by the following relationship with the corresponding moisture content:

$$\mu_{steel} = 0.0319m + 0.2618 \quad (\text{‘Hybrid’}: R^2 = 0.9037)$$

$$\mu_{steel} = 0.0261m + 0.3629 \quad (\text{‘Amelonado’}: R^2 = 0.8472)$$

The reason for the increasing friction co-efficient at higher moisture content may be due to the reduction of pore space inside the particle heap as the particle sizes were reduced. The difference in sizes (weight) and differences in surface characteristics could also account for the reason why ‘Amelonado’ cocoa bean shows higher frictional values than that of ‘Hybrid’ cocoa bean. Chandrasekar et al. (1999) found a linear relation between moisture content and the co-efficient of static friction for coffee on mild steel.

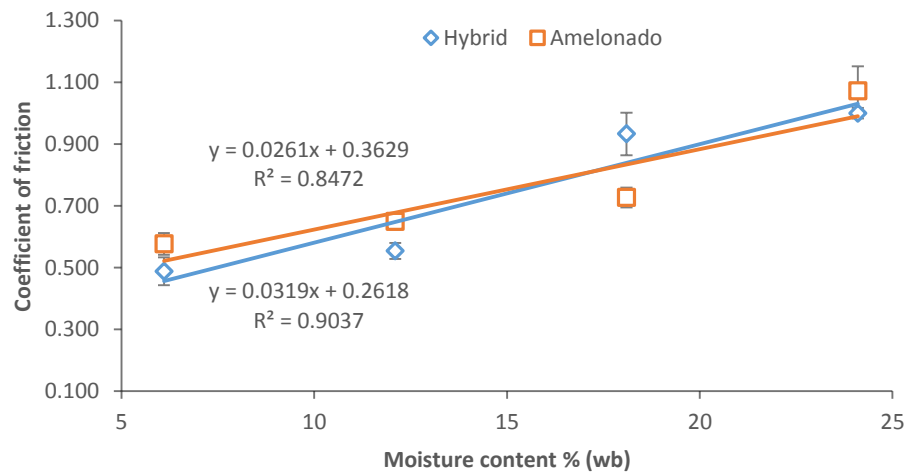


Fig 3.1.1. Effect of moisture content on coefficient of friction on steel.

Glass

The variation of frictional co-efficient against moisture content for glass surface is given in Fig. 3.1.2 for both ‘Hybrid’ and ‘Amelonado’ cocoa beans. The co-efficient of static friction increased linearly ($p < 0.05$) from 0.364 to 0.966 and 0.488 to 1.000 for ‘Hybrid’ and ‘Amelonado’ cocoa beans respectively as moisture content increased from 6.1 to 24.1% (wb) correspondingly. It also revealed a

significant difference ($p < 0.05$) between the average value of ‘Hybrid’ and ‘Amelonado’ varieties. The co-efficient of static friction showed a positive linear correlation with moisture content for both varieties with the relation:

$$\mu_{glass} = 0.0365m + 0.1214 \quad (\text{‘Hybrid’}: R^2 = 0.9417)$$

$$\mu_{glass} = 0.0273m + 0.2858 \quad (\text{‘Amelonado’}: R^2 = 0.9236)$$

The friction offered was less for ‘Hybrid’ cocoa beans than for ‘Amelonado’ cocoa beans at all moisture contents. This behavior may be due to the reduction of pore space inside the particle heap as the particle sizes were reduced. The difference in sizes as well as rougher surface development could also account for the reason why ‘Amelonado’ cocoa beans show higher frictional values than ‘Hybrid’ cocoa beans. Davies and El-Okene (2010) reported similar trend for soybeans.

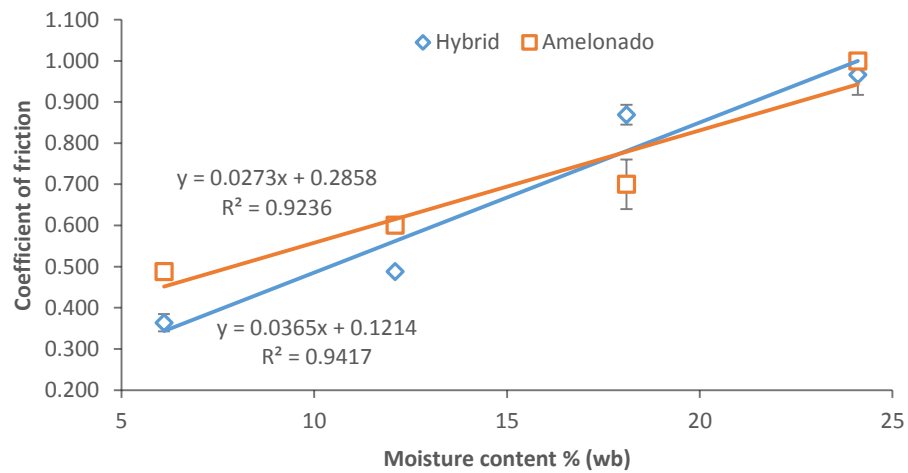


Fig. 3.1.2. Effect of moisture content on coefficient of friction on glass.

Rubber

Fig. 3.1.3 displays the effect of moisture content variations on coefficient of static friction on rubber. The static coefficient of friction increased linearly from 0.231 to 0.384 ($p < 0.05$) for ‘Hybrid’ cocoa beans and from 0.268 to 0.424 ($p < 0.01$) for ‘Amelonado’ cocoa beans in the corresponding moisture content range of 6.1 to 24.1% (wb) as depicted in Fig. 3.1.3. It, however, revealed a significant difference ($p < 0.05$) between the average value of ‘Hybrid’ and ‘Amelonado’ varieties. The effect of moisture content variations on coefficient of static friction on rubber for ‘Hybrid’ and ‘Amelonado’ can be expressed, respectively as follows:

$$\mu_{rubber} = 0.0086m + 0.1721 \quad (R^2 = 0.9898)$$

$$\mu_{rubber} = 0.0091m + 0.2081 \quad (R^2 = 0.9799)$$

It was observed that the friction offered was less for ‘Hybrid’ cocoa beans than for ‘Amelonado’ cocoa beans at all moisture content under investigation. Variations in the surface texture of the both varieties as well as the relatively smaller sizes of the ‘Amelonado’ variety might have accounted for this. The coefficient of static friction on rubber surface increased with increasing moisture content for lentil seeds, coffee and category B cocoa beans as reported by Carman, (1996), Chandrasekar and Visvanathan, (1999) and Bart- Plange and Baryeh, (2002). If a rubber surface is to be used for conveying cocoa beans, it will be advisable to roughen the surface to increase friction between the beans and the surface. On the other hand, discharging requires less friction to enhance the discharging process. In general, the values of the coefficient of static friction on the four (4) material surfaces obtained are used in the design of agricultural machine

hopper and other conveying equipment. It determine how a pack of grain or bean will flow in these systems.

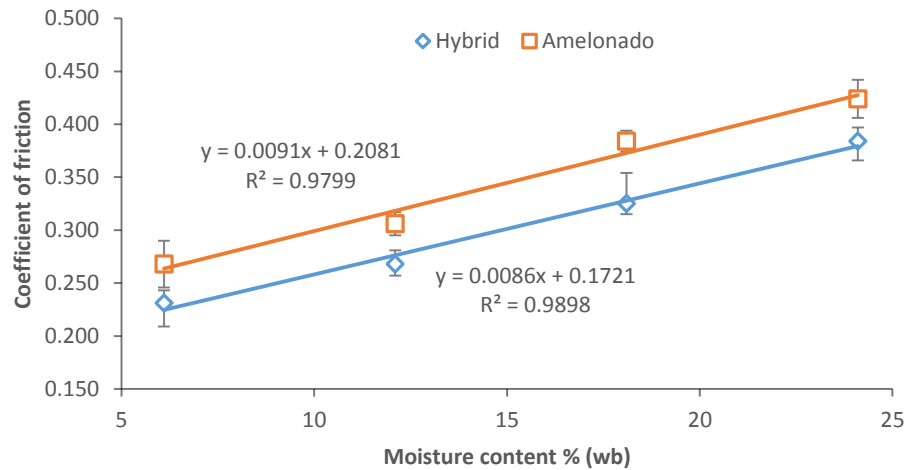


Fig. 3.1.3. Effect of moisture content on coefficient of friction on rubber.

Conclusions

This study was carried out to determine and to compare the physical properties of two varieties of cocoa beans ('Hybrid' and 'Amelonado') at four different levels of bean moisture contents (6.0, 12.0, 18.0, and 24.0% wb).

Conclusions are as follows:

1. In general, the principal dimensions increased with increasing moisture content. The mean principal dimensions increased slightly from 21.773 – 22.414 mm, 12.377 – 12.571 mm, and 8.383 – 8.710 mm for bean length, width, and thickness respectively, for 'Hybrid' cocoa beans. For 'Amelonado' cocoa beans, the mean principal dimensions increased slightly from 21.636 – 22.073 mm, 12.236 – 12.536

mm and 8.004 – 8.533 mm. The ‘Hybrid’ cocoa beans had higher values of principal dimensions as compared to the ‘Amelonado’ cocoa beans.

2. For the ‘Hybrid’ cocoa beans, the sphericity ranges from 0.599 to 0.602 using Eq. 3.0.9, and 0.894 to 0.896 using Eq. 3.0.6 in the moisture content range of 6.0 to 24.0% (wb). While the sphericity ranges from 0.591 to 0.605 using Eq. 3.0.5, and 0.890 to 0.897 using Eq. 3.0.6 for ‘Amelonado’ cocoa beans. The mean sphericity indicated that the bean shape (0.601 ± 0.01 for ‘Hybrid’ and 0.600 ± 0.003 for ‘Amelonado’) is quite far from the shape of a sphere and that the moisture content does not greatly affect the sphericity.
3. The bean mass increased linearly from 1.270 to 1.332g and 1.139 to 1.257g for ‘Hybrid’ and ‘Amelonado’ cocoa beans respectively with increase in the moisture content from 6.0 to 24.0% (wb).
4. The 1000-bean mass increased linearly from 1242.046 – 1345.342 g and 1133.236 – 1261.406 g for ‘Hybrid’ and ‘Amelonado’ cocoa beans respectively as moisture content increased from 6.0 – 24.0% (wb).
5. The average values of the particle density increased linearly from 946.21 kg/m³ to 1028.31 kg/m³ and 831.30 kg/m³ to 974.15 kg/m³ for ‘Hybrid’ and ‘Amelonado’ cocoa beans respectively with increase in moisture content.
6. The bulk density decreased linearly from 697.11 kg/m³ to 602.37 kg/m³ and from 649.86 kg/m³ to 563.90 kg/m³ with increase in moisture content for ‘Hybrid’ and ‘Amelonado’ cocoa beans respectively.

7. The porosity increased linearly with increasing moisture content from 26.3% to 41.4% and 21.8% to 42.1% for 'Hybrid' and 'Amelonado' cocoa beans respectively.
8. The filling angle of repose for 'Hybrid' cocoa beans increased linearly from 25.2 – 34.6° and that of 'Amelonado' cocoa beans also increased linearly from 27.9 – 36.5° between moisture content ranges of 6.0 – 24.0% (wb).
9. The coefficient of static friction increased linearly from 0.577 – 1.111, 0.488 – 1.000, 0.364 – 0.966 and 0.231 – 0.384 for plywood, steel, glass and rubber respectively for 'Hybrid' cocoa beans. For 'Amelonado' cocoa beans, a linear increment in coefficient of static friction from 0.675 – 1.150, 0.577 – 1.072, 0.488 – 1.000 and 0.268 – 0.424 was observed for plywood, steel, glass and rubber respectively. It was observed that the smoother the structural surface the lower the coefficient of friction of agricultural products.
10. The mean particle and bulk densities for both varieties are less than the density of water. This implies that both 'Hybrid' and 'Amelonado' cocoa beans will float in water. This makes it possible to separate them from materials that are denser than water.

CHAPTER FOUR

FRACTURE RESISTANCE OF COCOA BEAN AS A FUNCTION OF MOISTURE CONTENT, BEAN ORIENTATION AND VARIETY

Introduction

In processing operations like milling of foods mechanical force is applied. Cocoa beans like any other solid are deformed in proportion to the applied force. It is important to consider the types and the direction of forces involved during processing. In engineering design it is important to ensure that stresses in components do not exceed the strength of the agricultural materials (Gate, 2004). Knowledge of mechanical properties such as rupture force, deformation, energy, stress, strain and hardness is vital to engineers handling agricultural products. The study of mechanical properties of agricultural products under static or dynamic loading is aimed at textural measurement of unprocessed and processed food materials; the reduction of mechanical damage to agricultural produce during postharvest handling, processing, and storage; and the determination of design parameters for harvesting and postharvest systems. For instance, the hardness grains is an important feature of how they are processed for foods and feeds. (Morris *et al.*, 2011).

Basic information about the mechanical properties of cocoa beans are relevant in the design and construction of cocoa bean crushing machines. Several

studies have shown that mechanical properties are influenced by a number of factors including the variety, temperature, and moisture content (Shitanda *et al.*, 2002). Processing of cocoa bean into powder is greatly related to the external forces exerted on each bean between the attrition surfaces. A study of the correlation between the forces and orientation of the bean is needed for a better understanding of milling processes.

Simple compression tests are often termed uniaxial compression which means that the sample is compressed in one direction and is unrestrained in the other two dimensions. However some compression tests are performed in bulk where the sample is compressed in three dimensions. Several researchers have studied the mechanical properties of various food and biological materials such as wheat grains (Kalkan and Kara, 2011), pistachio nuts and kernel (Galedar *et al.*, 2009). Saiedirad *et al.*, (2008) reported an increase in the energy absorbed at seed rupture increased with increase in moisture content for quasi-statically loaded vertical and horizontal orientations, respectively, in their work involving small, medium, and large cumin seeds. Galedar *et al.*, (2009) studied the force required to cause deformation and subsequent rupture and crushing energy in pistachio nuts and kernel. It was reported that a nut breaking force and crushing energy varied when the nuts were compressed. The compression behaviour of agricultural materials does not obey the Hooke's law in the same way metals do. Example, Fig. 4.1 shows the force-deformation curve of an agricultural product. Most often in determining the mechanical properties of agricultural materials the rupture force,

energy, compressive stress and strain deformation, stiffness, Young's modulus are considered.

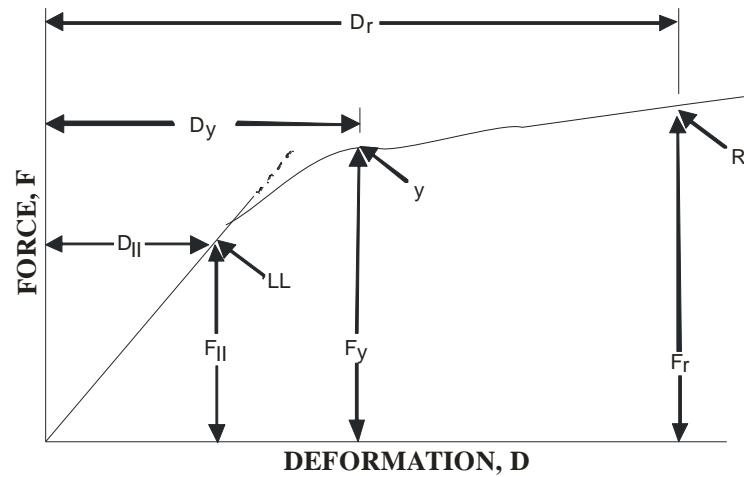


Fig. 4.1. Force-deformation curve for an agricultural product.

LL linear limit; y, “Bioyield point”; R, rupture point

Young's Modulus, being the stress per strain, gives an indication of the stiffness of a material within the limit of proportionality and therefore, the resistance to deformation under axial compression. Indeed Young's Modulus is more meaningfully defined for Hookean materials within the elastic region where it is constant (i.e. Young's modulus of elasticity). When the proportionality limit is exceeded, the modulus is no longer constant and the material deforms permanently until it eventually fractures. In food materials, apparent modulus is the more appropriate term to relate the stress to strain ratio as the stress-strain curve is not strictly linear and there is no single value for Modulus of Elasticity. The apparent modulus is expressed in terms of the secant or tangent modulus which are the apparent modulus of elasticity at a given point or the slope of the stress-strain curve at a given point on the curve, respectively (Sahin and Sumnu, 2006). In the food

industry, the modulus is commonly referred to as the stiffness, firmness or rigidity of the material (Rha, 1975).

This part of the research aimed to investigate the fracture resistance of two different varieties of cocoa beans ('Amelonado' and 'Hybrid') by examining the effect of moisture content, variety and bean orientation on rupture force, deformation at rupture point, energy absorbed, compressive stress, compressive strain, and apparent Young's modulus.

Materials and methods

Experimental location

The compression tests were conducted at the Department of Nutrition and Food Science, University of Ghana.

Determination of moisture content

Moisture content Moisture content was determined as recommended by the American Society of Agricultural Engineers (ASAE), (1999). This involves measuring the weight of sample before and after oven drying at temperature 105°C for 24 hours. The samples were cooled in a desiccator, reweighed and the weight loss of samples was recorded. The initial moisture content on wet basis was then estimated using Eq.3.1 and were found to 5.7 and 6.2 % for 'Amelonado' and 'Hybrid' cocoa beans respectively. The lower moisture content were obtained by drying to attain a sample mass using the expressions in Eq. 4.2. In order to attain

the desired moisture levels for the study, samples were conditioned by adding a calculated amount of distilled water based on Eq.4.3.

$$MC_{wb} = \frac{W_i - W_d}{W_i} * 100 \quad (4.1)$$

Where: MC_{wb} is the moisture content (% wb), W_i is the initial mass of sample (g) and W_d is the dried mass of sample (g).

In order to create an equal level of moisture content, 5 % (wb), the samples were evenly spread on raffia mat for sun drying at constant temperature of 34 °C until the desired moisture content of the samples was obtained. To attain the desired moisture levels for the study, samples were conditioned by drying or rewetting with a calculated amount of distilled water. The desired moisture contents for lower values were obtained by drying to attain a sample mass given by the expression:

$$M_f = M_i \left[\frac{100 - m_i}{100 - m_f} \right] \quad (4.2)$$

Whereas those of higher moisture levels were prepared by adding distilled water as calculated from the following equation:

$$M_w = M_i \left[\frac{m_f - m_i}{100 - m_f} \right] \quad (4.3)$$

Where: M_f is the mass of water added (g), M_i is the initial mass of the sample (g), m_i is the initial moisture content of the sample (% wb), m_f is the final moisture content (% wb) and M_w is the mass of water removed.

The samples were then poured into separate zip lock bags which were tightly sealed. The samples were kept at 5°C in a refrigerator for a week to enable the moisture to distribute uniformly throughout the sample. Before starting a test, the required quantity of the bean was taken out of the refrigerator and allowed to

equilibrate to the room temperature for 2 hours (Coskun *et al.*, 2006). All the physical properties of the beans were determined at five moisture levels in the range of 5.0–21.0% (wb) with four replications at each moisture content.

Experimental procedures

Preceding the uniaxial compression test, the average size of the cocoa beans was determined based on twenty randomly selected beans. To determine the size of the beans, four groups of samples consisting of twenty cocoa beans were randomly picked and their three axial dimensions namely, length (L), width (W) and thickness (T) were measured using a digital micrometer with 0.001mm sensitivity.

In determining the compressive properties of the cocoa bean under compression load, a biological material test device called TA-XT Plus texture analyzer (Stable Micro Systems, Godalming, UK) was used as shown in Fig. 3.2. This device, running with Exponent software is equipped with a 50-kg load cell and a stainless steel base plate. The compressive force was applied to the sample by a stainless disc plate (shown in Plate 4.1) at a constant crosshead speed of 0.5 mm/sec with an upper strain limit of 90% and a 0.2-N trigger force. Compression data curves were acquired at 200 points/sec and used to calculate all other stress vs. strain material properties. These and all other procedures followed those detailed by (Abano *et al.*, 2011).



