KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY
COLLEGE OF SCIENCE

DEPARTMENT OF FOOD SCIENCE AND TECHNOLOGY

COMPARATIVE STUDY OF GRADED COCOA BEAN QUALITY

BY

ISAAC BOAMAH

FEBRUARY, 2016

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A DISSERTATION SUBMITTED IN PARTIAL FULFILMENT FOR THE DEGREE OF

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BY

ISAAC BOAMAH

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DECLARATION

This is to certify that the thesis entitled "Comparative Study of Graded Cocoa Bean Quality" which is being submitted by me, to the Department of Food Science and Technology, Kwame Nkrumah University of Science and Technology for the award of Master of Science (Food Quality Management). It is a record bona fide research work carried out by me under the guidance of my supervisor and has fulfilled the requirements for the submission of thesis which to my knowledge has reached the requisite standard. The results contained in this dissertation have not been submitted in part or in full to any institution or university for an award or any degree.

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ABSTRACT

Cocoa product quality has been argued to be dependent on the bean size both from the marketers and some processors who attribute some processing difficulties to this observation, though some still disagree. This study was aimed to determine the yield and quality of fat as a basis for standardization of the gradation of cocoa bean. Specifically, the project sought to determine the butter characteristics of the graded beans with regards to fat yield and other biochemical properties. Five different categories of cocoa originating from the three take-over centres of Cocoa Marketing Company within the same crop year (2014/2015) were processed into liquor. The cocoa butter extracted from these categories were evaluated for their iodine value (IV), peroxide value (PV), saponification value (SV), unsaponification value, slip melting point value, free fatty acid (FFA), tempering cooling curves, refractive index, colour and yield fat levels. The outcome of the experiment was that cocoa bean quality was in decreasing order of; super main crop > main crop > super light crop > light crop > small beans in terms of many of the attributes that were studied. Yield-fat decreased respectively in this order 55.24%, 54.71%, 53.01%, 52.67% and 52.21% while FFA increased along the same order as 0.89%, 0.90%, 1.05%, 1.06% and 1.23%. Again the larger Q-factor values explains a good crystallization behavior for cocoa butter from the cooling curves evaluated in the Shukoff tempering studies presented similar order as 0.16, 0.14, 0.12, 0.11and 0.12. All the other parameters studied showed similar trends. The IV, PV, SV and unsaponification values were significantly ($p<0.05$) lower as compared to codex standards. Thus, it appears the marketers are indeed within their rights if cocoa beans are graded and marketed based on their sizes.

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CHAPTER ONE

INTRODUCTION

1.1 Background

Cocoa bean quality has been proven to be tainted by several extraneous factors over the years. The morphological difference in bean category or size is one of such factors affecting product quality. A couple of years back, cocoa beans were processed without any categorisation. The noncategorized cocoa beans which are also termed as admixture cocoa beans were processed together. The smaller size cocoa beans frequently slipped through the main production stream without crushing in the winnowing stage which often led to poorly removed shell contamination. The resulted liquor produced are more viscous and usually low in production yield. Cocoa bean categorization was then introduced by the Quality Control Company a division of COCOBOD to grade or segregate cocoa beans for sale and for better machine handling during processing.

The corollary of the work of Burubai (2007) confirmed that assorted category of cocoa beans emerged due to differences in their physical and chemical traits, the soil type, climatic conditions or seasons, the harvest condition, the post-harvest handling which includes fermentation, drying and storage. The above listed differences may have direct effect on the yield-fat content as well as the sensory or organoleptic properties, the butter tempering effect, the biochemical properties and the oil quality with regards to the saponification value, unsaponification value, iodine value, peroxide value, colour, free fatty acids, viscosity, clarity and the refractive index.

In an effort to improve consistency in producing quality products, control programs are being investigated and evaluated so as to overcome the quality degradation. Nonetheless, this is not always feasible under certain agronomic and post-harvest practices in terms of storage. A

comparative study of drying methods on the quality of cocoa done by Lasisi (2014) showed that the moisture content of cocoa beans after fermentation is 55% and this needs to be reduced to a range of 6% to 8% for safe storage. In their study, two drying methods which are sun drying and oven drying were focused on. Other drying methods such as silo storage drying and naked fire drying could have been discussed, since each method has a unique effect on the organoleptic properties of cocoa beans. External moulds are mostly the predominant effect with consignment stored in silos and microbes thrive well in such ambiences. The consumer usually detects smoke when the beans are dried by naked fire due to the hydroscopic nature of cocoa.

Cocoa bean drying is very essential when developing flavour and excessive exposure of cocoa to air to a larger extent affects its shelf life. Comparatively, the two are negatively skewed on graph, that is, when the moisture levels are high, the shelf life turns to shorten. Oke and Omotayo (2012) observed replica of such trend.

Redovnikovic *et al.* (2009) carried out an experiment to compare the polyphenolic levels and composition against the oxidative activity of different cocoa liquors originated from the varieties of cocoa beans; *Forastero, Criollo* and their hybrid *Trinitario* cultivated globally with their Fullgrown pods and beans vary significantly in shape, texture and **size**. The inference for their work ascertained that the varieties of the cocoa beans, growing conditions and fermentation affected the polyphenols and also established that, the polyphenol profile of the liquor were similar but in varying quantities.

Research has been done to evaluate the effects of large and medium size cocoa beans from Ghana by Bart-Plange (2012). The focal point for this study was to determine the physical and mechanical properties of cocoa beans as a function of moisture content to establish data for an equipment design. The experiment was to compare the differences that existed between two categories of Ghana cocoa by varying their moisture levels. Their inference was that the mechanical properties of the cocoa enable optimization limits for proficient and effective equipment design. The efficacy of winnowing depends greatly on the size of the beans. The effects of admixture consignment due to bad grading affect the processor to a large extent. Most often than not, traces of smaller cocoa beans are seen in the product after the winnowing stage.

A replica of the above study was done on maize, by Bart-Plange (2005), Bambara groundnut, by Baryeh (2001) and on rice by Varnamkhasti (2007). Cocoa bean quality in relation to their category or size has been proven to be varied by their bioactive compounds (Belscak *et al*. 2009). Wood (1986) also conducted an experiment on cocoa bean quality in relation to the bean size with respect to fermentation. The extractives of polyphenol levels and the antioxidant activities which have been upheld to be important compounds in comparing different breeds of cocoa bean quality in relation to their sizes were also studied (Redovnikovic *et al.* 2009).

The purpose for this work aimed to determine the yield and quality of fat as a basis for standardization of the gradation of cocoa bean. The specific objective was to determine the butter characterization of the graded cocoa beans with respect to their tempering effect, saponification value, unsaponification value, peroxide value, iodine value, free fatty acids, refractive index, colour, slip point and their fat content.

1.2 Problem Statement and Justification

The introduction of cocoa bean gradation has led to the development of cocoa purchasing premium. The concept has affected purchasing price of cocoa which has constrained many processing industries to purchase lower graded cocoa beans. The severity of the problem is that product produced from lower categories often do not meet the quality specifications and product consignment usually are rejected or discounted. The consequence for not tackling the issue could have serious food quality and safety implications on one hand and fair trade on the other. Fair trade would remove any doubts of cheating in the minds of the License buyers and sellers of cocoa in that, larger sizes of cocoa beans would attract premium due to their high quality. Although fair trade would clear any suspicion it is the probable health risks implication that is of utmost importance. Since processing lower categories alone generate fines that burns during roasting to produce chars and also render poor quality cocoa liquor. The resulted liquor produced are gummy which occasionally trip off production machines causing down times which greatly affect production throughput. The abundance of shell fines in nibs found in processing lower categories are physical hazards which char during roasting to produce smoke leading to a probable production of polycyclic aromatic hydrocarbons (PAH) and other browning hazards that could be a source of carcinogenicity and hence adverse health effect.

1.3 Objective

The objective for this project is to determine the yield-fat and quality of cocoa beans as a basis for standardization of the gradation of cocoa bean. Specifically, the project sought to determine the characteristics of the cocoa butter of the graded beans with regards to fat-yield and biochemical qualities.

CHAPTER TWO
LITERATURE REVIEW

2.1 Health benefits of cocoa

There is no disputable fact that cocoa is the most important cash crop with high marketable value worldwide. Moderate intake of cocoa possibly will catalyze several beneficial effect on preventing cancer (stabling *et al.,* 2013) and other cardiovascular diseases. Cocoa phenolic compounds have been agreeably endorsed as potential protective and also therapeutic agents to reduce liver damage, (Ramos, (2008); (Vitaglione *et al.,* 2004). The cash crop has been demonstrated to catalyze the activity of phase I enzymes in hepatic and thymocyte cells in phase II (Martin *et al.,* 2009); (Ramiro-Puig *et al.,* 2007). The phase I involves glutathione reductase (GR), glutathione peroxidase (GRC) and catalase (CAT) and the phase II also involves glutathione S-transferase (GST) enzymes and glutathione (GSI) These levels plays a vital role in the balance of the redox status of living organism and also in the detoxification of xenobiotion (Ramiro-Puig *et al.,* 2007). For this and many other reasons it was attributed as the "golden tree". In as much as a mere cocoa bean preparation fights against numerous types of cancers, (Yamagishi *et al.,* 2002, 2003), it appears to also protect against several hepatotic agents that nitrosamines are inclusive (Amin *et al.,* 2004); (Yamagishi *et al.,* 2000).