Plate 4.1. TA-XT Plus Texture Analyser

For each treatment twenty beans were randomly selected and the average values of all the twenty tests were reported. In order to determine the effect of the orientation of bean against loading, the bean was positioned horizontally (Plate 4.2a), with the major axis of the bean lying normal to the direction of loading, or lengthwise. For vertical loading (Plate 4.2b), the major axis of the bean was parallel to (perpendicular to the stainless steel base plate) the direction of loading, or widthwise. The test was conducted on the cocoa beans at five moisture content levels - 5%, 9%, 13%, 17% and 21% (wb) .The mechanical properties of cocoa bean were determined in terms of maximum compressive stress, strain, apparent Young's modulus, axial deformation, rupture force (strength) and energy at horizontal and vertical orientations for two different varieties 'Amelonado' and 'Hybrid' using the following relations:

$$\sigma_c = \frac{F_r}{TL} \quad (4.4)$$

$$\varepsilon_c = \frac{L}{L_o} - 1 = \lambda - 1 \quad (4.5)$$

$$E = \frac{\sigma_c}{\varepsilon_c} \quad (4.6)$$

$$E_a = \frac{1}{2} F_r D_r \quad (4.7)$$

Where σ_c is the compressive stress (Nmm⁻²), F is the rupture force (N), L is the mean length (mm), T is the thickness (mm), ε_c is the compressive strain (mm/mm), L_o is the original length (mm), λ is the extension ratio, E is the apparent Young's modulus, E_a is the energy absorbed (J) and D_r is the deformation at rupture point (mm).



(a) Horizontal (bean length section)



(b) Vertical (bean width section)

Plate 4.2. Orientations of cocoa bean under compressive loading

Experimental design and statistical analysis of data

This study was carried out based on a 5×2^2 factorial design. The treatments (5 moisture contents, 2 varieties and 2 orientations) were planned and evaluated based on completely randomized design (CRD). The mean values, standard deviations and correlation coefficients of the rupture force, deformation and energy

absorbed were determined using Microsoft Excel 2013 (Microsoft Corp., USA) software program. While the effects of moisture contents, variety and orientation on the bean mechanical properties were investigated using analysis of variance (ANOVA) using GenStat Release 9.2 (Ninth Edition) software. A confidence interval of 95% was used for all analysis. Mean differences in the treatments were tested for significance using Fisher's Least Significant Difference (LSD). Where significant differences were observed, the Duncan Multiple Range Test (DMRT) was used to separate the means.

Results and discussion

The effect of bean moisture content on the axial dimensions of the two varieties of cocoa beans used for the compression test is shown in Table 3.2. Similar trends of increase in the average axial dimensions were noted by other researchers like (Asoiro, et al., 2011). This situation of average increase in the axial dimensions of the beans as moisture content increased stems from water absorption of the beans. The importance of these dimensions in the determination of sieve apertures in could not be overemphasised as discussed Heidarbeigi *et al.* (2009).

The results obtained from effects of the bean moisture content, orientation and variety on cocoa bean rupture force, deformation and energy absorbed are presented in Table 4.1. The amount of rupture force and deformation at rupture point for cocoa beans were directly obtained as a function of bean moisture content, orientation and variety.

Table 4.1 shows that the rupture force, deformation and energy absorbed values of the ‘Amelonado’ and ‘Hybrid’ varieties at horizontal and vertical orientations. It has been observed that as the bean moisture content increases the rupture force of both ‘Amelonado’ and ‘Hybrid’ varieties decreases for both horizontal and vertical orientations. However, the deformation at rupture point and energy absorbed increased as moisture content increased. The rupture force and energy absorbed for horizontal orientation were the highest for both varieties whilst the highest values for deformation was obtained at vertical orientation for both varieties. These properties may be useful in designing equipment for post-harvest handling and processing operations.

The results of ANOVA considering the interaction effects of moisture content, orientation and variety on the rupture force, energy and deformation of cocoa bean is presented in Tables 4.3, 4.4 and 4.5. As shown, the effects of moisture content, orientation and variety on the rupture force, energy and deformation of cocoa bean were significant ($P < 0.05$). Also, the interaction effects of moisture content \times orientation, moisture content \times variety, orientation \times variety, and moisture content \times orientation \times variety on the rupture force, energy and deformation were significant ($P < 0.05$).

Table 4.1. Compressive properties of two varieties of cocoa beans.

Variety	MC % wb	Compressive Parameters					
		Rupture Force (N)		Deformation (mm)		Energy Absorbed (J)	
		Horizontal	Vertical	Horizontal	Vertical	Horizontal	Vertical
Amelonado	5	110.895 (3.839)	65.354 (1.392)	1.102 (0.027)	1.202 (0.0290)	0.061 (0.002)	0.039 (0.001)
	9	94.258 (2.144)	56.324 (1.156)	1.389 (0.042)	1.453 (0.043)	0.065 (0.003)	0.041 (0.001)
	13	68.654 (1.496)	37.587 (1.021)	2.033 (0.062)	2.321 (0.055)	0.069 (0.002)	0.044 (0.002)
	17	53.854 (1.247)	24.853 (0.610)	2.658 (0.069)	3.654 (0.074)	0.072 (0.003)	0.045 (0.001)
	21	39.421 (1.014)	21.365 (0.189)	3.804 (0.105)	4.425 (0.087)	0.075 (0.002)	0.047 (0.001)
Hybrid	5	289.589 (9.119)	81.721 (1.378)	0.684 (0.014)	0.969 (0.011)	0.099 (0.004)	0.040 (0.001)
	9	234.897 (4.742)	65.528 (1.203)	0.986 (0.025)	1.401 (0.040)	0.116 (0.004)	0.046 (0.002)
	13	180.122 (3.207)	48.988 (1.032)	1.448 (0.034)	2.118 (0.060)	0.130 (0.004)	0.052 (0.002)
	17	141.102 (1.926)	35.619 (0.814)	2.001 (0.045)	3.095 (0.083)	0.141 (0.003)	0.055 (0.002)
	21	105.137 (1.041)	28.415 (0.521)	2.895 (0.067)	4.011 (0.094)	0.152 (0.004)	0.057 (0.001)

Figures in the parenthesis are standard deviation

Rupture force

Interactively, the rupture force decreased from 136.89 to 48.58 N as the moisture content increased ($P < 0.05$) (Table 4.3), with an average force of 89.18 N to rupture the bean. This could possibly due to the fact that at a higher moisture content the bean became softer and required less force. The beans became more sensitive to cracking at a higher moisture content; hence, they required less force to rupture. Altuntaş and Yildiz (2007) conducted a study on the effects of the moisture content on some physical and mechanical properties of faba bean (*Vicia faba L.*) grains and reported that, as the moisture content increased from 9.89% to 25.08%, the rupture forces ranged from 314.17 to 185.10 N; from 242.2 to 205.56 N; and from 551.43 to 548.75 N for X-, Y-, and Z-axes, respectively. Liu *et al.* (1990) reported a decrease in the rupture force values for soybean with increase in the moisture content, which is true for the present work, too. Similarly, Saiedirad *et al.* (2008) reported that as the moisture content increased from 5.7% to 15%, the rupture force decreased from 36.977 to 20.358 N.

Table 4.1, showed that the force required for initiating bean rupture for the ‘Amelonado’ variety decreased from 110.895 to 39.421 N and 65.354 to 21.365 N at horizontal and vertical orientations, respectively; while the rupture force for ‘Hybrid’ variety decreased from 289.589 to 105.137 N and 81.721 to 28.415 N at horizontal and vertical orientations, respectively as moisture content increased from 5% - 21% (wb). The required force to initiate the bean rupture in the case of ‘Hybrid’ variety was higher than that of the ‘Amelonado’ variety, at similar bean moisture content and orientation. The results also revealed that the bean rupture

force at horizontal orientation was higher than that of vertical orientation, for both the ‘Hybrid’ and ‘Amelonado’ varieties. This is could be due to the higher rupturing dimensional axis of the beans at vertical orientation. The forces required for initiating the bean rupture at different moisture contents and bean orientations for ‘Amelonado’ and ‘Hybrid’ varieties are shown in Fig 4.2a and 4.2b respectively. The interaction effect of moisture content and bean orientation on force required to initiate bean rupture for ‘Amelonado’ and ‘Hybrid’ varieties can be represented in the following equations:

$$F_r = -4.5838m + 133.01 \quad \text{Amelonado (Horizontal): } R^2 = 0.9887$$

$$F_r = -2.9862m + 79.918 \quad \text{Amelonado (Vertical): } R^2 = 0.9603$$

$$F_r = -11.567m + 340.55 \quad \text{Hybrid (Horizontal): } R^2 = 0.9901$$

$$F_r = -3.413m + 96.424 \quad \text{Hybrid (Vertical): } R^2 = 0.981$$

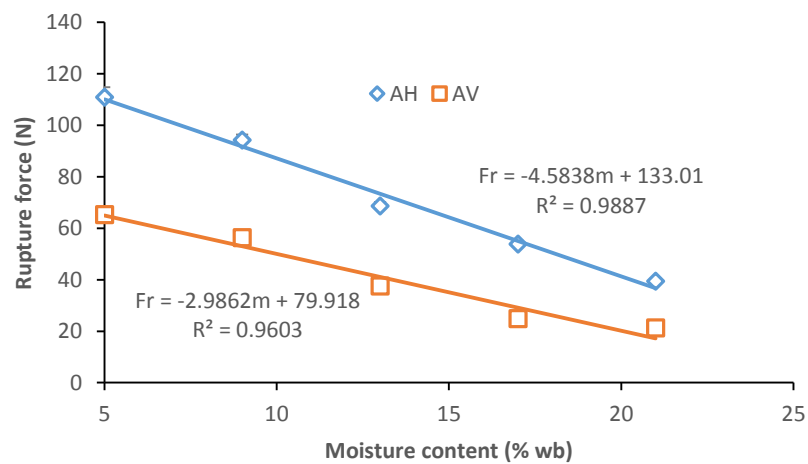


Fig. 4.2a. Interaction effect of moisture content and bean orientation on force required to initiate bean rupture for ‘Amelonado’ cocoa bean.

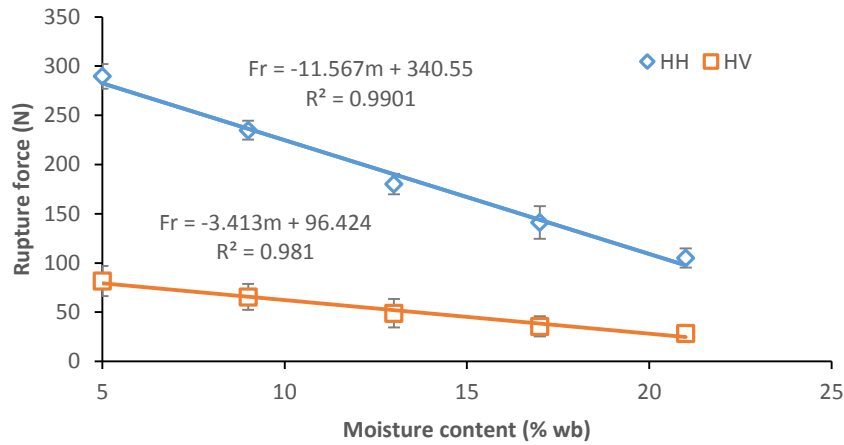


Fig. 4.2b. Interaction effect of moisture content and bean orientation on force required to initiate bean rupture for ‘Hybrid’ cocoa bean.

Energy absorbed

The energy absorbed by the bean before initiating its rupture in the case of ‘Amelonado’ variety was obtained lower than that of the ‘Hybrid’ variety, at same bean moisture content and orientation. The results also showed that the bean is more flexible and more resistant to rupturing in the horizontal direction of loading as compared to the vertical, for both varieties examined. During vertical loading, the bean area in contact with the compressing probes is smaller resulting in the expansion of high stress in the bean. Gupta and Das (2000) reported that sunflower seeds loaded in a vertical orientation absorbed more energy prior to rupture than those loaded in the horizontal orientation; while the sunflower kernels loaded in a vertical orientation required less energy to rupture than those loaded in the horizontal orientation. The results reported by Gupta and Das (2000) about the

effect of orientation on the energy absorption in the case of sunflower kernels were consistent with the findings in the current research.

The energy absorbed at bean rupture increased from 0.061 J at a moisture level of 5% (wb) to 0.075 J at a moisture level of 21% (wb) for ‘Amelonado’ variety in horizontal orientation and from 0.039 to 0.047 J in vertical orientation. On the other hand, the energy absorbed for the ‘Hybrid’ variety increased from 0.099 to 0.152 J and 0.040 to 0.057 J at horizontal and vertical orientations, respectively (Table 4.1). It is clearly seen that the energy absorbed by the cocoa beans increased with increase in bean moisture content for both varieties. This increase was significantly higher at horizontal orientation than vertical orientation for both varieties. This result means that in the case of horizontal orientation, the probe deforms the bean in the direction of the shorter axis of the bean, which has lower compression depth and therefore requires higher energy. The Effect of moisture content and bean orientation on energy absorbed by ‘Amelonado’ and ‘Hybrid’ varieties is shown in Fig. 4.3a and 4.3b respectively. The relationship between moisture content and bean orientation on energy absorbed was best described by a linear function with a very high correlation coefficients as shown below.

$$E_a = 0.0009m + 0.0572 \qquad \text{Amelonado (Horizontal): } R^2 = 0.9945$$

$$E_a = 0.0005m + 0.0367 \qquad \text{Amelonado (Vertical): } R^2 = 0.9804$$

$$E_a = 0.0033m + 0.085 \qquad \text{Hybrid (Horizontal): } R^2 = 0.9901$$

$$E_a = 0.0011m + 0.036 \qquad \text{Hybrid (Vertical): } R^2 = 0.9531$$

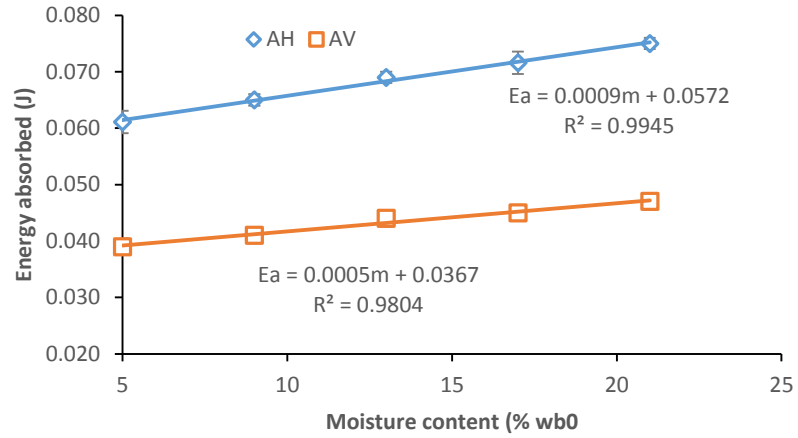


Fig 4.3a. Effect of moisture content and bean orientation on energy absorbed by 'Amelonado' cocoa bean.

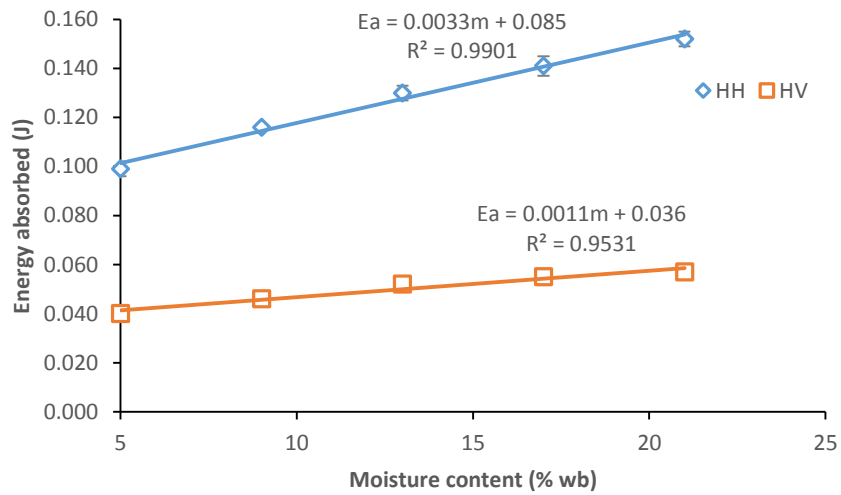


Fig 4.3b. Effect of moisture content and bean orientation on energy absorbed by 'Hybrid' cocoa bean.

Deformation

Cocoa beans and other Agricultural materials deform in response to the applied forces. The amount of force and energy needed to produce a given

deformation can be used to study the damage which occurs during compressive handling. Knowledge about this gives insight into the specific circumstances that lead to failure (i.e. breaking or milling).

It is observed that the deformation at rupture point increased as the moisture content increased ($P < 0.05$) for both varieties either at horizontal or vertical orientation (Table 4.5). Generally, the average deformation at rupture point was obtained as 2.1842 mm/mm varying from 0.9893 to 3.7836mm/mm. Specifically, Table 4.1 showed that deformation increased from 1.102 - 3.804 mm and 1.202 - 4.425 mm at horizontal and vertical orientations, respectively for the 'Amelonado' variety; while the deformation for 'Hybrid' variety increased from 0.684 - 2.895 mm and 0.969 - 4.011 mm at horizontal and vertical orientations, respectively as moisture content increased from 5% - 21% (wb). The energy absorbed at bean rupture was a function of both force and deformation up to rupture point. At low moisture content, the bean requires high force to rupture and its deformation was low but at high moisture content, the rupture force was low and the deformation was high. It could be deduced, from this that during compressive loading energy absorbed at bean rupture increases as the moisture content of the bean increases indicating high resistance. The results suggest that the 'Amelonado' is softer as compared to the 'Hybrid' and therefore the 'Amelonado' required a higher compression depth than the 'Hybrid' beans. The Relationship between moisture content and bean orientation on deformation of 'Amelonado' and 'Hybrid' cocoa beans is shown in Fig. 4.4a and 4.4b. The trend of the variation illustrates that as moisture content increases, the deformation of the bean also increased. In a study by Kalkan and

Kara (2011) the deformation at rupture point of wheat grains was found not to show any regular variation with the moisture content. However, Altuntas and Yildiz (2007) studied the deformation in faba bean grain and reported that specific deformation increased with moisture content along the X-, Y-, and Z-axes, respectively. The experimental values of the ‘Amelonado’ and ‘Hybrid’ varieties as a function of between moisture content and bean orientation on deformation were correlated using the regression equations:

$$D_r = 0.0009m + 0.0572 \quad \text{Amelonado (Horizontal): } R^2 = 0.9945$$

$$D_r = 0.0005m + 0.0367 \quad \text{Amelonado (Vertical): } R^2 = 0.9804$$

$$D_r = 0.0033m + 0.085 \quad \text{Hybrid (Horizontal): } R^2 = 0.9901$$

$$D_r = 0.0011m + 0.036 \quad \text{Hybrid (Vertical): } R^2 = 0.9531$$

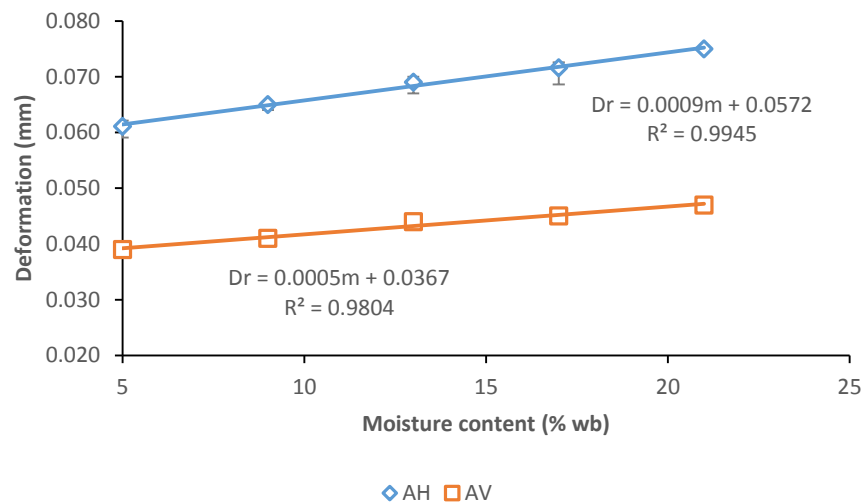


Fig 4.4a. Relationship between moisture content and bean orientation on deformation of ‘Amelonado’ cocoa bean.

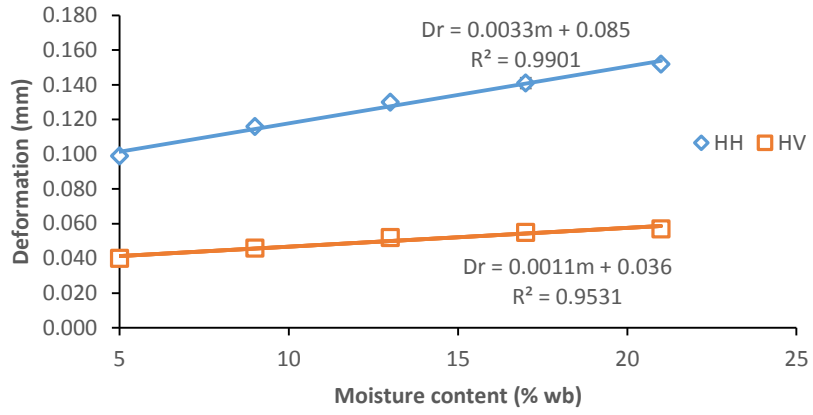


Fig. 4.4b. Relationship between moisture content and bean orientation on deformation of 'Hybrid' cocoa bean

Table 4.2. Other Compressive properties.

Variety	MC % wb	Compressive Parameters					
		Compressive Stress (Nmm ⁻²)		Compressive Strain (mm/mm)		Apparent Modulus (Nmm ⁻²)	
		Horizontal	Vertical	Horizontal	Vertical	Horizontal	Vertical
Amelonado	5	0.685 (0.010)	0.404 (0.018)	0.080 (0.094)	0.088 (0.078)	0.080 (0.015)	0.088 (0.031)
	9	0.569 (0.015)	0.340 (0.006)	0.101 (0.091)	0.105 (0.075)	0.101 (0.086)	0.105 (0.054)
	13	0.389 (0.001)	0.213 (0.004)	0.143 (0.024)	0.165 (0.057)	0.143 (0.064)	0.165 (0.032)
	17	0.297 (0.002)	0.137 (0.002)	0.187 (0.049)	0.258 (0.058)	0.187 (0.014)	0.258 (0.014)
	21	0.214 (0.001)	0.116 (0.002)	0.267 (0.070)	0.310 (0.065)	0.267 (0.041)	0.310 (0.104)
Hybrid	5	1.673 (0.015)	0.472 (0.045)	0.049 (0.057)	0.069 (0.031)	0.049 (0.031)	0.069 (0.021)
	9	1.317 (0.014)	0.367 (0.011)	0.070 (0.086)	0.099 (0.044)	0.070 (0.054)	0.099 (0.031)
	13	1.001 (0.124)	0.272 (0.013)	0.102 (0.191)	0.149 (0.067)	0.102 (0.014)	0.149 (0.056)
	17	0.764 (0.010)	0.193 (0.008)	0.139 (0.129)	0.215 (0.088)	0.139 (0.087)	0.215 (0.014)
	21	0.565 (0.101)	0.153 (0.012)	0.200 (0.085)	0.277 (0.045)	0.200 (0.055)	0.277 (0.032)

Figures in the parenthesis are standard deviations

Compressive stress, strain and apparent Young's modulus

Table 4.2 shows that the compressive stress, compressive strain and apparent Young's modulus values of the 'Amelonado' and 'Hybrid' varieties at horizontal and vertical orientations. It was observed that as the bean moisture content increased the experimental values of compressive strain for both 'Amelonado' and 'Hybrid' varieties increased at both horizontal and vertical orientations. However, compressive stress and apparent Young's modulus values for both varieties decreased as the moisture content increased from 5% to 21% (wb) at both horizontal and vertical loading orientations. It was noted that the highest values for compressive stress and apparent Young's modulus were obtained for horizontal orientation for both varieties. These properties may be useful in designing equipment for postharvest handling and processing operations.

The analysis of variance (ANOVA) of the data (Tables 4.6, 4.7 and 4.8) indicated that the moisture content, orientation and variety exerted a significant effect on the compressive stress, compressive strain and apparent Young's modulus ($P < 0.05$). Likewise, the interaction effects of moisture content \times orientation, moisture content \times variety, orientation \times variety, and moisture content \times orientation \times variety on the compressive stress, compressive strain and apparent Young's modulus were significantly different at $P = 0.05$ level.

Compressive stress

The ANOVA Table 4.6 showed that the compressive stress decreased from 0.8085 to 0.2620 Nmm⁻² as the moisture content increased ($P < 0.05$) with an average value of 0.50703 Nmm⁻². Fig. 4.5 illustrate the effect of moisture content and bean orientation on the compressive stress of ‘Amelonado’ and ‘Hybrid’ varieties of cocoa bean. Table 4.2 showed that the experimental values of compressive stress decreased from 0.685 - 214 Nmm⁻² and 0.404 - 0.116 Nmm⁻², and 1.673 - 0.565 Nmm⁻² and 0.472 - 0.153 Nmm⁻² for ‘Amelonado’ and ‘Hybrid’ varieties at both horizontal and vertical orientations, respectively when moisture content increased from 5% - 21% (wb). Similar decreasing trend was observed with moisture increase in the determination of the strength for filbert nut and kernel (Pliestic *et al.*, 2006) African nutmeg (Burubai *et al.*, 2007), barley grains that were quasi-statically loaded in horizontal and vertical orientations (Tavakoli *et al.*, 2009). Gereke and Niemz (2010) also, reported a decrease in the compressive stress of cross laminated solid wood panels in the moisture range of 10 to 13% (wb). The influences of bean moisture content and orientation on the compressive stress were well expressed by the following equations, which had high correlation coefficients.

$$\sigma_c = -0.0304m + 0.8254 \quad \text{Amelonado (Horizontal): } R^2 = 0.9801$$

$$\sigma_c = -0.0195m + 0.4952 \quad \text{Amelonado (Vertical): } R^2 = 0.9543$$

$$\sigma_c = -0.0692m + 1.9635 \quad \text{Hybrid (Horizontal): } R^2 = 0.9858$$

$$\sigma_c = -0.0203m + 0.5553 \quad \text{Hybrid (Vertical): } R^2 = 0.9762$$

The decreasing trend of compressive stress might have been caused by the interactions between the starch and protein matrix in the cocoa beans. These inherent properties of the cocoa beans may have decreased the toughness of the beans as the moisture content increased. The decrease of compressive stress, and increase of deformation of the cocoa bean as the moisture content increased support the hypothesis that the energy absorption capability of wet cocoa bean is higher than the dry ones leading to higher mechanical strength to rupture during the compressive loading (Saiedirad *et al.*, 2008). Fig. 4.5 illustrates the effect of moisture content and bean orientation on the compressive stress of ‘Amelonado’ and ‘Hybrid’ varieties of cocoa bean.

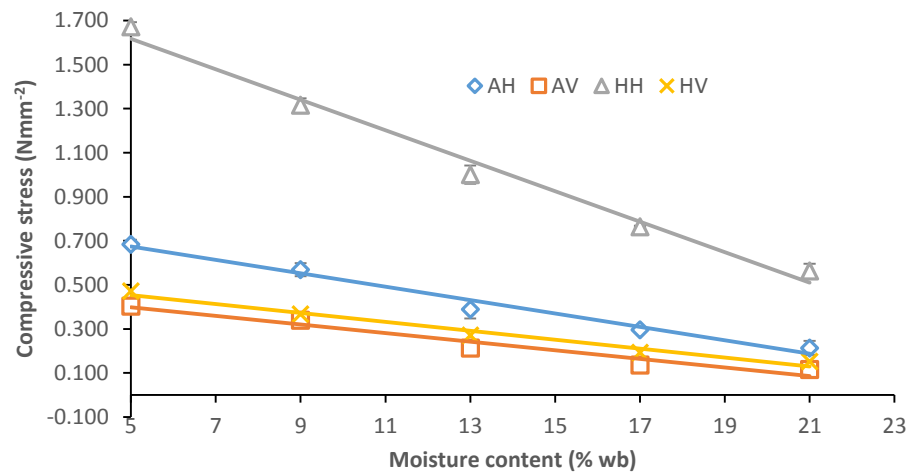


Fig 4.5. Effect of moisture content and bean orientation on compressive stress of ‘Amelonado’ and ‘Hybrid’ cocoa beans.

Compressive strain

Analysis of variance test (Table 4.7) indicates that the compressive strain significantly differed at the various moisture levels. Similarly, significant difference existed between ‘Amelonado’ and ‘Hybrid’ varieties. Likewise significant difference between horizontal and vertical orientations existed. The relationship between moisture content and bean orientation on compressive stress for ‘Amelonado’ and ‘Hybrid’ cocoa beans are shown in Fig. 4.6. The mean values for ‘Amelonado’ and ‘Hybrid’ varieties increased as moisture content increased. The compressive strain of the ‘Amelonado’ increased from 0.080 mm/mm at a moisture content of 5% (wb) to 0.267 mm/mm at a moisture content of 21% (wb) at horizontal orientation and from 0.088 to 0.310 mm/mm at vertical orientation. Similarly, the compressive strain for the ‘Hybrid’ variety increased from 0.049 to 0.200 mm/mm and 0.069 to 0.277 mm/mm at horizontal and vertical orientations, respectively at the same moisture content range. The mean compressive strain values of the ‘Hybrid’ variety were lesser than that of the ‘Amelonado’. The relationship between compressive strain and moisture content was found to be significant at 0.05. However, the increase in compressive strain was better explained by a linear relationship.

$$\varepsilon_c = 0.0115m + 0.0063 \quad \text{Amelonado (Horizontal): } R^2 = 0.9508$$

$$\varepsilon_c = 0.0149m - 0.009 \quad \text{Amelonado (Vertical): } R^2 = 0.9602$$

$$\varepsilon_c = 0.0093m - 0.0086 \quad \text{Hybrid (Horizontal): } R^2 = 0.962$$

$$\varepsilon_c = 0.0133m - 0.0106 \quad \text{Hybrid (Vertical): } R^2 = 0.9818$$

The increasing trend of compressive strain may have been caused by the interactions between the starch and protein matrix in the cocoa beans. These inherent properties of the cocoa beans may have increased the toughness of the beans as the moisture content increased. The increase of compressive strain, and increase of deformation capability of the cocoa bean as the moisture content increased support the hypothesis that the energy absorption capability of wet cocoa bean is higher than the dry ones leading to higher.

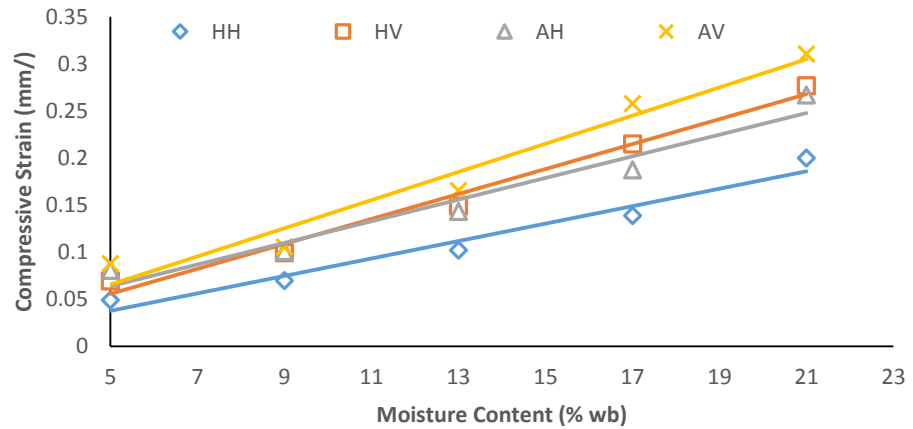


Fig. 4.6. Effect of moisture content and bean orientation on compressive strain of ‘Amelonado’ and ‘Hybrid’ cocoa beans.

Apparent Young's modulus

The variation of apparent Young's modulus considering the influence of moisture content and bean orientation is shown in Fig. 4.7. Increasing the moisture content increased the apparent Young's modulus linearly with a at probability level of 5% (Table 4.8). The mean values of the apparent Young's modulus of the 'Amelonado' variety respectively increased from 0.080 Nmm⁻² to 0.267 Nmm⁻² and 0.088 Nmm⁻² to 0.310 Nmm⁻² at a moisture content range 5% - 21% (wb) at horizontal and vertical orientations. Similarly, the mean values of the apparent Young's modulus for the 'Hybrid' variety decreased from 0.049 to 0.200 Nmm⁻² and 0.069 to 0.277 Nmm⁻² at horizontal and vertical orientations, respectively at the same moisture content range. A reported study by Delwiche (2000) suggests a similar decrease in apparent modulus as wheat kernel moisture content increased. The regression equations between cocoa bean moisture content and bean orientation on apparent Young's modulus were as shown below.

$$E = -0.4874m + 10.191 \quad \text{Amelonado (Horizontal): } R^2 = 0.9333$$

$$E = -0.279m + 5.6326 \quad \text{Amelonado (Vertical): } R^2 = 0.9156$$

$$E = -1.9017m + 38.963 \quad \text{Hybrid (Horizontal): } R^2 = 0.897$$

$$E = -0.3828m + 7.7343 \quad \text{Hybrid (Vertical): } R^2 = 0.8854$$

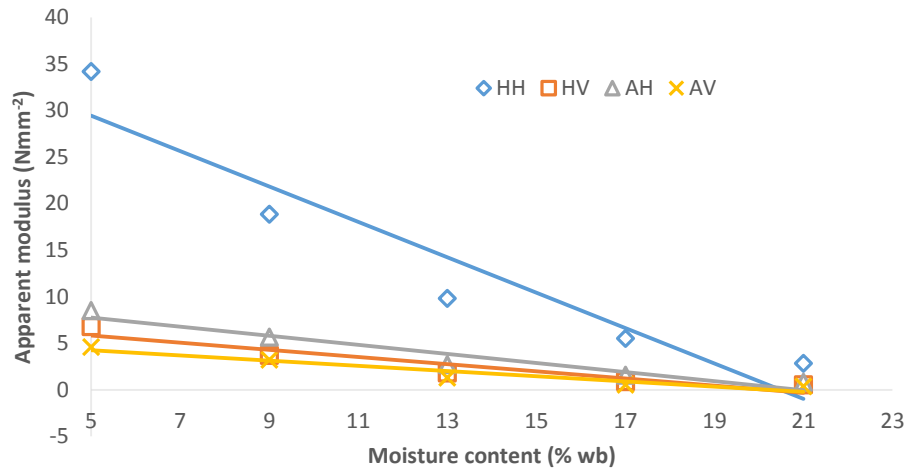


Fig. 4.7. Variation of apparent Young's modulus considering the influence of moisture content and bean orientation.

Conclusion

The purpose of this study was to investigate the compressive properties of 'Amelonado' and 'Hybrid' varieties of cocoa beans, by examining the effect of moisture content, variety and bean orientation on rupture force, deformation and energy of the bean. Statistical test showed that there are significant differences between the compressive properties of the two varieties studied ($P < 0.05$). Moisture content has significant effects on the compressive properties of both varieties of cocoa beans. An increase in the axial dimensions of the cocoa beans as moisture content increased was observed and this could stem from water absorption by the beans.

The force required for initiating bean rupture for the 'Amelonado' variety decreased from 110.895 - 39.421 N and 65.354 - 21.365 N at horizontal and vertical

orientations, respectively; while the rupture force for 'Hybrid' variety decreased from 289.589 - 105.137 N and 81.721 - 28.415 N at horizontal and vertical orientations, respectively as moisture content increased from 5% - 21% (wb). Comparatively, the required force to initiate the bean rupture in the case of 'Hybrid' variety was significantly higher than that of the 'Amelonado', at similar conditions of bean moisture content and orientation. The mean value of bean rupture force at horizontal orientation was significantly higher than that of vertical orientation, for both the 'Hybrid' and 'Amelonado' varieties.

The energy absorbed at bean rupture increased from 0.061 J at a moisture level of 5% (wb) to 0.075 J at a moisture level of 21% (wb) for 'Amelonado' variety in horizontal orientation and from 0.039 - 0.047 J in vertical orientation. On the other hand, the energy absorbed for the 'Hybrid' variety increased from 0.099 - 0.152 J and 0.040 - 0.057 J at horizontal and vertical orientations, respectively. This increase was significantly higher at horizontal orientation than vertical orientation for both varieties. The energy absorbed by the bean before initiating its rupture in the case of 'Amelonado' variety was obtained lower than that of the 'Hybrid', at similar conditions of the bean moisture content and orientation.

The deformation at rupture point increased from 0.061-3.836mm/mm and 0.039-0.047mm/mm, and 0.099-0.152mm/mm and 0.040-0.057mm/mm at horizontal and vertical orientation of 'Amelonado' and 'Hybrid' varieties respectively as the moisture content increased from 5 to 21 (% wb).

When moisture content increased from 5 to 21% (wb) the compressive stress decreased from 0.685 - 214 Nmm⁻² and 0.404 - 0.116 Nmm⁻², and 1.673 -

0.565 Nmm⁻² and 0.472 - 0.153 Nmm⁻² for 'Amelonado' and 'Hybrid' varieties at both horizontal and vertical orientations, respectively.

The mean compressive strain values for 'Amelonado' and 'Hybrid' varieties increased as moisture content increased. The relationship between compressive strain and moisture content was found to be significant at 0.05. The compressive strain values of the 'Hybrid' variety were higher than that of the 'Amelonado'.

The increase in moisture content increased the apparent Young's modulus linearly. The mean values of the apparent Young's modulus of the 'Amelonado' variety respectively increased from 0.080 Nmm⁻² to 0.267 Nmm⁻² and 0.088 Nmm⁻² to 0.310 Nmm⁻² at a moisture content range 5% - 21% (wb) at horizontal and vertical orientations. Similarly, the mean values of the apparent Young's modulus for the 'Hybrid' variety increased from 0.049 - 0.200 Nmm⁻² and 0.069 - 0.277 Nmm⁻² at horizontal and vertical orientations, respectively at the same moisture content range.

CHAPTER FIVE

EFFECTS OF FERMENTATION ON SOME PHYTOCHEMICAL PROPERTIES OF 'HYBRID' AND 'AMELONADO' COCOA VARIETIES

Introduction

Cocoa and chocolate have a fascinating history. Pre-Columbian cultures in Latin America cultivated cacao trees over 3,000 years ago. The main use was a chocolate beverage called xocolatl. In Mayan and Aztec cultures the cacao beans were not only used for xocolatl, but also as a very valuable currency. In the early 16th century, Spanish conquerors brought the first cacao beans in their ships, and began to conquer Europe. By 1653, cocoa was used in Europe as a medicine rather than as a delicious foodstuff (Barry, 2008).

The largest consumers of chocolate today are the countries in the western world, while the largest cocoa-producing countries are Ivory Coast, Ghana and Indonesia. Nearly 75% of the world's cocoa crop comes from Africa (ICCO, 2013). Cocoa is a prominent commercial cash crop in West Africa. The most useful and valuable part of the crop is the bean. Cocoa beans are the fermented and dried seeds of *Theobroma cacao*, and the fundamental ingredient in chocolate manufacture. Processing of cocoa beans into various cocoa and chocolate products involves two unique stages: The primary stage which includes harvesting, fermentation, drying of fermented beans, sorting and packaging, while the secondary stage consists of

roasting, alkalization, pressing and pulverization (Afoakwa, 2010). These postharvest processes according to Adeyeye *et al.* (2010) are very crucial to the quality of finished products as they initiate the formation of chocolate flavour precursors and the brown colour of cocoa products.

The nutritional quality of cocoa beans and its products are determined largely by the chemical composition of the cocoa powder, which is dependent on the quantum of proteins, carbohydrates, fats, minerals and phytochemicals in the cocoa products (Adeyeye *et al.*, 2010). It very imperative to know the nutritional status of materials (Belscak *et al.*, 2009). Nowadays, consumers are more concerned with the nutritional status of foodstuffs (Ieggli *et al.*, 2011). Jonfia-Essien and Navarro (2010) stated that the free fatty acids (FFA) content must be less than 1.00% to meet the acceptable level of 1.75% in cocoa butter extracted from the dry cocoa beans.