2.2 Effect of physical, chemical and mechanical properties of cocoa bean size on processing and product quality

The effect of cocoa quality may have resulted from several extraneous factors over the years according to some researchers. The morphological differences in terms of the bean category is one of the key factors affecting product quality and are extremely important for the equipment design, to process, handle and transport such commodity during production. Cocoa bean categories have been proven by many researchers including Burubai (2007) to have been resulted from variations

in the; physical properties, genotype, geographical locations, soil type, climatic conditions and the post-harvest handling of the bean during fermentation, drying and storage. In as much as the aforementioned differences may have some direct effect on the yield, fat levels and the organoleptic properties, this might also contribute to product defects such as butter tempering effect, biochemical properties, polyphenol levels, antioxidant activities and oil quality with regards to their unsaponification value, saponification value, iodine value, peroxide value, colour, refractive index slip point, viscosity just to mention a few.

The quest to resolve such anomalies associated with the aforementioned parameters with regards to product quality of the cash crop (cocoa) has ensued in lots of findings by interested researchers around the globe and the following studies are outcomes in several attempts to minimize these ambiguities. A comparative study of some physical and chemical properties of large and medium size cocoa beans from Ghana was done to determine the physical and mechanical properties of cocoa bean as a function of moisture content so as to establish vital information for the design of equipment for the handling, transporting, segregation, desiccating, aeration, storage and processing cocoa beans (Bart-Plange *et al.,* 2012). Similar experiment was conducted by several researchers for maize (Bart-Plange *et al.,* 2005), Bambara groundnuts (Baryeh, 2001), rice (Varnamkhasti *et al.,* 2007). The objective for this experiment was to measure and compare the differences that exist between two categories of beans from Ghana by varying their moisture content. From the engineering point of view, such information on the mechanical properties of the crop is vital and aids in the progression of optimization limits for proficient and effective equipment (Burubai *et al.,* 2007). More than a few researchers including Burubai, (2007) have determined the physical and mechanical properties of different agricultural products as a function of moisture content in

order to provide essential data for the design of equipment. A replica work on bitter kola by Davies and Mohammed (2013); Soya bean by Davies and El-Okene (2009); the work of Razari *et al.* (2007) on pistachio nut and its kernel; the work of Sessiz *et al.* (2005) on caper fruit; Almond nut by Aydin (2003); Tabatabaefa (2003) work on wheat; Bart-plange and Baryeh's (2003) work on cocoa bean; the work of Ogunjimi *et al.* (2002) on locust bean seed ; Shepherd and Bhardwaj's (1986) work on pigeon pea. Conversely, according to the work of Saldana *et al.* (2002), the chemical quality of cocoa butter largely influences the physical quality characteristics of chocolate such as hardness at room temperature, brightness, fast and melting behaviour. It is empirical, therefore, a comprehensive understanding of the physicochemical properties of cocoa is obtained so as to be able to make a much informed decision on its use.

2.2.1 Effect of cocoa bean quality in relation to moisture and fermentation

It is important to have a good understanding of the physical properties of food materials and also the physical laws governing the response to these biological materials so that machine processes and handling operations can be designed for maximum efficiency so as to attain the highest quality of end products. This information should be valuable to engineers and processors who might need them to meet the world's standards. Bart-Plange (2003) conditioned cocoa beans of good quality to obtain moistures of 7%, 10%, 14%, 18% and 22%, then the principal dimensions (length, breadth and thickness) of 100 randomly selected beans were measured to determine the average size using a micrometre screw gauge with a precision of 0.01mm. The findings of this experiment argued that the rate of deformation of the cocoa increased linearly with moisture content, the sphericity values or the bean size increased with increasing moisture content and also energy required to crush the beans increased with increasing moisture content. Lasisi (2014) also did a

comparative study of drying methods on the quality of cocoa and found out that there was about 55% moisture in cocoa beans after fermentation and this needed to be reduced to between 6% and 8% for safe storage which is a follow up experiment of Oke and Omotayo (2012). It was argued that not only will the moisture content be reduced but it would help in the completion of the chemical reactions that commenced during fermentation process as well as the eruption of the chocolate brown colour of well fermented beans (Wood and Lass, 1986). Two different methods of drying were the focal point here and these were the sun drying and oven drying. Sun drying which employs the use of sun rays is a natural method employed by most farmers. This method is most effective in the dry season since insufficient drying in the wet season may cause microbial growth on beans or what is termed as moldy beans. This defect usually gives off- flavours and also a clear indication of rancidity in a product. Few large farms employ artificial drying which employs the use of heat. Less time is used in this method as compared to sun drying which solely depends on the weather conditions. However, this method also has negative sensory effects on the cocoa since the beans do not have their usual duration in the fermentation cycle.

The study also established the fact that the faster way of drying cocoa beans which is by artificial method, does not permit for the completion of the required oxidation reaction and acid diffusion process. This thus results in high acidity and off-flavoured beans. The main objective for their study was to determine the effects of forced-air and sun-drying at different temperatures, moisture contents, relative humidity and time of drying on cocoa bean quality and establish the best method of drying. In the method, the initial moisture content of the cocoa beans was determined by the International Standard of Organization and AOAC (2005) method. A sample of cocoa beans was sun dried by spreading them on a concrete floor and other samples were also dried in an oven at

35%, 40%, 45%, 50% and 55% to obtained 6% to 8% the equilibrium moisture content were determined. Good fermentation also depends on the cocoa bean size, the smaller size beans are usually well fermented as compared to the larger size beans exposed to the same conditions. The above experiment endorses on the fact that bean size matters with regards to quality fermentation.

The quality of cocoa was assessed based on the acetic acid value, pH, and the Free Fatty Acid (FFA) levels as well as the grading. In their study the acetic acid content was determined by the AOAC (2005) method and the pH according to Opeke (2012). The FFA levels were determined according to AOAC (2005). It was established that the best drying method with maximum quality of expectation was the sun drying. The outcome of their work was quite convincing, nonetheless, the study could have been more educative for the researcher to include other methods like naked fire drying, silo storage that naturally generate heat to keep the beans dry. The former is most practiced in several countries where much rainfall is experienced. The effect of polycyclic aromatic hydrocarbons (PAH) can possibly result from cocoa beans coming into direct contact with the smoke. The practice usually has much organoleptic effect on the products due to the hygroscopic nature of the beans which easily absorbs odors and moisture. The effect of the naked fire can give the beans a smoky and a hammy flavor.

2.2.2 Effect of moisture content on microbial activities in cocoa beans of varying sizes

Poorly dried cocoa beans mostly the larger bean sizes due to their hygroscopicity retained some amount of humid ambience when drying is not effectively done. This anomaly are relatively not seen in smaller beans exposed to the same drying condition. Moisture affects the organoleptic properties of cocoa and also catalyzes the microbial growth on such produce, and the beans are mostly seen to develop moulds which are ubiquitous and are prone to grow in relatively high humid

ambience (Archer, 2006). Moulds are replicated by spores which begin to grow on moist surfaces that are suitable for life and most often these microbes thrives well in areas with very high humidity.

2.2.3 Effect of processing methods on the formation of free fatty acids in cocoa beans

The triacyl glycerols (TAGs) in the cocoa butter are molecules made of glycerol backbone to which three fatty acids are bound via ester bonds. These fatty acids vary, from stearic, oleic to palmitic acids. The action of the micro flora in molds, lipolyses the fatty acids from the triacyl backbone causing them to become free. The resulted free fatty acids (FFA) means both the mono and the diglycerides are present with the triglycerides due to the slower disintegration of the triglycerides as compared to the oxidative attacks which are mostly randomized. This causes spikes in FFA values during processing, prevents the chocolate bar or cocoa paste from hardening efficiently to enable the 'popping' in chocolate bars, affects end product organoleptic properties and poses food safety problems and lastly, it increases the probability of aflatoxins present in the cocoa which poses a health danger (Jay *et al.*, 2005). Semi-finished products like butter and liquor crystallize as well as finished products like chocolate which are greatly affected in the presence of the mono, di, and triglycerides together with the free fatty acids. Interruption of the crystals is usually triggered by the emulsifying action of the fat as well as its solubilizing effects.

A comparative study of cocoa bean quality with respect to their free fatty acids (FFA) content was conducted by Guehi *et al.* (2008). The experiment was to assess the impact of cocoa processing technologies on free fatty acids formation in stored raw cocoa beans. In their study different fermented dry cocoa beans were purchased in Cote d'Ivoire, stored and analyzed for their free fatty acid values. Pontillon (1998) confirmed that increase in Free Fatty Acid content reduces the

hardness of cocoa butter which further reduces the commercial value of finish product like chocolate. In accordance with delivering safe quality product, 1.75% was stipulated to be the allowable maximum limit and also directed in 73/241/EEC (Guehi, 2007). Free fatty acids are usually carboxylic acids unleashed from the triglycerides (Selamat *et al.*, 1996) catalyzed by a lipase (E.C 3.1.1.3) or an oxidation. Oxidation reaction in the butter of cocoa is insignificant due to its low unsaturated fatty acid levels (Whitefield, 2005). The lipase activities are mostly conspicuous in germinated seed (Wanasundara *et. al.*, 2001) except in other crop plants namely castor oil plant (Ory *et al.,* 1962), nigella kernel (Mert *et al.,* 1995) and rice (Raghavendra and Prakash, 2002). The outcome of their study was that the FFA of these beans increases with time and their levels were higher in cocoa beans with inadequate drying. Microbial activities are enormous in high moisture ambient because water activity is high. This can be also confirmed by Raghavendra (2002).

The action of microbes produces lipase which unleashes FFA from triglycerides (Wood and Lass, 1985). The cotyledon of the bean is protected by the shell or the epithelia layer of the beans. The microbial activities reside mostly on the outer cover of the shell in humid environment.

Nonetheless the oxidation activities are faster or higher in the exposed kernel or the cocoa nib. Poor post-harvesting method is one key factor in spiking FFA levels. They did not also mention if the cultivation was done within the same crop season or not. The reason being that from data gathered over decades cocoa beans cultivated in the light crop season have relatively higher FFA levels than those in the main crop season due to their climatic condition differences. The lipase activity in dry beans is relatively lower than that of fresh germinated seed. The obvious reason lies in the differences in the moisture levels. Well dried beans are known to have lower moisture hence

would not support any microbial growth than germinated seed which are predominantly of higher moisture content. Traces of shells with high residual of moulds found in product after winnowing production are also contributing factor to FFA spikes. Temperature and moulds against FFA are positively skewed on a graph during processing.

2.2.4 Effect of polyphenolic content and antioxidative activities on cocoa beans with varying size, texture and shape

It is an unquestionable fact that cocoa bean is an abundant source of numerous structurally diversify biologically active compounds of which xanthine and polyphenolic alkaloids are the predominant. A comparative study of polyphenolic content and antioxidative activity of cocoa liquor from different countries including Ghana originating from the three varieties of cocoa beans cultivated worldwide which includes *Forastero* (bulk grade), *Criollo* (fine grade) and their hybrid *Trinitario* (fine grade) (Counet *et al.*, 2004) were purchased from *Kras* Food Industry (*d.d* Zagreb, Croatia). The effect of the polyphenols together with sugars and amino acids contribute to the flavor and colour of the roasted nibs of cocoa. Nonetheless, alkanoids are responsible for the bitterness to the fermented beans (Nazaruddin *et al*., 2006a). They also established that irrespective of the variety the phenolic profile of the liquor were similar but with varying proportion. In addition to their outcome the overall phenolic content and the antioxidant activity were in the order: Madagascar > Mexico > Ecuador > Venezuela > Sao Tome > Ghana.

The phytochemical constituent of cocoa has become objects of interest that has augmented scientific research. The recent trend in food marketing shows that the cash crop products acknowledge multiple- benefit foodstuffs. A comparative study of commercially available cocoa products in terms of the bioactive composition was conducted by Belscak *et al.* (2009). Though

tea and red wine seem to be known for their high content of polyphenolic substances, little did we know of cocoa bean and its derived products to possess abundant source of polyphenols which even have higher antioxidant capacity (Lee *et al.*, 2003). Their experiment was conducted to apply an array of assays for the routine determination of polyphenol and methyl xanthine composition of cocoa product extract and also to compare the antioxidant capacity of cocoa products affected by the extraction solvent used. Most often than not studies attribute health benefits of cocoa products to polyphenols. In this study little did we know cocoa is rich in methylxanthines of which theobromine and caffeine are the major constituents.

The polyphenols of cocoa have been published in many studies as bioactive components with antioxidant and antiradical properties. Folin-Ciocalteu, formic acid. Sodium carbonate, ferric chloride hexahydrate, DPPH (2, 2-diphenyl-1-picrylhydrazyl) were among the chemicals used for this study. In their research, the phenol was analysed and the flavonoid compounds were precipitated using formaldehyde, which reacted with the C6, or C8 on 5, 7 – dihydroxyflavonoids to yield methyl derivatives, and the resultant product reacted with other flavonoid compounds. The corollary of their work was that the interests of scientists around the globe on this subject were due to the health benefits obtain from the numerous cocoa products evolved from the cocoa phenols and their antioxidant capacity.

The limitation of their work has to do with the fact that standardized method for quantification of these polyphenols and antioxidant capacity of most plant derived products have not yet been established and these have resulted in less consideration dedicated to specific examination of polyphenolic composition in several quantum of cocoa products.

The findings were that cocoa products with maximum content of cocoa solids contained the higher content of polyphenols and also antioxidant capacity in vitro likewise, theobromine was profuse in cocoa products of highest cocoa solids. Theobromine was the most abundant methylxanthines than caffeine and (-) -epicatechin was the most present followed by procyandin be and (+)-catechin among the flavan-3-ols.

2.3 Effect of geographical differences on the quality of cocoa beans

Comparison of cocoa beans from China, Indonesia and Papua New Guinea based on quality was a survey which was also done. The main objective of their survey was to investigate the influence of fermented, unfermented and well dried cocoa beans from box fermentation practiced in different geographical locations. Improper fermentation, when roasted may not develop any chocolate flavour and are usually bitter and astringent (Biehl *et al.,* 1996). In this experiment, the average bean weight and fat level of cocoa samples prepared was analyzed using oven at 600 ˚C and Soxhlet extraction respectively. Also colour absorbance at 420 nm using UV-Vis Shimadzu UV 60 spectrophotometer, total phenolic and total flavonoid content were measured. The former was measured with Folin-Ciocalteu method reported by (Lee *et al.,* 2003) whilst the latter was measured by using colorimetric assay developed by (Jia *et al.,* 1999). Other quality analysis done include; measurement of the total amino acids, free amino acids investigated by extraction method of Noor-Soffalina (2009), garlic acid and epicatelin content with the replicated method of (Kyi *et al.,* 2005).

The outcome of this survey were that, the breed, germinating conditions as well as fermentation influences cocoa bean average weight, polyphenols and amino acid levels. The study also provided data to promote cocoa plantation in China. The study aimed to experiment the strength of the three

methods of fermentation and the effect of duration on the physical, chemical and microbial effects of quality attributed to raw cocoa. Materials used were cocoa (*Theobroma cacao*) of mixed crops harvested from May to July 2009 and the origin of consignment was at Kpada. These cocoa pods were initially stored and unveiled three days after harvesting as described by Meyer *et al.* (1989) and fermentation was carried on as specified by Lopez and Dimich (1995) and (Mounjouenpou *et al.*, 2008).

The beans after drying through the sun were set for cut test cross-sectional to examine the defects as described by Hamid and Lopez (2000) and (Hii *et al.*, 2006). The pH and terrible acidity were analyzed as well as the microbial loads. Duration of six days fermentation of cocoa beans was proven to have the best quality. However long duration of fermentation also termed overfermentation gave off ammonia smell. Heap of fermentation using banana leaves was acknowledged as the best practice for good quality cocoa.

Cocoa beans are naturally hygroscopic and would absorb moisture under humid ambient until it becomes equipoise with the environment. The cash crop would detect any off flavours and other organoleptic defects like earthy when dried on the bare land, smoky when fire is use to catalyzed drying, baggy when dried on jute sacks, woody when dried on freshly woods just to mention a few. Furthermore, the bean size has a direct correlation with this effect.

Fermentation and bean drying are the instantaneous steps after harvesting. That is after the removal of the beans from the mucilaginous pulp, the fermentation process is carried out to develop the flavor. Well fermented cocoa beans are brown when in their cross sectional view. The best

fermentation oven takes averagely seven days. The after taste is mostly unpleasant, astringent acidic, bitter flavours when fermentation is poorly done or the aforementioned duration is not met or exceeded. The cross sectional view of the cut beans is examined and the beans are graded base on the percentage of moulds, slate and the purple colour present. The blooming of moulds may be as a result of poor drying after fermentation and also poor storage conditions. In situation where the farmer applies heat to dry the beans faster than the usual duration usually experience this challenge. Application of heat usually dries the peripheral parts leaving moist the cotyledon resulting in the growth of moulds, which are usually prolific in humid ambient hence the anomaly.