On the other hand, the poultry industry is faced with several challenges among which is the scarcity of conventional energy source feedstuffs particularly maize, a major energy source in animal feed. Several attempts have been made by researchers to address this pestering issue facing the poultry industry by the use of alternative and cheaper sources of ingredients to replace the less available and expensive ones. One such alternative source is the use of agro-industrial by-products which are abundantly found in the environment produced by processing industries. One such agro-industrial by-product is cocoa bean shells produced from cocoa and chocolate factories. Several researchers have established alternative use

of cocoa bean shell for animal feed especially in poultry diets (Hamzat and Babatunde, 2006).

Recently, cocoa and cocoa products have been recognized as significant sources of phytochemicals, with many health promoting effects. For cocoa, the terms that are used to describe the particular compounds of interest are flavanols. Flavanols are a subclass of flavonoids which are, in turn, a subclass of polyphenols (Cooper *et al.*, 2008). Flavonoids are a group of phenolic compounds that occur widely in fruits, vegetables, tea, red wine, and chocolate. Cocoa and chocolate products have the highest concentration of flavonoids among commonly consumed foods (Roberto *et al.*, 2009). The nutritional quality of cocoa products are determined largely by the chemical composition of the cocoa powder, which is dependent on the quantum of proteins, carbohydrates, fats, minerals and phytochemicals in the cocoa products and the corresponding digestibility coefficient (Belscak *et al.*, 2009; Adeyeye *et al.*, 2010).

Considering that cocoa and cocoa products are extremely rich sources of many phytochemicals that can contribute to a healthy diet, it is imperative to periodically research into the raw cocoa beans and its food products. Therefore, in this study, the effect of fermentation of cocoa beans on the phytochemicals such as polyphenols, free fatty acid (FFA), titratable acidity, total soluble solids and pH were determined for ‘Amelonado’ and ‘Hybrid’ varieties. Specifically, the phytochemicals present in the unfermented and fermented cocoa beans were examined. The investigations were conducted on whole bean, cocoa nib and shell in this study.

Materials and methods

Experimental location

The laboratory analysis of the cocoa samples for total polyphenols, free fatty acids, total soluble solids, pH, and titratable acidity were conducted in the Chemistry Laboratory of the Department of Chemistry of the University of Cape Coast.

Experiments

A 4 x 2 x 3 factorial experiment with the experimental factors as fermentation periods (0, 4, 6 and 8 days), varieties ('Amelonado' and 'Tafo Hybrid') and bean parts (cocoa bean, nib and shell) were used. The treatments were planned and evaluated based on a completely randomized design. Three experiments were conducted and phytochemical analysis were performed on the dried cocoa beans. The experimental procedures are described below.

Determination of impact of fermentation duration on cocoa beans

Prior to the process of pod breaking, the necessary quality checks involving separation of bad pods (i.e. pest damaged pods, black pods, and immature ripe pods) from the good pods were performed. Wooden clubs were used to break the pods instead of cutlasses to avoid injury to the beans inside the pod. The beans were scooped out of the broken pods by hand whilst the husk and placenta were discarded. All black, caked and germinated beans as well as other foreign materials

were also disposed off. The good beans obtained from the good pods were weighed and the wet weight determined.

There are four methods of fermentation. They are the heap, basket, box and tray methods but the most commonly used are the heap, basket and box methods. The heap method of fermentation was used (Plate 5.1). Under the heap fermentation, fresh plantain leaves were spread in a circular pattern on the ground and the fresh cocoa beans heaped on them. This allows easy pulp drainage. The heap of beans was then covered with more leaves and held in place by small logs. The cover protects the fermenting beans against mould growth and also helps to maintain the heat generated within the heap. Each heap was filled with cocoa beans which weighed 100kg and beans were poured in the centre of each heap and covered very well to prevent the entry of air. The beans were turned on the second day of fermentation and covered again. To facilitate uniform fermentation, the beans were turned after every 48 hours. Fermentation was done for four, six and eight days and on each of these days, after which beans were sun dried on a raffia mat.



Plate 5.1: Heap method of fermentation

Laboratory analysis

Phytochemical analysis

The phytochemical parameters that were determined included the polyphenols, free fatty acid (FFA), titratable acidity, total soluble solids and pH were determined for ‘Amelonado’ and ‘Hybrid’ varieties. The examination of these phytochemicals were conducted on the unfermented and fermented cocoa beans.

After sun drying to an initial moisture content of 7% (wb) the dried beans were manually separated into nib and shell. The nib, shell and whole bean were ground into their various forms of powdered using lab mill (Model Brook Crompton, Series 2000, Glen Creston Ltd, UK). The investigations were specifically conducted on these dried powdered samples of nib, shell and whole bean of the two varieties.

pH determination

The pH for the powdered nib, shell and whole bean was determined according to the International Office of Cocoa, Chocolate and Sugar Confectionery method (IOCCC (1996). Five (5) grams of each sample was poured in different conical flasks and 50ml of boiling distilled water added. Samples were filtered and allowed to cool to a temperature of 27°C. The pH of the resulting filtrate was measured using a pH meter (Jenway Model 3510, Wagtech Bibby Scientific Limited, UK) calibrated with buffers at pH 4.1, 7.0 and 9.2. Each sample was replicated three times.

Determination of titratable acidity

The titratable acidity was determined according to the International Office of Cocoa, Chocolate and Sugar Confectionery method (IOCCC, 1996). 25 ml of the aliquot collected for the above pH determination was titrated with 0.1 N NaOH drop wise to a pH of 8.2, determined using a pH meter (Jenway Model 3510, Wagtech Bibby Scientific Limited, UK) which was calibrated with buffers of pH of 4.1, 7.0 and 9.2. The titratable acidity was calculated using the titre values and reported as milliequivalent sodium hydroxide per gram of dry powdered nibs, shell and whole bean samples. Triplicate readings were made.

Free fatty acid determination

The Federation of Cocoa Commerce (FCC) recommended method was used for the free fatty acid (FFA) analysis. Round bottomed flasks of 250 mL were dried in the oven at 105°C, cooled in the desiccator, weighed and 150 mL of petroleum ether (40°C -60°C) was measured into the round bottomed flasks. Each test sample of 5 g was measured into a thimble and was set up for extraction for three hours using the Soxhlet apparatus. The set up was allowed to cool and the solvent drained into the round bottomed flask. Each sample was ground with sand and set up for two 3 h again. The solvent was concentrated into fat by evaporating the petroleum ether (40°C -60°C) using the rotary evaporator. The fat content was dried in the oven for 2 h and cooled in the desiccator. Weight of the extract and the flask were taken and recorded. The weighed fat extract was dissolved in 50 mL diethyl ether-ethanol mixture (1:1), [v:v]. Two drops of phenolphthalein indicator were added to

the fat in 50 mL diethyl ether-ethanol. The sample was swirled to mix and titrated against 0.1 M sodium hydroxide in ethanol solution till a faint pink colour was obtained and the end point taken and recorded for the FFA calculation as follows:

$$FFA = (282 \times V \times C) / 10 \times M$$

$$M = (m_a - m_b)$$

Where: 282 = molecular mass of oleic acid

V = volume (mL) of standardised sodium hydroxide used for titration.

C = concentration (mol L⁻¹) of the standardised sodium hydroxide used for titration.

$$C = W_p / (M_p \times V_p)$$

Where: M_p = molecular weight of hydrogen phthalate

V_p = volume of sodium hydroxide solution

W_p = weight of sodium hydroxide phthalate

M = mass of extracted fat

m_b = mass of conical flask and pumice stones before extraction

m_a = mass of conical flask after extraction

Determination of total polyphenol content

Total polyphenol content was estimated using Folin-Ciocalteu reagent based assay as previously described in Victor *et al.* (2013) with little modification.

To one ml of each extract (100µg/ml) in methanol, 5ml of Folin-Ciocalteu reagent

(diluted ten-fold) and 4 ml (75 g/l) of Na₂CO₃ were added. The mixture was allowed to stand at 20°C for 30 min and the absorbance of the developed colour was recorded at 765 nm using UV-VIS spectrophotometer. 1 ml aliquots of 20, 40, 60, 80, 100 µg/ml methanol gallic acid solutions were used as standard for calibration curve. All determinations were performed in triplicate. Total phenol value was obtained from the regression equation: $y = 0.00048x + 0.0055$ and expressed as mg/g gallic acid equivalent using the formula, $C = cV/M$; where C = total content of phenolic compounds in mg/g GAE, c = the concentration of gallic acid (mg/L) established from the calibration curve, V = volume of extract (0.5ml) and m = the weight of pure plant methanolic extract (0.052g).

Determination of total soluble solids

Total soluble solids were measured with a refractometer (JP SELECTA, Spain) graduated from 0-30 and results were expressed in degree Brix.

Results and discussion

Fermentation temperature

Table 5.1b: Effect of fermentation duration on temperature of cocoa beans

Fermentation Days	Temperature (°C)		
	‘Amelonado’	‘Hybrid’	‘Amelonado’ & ‘Hybrid’
1	26.25g	26.45g	26.35g
2	27.90f	27.85f	27.88f
3	34.70d	33.60e	34.15e
4	36.77c	37.45c	37.11c
5	39.75b	42.67b	41.21b
6	41.70a	45.33a	43.51a
7	34.19d	37.92c	36.06d
8	33.30e	35.33d	34.31e
LSD	0.8722	1.077	0.9008

Values are means of duplicate determinations. Means with same letters within a column are not significantly different based on LSD test at $P = 0.05$.

‘Amelonado’ and ‘Hybrid’ cocoa beans is presented in Table 5.1b. The duration of fermentation influenced the temperature of the beans ($p < 0.05$). The temperature of the fermented beans for both varieties increased significantly as days of fermentation increased from day one to day seven. The temperature of the fermented beans began to fall after the sixth day of fermentation. The temperatures recorded before the seventh day are significantly different from those recorded for eighth day of fermentation at ($p < 0.05$). Fig. 5.1 illustrates the effect of days of fermentation on temperature of fermented cocoa beans (‘Amelonado’ and ‘Hybrid’). It also demonstrates how the temperature began to fall after sixth day of fermentation. This fall in temperature well corresponded with the development of ammonia odour when the fermentation can be considered to have completed. The experimental values demonstrated that as the days of fermentation increased the

temperature in the fermented cocoa beans increased with ‘Hybrid’ variety recording the highest temperatures as compared with ‘Amelonado’ variety.

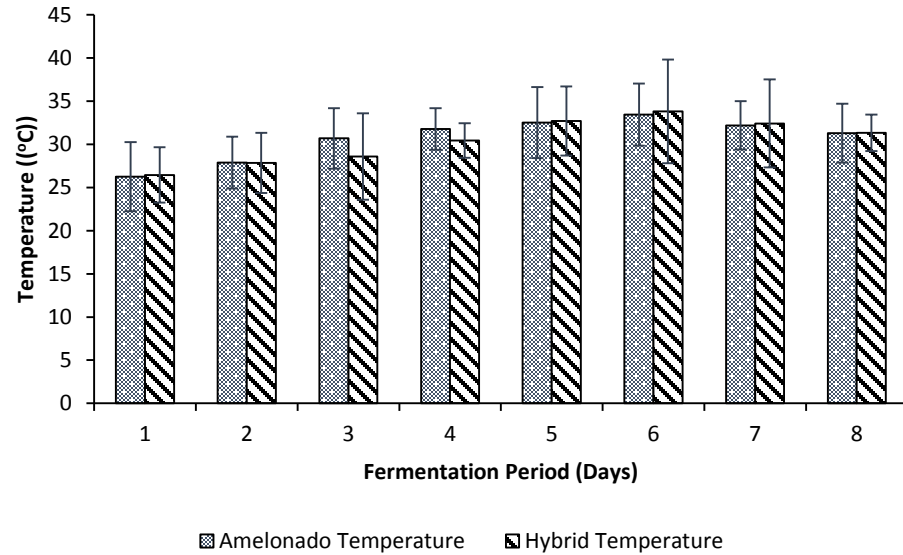


Fig. 5.1. Effect of fermentation period on temperature of fermented cocoa beans

pH content of cocoa beans

Table 5.2b: Effect of fermentation duration on pH in different parts of cocoa beans

Fermentation Day	‘Amelonado’			‘Hybrid’		
	WB	NI	SH	WB	NI	SH
0	3.612d	4.145d	3.505d	3.484d	4.099b	3.391c
4	4.277c	4.817c	3.915c	3.920c	4.492b	3.546c
6	4.580b	5.389b	4.559b	4.322b	5.296a	3.883b
8	5.713a	6.527a	5.613a	5.618a	5.698a	5.608a
LSD	0.1656	0.1280	0.2664	0.2606	0.6937	0.2970

Values are means of duplicate determinations. Means with same letters within a column are not significantly different based on LSD test at probability level 0.05. Where; WB – Whole bean, NI – Nib and SH – Shell.

The pH of cocoa beans is an important phytochemical property as it gives an indication on the degree of acidification of the nibs during fermentation and the quality of fermentation. It also gives an indication of the degree of biochemical reactions that occurred during the fermentation as well as the taste or sourness of the bean. Table 5.2b shows the pH values of the whole cocoa beans, nib and shell for both 'Amelonado' and 'Hybrid' varieties as affected by fermentation duration. Whole Cocoa beans from the 'Amelonado' and 'Hybrid' pods without fermentation before drying had a pH of 3.61 and 3.48 and those from the cocoa nib and shell had pH values of 4.15 and 3.51, and 4.10 and 3.39, respectively. The unfermented cocoa beans had the lowest pH for both varieties and all categories while 8-day fermentation had the highest pH. Fermentation within 4-day and 6-day had pH values ranging from 3.55 to 5.30. Fermented and dried cocoa beans with pH range 5.0-5.5 produced higher flavour potentials while that with pH range 4.0-4.5 give low flavour potential. Similar trends were observed by Nazaruddin *et al.* (2001) and Afoakwa *et al.* (2008). It is observed that the pH of all the three parts increased as the number of days for fermentation increased for both varieties (Fig. 5.2). The values show a level of significant difference among the samples considering the fermentation duration, bean part and variety involved ($p < 0.05$) (Table 5.2a). The pH of cocoa beans during fermentation is crucial as it dictates the fermentative quality of the beans. There were are significant differences in the pH content of beans obtained from 'Amelonado' and 'Hybrid' varieties including the part of the bean examined. This could be as a result of the differences in the duration of fermentation. On the average pH was observed to be increasing with increasing

days of fermentation irrespective of the variety and the part of the cocoa bean examined. Duration of fermentation have affected the pH of beans by influencing enzyme activities and flavour development and hence acidity.

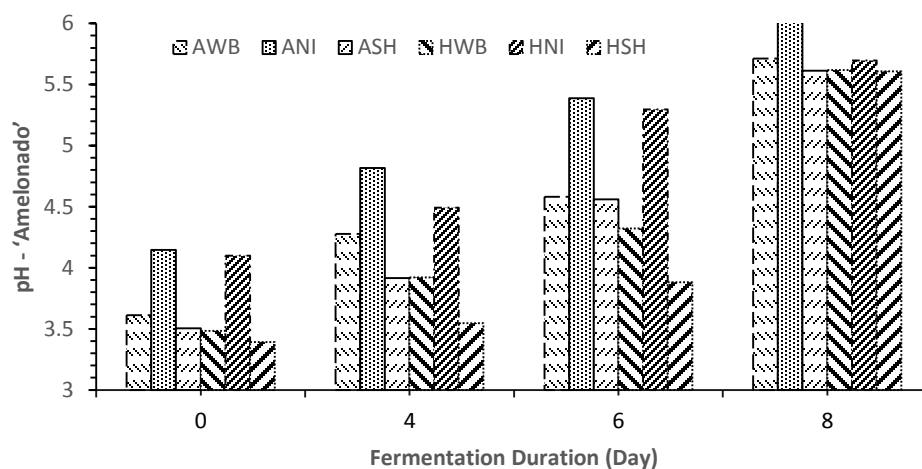


Fig. 5.2 Effect of fermentation on pH content of 'Amelonado' and 'Hybrid' varieties of cocoa beans.

Titrateable acidity content

Table 5.3b: Effect of fermentation duration on titrateable acidity in different parts of cocoa beans.

Fermentation Day	'Amelonado'			'Hybrid'		
	WB	NI	SH	WB	NI	SH
0	0.9812a	0.7942a	1.2870a	1.3860a	1.0369a	3.858a
4	0.6405b	0.5460b	1.0130b	1.1780b	0.5470b	1.358b
6	0.5307c	0.4365c	0.6780c	0.781c	0.4254c	0.658c
8	0.2271d	0.3749d	0.4670d	0.5730d	0.3260d	0.482d
LSD	0.01328	0.04665	0.00900	0.01943	0.03074	0.02709

Values are means of duplicate determinations. Means with same letters within a column are not significantly different based on LSD test at probability level 0.05.

The effect of fermentation duration on titratable acidity of whole cocoa bean, cocoa nib and cocoa bean shell of ‘Amelonado’ and ‘Hybrid’ varieties is presented in Table 5.3b. Titratable acidity is one of the main quality parameters determined during processing of cocoa both on farm and industrial processing. Cocoa nibs with very high titratable acidity after fermentation is an indication of poor fermentation. The titratable acidity content of whole cocoa bean, cocoa nib and cocoa bean shell decreased significantly ($p < 0.05$) as duration of fermentation increased for both varieties of cocoa used in this research (Table 5.3a).

Fig. 5.3 shows the effect of fermentation duration on the whole cocoa bean, nib and cocoa bean shell of ‘Amelonado’ and ‘Hybrid’ varieties. There was a gradual decrease in average titratable acidity in all the three parts of the cocoa bean investigated into as the duration of fermentation increased, irrespective of the variety. This decrease corresponded with a general increase in average pH. The pH and acidity of fermented cocoa beans were reported in different researches to influence both the taste and flavour of the products (Adeyeye *et al.*, 2010).

Nazaruddin *et al.* (2001) and Afoakwa *et al.* (2008) reported similar decrease in titratable acidity of the cocoa beans with increasing pod storage, from 0 day to 7 days. The decreases in titratable acidity of the beans with increasing fermentation duration might be due to the loss of moisture from the beans. This causes reduction in the pulp volume as well as sugar content due to respiration by the cocoa bean, thereby decreasing alcohol production by the yeast from sugar metabolism at the anaerobic phase of the fermentation process. This might have affected the rate of acid production with beans from the fermented beans.

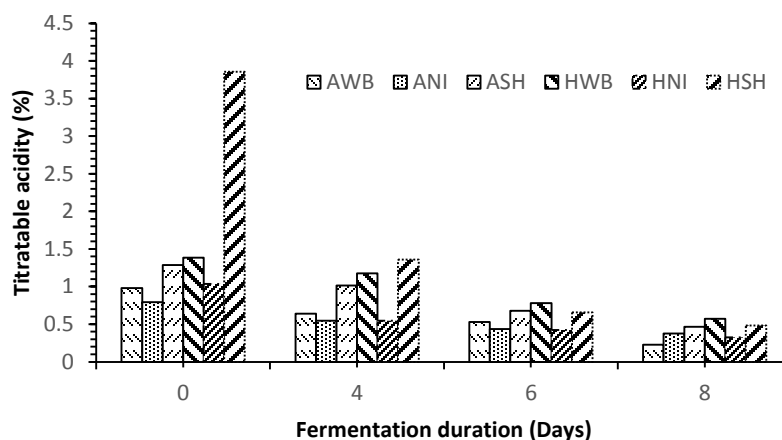


Fig. 5.3 Effect of fermentation on titratable acidity content of ‘Amelonado’ and ‘Hybrid’ varieties of cocoa bean.

Free fatty acid (FFA) content

Table 5.4b: Effect of fermentation period on FFA in different parts of cocoa beans

Fermentation Day	‘Amelonado’			‘Hybrid’		
	WB	NI	SH	WB	NI	SH
0	1.430b	1.225b	0.880b	1.220a	1.035b	0.660a
4	1.020c	0.925c	0.680c	0.975b	0.775c	0.520b
6	0.845d	0.750d	0.570d	0.790c	0.625d	0.450c
8	1.565a	1.340a	0.970a	1.245a	1.100a	0.695a
LSD	0.061	0.075	0.039	0.046	0.047	0.056

Values are means of duplicate determinations. Means with same letters within a column are not significantly different based on LSD test at probability level 0.05.

The effect of fermentation duration on free fatty acids (FFA) content of whole cocoa bean, cocoa nib and cocoa bean shell of ‘Amelonado’ and ‘Hybrid’ varieties is presented in Table 5.4b. The internationally acceptable level of free fatty

acids in cocoa butter extracted from the dry cocoa bean is 1.75% (Jonfia-Essien and Navarro, 2010). The level of free fatty acids in the fat of cocoa beans gives the measure of rancidity of the cocoa, and high levels of free fatty acid (> 1.75% in dried beans) in cocoa are not acceptable. The ANOVA in table 5.4a shows a significant difference ($p < 0.05$) in the FFA content of whole bean, nib and bean shell from both varieties. Even though there were significant differences in FFA content of the whole bean, nib and bean shell from both varieties, both varieties produced good beans with respect to the percentage FFA. The significant differences could be as a result of the fermentation duration and the part of bean involved. The cocoa bean shell recorded the lowest FFA content in respect to both the bean part and variety. Fermenting beans for six days was the best since it resulted in the production of the least FFA for both ‘Amelonado’ and ‘Hybrid’ varieties of cocoa beans (Fig. 5.4).

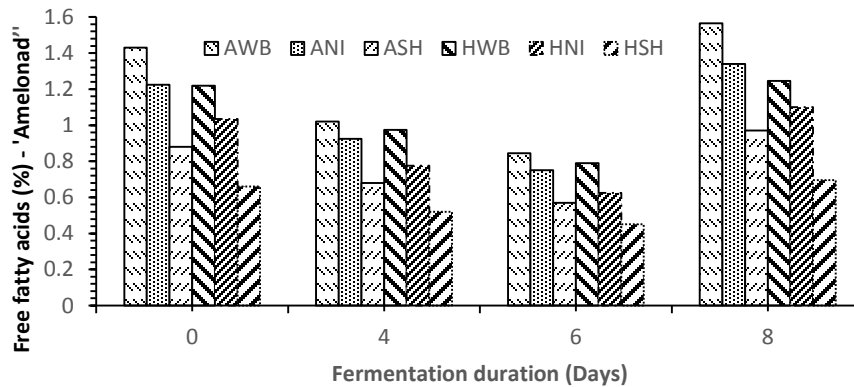


Fig. 5.4: Free fatty acid content in cocoa beans from ‘Amelonado’ and ‘Hybrid’ varieties.

Total polyphenol content

Table 5.5b: Effect of fermentation duration on total polyphenol in different parts of cocoa beans

Fermentation Day	‘Amelonado’			‘Hybrid’		
	WB	NI	SH	WB	NI	SH
0	32.08d	29.04c	25.77c	34.25d	31.55b	27.60d
4	47.01b	43.97b	29.15b	50.25b	44.42a	29.18c
6	50.89a	48.15a	34.64a	54.43a	48.64a	35.65a
8	34.94c	29.63c	29.32b	41.42c	32.30b	30.37b
LSD	1.765	1.560	1.156	0.2919	0.831	0.4190

Values are means of duplicate determinations. Means with same letters within a column are not significantly different based on LSD test at $P = 0.05$.

Polyphenols have gained a lot of attention in recent times, owing to their antioxidant capacity and their beneficial implications in human health, such as in the treatment and prevention of cancer, cardiovascular disease, anti-microbial and other pathologies (Lettieri-Barbato *et al.*, 2012). Polyphenol reactions with sugar and amino acids contribute flavour and colour to cocoa bean whereas the alkaloids contribute to the bitterness (Afoakwa and Paterson, 2010). Polyphenols also have bitter, astringent flavours and their antioxidant properties help protect the seed from damage and disease (Nazaruddin *et al.*, 2001)

The total polyphenol content of whole cocoa bean, cocoa nib and cocoa bean shell decreased significantly ($p < 0.05$) (Table 5.5a) as duration of fermentation increased for both varieties of cocoa used in this research. It is seen that the total polyphenol content of whole cocoa bean, nib and shell from the ‘Hybrid’ variety recorded the highest as compared with those obtained from ‘Amelonado’. Fermenting beans for six days yielded the highest polyphenol content for both

‘Amelonado’ and ‘Hybrid’ varieties of cocoa beans of all the three parts considered in this study (Fig. 5.5). The results from this work is similar to the work done by Nazaruddin *et al.* (2001) who reported that the total polyphenols ranged from 34 to 60 mg/g in cocoa beans. For ‘Amelonado’ variety there was no significant difference ($p < 0.05$) in the polyphenol content of cocoa nib unfermented and those fermented for 8 days. Similarly fermenting beans for four and six days recorded no significant difference in the shell polyphenol content of ‘Amelonado’ variety. On the other hand, experimental values as seen in Table 5.5b shows that ‘Hybrid’ beans fermented for four and six days were not significantly different in respect to nib polyphenol content.

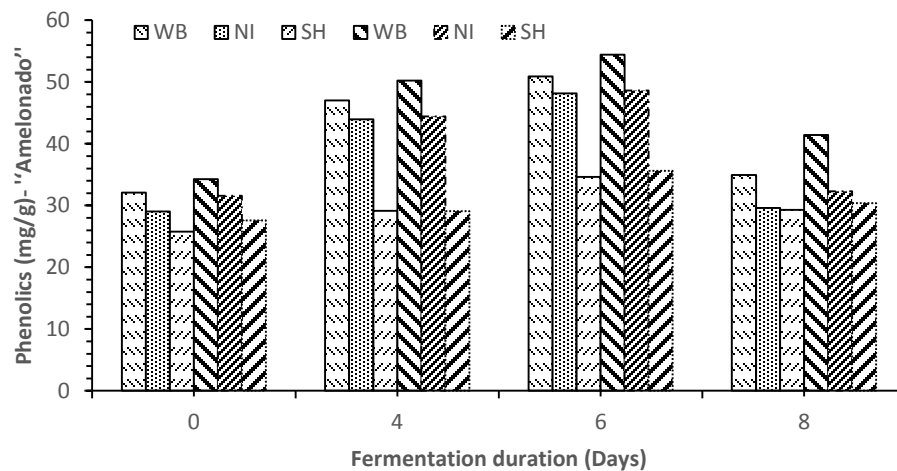


Fig. 5.5 Effect of fermentation on total polyphenols content of ‘Amelonado’ and ‘Hybrid’ varieties of cocoa bean.

Total soluble solids content

Table 5.6b: Effect of fermentation duration on total soluble solids in parts of cocoa beans

Fermentation Day	‘Amelonado’			‘Hybrid’		
	WB	NI	SH	WB	NI	SH
0	67.30a	67.35a	66.60b	66.80a	67.55a	67.50a
4	67.40a	67.65a	66.25b	67.30a	67.95a	67.15a
6	67.40a	67.15a	67.75a	67.35a	67.10a	67.15a
8	67.40a	67.55a	67.40a	67.30a	67.35a	66.60a
LSD	1.039	0.942	0.5376	1.622	1.517	1.048

Values are means of duplicate determinations. Means with same letters within a column are not significantly different based on LSD test at P = 0.05.

Table 5.6b presents the effect of days of fermentation on total soluble solids (TSS) content of whole cocoa bean, cocoa nib and cocoa bean shell of ‘Amelonado’ and ‘Hybrid’. The analysis of variance in Table 5.6a showed that no significant difference ($p < 0.05$) exist in the total soluble solids content of the ‘Amelonado’ and ‘Hybrid’ varieties, irrespective of bean part used. However, cocoa bean shell from ‘Amelonado’ variety unfermented and fermented for four days are significantly different from others. Generally, the mean values of total soluble solids content of the two varieties of cocoa beans ranges from 66.2 to 67.75° Brix (Fig. 5.5). The outcome of this study is similar to results obtained by Anyoh *et al.* (2009) who reported the total soluble solids content of cocoa marmalade to be 67.14° Brix. The total soluble solids content has been strongly correlated with sweetness.

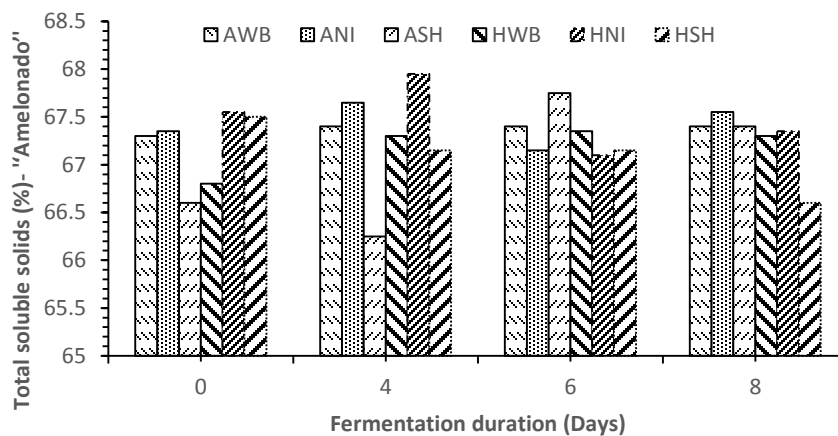


Fig. 5.6 Effect fermentation on total soluble solids content of ‘Amelonado’ and ‘Hybrid’ varieties of cocoa bean.

Conclusion

In this study, the effect of fermentation duration of cocoa beans on the phytochemicals such as polyphenols, free fatty acid, titratable acidity, total soluble solids and pH were determined for ‘Amelonado’ and ‘Hybrid’ varieties. Specifically, the investigations were conducted on whole bean, nib and shell.

It is observed that the pH content of all the cocoa bean parts considered for this study increased as days for fermentation increased for both varieties. The values show a level of significant difference among the samples on LSD test at $P = 0.05$. The ‘Hybrid’ variety recorded the highest pH value of 6.152 while ‘Amelonado’ variety had 4.721. The experimental values obtained showed that cocoa nib had the highest pH, while cocoa bean shell had the lowest pH for both ‘Amelonado’ and ‘Hybrid’ varieties. There was a significant decrease in the

average titratable acidity in all the three spatial regions of both varieties of cocoa bean investigated as the days of fermentation increased.

Though there were significant differences ($p < 0.05$) in FFA content of the whole bean, nib and bean shell, both varieties produced good beans with respect to the percentage FFA. The significant differences could be as a result of the fermentation duration and the differential composition of the biochemical compounds in the parts of bean involved. The cocoa bean shell recorded the lowest FFA content in respect of both the bean part and variety. It could be possible because the outermost part and therefore had greater interaction with oxygen and therefore oxidation of FFA. Fermenting beans for six days was the best since it resulted in the production of the least FFA for both ‘Amelonado’ and ‘Hybrid’ varieties of cocoa beans.

The total polyphenol content of whole cocoa bean, nib and shell from the ‘Hybrid’ variety was the highest as compared to those obtained from ‘Amelonado’. Fermenting beans for six days yielded the highest polyphenol content for both ‘Amelonado’ and ‘Hybrid’ varieties of cocoa beans of all the three parts considered in this study. For ‘Amelonado’ variety there was no significant difference ($p < 0.05$) in the polyphenol content of cocoa nib unfermented and those fermented for 8 days.

No significant difference ($p < 0.05$) exist in the total soluble solids content of the ‘Amelonado’ and ‘Hybrid’ varieties. However, the soluble solids content of cocoa bean shell from ‘Amelonado’ variety unfermented and fermented for four days are significantly different?. Generally, the mean values of total soluble solids content of the two varieties of cocoa beans ranged from 66.2 to 67.75° Brix.

CHAPTER SIX

EFFECTS OF FERMENTATION ON PROXIMATE COMPOSITION OF TWO VARIETIES OF COCOA BEANS

Introduction

The fruit of the tropical plant, cocoa (*Theobroma cacao L.*) is known world-wide for its beans. Cocoa is typically known to be an evergreen tree which can grow to a height of 4-8m tall. Cocoa is very important ingredient in several kinds of foods, such as chocolate, cakes, biscuit, child-foods, ice creams and sweet consumed in developed countries (Guehi *et al.*, 2007). For a long time the production and commercialisation of cocoa has been the basis for the economy of Ghana. Cocoa cultivation is a major source of income for many people in Ghana (Mingle, 2010). In addition to the highly flavoured cocoa products, cocoa tree provides by-products such as cocoa bean meal, cocoa pod husk and cocoa bean shell, among others.

Cocoa bean shell is a potential tropical feed resource and its utilization in animal feed will greatly reduce the disposal problem facing the cocoa processing factories. The dried cocoa bean shell contains 13.12% crude protein; 13.00% crude fibre; 8.71% ether extract; 9.15% ash. Several studies on broilers, cockerel chick finishers and laying hens have established the inclusion rate of cocoa bean shell in

these poultry rations though they reported a low growth performance at higher inclusions due to several factors (Hamzat and Babatunde, 2006). Gohl (1981) attributed the limited use of cocoa bean shell in animal feeds to its theobromine content in spite of its high nutritive value. Theobromine belongs to the same naturally occurring methylated xanthine group as caffeine (Ching and Wong, 1986). When taken in modest quantities, it acts as a stimulant like caffeine but intake of more than 0.0279kg per body weight is injurious to animals (Menon, 1982). Menon (1982) indicated that the anti-nutritional compound could be reduced by heat, sun-drying and boiling. Cocoa processing and chocolate manufacturing are two different processes that, although linked, require different procedures to obtain the products wanted. Cocoa processing is basically a means of converting the cocoa beans into nib, liquor, butter, cake and powder. Much emphasis is laid rather on the by-products produced from the processing of the beans especially the production of the shells which occurs at the initial stage where the beans are de-shelled before or after the roasting of the nib.

The main objective of this research was to investigate and compare proximate compositions of two varieties of cocoa beans 'Amelonado' and 'Hybrid'. The effect of fermentation on the nutritive values such as crude protein, carbohydrate, fat, ash and moisture contents of whole cocoa bean, nib and shell use as human food and animal feed was investigated.

Materials and methods

Raw materials and experimental location

For the experiment, 350 pods each of ‘Amelonado’ and ‘Hybrid’ varieties were obtained from the Seed Production Unit of COCOBOD located at Saamang, Wasa Akropong in the Western Region of Ghana. The laboratory analysis of the cocoa samples for total polyphenols, free fatty acids, total soluble solids, pH, and titrable acidity were conducted in the Chemistry Laboratory of the Department of Chemistry of the University of Cape Coast.

Experimental design

This study was carried out based on a factorial combination of 4 fermentation periods (0, 4, 6 and 8 days), 2 cocoa varieties (‘Amelonado’ and ‘Tafo ‘Hybrid’) and 3 bean parts (cocoa bean, nib and shell) in a completely randomized design with three replications. The experimental procedures are described below. The effects of fermentation periods, variety and bean parts on the proximate compositions were investigated using analysis of variance using GenStat Release 9.2 (Ninth Edition) software.

Laboratory analysis

Proximate analysis

The proximate compositions that were determined included the crude protein, carbohydrate, fat, ash and moisture contents were determined for ‘Amelonado’ and ‘Hybrid’ varieties. The examination of these proximate compositions were conducted on the unfermented and fermented cocoa beans of ‘Amelonado’ and ‘Hybrid’ varieties. After sun drying to an initial moisture content of 7% (wb) the dried beans were manually separated into nib and shell. The whole bean, nib and shell were ground into their various forms of powdered using lab mill (Model Brook Crompton, Series 2000, Glen Creston Ltd, UK). The investigations were specifically conducted on these dried powdered samples of nib, shell and whole bean of the two varieties.

Moisture content determination

Two (2.0) grams each of whole cocoa bean, nib and shell samples were weighed into already cleaned and weighed crucibles in duplicate. The crucibles were placed in a thermostatically controlled oven (Wagtech) at 105°C for drying. The crucibles were then removed and placed in dessicators, allowed to cool and reweighed. The procedure was repeated until a constant weight was obtained. Moisture content was calculated by difference in weight and expressed as a percentage of the initial weight of the samples.

$$\text{Percentage Moisture} = \frac{W_2 - W_3}{W_2 - W_1} \times 100$$

Where: W_1 = Initial weight of empty crucible, W_2 = Weight of crucible + undried sample and W_3 = Weight of crucible + dried sample.

Determination of ash

After the determination of the moisture content the dried samples were then transferred into a muffle furnace and heated at a temperature of 550°C until it turned white and free of carbon. The samples were then removed from the furnace, cooled in a desiccator and reweighed immediately. The weight of the residue was then calculated as ash content expressed in percentage.

$$\text{Percentage Ash} = \frac{\text{Weight of Ash}}{\text{Weight of Sample}} \times 100$$

Carbohydrate determination

50 mg of air-dry ground sample was weighed into a 100 ml conical flask and 30 ml water was added. A glass bubble was placed in the neck and simmered gently on a hotplate for 2 hours. It was periodically topped up to 30 ml. It was then allowed to cool slightly and filtered through a No. 44 Whatman paper into a 50 ml volumetric flask. The paper was washed, and diluted to volume after cooling. The extract was prepared shortly before colour development. Two millilitres of each standard was pipetted into a set of boiling tubes. Also 2 ml of extract was pipetted into a boiling tube. From this point the standards and extract were treated in the same way. 10 ml

of anthrone reagent was added rapidly and mixed with the tube immersed in running cold water. The tubes were placed in a beaker of boiling water in a darkened fume cupboard and boiled for 10 minutes. The tubes were placed in cold water and allowed to cool in the dark. The optical density was determined at 625 nm using water as a reference. A calibration graph from the standards were prepared and used to obtain mg in the sample aliquot. The blank determinations were done in the same way. Calculation;

If C =mg glucose obtained from the graph then for

$$\text{Soluble Carbohydrates (\%)} = \frac{C(\text{mg}) \times \text{Extract Volume}}{10 \times \text{Aliquot}(\text{ml}) \times \text{Sample Weight}(\text{g})}$$

Fat determination

Two grams sample was loosely wrapped with a filter paper and put into the thimble which was placed in Soxhlet extractor which was fitted to a clean round bottom flask, which has been cleaned, dried and weighed. An amount of petroleum ether (40°C – 60°C) was poured into the extractor and the fat was extracted for 6 hrs. The petroleum ether (40°C – 60°C) in the round bottom flask containing the fat was evaporated in an oven at temperature of 70°C. The round bottom flask containing the fat was then placed in the desiccator for cooling and then reweighed. The difference in weight was calculated as mass of fat and is expressed as percentage of the sample. The percentage fat content is calculated as;

$$\text{Percentage fat} = \frac{W_2 - W_1}{W_3} \times 100$$

Where: W_1 = Weight of the empty extraction flask, W_2 = Weight of the flask and oil extracted and W_3 = Weight of the sample

Protein determination

The micro kjeldahl method described by A.O.A.C (Horwitz, 1980) was used. 0.5 gram each of the samples was mixed with 10 ml of concentrated H_2SO_4 in a heating tube. One tablet of selenium catalyst was added to the tube and mixture heated inside a fume cupboard. The digest was transferred into a 100 ml volumetric flask and made up with distilled water. Twenty milliliter portion of the digest was mixed with ten milliliter of 45% NaOH solution and poured into a kjeldahl distillation apparatus. The mixture was distilled and the distillate collected into 4% boric acid solution containing bromocresol green and methyl red indicators. A total of 50 ml distillate was collected and titrated as well. The sample was duplicated and the average value taken. The nitrogen content was calculated and multiplied with 6.25 to obtain the crude protein content. This is given as:

$$\text{Percentage Nitrogen} = \frac{\text{Titre}(ml) \times \text{Solution Volume}(ml)}{100 \times \text{Aliquot}(ml) \times \text{Sample Weight}}$$

Results and discussions

Moisture content

Table 6.1: Effect of fermentation duration on moisture content in different parts of cocoa beans

Fermentation Day	‘Amelonado’			‘Hybrid’		
	WB	NI	SH	WB	NI	SH
0	7.700c	7.720ab	11.63ab	11.97a	14.760a	14.67b
4	9.700a	7.025b	13.72a	9.20b	7.085b	17.98a
6	8.285b	5.730c	8.62c	9.96b	7.465b	17.75a
8	8.215b	8.235a	13.87a	9.63b	7.285b	14.57b
LSD	0.2889	0.954	4.147	0.836	0.6189	1.136

Values are means of duplicate determinations. Means with same letters within a column are not significantly different based on LSD test at $P = 0.05$.