2.4 Cocoa bean gradation

The percentage of slaty beans, purplish beans and other colour defects are mostly the cause of poor fermentation. Most often than not, farmers who turn to ignore the usual length of the fermentation cycle which is stipulated between 6 to 7 days by the quality control division of Ghana COCOBOD would experience the above listed defects. The root cause of most organoleptic defects and off flavored cocoa are typical characteristics of poor fermentation process apart from poor roasting. Cocoa are graded into grade 1, 2 or substandard due the level of moulds, slaty or purple colour after a critical scrutiny of the interior surface. A summary of these grading system according to Ghana COCOBOD is as tabulated in table 1.

Table 1: Bean Grading System according to Ghana Cocoa Board

Grade	%Total Moldy	%Total Slaty	%All other defects	%Purple
Grade I	3.0	3.0	3.0	20
Grade II	4.0	8.0	6.0	20.3 – 45
Substandard (SS)	>4.0	>8.0	>6.0	>45

In a situation where one particular cotyledon has all the three defects, the moldy defects are prioritized and again slaty over purple defects. Fermentation and drying therefore are the major

pre-requisite steps to stabilize or improve the shelf- life of the freshly cultivated beans against microbial degradation during storage (Hii *et al.,* 2009).

There are lots of other extraneous factors that have vital effects on the characteristics of cocoa quality. These includes the, cocoa bean type or category, soil type, climatic conditions or season, harvest condition and post-harvest handling (fermentation, drying and storage. The cocoa beans generally cultivated from the ripe pods are greatly found in tropical areas across the globe (Ardhana *et al.,* 2003). This include South America, Southeast Asia and the West Africa Regions. The cash crop (cocoa) is mostly used in beverages, toiletries, pharmaceuticals, agricultural field as manure and animal feeds and cosmetics (Tafuri *et al.,* 2004).

Among these prominent cocoa growing areas, Ghana cocoa which is geographically located in the West Africa Region is the best. The higher standard of Ghana cocoa attracts a substantial premium which was most often absent in other countries (Wahyudi, 2008). The enormous increment of the Ghanaian revenue is partly explained by these quality premium which is estimated to about 30 % of Ghana's export revenue with 4 % GDP (Quarmine *et al.,* 2012). The *Theobroma Cacao* is the most important cash crop grown in Ghana. Ghana produced 680,385 metric tons of cocoa in 2007/08, about 18.2 % of the global total. (Nsiah *et al.,* 2009). It is difficult to over-estimate the importance of cocoa to Ghana's economy or of Ghana's production to the world cocoa industry.

Cocoa bean segregation was first instigated in 1991 according to COCOBOD when the said organization was experiencing numerous reports of admixture beans after harvesting. The beans were segregated by size due to the number of beans counted from weighing 100 g. The effect of admixture and smaller beans were due to seasonal factors, environment factors, the genotype, the

breed, the type of planting materials or method used, the type of application of chemicals. These practices are regulated and strictly monitored by the Quality Control Division of COCOBOD which again explains why cocoa beans from Ghana are tagged as the best world-wide (Jonfia *et al.*, 2004).

The differences in bean size affect product quality during bean cleaning, winnowing or production in diverse ways to mention a few are the yield, fat content, free fatty acids, colour, viscosity, texture, ash levels, saponification value, unsaponification value, the peroxide value. The processing of smaller sized cocoa beans are those kind that usually demand attention. The liquor produced from this category of beans are usually gammy, more gelatinous or viscous. This anomaly turns to trip off milling machines, retards production and processors most often do not meet their production target as a result of these stoppages.

2.5 Processing of cocoa beans into liquor and butter

The segregation of shells from nibs during production or winnowing process are mostly inefficient when in handling such smaller consignment. The cocoa beans are usually pre-roasted to enable the shell to pop out from the cotyledon for easier separation. The beans after pre-drying are conveyed to the winnower which are then crushed to break. The small category of beans after crushing generate a lot of fines and that makes it impossible for the winnower to separate the shells from the nibs.

Admixture beans which are basically mixtures of smaller and larger beans are one of the major root causes of bad product quality. Processing of admixture beans can affect your yield especially during the cleaning and winnowing stage of your production line where the lighter weighed beans

are sucked up together with other extraneous materials in the cleaning. The cleaning phase in the production process the beans are aspirated to create a fluidize bed or condition to give the beans the level of freedom to align themselves in the direction of the vibration of the de-stoner because when the beans becomes static or sit on the bed of the sieve of the de-stoner, they cannot propel but rather obeys Newton's law which states that; everybody continuous to be in its state of rest or uniform motion unless an external force is applied to act otherwise. Applying this principle as much as the beans are seated on the bed of the de-stoner it becomes difficult to sail the beans and to make that easier the beans slightly lifted from their state of rest by vibration. This allows the cocoa surge to for winnowing whilst leaving the stones static on the bed. Cocoa flavours are generated during roasting; the condition of it defines quality for finished products. This was recognised by Krysiak and Motlyl-Patelska (2006). The critical roasting parameters are usually temperature and time. The browning effect or colour generation through Maillard reaction according to Afoakwa (2010) is one of the numerous physic-chemical changes occur during roasting the reduction of acidic level, sourness as well as bitterness are key examples of physical and chemical activities of the cocoa during roasting.

A study of different cocoa cultivars evaluating their bioactive compounds during the process of fermentation was conducted by Cruz *et al.* (2013). The purpose for their experiment was to study the characteristics of the bioactive compounds during fermentation and drying process and also to investigate their influence with regards to sensory and organoleptic quality of different cultivars.

In the study cultivars of cocoa beans namely PH16 which was known to have originated from a selection carried out in commercial area. SR 162 and a blend of *Parazinho* and *Maranhao* which

belong to the *Forastero* group of cocoa plant species were used. Lopez (1986) and Leite *et al.* (2013), confirmed that the pulp of cocoa bean was degraded by the activities of microbes during the process of fermentation terminating to the formation of lactic acid and ethanol resulting in the formation of flavor and aroma precursors. The constituent of this process were the polyphenols. The flavour development process continues during drying and the browning process was the most important process occurring at this stage (McDonald *et al.*, 1981). The flavour forming reactions occurred during sun drying coupling with oxidation or browning of polyphenols resulting astringency and bitterness reduction (Opoku-Ameyaw *et al.*, 2010).

Bonvehi and Cool (2000) argued that the development of bitterness and astringency in cocoa beans were the role of the polyphenols, continued by alkaloids, pyrazines and peptides. The polyphenol content of cocoa beans declines to about 70% during the process of fermentation whilst the epicatechin which happens to be the main substrate for polyphenol obtained a reduction of 90 % of its initial concentration (Efraim *et al.*, 2011).

The process of fermentation for the different cultivars was done using wooden boxes with the dimension 70 by 70 by 75 cm having about 20 holes which facilitated the flow of the liquefied pulp. 400 kg mass was generated in each box, the mass was then covered with banana leaves. The cocoa beans were then subjected to excessive drying for 5 to 7 days up to about 8.0 % moisture content.

The polyphenol compounds (catechin, caffeic acid and epicatechin) and methyxanthine (Caffeine and theobromine) were determined by the method explained by Elwers *et al.* (2009) were 10

microlitres of each sample was analyzed by HPLC system. The compound was monitored by UV detection at 280 nm wavelength. The total run time was 20 min and temperature was 26 ^{o}C. It was revealed that during fermentation a wide variation of methylxanthines were discovered and was attributed to fermentation conditions like temperature and pH. Nonetheless the enormous reduction in phenolic compounds were observed after drying and this could be as a result of enzymatic browning coupled with non-enzymatic reaction with increase in pH and high oxygen uptake during sun drying. Cocoa cultivars exhibit different traits during fermentation and drying respectively taking into consideration the polyphenolic and methlyxantine contents which contributes to the differences in sensory characteristics of these cultivars.

A comparative study was carried out by Hii *et al.* (2008) to evaluate effects of drying kinetics of natural and artificial drying methods on the quality of cocoa beans. The temperature and relative humidity during the drying period fluctuated between 26 ˚C – 33 ˚C and 56% - 82% respectively. Starting with beans with initial moisture content of 51% (wet base), they observed that moisture content decreased steadily with drying time. The artificial technique ended drying (that is 7% mc) in 52 h due to the faster drying rate while the natural technique ended drying in 73.5 h. Bharath and Bowen (2008) assessed the drying rate of cocoa beans with small samples, also reported that the smaller the bean masses, the thinner the bean layer and the faster the drying rate. According to Fagunwa *et al.* (2009) the drying rate of cocoa beans were largely determined by the ambient temperature and the relative humidity. The above assertion seemed to reflect the study of Ndukwu (2009) in which the effect of drying temperature and drying air velocity on the drying rate of cocoa beans were determined.