Table 6.1 shows the effect of days of fermentation on moisture content of whole cocoa bean, cocoa nib and cocoa bean shell of ‘Amelonado’ and ‘Hybrid’ varieties. The moisture content of a food material gives an indication of the extent to which the nutritive value of the food material can be maintained (i.e. its shelf life). Therefore, low moisture content is required for a longer shelf life. Low moisture content confers higher shelf-life to the cocoa powder as microbial attack is minimal thereby keeping the nutritional ingenuity intact. Furthermore, effective control of moisture content of the powder reduces the water activity, oxidation and rancidity which inhibit good quality in cocoa beans.

The whole cocoa beans obtained from ‘Amelonado’ cocoa beans fermented for six and eight days had no significant difference ($p > 0.05$) in the moisture content. Similarly, the unfermented cocoa nib and bean shell and those fermented for eight days recorded no significant difference in moisture content. Also, the whole cocoa

beans and nib obtained from ‘Amelonado’ cocoa beans fermented for four, six and eight days showed no significant difference ($p>0.05$) in the moisture content. Fig. 6.1 depicted the effect of days of fermentation on the moisture content of different parts of ‘Amelonado’ and ‘Hybrid’ cocoa varieties.

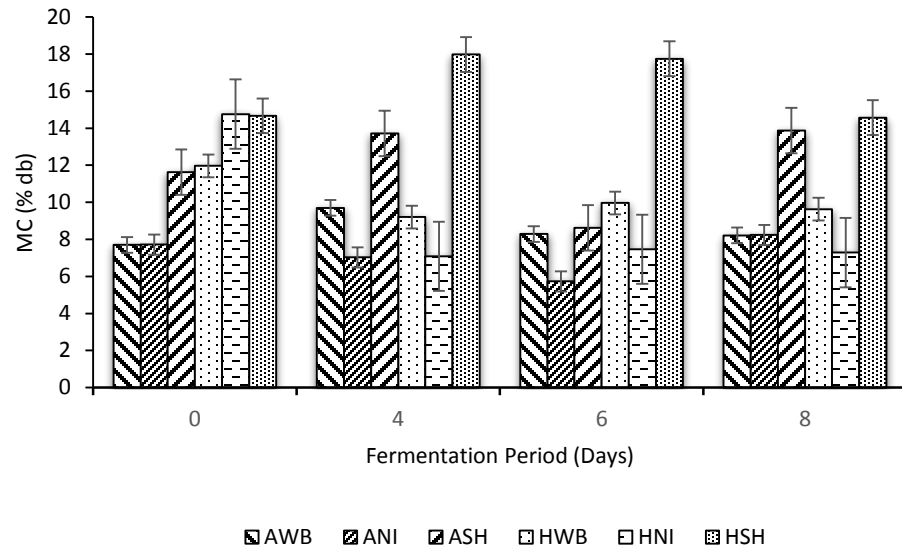


Fig. 6.1. Effect of fermentation duration on the moisture content of cocoa beans.

Where: AWB- whole bean of ‘Amelonado’, ANI- nib of ‘Amelonado’, ASH- shell of ‘Amelonado’, HWB- whole bean of ‘Hybrid’, HNI- nib of ‘Hybrid’ and HSH- shell of ‘Hybrid’.

Ash content

Table 6.2b: Effect of fermentation duration on ash content in different parts of cocoa beans

Fermentation Day	‘Amelonado’			‘Hybrid’		
	WB	NI	SH	WB	NI	SH
0	3.660c	3.390c	5.955c	4.350d	1.195d	7.75d
4	3.935b	3.715b	8.635b	4.900bc	3.340c	11.68c
6	3.965b	3.860ab	9.745a	5.630b	3.565b	12.45b
8	4.180a	3.945a	10.105a	7.630a	3.725a	13.84a
LSD	0.1601	0.1958	0.4716	0.892	0.0957	0.3981

Values are means of duplicate determinations. Means with same letters within a column are not significantly different based on LSD test at $P = 0.05$.

The ANOVA conducted on the experimental values as seen in Table 6.2a show that the ash content of the whole cocoa bean, cocoa nib and bean shell from both ‘Amelonado’ and ‘Hybrid’ varieties increased as the days of fermentation increased. Also, the ash content in the various part of the bean increased significantly at 5% level of probability (Table 6.2a) as the days of fermentation increased, irrespective of the variety. However, the ash content of whole cocoa beans fermented for four and six days are not significantly different based on LSD test at $p = 0.05$ (Table 6.2b). The values obtained from this study show a direct relationship with the days of fermentation because as the days of fermentation increased, the ash content increased Fig. 6.2. Ash is an indication of mineral contents of foods and has been shown by Ieggli *et al.* (2011) to be high in cocoa products. Cocoa contains iron for red blood cells, however, it boost the white blood cells which are responsible for the protection against infection (Abrokwah *et al.*,

2009). It has been earlier reported that cocoa can strengthened the body immune system and prevents many viral diseases.

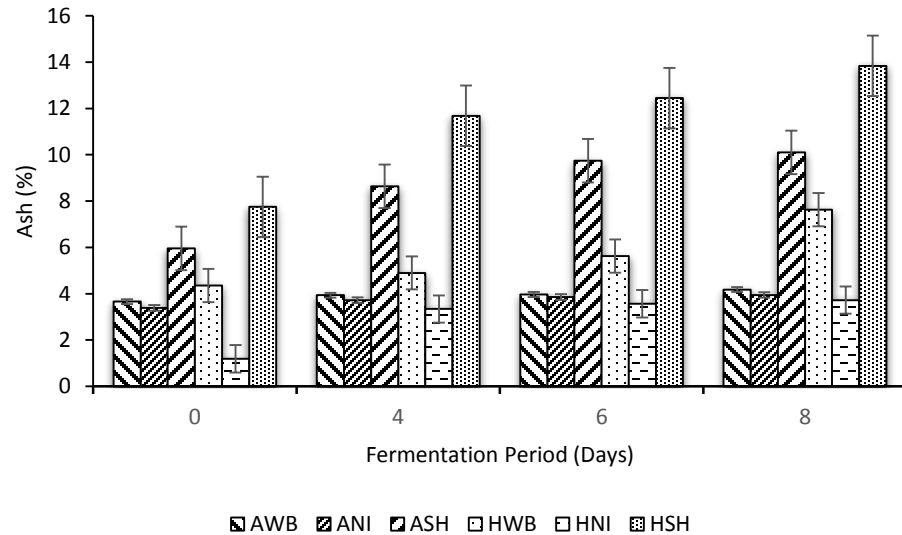


Fig. 6.2. Effect of fermentation on ash content of ‘Amelonado’ and ‘Hybrid’ cocoa beans.

Carbohydrate content

Table 6.3b: Effect of fermentation duration on carbohydrate in different parts of cocoa beans.

Fermentation Day	‘Amelonado’			‘Hybrid’		
	WB	NI	SH	WB	NI	SH
0	23.37a	34.19c	19.96a	15.13a	28.12d	24.56d
4	24.55a	34.81bc	23.14a	20.99a	32.25c	27.87c
6	27.50a	36.67ab	24.42a	25.02a	33.83b	29.19b
8	27.68a	38.00a	25.42a	26.45a	34.20a	37.66a
LSD	4.792	1.938	6.728	11.43	16.53	0.971

Values are means of duplicate determinations. Means with same letters within a column are not significantly different based on LSD test at P = 0.05.

From Table 6.3a, as the days of fermentation increased, the total soluble carbohydrate content increased. Generally, the total soluble carbohydrate of ‘Amelonado’ and ‘Hybrid’ varieties of cocoa beans increased ($P < 0.05$) with fermentation duration (Fig. 6.3). However, the carbohydrate content of whole cocoa beans from both varieties are not significantly different based on LSD test at $p = 0.05$ (Table 6.3b). This explains that days of fermentation had no influence on the whole bean carbohydrate content.

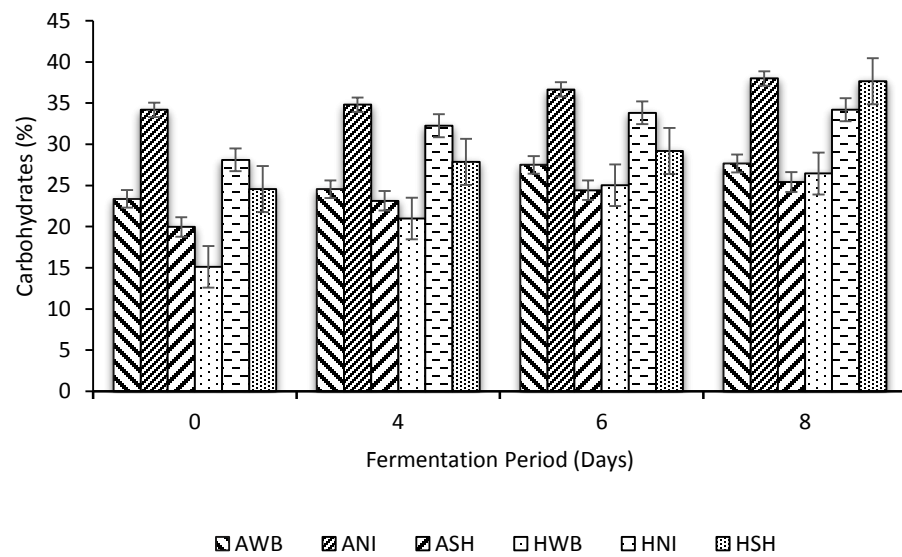


Fig. 6.3 Effect of days of fermentation on the carbohydrate content of cocoa beans.

Fat content

Table 6.4b: Effect of fermentation period on fat in different parts of cocoa beans

Fermentation Day	‘Amelonado’			‘Hybrid’		
	WB	NI	SH	WB	NI	SH
0	45.27a	39.08a	12.28a	47.77a	46.31ab	17.52a
4	37.53b	38.21a	11.23b	40.67b	44.32c	15.09b
6	37.62b	31.95a	10.03c	38.41b	41.22d	12.28d
8	39.38b	39.08a	12.09a	39.23b	48.82a	13.84c
LSD	2.682	17.79	0.2144	3.415	2.511	1.185

Values are means of duplicate determinations. Means with same letters within a column are not significantly different based on LSD test at $P = 0.05$.

The effect of fermentation duration on fat content of whole cocoa bean, cocoa nib and cocoa bean shell of ‘Amelonado’ and ‘Hybrid’ varieties is presented in Table 6.4b. It is noted from ANOVA Table 6.4a that fermentation duration had significant effect on fat content considering the variety and part of bean used. The values exhibited a level of significant difference among each other ($p < 0.05$). The significant differences could be as a result of the duration of fermentation and the part of bean involved. The cocoa bean shell recorded the lowest fat content in respect to both the bean part and variety. Fermenting beans for six days was the best since it resulted in the production of the least fat for both ‘Amelonado’ and ‘Hybrid’ varieties of cocoa beans (Fig. 6.4). The fat profile helps to reduce the risk of coronary heart disease because the flavonoids in cocoa are capable of causing modulation and preventing the oxidation and increase in cholesterol which could cause higher risk of heart disease as reported by Osakebe, *et al.* (2000).

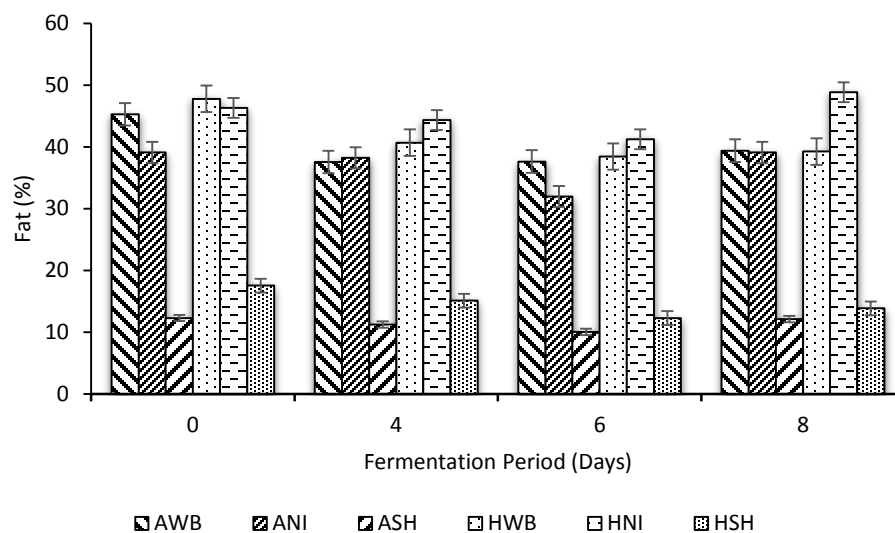


Fig. 6.4 Effect of fermentation duration on the fat content of cocoa beans.

Protein content

Table 6.5b: Effect of fermentation duration on protein in different parts of cocoa beans

Fermentation Day	Amelonado			Hybrid		
	WB	NI	SH	WB	NI	SH
0	15.47a	16.81a	12.390a	17.12a	17.24a	13.52a
4	15.19a	14.87ab	10.250ab	16.55a	16.74ab	13.33a
6	14.91a	13.96b	9.250bc	15.90a	16.55ab	9.82b
8	13.21b	13.23b	7.745c	14.48a	15.29b	9.30b
LSD	0.7559	1.992	2.405	2.617	1.660	1.864

Values are means of duplicate determinations. Means with same letters within a column are not significantly different based on LSD test at P = 0.05.

As the days of fermentation increased, the protein content of all the different parts of cocoa beans considered in this study reduced (Table 6.5b). The experimental values show a level of significant difference among the part of the bean used and duration of fermentation ($p < 0.05$) (Table 6.5a). The protein values

in this work are comparable with the values reported by (Abrokwah *et al.*, 2009). In their work, (Abrokwah *et al.*, 2009) reported that the protein content decreased as the drying temperature increased. The protein content of cocoa is health improving as it helps in the functioning of liver and kidney, alanine aminotransferase, aspartate aminotransferase of cocoa helps to detect and monitor cardiac disease (Abrokwah *et al.*, 2009). In this experiment, the protein content values obtained ranged between 7.75% - 17.24%. The protein content was similar to that reported by Spencer and Hodge (1992), who reported protein content of 15-20% in dried cocoa beans.

Irrespective of the variety and part of the bean used, the protein content reduced as the days of fermentation increased (Fig. 6.5). Protein content in the dried beans was affected by the duration of fermentation. As fermentation time increased, protein content reduced ($p < 0.05$) (Table 6.5b). The observed decreases in protein content with fermentation might be due to protein breakdown during the curing process, partly due to hydrolysis into amino acids and peptides and partly by conversion to insoluble forms by the action of polyphenols as well as losses by diffusion (Afoakwa *et al.*, 2008).

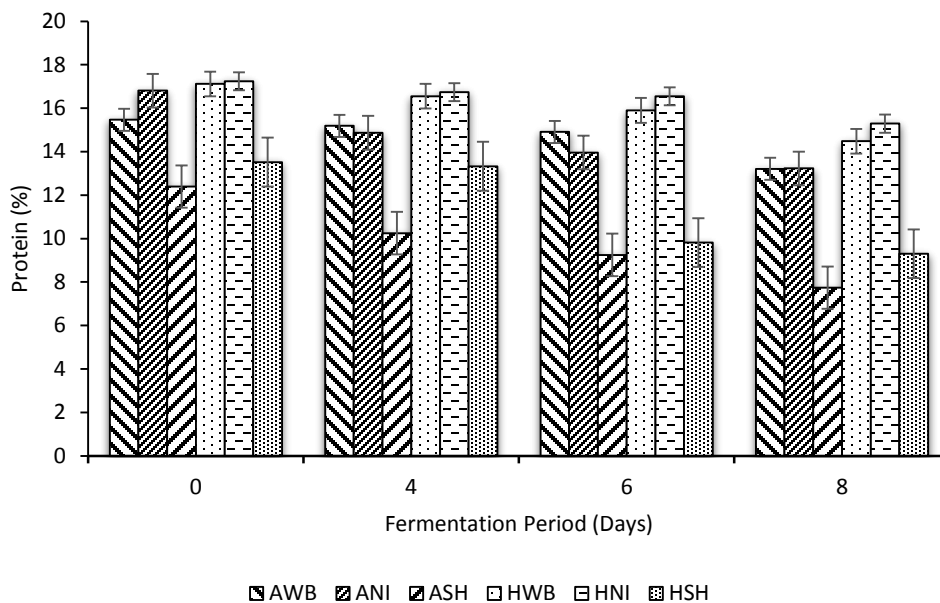


Fig. 6.5 Effect of duration of fermentation on the protein content of ‘Amelonado’ and ‘Hybrid’ cocoa beans.

Conclusion

The objective of this part of the research was to investigate and compare the proximate compositions of two varieties of cocoa beans ‘Amelonado’ and ‘Hybrid’. The impact of fermentation on the nutritive values such moisture contents, ash, carbohydrate, fat, and crude protein of dry cocoa nib, cocoa shell and whole cocoa bean use as human food and animal feed was investigated.

The moisture content of a food material gives an indication of the extent to which the nutritive value of the food material can be maintained. The raw (whole) cocoa beans obtained from ‘Amelonado’ cocoa beans fermented for six and eight days had no significant difference ($p>0.05$) in the moisture content. Similarly, the

unfermented cocoa nib and bean shell and those fermented for eight days recorded no significant difference in moisture content. Also, the raw (whole) cocoa beans and nib obtained from 'Amelonado' cocoa beans fermented for four, six and eight days had no significant difference ($p > 0.05$) in the moisture content.

The mean ash content of the whole cocoa bean, cocoa nib and bean shell from both 'Amelonado' and 'Hybrid' varieties increased as the days of fermentation increased. The values obtained from this study show a direct relationship with the days of fermentation because as the days of fermentation increased, the ash content increase.

As the days of fermentation increased, the total soluble carbohydrate content increased for both varieties considered for this study. Generally, the total soluble carbohydrate of 'Amelonado' and 'Hybrid' varieties of cocoa beans increased ($P < 0.05$) with fermentation duration.

There was a significant difference in fat content among each part of cocoa bean involved ($p < 0.05$). The significant differences could be as a result of the duration of fermentation and the part of bean involved. The cocoa bean shell recorded the lowest fat content in respect of both the bean part and variety. Fermenting beans for six days was the best since it resulted in the production of the least fat for both 'Amelonado' and 'Hybrid' varieties of cocoa beans.

As the days of fermentation increased, the protein content in all the three parts of the beans reduced, irrespective of the variety. The values show a level of significant difference among the samples at a significant level of $p = 0.05$.

CHAPTER SEVEN

GENERAL DISCUSSIONS

The particle density linearly increased (probability < 0.05) from 946.21 to 1028.31 kg/m³ and 831.30 to 974.15 kg/m³ for 'Hybrid' and 'Amelonado' cocoa varieties, respectively. Comparatively, the 'Hybrid' cocoa beans displayed a higher particle density than the 'Amelonado' cocoa beans. The variation could be attributed to the higher increase in the mass of the bean as compared to its volumetric increase as bean moisture content increases. The average values of the bulk density for 'Hybrid' and 'Amelonado' beans decreased linearly from 697.11 to 602.37kg/m³ and 649.86 kg/m³ to 563.90 kg/m³ respectively, with an increase in moisture content from 6.1 to 24.1% (wb). This can be attributed to the fact that an increase in mass owing to moisture bean in the bean sample was lower than the accompanying volumetric expansion of the bulk. These observed discrepancies could be due to the cell structure, volume and mass increase characteristics of the grains and seeds as moisture content increases. The implication may be that the shells absorptivity of moisture is high and it has a reducing effect on the bulk density.

The experimental values showed that as the bean moisture level increased porosity of the bean also increased linearly irrespective of variety. This could be as a result of a decrease in the cohesion of the cell structure of the beans as a result of

moisture absorption. The increase in porosity is certainly the result of a more expanded shape of the beans, leading to a decrease in the contact surface. Bart-Plange and Baryeh (2002) category B cocoa beans. This observation was, however, opposite to Tunde-Akintunde and Akintunde (2007) who found a decrease in porosity with increase in moisture content for beniseed. Less quantity of beans can be stored at high moisture as a result of the increased porosity. The ‘Amelonado’ variety depicted lower values of porosity as compared to ‘Hybrid’ cocoa beans.

The angle of repose increased linearly with the moisture content in all the varieties under investigation. The increasing trend of repose angle with moisture content occurs because surface layer of moisture surrounding the bean holds the aggregate of beans together by the surface tension. Between moisture content of 6.1 to 24.1% (wb), the filling angle of repose increased from 25.2° to 34.6° and 27.9° to 36.5° for ‘Hybrid’ and ‘Amelonado’ beans respectively. ‘Amelonado’ variety exhibits higher values than ‘Hybrid’ cocoa beans. This could be due to the smaller sizes of the ‘Amelonado’ beans which interlock more to cause a higher heap formation than relatively bigger sizes of ‘Hybrid’ cocoa beans. This property is needed in determining the minimum slope of flow in hoppers.

The rupture force decreased with an increase in the bean moisture content. This is possibly due to the fact that at a higher moisture content the bean became softer and required less force to rupture. Comparatively, the force required to initiate the bean rupture in the case of ‘Hybrid’ variety was higher than that of the ‘Amelonado’ variety, at similar conditions of bean moisture content and orientation. The results also revealed that the bean rupture force at horizontal

loading was higher than that of vertical loading, irrespective of variety. This is could be due to the higher rupturing dimensional axis of the beans at vertical orientation.

The energy absorbed by the bean before initiating its rupture in the case of 'Amelonado' variety was lower than that of the 'Hybrid' variety, at similar conditions of the bean moisture content and orientation. The results also showed that the bean was more resistant to rupturing in the horizontal direction of loading as compared to the vertical, for both varieties examined. In size reduction process, the energy required for particle breakdown increases with decrease in the size of the particles (Sahay and Singh, 2001). It was noted that the energy absorbed by the cocoa beans increased with increase in bean moisture content for both varieties.

It is observed that the deformation at rupture point increased as the moisture content increased for both varieties. The energy absorbed at bean rupture was a function of both force and deformation up to rupture point. At low moisture content, the bean requires high force to be ruptured and its deformation was low but at high moisture content, the rupture force was low and the deformation was high. This fact showed that energy absorbed at bean rupture increases as the moisture content of the bean increases indicating high resistance to bean rupture during compressive loading. The experimental values suggested that the 'Amelonado' is softer as compared to the 'Hybrid' and therefore the 'Amelonado' required a higher compression depth than the 'Hybrid' beans.

The temperature of the fermented beans for both varieties increased significantly as days of fermentation increased from day one to day seven. The

beans temperature began to fall after the sixth day of fermentation. This fall in temperature well corresponded with the development of ammonia odour when the fermentation can be considered to have completed. The experimental values demonstrated that as the days of fermentation increased the temperature in the fermented cocoa beans increased with 'Hybrid' variety recording the highest temperatures compared to 'Amelonado' variety.

The pH of cocoa beans is an important phytochemical property as it gives an indication on the degree of acidification of the nibs during fermentation and the quality of fermentation. Fermented and dried cocoa beans with pH range 5.0-5.5 produced higher flavour potentials while that with pH range 4.0-4.5 give low flavour potential. There were significant differences in the pH content of beans obtained from 'Amelonado' and 'Hybrid' varieties including the part of the bean examined. This could be as a result of the differences in the duration of fermentation. On the average pH was observed to be increasing with increasing days of fermentation irrespective of the variety and the part of the cocoa bean examined. Duration of fermentation have affected the pH of beans by influencing enzyme activities and flavour development and hence acidity, bitterness and astringency of the cocoa beans.

The level of free fatty acids in the fat of cocoa beans gives the measure of rancidity of the cocoa, and high levels of free fatty acid (> 1.75% in dried beans) in cocoa are not acceptable. Even though there were significant differences in FFA content of the whole bean, nib and bean shell from both varieties, both varieties produced good beans with respect to the percentage FFA. The significant

differences could be as a result of the fermentation duration and the part of bean involved. The cocoa bean shell recorded the lowest FFA content in respect to both the bean part and variety. Fermenting beans for six days was the best since it resulted in the production of the least FFA for both ‘Amelonado’ and ‘Hybrid’ varieties of cocoa beans, irrespective of the bean part used.

The experimental values showed that the total polyphenol content of whole cocoa bean, nib and shell from the ‘Hybrid’ variety recorded the highest as compared with those obtained from ‘Amelonado’. Fermenting beans for six days yielded the highest polyphenol content for both ‘Amelonado’ and ‘Hybrid’ varieties of cocoa beans of all the three parts considered in this study.

The experimental values showed that no significant difference ($p < 0.05$) exist in the total soluble solids content of the ‘Amelonado’ and ‘Hybrid’ varieties. However, cocoa bean shell from ‘Amelonado’ variety unfermented and fermented for four days are significantly different from others. Generally, the mean values of total soluble solids content of the two varieties of cocoa beans ranges from 66.2 to 67.75° Brix (Fig. 5.5). The total soluble solids content correlated with sweetness.

The experimental values show that the ash content of the whole cocoa bean, cocoa nib and bean shell from both ‘Amelonado’ and ‘Hybrid’ varieties increased as the days of fermentation increased. The values further showed that among the three regions of cocoa bean considered in this research the ash content is highest in the shell of the bean, irrespective of the variety. This result obtained actually confirms the assertion that the observed increase in the ash content of the fermented cocoa bean shells was as a result of the mycelia growth on the cocoa bean shells.

There were significant differences in carbohydrate content in cocoa nib and shell from both varieties of cocoa ‘Amelonado’ and ‘Hybrid’. Meanwhile the cocoa nib showed the highest levels of carbohydrate content as the days of fermentation increase irrespective of the variety. However, cocoa nib from ‘Amelonado’ variety showed significantly higher levels in carbohydrate content than cocoa nib from ‘Hybrid’ variety. The bean carbohydrate changes are due to hydrolytic enzymes in the beans that were released during fermentation by de-compartmentalization of cells within the bean

The cocoa bean shell recorded the lowest fat content in respect to both the bean part and variety. Fermenting beans for six days was the best since it resulted in the production of the least fat for both ‘Amelonado’ and ‘Hybrid’ varieties of cocoa beans. No significant difference ($p < 0.05$) existed in the unfermented and fermented cocoa nib of ‘Amelonado’ variety in the fat content over the period of fermentation. As the days of fermentation increased, the protein content reduced irrespective of the variety and part of the bean used. The cocoa nib from ‘Hybrid’ variety had the highest level protein content (16.46 %). On the other hand the cocoa bean shell recorded the lowest levels of protein content irrespective of the variety and part of the bean considered. However, unfermented recorded significantly highest levels in the protein content irrespective of the variety and part of the bean considered.

CHAPTER EIGHT

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The entire study investigated the physical, mechanical and biochemical properties of ‘Amelonado’ and ‘Hybrid’ cocoa varieties, as affected by moisture content and fermentation. There are several conclusions that could be drawn from this study:

1. There is a tendency for the axial dimensions to increase slightly with increasing moisture content.
2. For the same quantity of cocoa beans the ‘Hybrid’ variety is more likely to give a higher weight than the ‘Amelonado’ variety.
3. The mean particle and bulk densities for both varieties are less than the density of water. This implies that both ‘Hybrid’ and ‘Amelonado’ cocoa beans will float in water. This makes it possible to separate them from materials that are denser than water.
4. The values of rupture force and energy of cocoa beans in the case of ‘Hybrid’ variety was higher than those of ‘Amelonado’ variety. So, it can be concluded that the ‘Hybrid’ variety is more resistant to breakage than the ‘Amelonado’ variety during the bean processing operations such as de-shelling and milling.
5. The results also showed that the cocoa bean is more resistant to rupturing in the horizontal direction of loading than vertical direction, for both varieties examined.

6. The results revealed that cocoa beans rupture under vertical loading direction demand less energy than under horizontal loading direction. This is may be due to decreasing contact area of the beans with loading plate and probably the occurring buckling phenomenon.
7. The experimental values of compressive stress decreased from 0.685 - 214 Nmm⁻² and 0.404 - 0.116 Nmm⁻², and 1.673 - 0.565 Nmm⁻² and 0.472 - 0.153 Nmm⁻² for 'Amelonado' and 'Hybrid' varieties at both horizontal and vertical orientations, respectively when moisture content increased from 5% - 21% (wb).
8. The mean compressive strain values for 'Amelonado' and 'Hybrid' varieties increased as moisture content increased. The relationship between compressive strain and moisture content was found to be significant at 0.05. The compressive strain values of the 'Hybrid' variety were higher than that of the 'Amelonado'.
9. The increase of moisture content increased the apparent Young's modulus of deformability linearly.
10. As the days of fermentation increased the temperature in the fermented cocoa beans increased with 'Hybrid' variety recording the highest temperature as compared with 'Amelonado' variety. It was realized that there was an increasing trend of the fermentation temperature with increase in fermentation duration and then peaked by the sixth day after which there was a decline at day eight.
11. Fermenting beans for six days was the best since it resulted in the production of the least FFA (less than 1.75) in all the different parts of cocoa beans of both 'Amelonado' and 'Hybrid' varieties.

12. The total polyphenol content of whole cocoa bean, nib and shell from the 'Hybrid' variety recorded the highest as compared with those obtained from 'Amelonado' variety. Fermenting beans for six days yielded the highest polyphenol content for both 'Amelonado' and 'Hybrid' varieties of cocoa beans of all the three parts considered in the present study.
13. The mean ash content of the whole cocoa bean, cocoa nib and bean shell from both 'Amelonado' and 'Hybrid' varieties increased as the days of fermentation increased.
14. As the days of fermentation increased, the total soluble carbohydrate content increased for both varieties considered for this study.
15. The cocoa bean shell recorded the lowest fat content in respect to both the bean part and variety.
16. It can be concluded from this study that as the days of fermentation increased, the protein content of all the different parts of the beans reduced, irrespective of the variety considered for the examination.

Recommendations

1. Further research on the effect of different drying methods on the physical characteristics and nutritional compositions of the beans should be investigated.
2. The effect of storage on the nutritive compositions in raw cocoa bean, nib and shell should be studied.

REFERENCES

- Abano, E.E. and Amoah, K.K. (2012). Effect of moisture content on the physical properties of tiger nut. *Asian Journal of Agricultural Research*, 5 (1): 55-56.
- Abano, E.E., Ma, H. and Qu, W. (2011). Effects of Pretreatments on the Drying Characteristics and Chemical Composition of Garlic Slices in a Convective Hot Air Dryer. *Journal of Agricultural and Food Technology*, 1(5): 50-58.
- Abrokwah, F.K., Asamoah, K.A. and Esubonteng, P.K.A. (2009). Effect of intake of natural cocoa powder on some biochemical and heamatological indices in the rat. *Ghana Med. Journal*, 43(4): 164-168).
- Adeyeye, E.I., Akinyeye, R.O., Ogunlade, I., Olaofe, O. and Boluwade, J.O. (2010). Effect of farm and industrial processing on the amino acid profile of cocoa beans. *Food Chemistry*, 118:357–363
- Afoakwa E.O. (2010). *Chocolate science and technology*. Wiley- Blackwell Publishers, Oxford, UK, pp 3–22.
- Afoakwa E.O., Paterson A., Fowler M. and Ryan A. (2008). Flavour formation and character in cocoa and chocolate: a critical review. *Crit Rev Food Sci Nutr*, 48:840–857.
- Akaaimo, D.I. and Raji, A.O. (2006). Some Physical and Engineering Properties of *prosopis africana* Seed. *Journal of Biosystems engineering*, 95:197-205.

- Altuntaş E. and Yildiz M. (2007): Effect of moisture content on some physical and mechanical properties of faba bean (*Vicia faba L.*) grains. *Journal of Food Engineering*, 78: 174–183.
- Anvoh, K.Y.B., Zoro Bi A. and Gnakri, D. (2009). Production and Characterization of Juice from Mucilage of Cocoa Beans and its Transformation into Marmalade. *Pakistan Journal of Nutrition*, 8 (2): 129-133.
- Aregheore, E. M. (2002). Chemical evaluation and digestibility of cocoa (Theobroma cacao) by-products fed to goats. *Tropical Animal Health and Production*, 34: 339-348.
- ASAE Standards 358.2. (1999). *Moisture measurement of unground grains and seeds*. ASAE Press, St. Joseph, MI, USA.
- Asiedu, J.J., 1991. *Transformation des produits agricoles en zone tropicale CTA Karthala*, page: 335.
- Asoiro, F.U. and Anthony, O.A., (2011). *Determination of some Physical Properties of African Yam Beans*. 12(1): 374-80.
- Aviara, N. A., Oluwole, F. A. and Haque, M. A. (2005). Effect of moisture content on some physical properties of sheanut (*Butyrospermum Paradoxum*), *International Agrophysics*, 19:193-198.
- Aviara, N.A., Gwandzang, M.I. and Hague, M.A. (1999). Physical properties of guna seeds. *Journal of Agricultural Engineering Research*, 73, 105-11.

- Bagheri, I. Dehpour, M.B., Payman, S.H. and Zareiforoush, H. (2011). Rupture Strength of Brown Rice varieties as Affected by Moisture Content and Loading rate. *Australian Journal of Crop Science*, 5(10):1239- 1246.
- Bahnasawy, A. H., El-Haddad, Z. A., El-Ansary, M. Y. and Sorour, H. M. (2004). Physical and mechanical properties of some Egyptian onion cultivars. *Journal of Food Engineering*. 62, 255-261.
- Barker, Helen M. (2002). *Nutrition and dietetics for health care*. Edinburgh: Churchill Livingstone. p. 17. ISBN 0-443-07021-0. OCLC 48917971
- Bart-Plange, A. and Baryeh, E.A. (2002). The physical properties of category B Cocoa beans. *Journal of Food Engineering*. 60, 219-227.
- Barry Callebaut (2008). *History of chocolates*. <http://www.barry-callebaut.com/158>
- Baryeh, E.A. and Mangope, B.K. (2002). Some Physical Properties of QP-38 Variety Pigeon Pea. *Journal of Food Engineering*. 56 (2002) 59–65.
- Baryeh, E.A. (2001). Physical properties of Bambara groundnuts. *Journal of Food Engineering*, 2001, 47, 321-326.
- Bello, M., Tolaba, M.P., Suarez, C. (2004). *Factors affecting water uptake of rice grain during soaking*. *Lebensm. Wiss. Technology*, 37 (2004) 811-816.
- Belscak, A., Komes, D., Horzic, D., Ganic, K. and Damir, K.D. (2009). Comparative study of commercially available cocoa products in terms of their bioactive composition. *Food Research Internationa*, 42: 707-716.
- Bhave, M., and Morris, C.F. (2008). Molecular genetics of puroindolines and related genes: Allelic diversity in wheat and other grasses. *Plant Mol. Biology*, 66:205-219.

- Burubai, W., Ako, A.J., Igoni, A.H. and Uyate, Y.T. (2007). Effects of Temperature and Moisture Content on the Strength Properties of African Nutmeg (*Monodora Myristica*). *Bulgarian Journal of Agricultural Science*. 13:703-712.
- Ching, A.L. and Wong, H.M. (1986). Utilization of cocoa shell in pig feed. *Singapore Journal. Pri. Ind.*, 14: 133-139.
- COCOBOD, (2012). Socio-economic study. Final report [MASDAR]. Ghana Cocoa Board.
- Cooper, K.A., Donovan, J.L., Waterhouse, A.L., & Williamson, G. (2008). Cocoa and health : a decade of research *British Journal of Nutrition*, 99:1–11.
- Coskun, M.B., Yalcin, I., & Ozarslan, C. (2006). Physical properties of sweet corn seed (*Zea mays saccharata sturt*). *Jour. Food Eng.*, 74, 523-528.
- CRIG. (2010). *Cocoa Manual: A source book for Sustainable Cocoa Production*. Tafo: Cocoa Research Institute of Ghana, 104pages.
- Davies, R.M. and El-Okene, A.M. (2010). *Moisture-Dependent Physical Properties of Soybeans*. 23, 299-303.
- Delwiche, S.R. 2000. “*Wheat Endosperm Compressive Strength as Affected by Moisture*”. Transaction of ASAE. 43(2):365-373.
- Dutta S.K., Nema V.K., and Bhardwaj R.K. (1988). Physical properties of gram. *J. Agric. Eng. Res.*, 39; 259-268.
- Eke C.N.U., Asoegwu S.U. and Nwandikom G.I. (2007) Physical Properties of Jackbean (*Canavalia ensiformis*) *Agricultural Engineering International: the CIGR Ejournal Manuscript FP 07 014 Vol. IX*.

- Food and Agriculture Organization of the United Nations (FAO), (2013). FAOStat. Retrieved from <http://faostat.fao.org/default.aspx?lang=en>.
- Galedar M.N., Jafari A. and Tabatabaeefar A. (2008). Some physical properties of wild pistachio nut and kernel as a function of moisture content. *J. Physics Environ. Agric. Sci.*, 22; 117-124.
- Gates, Fred K. (2004). *Mechanical Properties of Oats and Oat Products*. Agricultural and Food Science, 13(2004): 113–123.
- Gereke, T. and Niemz, P., (2010). Moisture- induced stresses in spruce cross-laminates. *Engineering Structures*, 32, 600-606.
- Gharibzahedi, S.M.T., Mousavi, S.M., Moayedi, A., Garavand, A.T. and Alizadeh S.M. (2010). Moisture-dependent engineering properties of black cumin (*Nigella sativa L.*) seed. *Agric. Eng. Int: CIGR Vol. 12, No.1*.
- Gohl, B. (1981). *Tropical Feeds*. Publishers, FAO of UN, Rome, pp 38-39.
- Guehi, T.S., Dingkuhn, M., Cros, E., Fourny, G., Ratomahenina, R., Moulin G. and Clement, A. (2007). Identification and lipase-producing abilities of moulds isolated from Ivorian raw cocoa beans. *Res. J. Agric. Biol., Sci.*, 3: 838-843.
- Gupta R.K., Das S.K. (2000). Fracture resistance of sunflower seed and kernel to compressive loading. *Journal of Food Engineering*, 46:1- 8.
- Hamzat, R.A. and Babatunde A. (2006). *Utilization of cocoa bean shell as a feed ingredient for broiler chickens*. Proceedings of the 15th International Cocoa Research Conference, Costa Rica. pp. 84 -86.

- Heidarbeigi, K. H., Ahmadi, K.K. and Tabatabaeefar, A. (2009). Some Physical and Mechanical Properties of Khinjuk. *Pak. J. Nutr.*, 8(1): 74-77.
- Horwitz, W. (1980). *Official Methods of Analysis*. Association of official analytical chemists, 13th edition, Washington DC, USA.
- Ieggli, C., Bohrer, D., Nascimento, P. and Carvalho, L. (2011). Determination of sodium, potassium, calcium, magnesium, zinc and iron in emulsified chocolate samples by flame atomic absorption spectrometry. *Food Chemistry*, 124:1189-1193.
- International Cocoa Organization (ICCO). (2009). Annual report 2007/2008. International Cocoa Organization, London U.K.
- International Cocoa Organization (ICCO). (2011). Also available at www.icco.org.
- International Cocoa Organization (ICCO). (2013). *ICCO quarterly bulletin of cocoa statistics*, XXXIX (2). London, UK.
- International Office of Cocoa, Chocolate and Sugar Confectionery (IOCCC), (1996). *Determination of free fatty acids (FFA) content of cocoa fat as a measure of cocoa nib acidity*, *Anal. Method* 42 130-136.
- Irtwange S. V., Igbeka J.C. (2002). Some physical properties of two African yam bean (*Sphenostylis stenocarpa*) accessions and their interrelations with moisture content. *Applied Engineering in Agriculture*, 18(5), 567–576.
- Jain, R. K. and Bal. S. (1997). Physical properties of pearl millet. *Journal of Agricultural Engineering Research*, 66, 85-91.
- Jonfia-Essien, W. A. (2004). Cocoa: West Africa (Ghana). In R. Hodges and G. Farrell (Eds), *Crop Post Harvest: Science and Technology* volume 2 (pp 216- 245). Blackwell Publishing, Oxford, UK.