2.6 Cocoa butter characterisation

Cocoa butter is the most abundant component of the cocoa nib, constituting about 53% to 65% of the nibs on a dry weight basis compared to the other components (sugars, polyphenols, alkaloids, starch, proteins, theobromine, caffeine, non-volatile acids such as oxalic acids, malic acid and minerals (Biehl and Ziegleder, 2003); Borges *et al.* (2006); (Afoakwa, 2010). Cocoa butter is the most valuable component of the cocoa beans, due to its unique physical and chemical characteristics that gives it great demand in the, pharmaceutical field, food and cosmetic industries.

2.6.1 Cocoa butter characterisation with respect to their cooling curves

The commodity or the butter is the only continuous phase in chocolate. The dispersion of all other constituents and the physical behaviour of chocolate is attributed to be instigated by the cocoa butter. The distinctive nature of cocoa butters that is, its fragility at room temperature and its rapidity way of melting at body temperature (Lipp and Anklam, 1997). These special traits, are clearly not analogous to any other vegetable fats and oils, which makes it are very beneficial in the manufacture of a wide variety of products in the chocolate, cosmetic and pharmaceutical industries (Liendo *et al.,* 1997); (Sukha, 2003); (Howell *et al.*, 2005); (Beckett, 2008) during crystallization gives a clue about how good or bad a butter. $Q>0.15$ connotes a good or soft butter and $Q < 0.05$ refers bad or hard butter.

2.6.2 Cocoa butter characterisation with respect to their peroxide values

Peroxide value (P.V.) of cocoa butter is the number of mill-equivalent of active oxygen (peroxides) per kg of fat; the PV relates to the oxidative stability (rancidity) of the fat (Archer, 2006). Identification of peroxides in a fat sample gives an initial evidence of rancidity in unsaturated fats and oils. Peroxide value gives a measure of the extent to which an oil sample has undergone

primary oxidation. Double bonds found in fats and oils play a role in autoxidation. Oils with high degree of unsaturation are most susceptible to autoxidation. Peroxides are intermediates in the autoxidation reaction (Chakrabarty, 2003).

Autoxidation is a free radical reaction involving oxygen that leads to deterioration of fats and oils which forms off-flavours and off-flavours and off-odours. Peroxide value, concentration of peroxide in an oil or fat is useful for assessing the extent to which spoilage has advanced. The peroxide value is determined by measuring the amount of iodine which is formed by the reaction of peroxides (formed in fat or oil) with iodide ion. Note that the base produced in this reaction is taken up by the excess of acetic acid present, the iodine liberated is treated with sodium thiosulfate. The acidic conditions (excess acetic acid) prevent formation of hypoiodite (analogous to hypochlorite) which would interfere with the reaction. The indicator used in this reaction is starch solution where amylose forms a blue to black solution with iodine and is colourless where iodine is titrated. A precaution that should be observed is to add the starch indicator only near the end point (the end point is near when fading of the yellowish iodine colour occurs) because at high iodine concentration starch is decomposed to products whose indicator properties are not entirely reversible (Chakrabarty, 2003). According to Leo *et al*. (2011) peroxide value can be measured based on their ability to liberate iodine from potassium Iodide. Determination of peroxide value involves the reaction of the fat sample dissolved in acetic or chloroform or isooctane with aqueous potassium iodide for 1 min. The amount of released iodine is assessed by titration against a standardized solution of sodium thiosulfate ($Na_2S_2O_3$) using a starch indicator.

2.6. 3 Cocoa butter characterisation with respect to their saponification values

The saponification value (SV) measures quality and give account to the purity of oils and fats. The mean molecular weight of the fatty acids available in oil is also measured by the saponification value according to Krysiak (2011). The bonded and unbonded acids exist in an oil or fat are usually measured by SV Saponification is basically the hydrolysis of fats or oils under basic conditions to afford glycerol and the salt of the corresponding fatty acid. Saponification value determination of cocoa butter gives information concerning the character of the fatty acids of the fat; the longer the carbon chain; the less acid is liberated per gram of fat hydrolyzed. The saponification value measures the bonded and unbonded acid present in an oil/fat. The bonded and unbonded acid present in an oil or fat is measured by the saponification number or value. That is to say the smaller the molar mass of the oil, the higher the saponification value (Choudhary and Grover, 2013).

2.6.4 Cocoa butter characterisation with respect to their iodine values

The value of iodine is the mass of iodine that is consumed by 100 g of a fat sample. The iodine numbers are very often used to determine the degree of unsaturation in fatty acids. According to Thomas (2002), the higher the iodine number, the more double bonds were present in a fat.

Firestone (1994) said in a typical procedure that fatty acid was treated with an excess Hanus or Wijs solution of iodine monobromide and iodine monochloride in glacial acetic acid. Untreated iodine monochloride is then allowed to react with KI converting it to iodine whose concentration can be determined by titrating with sodium thiosulfate

2.6.5 Cocoa butter characterisation with respect to their free fatty acid values

The free fatty acid content of cocoa butter are of interest to both producers and chocolate manufacturers since higher percentage leads to quality reduction in fermented cocoa beans as well as decrease in hardness of the cocoa butter (Afoakwa *et al.*, 2014). Fat crystallization traits usually

define the technical behavior of the product and this is affected by extraneous factors like oxidation which are responsible to the modification triglycerides characteristics.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

Five different cocoa bean categories of *Amelonado* genotype originated from the *Forastero* variety largely grown in West Africa including Ghana were collected for this work. The bean categories includes; 'Super Main Crop', 'Main crop', 'Super Light Crop', 'Light Crop' and 'Small beans'(Table 1). The aforementioned cocoa beans were obtained from consignment purchased by Niche Cocoa Industry Limited and dispatched from Cocoa Marketing Company (CMC) after Quality control Company's clearance both division under Ghana COCOBOD. The cocoa beans were delivered from the three points of sale CMC including; Kumasi, Takoradi and Tema.

Table 2 : Cocoa bean categories and their respective counts –Ghana COCOBOD.

Bean Types (Categories)	Bean Count 100/g
Super Main Crop	Up to 90
Main Crop	91-100
Super Light Crop	101-110
Light Crop	111-120
Small Beans	121-130
Type 4	131-150
Remnant	151-180

3.1.1 Cocoa bean Sampling

The five categories of cocoa beans originating from the three sales point regions; Greater Accra, Ashanti and the Western part of Ghana were confirmed by their waybills. The jute sacks were

critically examined before sampling to note the station marks and other identifications which included the; type of grade, category, origin's code that denoted the license buying companies (LBCs). Samples were taken from each truck on arrival to the factory. The cocoa beans were drawn from the selected identified bags with a sampling horn. Samples were randomly taken from top, bottom and center of each truck. The Federation of Cocoa Commerce, sampling rules 3.2 (FCC 3.2) was applied (Dand, 2010). According to this rule, 30 % of each truck's consignment were taken. This was done for all the categories during reception for the same crop year for the two crop seasons (Main crop Season and the light crop season). The information for all consignment was clearly labeled.

3.1.2 Confirmation of cocoa categories and stacking

The categories of each truck sampled though clearly indicated on the attached waybills were also confirmed by weighing 100 g and counting the number of beans involved for each test sample after a thorough mixing and quartering (Dand, 2010). The counted cocoa beans were segregated as designed by Quality Control Company – a division under Ghana COCOBOD. This study was focused on the first-five categories since they are the ones mainly processed in cocoa processing industries. The last two categories are mostly blended with bigger sized beans since they are small in size and uneconomical to process alone this because often than not traces of the smaller beans are seen in the product after the winnowing stage.

3.1.3 Production process and butting sampling

The cocoa beans with the right identifications were transferred to production for processing. The consignment were initially cleaned to take out all extraneous materials like woods, jute twines, strings, stones, ferrous and non-ferrous metals by means of operational pre-requisite programs (OPRPs) put in place. The beans were pre-roasted before winnowing for easy shell separation. The

de-shelled beans (nibs) were transported by means of pneumatic pump for roasting. The roasting parameters were altered to maintain equal recipe with respect to their moisture levels for all the various categories. The roasted beans were firstly ground into liquor or cocoa masse (cocoa solids and butter) in three different stages. That is; course grinding, intermediate and fine grinding to produce a liquor of fineness of above 99%. The obtained liquor samples were stored and conditioned in storage tanks for pressing.The crude butter obtained from the presses was filtered to attain a clarity of 90% and above. The filtered butter samples for un-saponification, saponification, iodine, peroxide, and colour and refractive index analyses were sampled from the filtration station and stored for further analysis.

3.2 **METHODS OF ANALYSIS**

3.2.1 Determination of Saponification Value

The saponification value was evaluated according to the method of the International Organization Standard (ISO) 3657-(2002). In the experiment exactly 2 g of melted cocoa butter was accurately weighed with Mettler Toledo analytical balance (model: MS204S/01, Switzerland), into a 250 ml conical flask. A volume of 25 ml of 0.5M methanolic KOH solution was added to the weighed cocoa butter in the flask with the aid of a pipette. The flask with its contents was connected to the reflux condenser and placed on heating mantle (10067655/00, UK,) to reflux gently. The contents of the flask were swirled gently but continuously for about one hour until all solid materials were dissolved. It was ensured, whilst swirling that, the vapor ring in the condenser did not rise to the top of the condenser to prevent losses. The condenser was disconnected, the flask removed and about 1ml of phenolphthalein indicator was added to pink colouration. The content of the flask was titrated with 0.5 N HCL till the pink color disappeared (Warra *et al.,* 2011). The volume of 0.5 N HCL required for the titration at the end-point was recorded. End point was attained when

the color of the solution in the flask changed from pink to colorless. A blank test was conducted following the same procedure using 25 ml of methanolic KOH solution but omitting the test portion. The procedure was repeated for butter processed from the various categories. The formula for calculating saponification value is as shown in **Appendix B 1**.

3.2.2 Determination of Unsaponification Value

The unsaponification value was determined according to the method of the International Organization Standard (ISO) 3596-2. An accurate weight of 2.5 g sample of the melted cocoa butter sample was weighed by Mettler Toledo analytical balance (model: MS204S/01, Switzerland) into a 250 ml round bottom flask and also a volume of 25 ml of 2 M ethanoic KOH solution was added. The flask was fixed to a reflux condenser and then heated on a heating mantle ((10067655/00, UK,) for an hour, whilst intermittent swirling until saponification was completed. Distilled water of 25 ml was again added and heating stopped. The contents of the flask were allowed to cool to room temperature and thereafter transferred into a 250 ml separating funnel. The flask was rinsed five times with 10 ml portions of petroleum ether and added to the contents in the separating funnel. The separating funnel was vigorously shaken for approximately 1 min, periodically releasing pressure buildup by inverting the separating funnel whilst opening the stop cork. The separating funnel was allowed to stand till separation was complete. The soap solution was drained as completely as possible into a second 250 ml separating funnel. It was ensured that no petroleum ether extract was added. Small amounts of absolute ethanol were added whenever emulsions were formed. The extraction from the soap solution was repeated twice with two 25 ml portions of petroleum ether and the petroleum ether extracts combined. Petroleum ether was washed out three times with 25 ml portion of 50% dilute ethanol. The last washing was checked with phenolphthalein to see if alkaline was $_{o}$ present. The solution was rewashed and rechecked. The solution

was poured into an accurately weighed flask (W_1) and the petroleum ether was completely evaporated in a fume hood. The residue was dried for about 30 min at 100 C in an oven by placing the flask horizontally in the drying oven.

The flask was then cooled for about an hour in the desiccator and weighed. This weight was noted as W_2. The drying was repeated successively for a period of 30 minutes until weight difference between successive weighing was less than 1.5 mg. The unsaponification value was then calculated by the formula presented at **Appendix B 2.** The experiment was repeated for all other butter samples processed from all other categories

3.2.3 Determination of Iodine Value

Iodine value procedure was followed according to the method of the International Organization Standard (ISO) 3961-(2009): animals and vegetable fats and oils, including the following steps: An accurate weight of 0.2 g 0f the cocoa butter was weighed with Mettler Toledo analytical balance (model: MS204S/01, Switzerland) to the nearest 1 mg into a 500 ml conical flask and 20 ml of solvent to one mixture of glacial acetic and cyclohexane. That is in a ratio of 10 ml to 10 ml.

Twenty-five (25.0) ml of 0.2 N Wij's solution was pipetted into the flask and mixed carefully and the flask was stoppered and contents swirled. Flasks were placed in the dark for one hour and 20 ml of potassium iodide (15%) solution and 150 ml of demineralized water were added. The free iodine in the contents of the flasks was titrated with the sodium thiosulfate solution (Normality 1) until yellow color due to iodine almost disappeared. A starch solution of 5 ml used as an indicator was added to obtain a dark blue color and the titration continued under vigorous shaking till the blue color just disappears (V_2 in ml). A blank test was carried out simultaneously under the same conditions and without cocoa butter (V_1 in ml). Iodine value was then calculated by the formula cited in **Appendix B 3.**

3.2.4 Determination of Peroxide Value

The peroxide value determination procedure was followed according to the International Organization Standard (ISO) 3960 method. The liquid cocoa butter was homogenized by stirring without introducing air. An accurate weight of 5.0 g of cocoa butter to the nearest 1mg was weighed with Mettler Toledo analytical balance (model: MS204S/01, Switzerland) into an Erlenmeyer flask of 250 ml. test sample was dissolve in 50ml glacial acetic acid / ISO-octane solution (60% glacial acetic acid and 40% isooctane) was added and subsequently, 0.5ml of saturated potassium iodide solution. The content was shaken for 1 min. 100ml of distilled water was added and immediately liberated iodine was titrated sodium thiosulfate solution 0.01 N (V in ml) from yellow orange to pale yellow.0.5 ml starch solution was added and titration continued from violet color to colorless. At the same time a blank analysis was carried out without the test sample. The iodine value was then calculated as presented under **Appendix B 4.** The experiment was repeated for all the cocoa bean categories.

3.2.5 Determination of butter colour

Lovibond Tintometer Model F Operators Instruction Manual was followed for this test. The optical cells (cuvette) were dried thoroughly whilst warming the butter samples in a 60 ˚C oven (Genlab oven, model: OV/150/SS/F/D/G, UK). The first sample was then poured gently into the one (1) inch sample optical cell of the lovibond (Tintometer Colorimeter, U.K.), positioned accurately in the chamber and then focusing the viewing tube until a sharp image of the aperture was obtained on one of the adjacent fields of view of the lovibond. The sample field and a white reflective surface in the comparison field were observed side by side. The racks controlling the colored filters were adjusted for the proportions of red, yellow and blue (Lovibond standard colors) until a color

match was obtained. The process was repeated with the other samples and the values (s) of the filter color combination used in the color measurement were recorded.

3.2.6 Determination of slip melting point

The slip melting point determination procedure was followed according to IOCCC 4 – 1961 method .The test samples to be analyzed were solidified at -5 ^{0}C. Capillary tube with opening at both ends was filled half-way by pressing the surface of the test sample with one of the open ends randomly to increase sample space. The capillary tube was inserted into a Grant water bath (GP 200, England), pre-conditioned at 30 °C with the ends that contains the butter. The temperature was increased by 0.2 °C unit intervals until sample was observed to melt and then rises up through the capillary tube. The temperature was then recorded as the slip melting point. The process was repeated with the other samples.

3.2.7 Determination of refractive index

The refractive index procedure was followed according to the method of the International Union of Pure Applied Chemistry (IUPAC) 2.102. The prism surface of the Abbe 60/DR refractometer (A 12005, U.K), was cleaned by a cotton soaked with alcohol. The refractometer was calibrated with distilled water to refractive index of 1.3333 by placing a drop onto the prism surface of the refractometer and adjusting the fine tuning knob to get the right fine tune. Test samples were warmed to about 40 °C by the attached water bath. A drop of the sample was placed onto the prism surface of the refractometer and closed. The refractive index was read by adjusting the two knobs on the side of the refractometer until two different regions (light and dark colored regions) separated at the intersection point of two lines were seen. The refractive index value of the sample was recorded. The process was repeated using the other samples.