- Jonfia-Essien, W. A. and Navarro, S (2010). *Effect of storage management on free fatty acid content in dry cocoa beans*. 10th International Working Conference on Stored Product Protection. DOI: 10.5073/jka.2010.425.167.160.
- Kabas O., Yilmaz E., Ozmerzi A. and Akinçi I. (2007). Some physical and nutritional properties of cowpea seed (*Vigna sinensis* L.). *Journal of Food Engineering*, 79: 1405-1409.
- Kalkan, F., Kara M. (2011). *Handling, frictional and technological properties of wheat as affected by moisture content and cultivar*. *Powder Technol* 213: 116-122.
- Karababa E. (2006). Physical properties of popcorn kernel. *Journal of Food Engineering*. 72, 100-107.
- Lefeber, T., Gobert, W., Vrancken, G. Camu, N., and Vuyst, L.D. (2011). Dynamics and species diversity of communities of lactic acid bacteria and acetic acid bacteria during spontaneous cocoa bean fermentation in vessel. *Food microbiology*, 28, 457-464.
- Lettieri-Barbato, D., Villano, D., Beheydt, B., Guadagni, F., Trogh, I. and Serafini, M. (2012). Effect of ingestion of dark chocolates with similar lipid composition and different cocoa content on antioxidant and lipid status in healthy humans. *Food Chemistry*, 132:1305-1310.
- Liu M, Haghghi K, Strohline RL, Ting EC (1990). Mechanical properties of the soybean cotyledon and failure strength of soybean kernels. *Trans ASAE* 33(2):559–566.
- MarketsandMarkets. (2013). *MarketsandMarkets: Global Chocolate Market worth \$ 98.3 billion by 2016*. Retrieved from <http://www.marketsandmarkets.com/PressReleases/global-chocolate-market.asp>.

- McCabe, W. L., Smith, J. C., and Harriott, P. (1986). *Unit operations of chemical engineering*. New York: McGraw-Hill.
- Menon, M. A. (1982). *Cocoa by-products and their uses*. *Planter*, Kuala Lumpur, 58: 286 – 295.
- Milani E., Razavi S.M.A., Koocheki A., Nikzadeh V., Vahedi N., Moein Ford M., and Gholamhossein Pour A. (2007). Moisture dependent physical properties of cucurbit seeds. *Int. Agro physics*, 21, 157-168.
- Mingle, J. (2010). *Ghana strides in cocoa production*. Ghana Broadcasting co-operation.
- Mohsenin, N.N. (1978). *Physical properties of plant and animal materials*. Vol. I. Gordon and Breach Sc. Pub. Inc. pp. 66-87, 205-207.
- Mohsenin, N.N. (1986). *Physical Properties of Plant and Animal Materials: Structure, Physical Characteristics and Mechanical Properties*. Updated and Revised Edition. Gordon and Breach Science Publishers, New York.
- Morris, Craig F., Delwiche, S.R., Bettge, A.D., Mabelle, F., Abécassis, J., Pitts, M.J., . . . Dowell, F.E., Deroo, C and Pearson, T. (2011) Collaborative Analysis of Wheat Endosperm Compressive Material Properties. *Cereal Chemistry*, 88(4): 391–96.
- Nazaruddin, R., Ayub, M. Y., Mamot, S. and Heng, C. H. (2001). HPLC determination of methylxanthines and polyphenols levels in cocoa and chocolate products, *Malaysian Journal Analytical Science*, 7, 377–386.
- Ntiamoah, A and Afrane, G. (2008). Environmental impacts of cocoa production and processing in Ghana: life cycle assessment approach. *Journal of Cleaner Production*, Vol. 16, issue 16, 1735-1740.

- Osakebe, N., Natsume M. A., T. Yamagashi, M., Hirano R., Takizawa T., Itakura H. and Kando, K. (2000). *Effect of cocoa liquor polyphenol on the susceptibility of low density lipoprotein to oxidation in hypercholesterolemic rabbit*. *J. Atheroscler Thomb*; 7(3): 164-165.
- Pliestic, S. Dobricevic, N. Filipovic, D., Gospodaric, Z. (2006). Physical Properties of Filbert Nut and Kernel. *Biosystems Engineering*, 93(2):173-178.
- Polly H. (1963), *The Migrant Cocoa--Farmers of Southern Ghana: A Study in Rural Capitalism* (England: Cambridge University Press), 171-173.
- Pradhan, R. C., Naik, S. N., Bhatnagar, N. & Vijay, V. K. (2009). Moisture dependent physical properties of Jatropha fruit. *Journal Industrial crops and products*, 29, 341-347.
- Roberto, C., Andreas J.F., Norman, K. and Thomas, F.L. (2009). *Cocoa and Cardiovascular Health*. *Circulation* 119:1433-1441.
- Rossini K, Noreña C.P.Z. and Brandelli A. (2011) Changes in the color of white chocolate during storage: potential roles of lipid oxidation and non-enzymatic browning reactions. *J Food Sci Technology*, 48:305–311.
- Rusconi, M. and Conti, A. (2010). *Theobroma cacao* L., the food of the Gods: a scientific approach beyond myths and claims. *Pharmacological Research*, vol. 61, no. 1, pp. 5–13.
- Saiedirad, M.H., Tabatabaeefar, A., Borghei, A., Mirsalehi, M., Badii, F. and Ghasemi Varnamkhasti, M. (2008). *Effects of Moisture Content, Seed size, Loading Rate and Seed Orientation on Force and Energy Required for Fracturing Cumin Seed*

- (*Cuminum cyminum* Linn.) under quasi-static loading. *Journal of Food Engineering*. 86:565-572.
- Sharma, S.K., Dubey, R.K. and Teckchandani, C.K. (1985). *Engineering properties of black gram, soybean and green gram* (Vol. pp. 118-185).
- Shitanda, D. Nishiyama, Y. and Koide, S. (2002). Compressive strength properties of rough rice considering variation of contact area. *Journal of Food Engineering*, 53, 53-58.
- Singh, K.K. and Goswami, T.K. (1996). Physical properties of cumin seed. *Journal of Agricultural Engineering Research*. 64, 93-98.
- Singh, K.K., Reddy, B.S., Varshney, A.C. and Mangraj, S. (2004). Physical and frictional properties of Orange and sweet lemon. *Applied Engineering in Agriculture*, 20(6), 821-825.
- Singh, R.P. and Dennis, R.H. (2009). *Introduction to Food Engineering*, International Series. Fourth Edition. Elsevier Inc. London, UK.
- Sirisomboon, P., Pornchaloeampong P. and Romphophak T. (2007). Physical Properties of Green Soybean: Criteria for Sorting. *Journal of Food Engineering*, 79:18–22.
- Spencer, M.E. and Hodge, R. (1992). Cloning and sequencing of a cDNA encoding the major storage proteins of *Theobroma cacao*. *Planta*, 186: 567-576.
- Stroshine, R. and Hamann, D. (1995). *Physical Properties of Agricultural Materials and Food Products*. Course Manual, Purdue University Press, Indiana.
- Sundiata, I.K. (1974). “Prelude to Scandal: Liberia and Fernando Po, 1880-1930”. *The Journal of African History*. Vol. 15, No. 1. 98; 98-99.
- Suthar S.H. and Das, S.K. (1996). Some physical properties of *Karingda Citrullus lamatus* (*Thurm*) Manst. Seeds. *J. Agric. Eng. Res.*, 65, 15-22.

- Taubert, D., Roesen, R., Schömig, E. (2007). Effect of cocoa and tea intake on blood pressure: a meta-analysis. *Arch. Intern. Med.*, 167(7):626-34.
- Tavakoli, H., Mohtasebi, S.S., Rajabipour, A. and Tavakoli, M. (2009). Effects of Moisture Content, Loading Rate and Grain Orientation on Fracture Resistance of Barley Grain. *Res. Agr. Eng.*, 3:85-93.
- Thompson, R.A. and Isaac, G.W. (1967). *Porosity determination of grains and seeds with air comparison pycnometer*. Transactions of ASAE, 10, 693-696.
- Victor, Y.A.B., Yaw, O.B., Ernest O.A., Nicholas, T.K.D.D. and Francis, E.M. (2013). In-Vitro Assessment of Antioxidant and Antimicrobial Activities of Methanol Extracts of Six Wound Healing Medicinal Plants. *Journal of Natural Sciences Research*. Vol. 3, No. 1, 74, 74-80.
- Visvanathan, R., Palanisamy, P.T., Gothandapani, P.T. and Sreenarayanan, V.V. (1996). Physical properties of neem nut. *Journal of Agricultural Engineering Research*, 63, 19-26.
- Wood, G.A.R. and Lass, R.A. (1985). *Cocoa*. 4th Edition. Longman Group, Scientific and Technical, Essex, London, England, pp 510-513.

APPENDICES

ANOVA TABLES

Appendix 1: Interactive effect of variety, moisture content and axial dimensions

Table 3.3: ANOVA of principal dimensions of cocoa beans

Source of variation	df	ss	ms	f	F pr
Variety (VA)	1	9.321	9.321	6.90	0.009
Moisture content (MC)	4	24.114	6.028	4.46	0.001
Dimension (D)	2	19380.7	9690.366	7169.91	<.001
VA × MC	4	0.399	0.100	0.07	0.990
Variety × Dimension	2	5.033	2.516	1.86	0.156
MC × D	8	1.674	0.209	0.15	0.996
VA × MC × D	8	6.985	0.873	0.65	0.739
Residual	570	770.373	1.352		
Total	599	20198.632			

Appendix 2: Effect of moisture content, orientation and variety on mechanical properties

Table 4.3: ANOVA on the effects of moisture content, orientation and variety on rupture force

Source of variation	df	ss	ms	f	F pr
Moisture content (MC)	4	4.120E+05	1.030E+05	13293.68	<.001
Variety (VA)	1	4.077E+05	4.077E+05	52630.33	<.001
Orientation (OR)	1	7.262E+05	7.262E+05	93734.79	<.001
MC × VA	4	4.475E+04	1.119E+04	1444.09	<.001
MC × OR	4	7.664E+04	1.916E+04	2473.11	<.001
VA × OR	1	2.798E+05	2.798E+05	36117.60	<.001
MC × VA × OR	4	3.483E+04	8.708E+03	1124.00	<.001
Residual	380	2.944E+03	7.747E+00		
Total	399	1.985E+06			

Table 4.4: ANOVA on the effects of moisture content, orientation and variety on energy absorbed

Source of variation	df	ss	ms	f	F pr
Moisture content (MC)	4	2.703E-02	6.757E-03	1027.32	<.001
Orientation (OR)	1	2.652E-01	2.652E-01	40322.26	<.001
Variety (VA)	1	1.086E-01	1.086E-01	16516.00	<.001
MC × OR	4	5.099E-03	1.275E-03	193.82	<.001
MC × VA	4	7.637E-03	1.909E-03	290.26	<.001
OR × VA	1	6.859E-02	6.859E-02	10428.01	<.001
MC × OR × VA	4	2.741E-03	6.852E-04	104.18	<.001
Residual	380	2.500E-03	6.578E-06		
Total	399	4.875E-01			

Table 4.5: ANOVA on the effects of moisture content, orientation and variety on deformation

Source of variation	df	ss	ms	f	F pr
Moisture content (MC)	4	420.361	105.090	21354.59	<.001
Orientation (OR)	1	32.345	32.345	6572.55	<.001
Variety (VA)	1	19.339	19.339	3929.80	<.001
MC × OR	4	11.854	2.963	602.17	<.001
MC × VA	4	2.639	0.659625	134.04	<.001
OR × VA	1	2.394	2.394	486.53	<.001
MC × OR × VA	4	0.442	0.111	22.46	<.001
Residual	380	1.870	0.005		
Total	399	491.243			

Table 4.6: ANOVA on the effects of moisture content, orientation and variety on compressive stress

Source of variation	df	ss	ms	f	F pr
Moisture content (MC)	4	2.373	0.593	14016.38	<.001
Orientation (OR)	1	3.466	3.466	81896.97	<.001
Variety (VA)	1	1.747	1.747	41282.65	<.001
MC × OR	4	0.434	0.108	2562.99	<.001
MC × VA	4	0.195	0.049	1153.66	<.001
OR × VA	1	1.278	1.278	30195.96	<.001
MC × OR × VA	4	0.177	0.044	1043.36	<.001
Residual	40	0.002	0.000042		
Total	59	9.670			

Table 4.7: ANOVA on the effects of moisture content, orientation and variety on compressive strain

Source of variation	df	ss	ms	f	F pr
Moisture content (MC)	4	1.250E-01	3.126E-02	22329.27	<.001
Orientation (OR)	1	9.907E-03	9.907E-03	7076.68	<.001
Variety (VA)	1	8.284E-03	8.284E-03	5916.96	<.001
MC × OR	4	3.574E-03	8.935E-04	638.20	<.001
MC × VA	4	1.457E-03	3.641E-04	260.09	<.001
OR × VA	1	6.338E-04	6.338E-04	452.68	<.001
MC × OR × VA	4	1.485E-04	3.713E-05	26.52	<.001
Residual	40	5.600E-05	1.400E-06		
Total	59	1.491E-01			

Table 4.8: ANOVA on the effects of moisture content, orientation and variety on apparent Young's modulus

Source of variation	df	ss	ms	f	F pr
Moisture content (MC)	4	2.264E+04	5.661E+03	4.698E+08	<.001
Orientation (OR)	1	3.877E+04	3.877E+04	3.217E+09	<.001
Variety (VA)	1	1.904E+04	1.904E+04	1.580E+09	<.001
MC × OR	4	4.169E+03	1.042E+03	8.649E+07	<.001
MC × VA	4	1.807E+03	4.518E+02	3.749E+07	<.001
OR × VA	1	1.397E+04	1.397E+04	1.159E+09	<.001
MC × OR × VA	4	1.676E+03	4.190E+02	3.477E+07	<.001
Residual	40	4.820E-04	1.205E-05		
Total	59	1.021E+05			

Appendix 3: Effect of fermentation periods on the phytochemical compositions

Table 5.1a: ANOVA on effect of fermentation duration on temperature of cocoa beans

Source of variation	df	ss	ms	f	F pr
Days	7	973.5186	139.0741	770.21	<.001
Variety	1	18.1052	18.1052	100.27	<.001
Days × Variety	7	23.3323	3.3332	18.46	<.001
Residual	16	2.8891	0.1806		
Total	31	1017.8450			

Table 5.2a: ANOVA on effect of fermentation duration on pH of cocoa beans

Source of variation	df	ss	ms	f	F pr
Days (D)	3	14.809744	4.936581	1088.03	<.001
Bean Part (BP)	2	2.454020	1.227010	270.43	<.001
Variety (V)	1	24.571701	24.571701	5415.62	<.001
D × BP	6	0.597983	0.099664	21.97	<.001
D × V	3	4.964216	1.654739	364.71	<.001
BP × V	2	0.858323	0.429161	94.59	<.001
D × BP × V	6	1.079879	0.179980	39.67	<.001
Residual	24	0.108892	0.004537		
Total	47	49.444758			

Table 5.3a: ANOVA on effect of days of fermentation on titratable acidity of cocoa beans

Source of variation	df	ss	ms	f	F pr
Days (D)	3	1.280E+01	4.267E+00	56197.07	<.001
Bean Part (BP)	2	1.108E+01	5.539E+00	72937.71	<.001
Variety (V)	1	4.188E-02	4.188E-02	551.51	<.001
D × BP	6	2.188E+01	3.647E+00	48025.56	<.001
D × V	3	2.880E+00	9.600E-01	12642.64	<.001
BP × V	2	9.438E-01	4.719E-01	6214.05	<.001
D × BP × V	6	1.368E+00	2.280E-01	3002.93	<.001
Residual	24	1.822E-03	7.594E-05		
Total	47	5.100E+01			

Table 5.4a: ANOVA on effect of days of fermentation on FFA of cocoa beans

Source of variation	df	ss	ms	f	F pr
Days (D)	3	14299.68	4766.56	102.43	<.001
Bean Part (BP)	2	1926.81	963.40	20.70	<.001
Variety (V)	1	648.61	648.61	13.94	0.001
D × BP	6	878.55	146.42	3.15	0.020
D × V	3	1603.46	534.49	11.49	<.001
BP × V	2	440.53	220.27	4.73	0.018
D × BP × V	6	962.68	160.45	3.45	0.013
Residual	24	1116.80	46.53		
Total	47	21877.12			

Table 5.5a: ANOVA on effect of fermentation on total polyphenol of beans

Source of variation	df	ss	ms	f	F pr
Days (D)	3	16752366.	5584122.	102.15	<.001
Bean Part (BP)	2	33350723.	16675362.	305.06	<.001
Variety (V)	1	28455587.	28455587.	520.56	<.001
D × BP	6	18790251.	3131709.	57.29	<.001
D × V	3	26661071.	8887024.	162.58	<.001
BP × V	2	32575646.	16287823.	297.97	<.001
D × BP × V	6	15862887.	2643814.	48.37	<.001
Residual	24	1311918.	54663.		
Total	47	173760449.			

Table 5.6a: ANOVA on effect of fermentation days on TSS of cocoa beans

Source of variation	df	ss	ms	f	F pr
Days (D)	3	0.0967	0.0322	0.19	0.906
Bean Part (BP)	2	1.2529	0.6265	3.60	0.043
Variety (V)	1	0.0000	0.0000	0.00	1.000
D × BP	6	2.3821	0.3970	2.28	0.070
D × V	3	1.0467	0.3489	2.00	0.140
BP × V	2	0.2112	0.1056	0.61	0.553
D × BP × V	6	1.8071	0.3012	1.73	0.157
Residual	24	4.1800	0.1742		
Total	47	10.9767			

Appendix 4: Effect of fermentation periods on the proximate compositions

Table 6.2a: ANOVA on effect of fermentation days on ash content of beans

Source of variation	df	ss	ms	f	F pr
Bean Part (BP)	2	282.4327	141.2164	210.13	<.001
Day (D)	3	22.3011	7.4337	11.06	<.001
Variety (V)	1	8.3378	8.3378	12.41	0.002
BP × D	6	19.3545	3.2257	4.80	0.002
BP × V	2	24.8108	12.4054	18.46	<.001
D × V	3	2.6008	0.8669	1.29	0.301
BP × D × V	6	7.8205	1.3034	1.94	0.115
Residual	24	16.1293	0.6721		
Total	47	383.7875			

Table 6.3a: ANOVA on effect of fermentation days on carbohydrate content of cocoa beans

Source of variation	df	ss	ms	f	F pr
Bean Part (BP)	2	568.06	284.03	19.50	<.001
Day (D)	3	21.36	7.12	0.49	0.693
Variety (V)	1	0.00	0.00	0.00	0.987
BP × D	6	277.18	46.20	3.17	0.020
BP × V	2	385.26	192.63	13.22	<.001
D × V	3	13.50	4.50	0.31	0.819
BP × D × V	6	169.58	28.26	1.94	0.115
Residual	24	349.64	14.57		
Total	47	1784.60			

Table 6.4a: ANOVA on effect of fermentation on fat content of cocoa beans

Source of variation	df	ss	ms	f	F pr
Bean Part (BP)	2	7352.528	3676.264	432.20	<.001
Day (D)	3	30.614	10.205	1.20	0.331
Variety (V)	1	326.153	326.153	38.34	<.001
BP × D	6	237.266	39.544	4.65	0.003
BP × V	2	147.381	73.691	8.66	0.001
D × V	3	29.666	9.889	1.16	0.345
BP × D × V	6	24.835	4.139	0.49	0.812
Residual	24	204.143	8.506		
Total	47	8352.584			

Table 6.5a: ANOVA on effect of fermentation days on protein content of cocoa bean

Source of variation	df	ss	ms	f	F pr
Bean Part (BP)	2	3.117	1.559	1.12	0.342
Day (D)	3	7.440	2.480	1.79	0.177
Variety (V)	1	18.119	18.119	13.05	0.001
BP × D	6	65.008	10.835	7.80	<.001
BP × V	2	0.680	0.340	0.24	0.785
D × V	3	3.913	1.304	0.94	0.437
BP × D × V	6	9.067	1.511	1.09	0.397
Residual	24	33.322	1.388		
Total	47	140.666			