3.2.8 **Determination of fat by Soxhlet extraction**

The determination of fat by Soxhlet extraction procedure was followed according to IOCCC 14(1972) method. An accurate weight of 2 g of the test sample (W_1) was weighed with Mettler Toledo analytical balance (MS204S/01, Switzerland) on to a filter paper and tightly wrapped. The wrapped sample was inserted in a thimble which was then placed in the Soxhlet extraction chamber. A clean, dry and a well-conditioned Round bottom flask (W_2) was weighed and recorded. The flask was filled with Petroleum Ether to about one-third of its volume and connected to the extraction chamber and the heating mantle ((10067655/00, UK,) turned on. Water tap connected to the condenser was turned on and the test sample was extracted for 12 h. Sample was removed after 12 h from the extractor and the petroleum ether was recovered. The round bottom flask was placed in a Genlab oven (OV/150/SS/F/D/G, UK) at 105 ° C for an hour to expel traces of petroleum ether. The flask with fat was cooled in a desiccator, weigh and recorded as (W_3). The fat content was then determined. This experiment was again determined for all the liquor samples for the five categories according to the formula stipulated in **Appendix B 5.**

3.2.9 Determination of Q-factor by Shukoff's cooling curve

The degree of tempering was determined according to the International Union of Pure Applied Chemistry (IUPAC), 2.132 method which consists of measuring the temperature of the fat to be tested during its cooling. The instrument used was the Exotherm 8000 Shukoff Tempermeter (8004, Germany). It consist of a special flask made of glass with double wall to carry the sample (pressure between the wall is 0.01 mm Hg). The tempered butter or oil was conditioned together with the Shukoff bottles in a Genlab oven (OV/150/SS/F/D/G, UK) at 60 °C. An acculturate volume of 25 ml of the test samples was poured in each of the four bottles and these were again

conditioned in the oven at 60 ºC. The bottles were inserted in the cooling bath after checking the water level was correct. The temperature probe was then inserted to start the measurement. Temperatures of 17 ºC to 40 ºC were the set limits for this experiment. The monitor connected to the Exotherm 8000 instrument displayed three peaks on the graph plotted; the prime stay, minimum curve and the maximum curve. The determination of the cooling curve as cited in **Appendix B 6.**

3.2.10 Determination of Free Fatty Acid

The determination of free fatty acid procedure was followed according to the method of the International Union of Pure Applied Chemistry (IUPAC), 2.201. An accurate weight of 10 g of the fat was weighed with a Mettler Toledo analytical balance (MS204S/01, Switzerland) into a 250 ml beaker and the weight was recorded. A volume of 50 ml of ethanol was measured into a beaker and heated. Three drops of phenolphthalein indicator was added to the ethanol and neutralized with 0.1 M of NaOH standard solution to a faint purple colour. The neutralized ethanol was poured onto the fat and warmed to aid dissolution by placing on Hot plate (23218, U.K.). A magnetic stirrer was dropped into the suspension and a stirrer attached to the dosimat was set on. The weight of the sample was inputted by using the numeric keypad of the dosimat. (MS: 00294780, Switzerland). The suspension was titrated against a standardized 0.1M NaOH solution whilst stirring until a deep pink colour which persisted for 15 s was obtained denoting an endpoint. The percentage FFA value automatically displayed on a screen after tapping the “fill” bottom.

3.2.11 Statistics Analysis

Analysis of Simple t-tests were performed using Minitab 17 software to evaluate the significance of differences between mean value of all parameters investigated for the various bean categories and the Codex standard at a level of $P < 0.05$

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 RESULTS

4.1.1 Saponification Value for the various test samples

The results indicated in figure 1 shows an increasing trend of saponification values from the Super Main Crop, Main Crop, Super Light Crop, and Light Crop to the Small bean size categories. The super main crop beans with the largest size recorded the least value of 189.48 mg KOH/g, whereas the small beans recorded the highest among the test samples of saponification 194.27 mg KOH/g. The saponification order for the rest of the categories increases as the size decreases in the order as follows; main crop (190.72 mg KOH/g) < super light crop (191.31 mg KOH/g) and light crop (192.04 mg KOH/g). The saponification value increases whilst the bean size decreases.

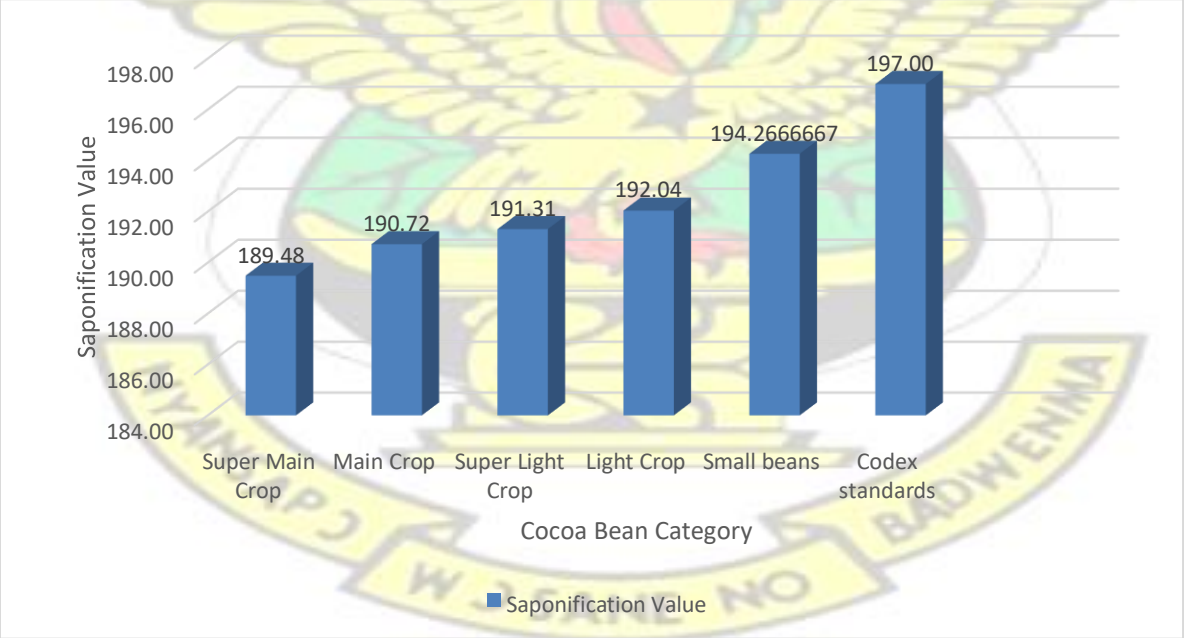

Figure 1 Effect of Bean Categories on Saponification values with the Codex Standard of 197mg KOH/g cocoa fat.

The main crop categories recorded the lowest with 189.48 mgKOH/g and the small beans recorded the highest value of 194.27 mgKOH/g of cocoa butter. The saponification values recorded as shown in table of Appendix A; were significantly lower ($p<0.05$) for all categories than the codex standard of 197 mgKOH/g cocoa fat. That also endorses the fact that Ghana's cocoa is or among the best in the world. There were significant differences ($p < 0.05$) of all the categories against the codex standard. The highest saponification value was found in small beans (194.27 mg KOH/g) and the lowest was found in super main crop beans (189.48 mg KOH/g).

The increase in the saponification values might also be due to increased aeration and diffusion of oxygen into the beans during fermentation, drying and storage which caused oxygen molecules to react with some of the double bonds (oleic and linoleic fatty acids) in the triacylglycerol molecules to form hydroperoxides (Afoakwa *et al.*, 2014). The oxygen passage effect was immensely seen in the lower categories than the larger size beans. This anomalies could be as a result of their size differences. The rate of oxygen exchange or passage was greater for the smaller categories when exposed to the same conditions with the larger size beans after cultivation and storage. Generation of nib and shell fines were most common for smaller categories during winnowing. The fragment or size of cocoa nibs from small beans were smaller than nibs processed from larger bean size. Roasted fines from lower categories have a shorter shelf life than larger categories. The roasting effect changes the microstructure of the fine nibs easily which then hasten lipid oxidation and rancidity. The oil in raw cocoa beans were basically protected from oxygen in the environment by the microstructure and the antioxidants naturally present. The membrane network of the oleosome was damaged through thermal activity during roasting thereby increasing the extracellular spaces.

The structural change exposed the oil within the cells more to oxygen which triggered the lipid oxidation reactions.

The saponification value serves as an indicator to determine the molecular weight of the triglycerides in oil. That is the chain length of the fatty acids or the average molecular weight is inversely proportional to the saponification value (Muhammad *et al.*, 2011). The shorter the average chain length, the higher the saponification value (Tamzid, *et al.*, 2007). The higher the amount of acid value, the higher the deterioration or rancidity of the oil. The oil achieves a foul smell along with a sour taste as the rancidity level increases.

The saponification values for cocoa butter extracted from all the various categories investigated were within the cited literature values of 188-198 mg KOH/g cocoa butter (Codex Standard 86, 1981; Chaiseri and Dimick, 1989; Shukla, 2003; Krysiak, 2011).

4.1.2 Unsaponification value trend exhibited by the various categories

The unsaponification values increased steadily (figure 2) as the bean size increased. The super main crop recorded the least unsaponification value of 0.17%, and the trend increases from 0.19%, 0.25%, 0.26% and 0.28% for main crop, super light crop, light crop and small beans respectively. The unsaponifiable levels were small in cocoa butter processed from larger sized cocoa beans than cocoa butter extracted from the smaller categories as shown in figure 2. Despite the maximum threshold value of 0.35 % by codex standard as presented in table 8 of Appendix A. The values recorded were significantly lower than codex threshold.

The unsaponifiables are components of an oily mixture that fail to form soaps when blended with sodium hydroxide. This type of analysis is important in the estimation of the oil or cocoa butter purity.

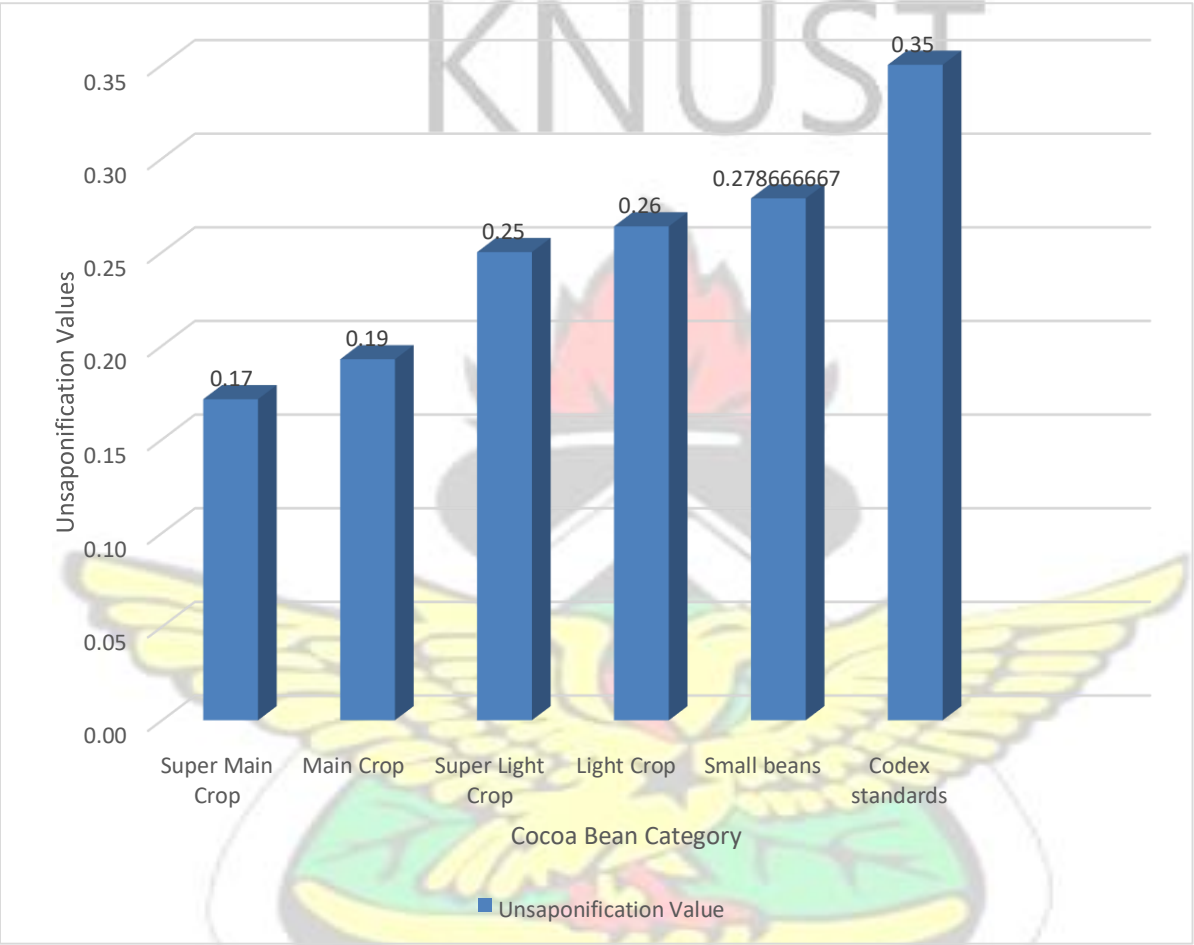

Figure 2 Effect of Bean Categories on Unsaponification values with the Codex Standard

The cocoa masse produced from the lower categories were more viscous due to the lower fat content attributed for smaller size beans as indicated in table 9 of Appendix A. The cocoa masse obtained from the smaller beans were usually gummy resulting to sieve blockage and spillages during liquor pressing leading to the trend as seen in figure 2.

4.1.3 Iodine value trend exhibited by the various categories

The trend in figure 3 showed a lowest recorded value of 31.67 gI_2/100g iodine value for the super main crop cocoa beans and the trend continued to increase from 31.99 gI_2/100g for the main crop, 32.17 gI_2/100g for the super light crop, 32.36 gI_2/100g also for the light crop size beans. The small beans recorded the highest value of 33.13 gI_2/100g and the interpretation is that there were few bonds that reacted with the iodine. The iodine number at 95 % confidence level as presented in table 8 indicated that all the various categories were far less significant ($p < 0.05$) to the codex standard.

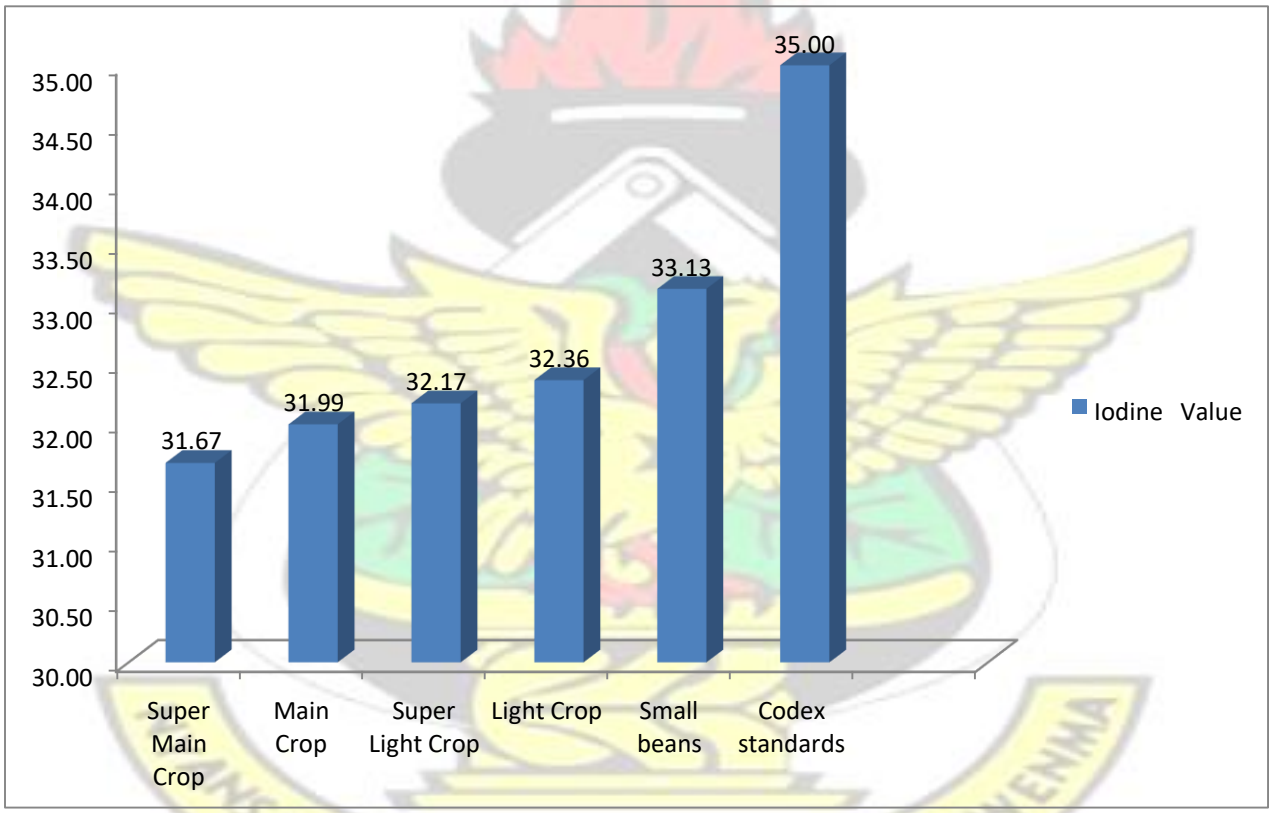

Figure 3 Effect of Cocoa Bean Categories on Iodine values with the Codex Standard of 35 gI_2/100g.

Iodine value is an index of the unsaturation (Otunola *et al.*, 2009). The iodine value of the bean categories are presented in figure 3. It was observed that the iodine value were less significant as

compared to the codex standard. Variable trends in iodine values were conspicuously seen during roasting and by definition the amount of iodine in grams that are consumed by 100 groms of a chemical substance. The iodine value analysis determines the degree of unsaturation in fatty acids like the cocoa butter. The unsaturation usually in the form of double bonds reacted with iodine compounds. These bonds are positively skewed on graph with the iodine levels. That is as the number of bounds increases, the iodine value also increases.

The iodine values (IV) often than not offers an estimation of unsaturation and hardness in cocoa butter. The highest recorded value of iodine value from test samples as shown in figure 3 indicates a high level of unsaturation of the triglycerides in the butter. The soft texture of cocoa butter is as a result of iodine value this was also confirmed by Liendo *et al*. (1997).

Cocoa beans with smaller size usually have a very shorter shelf life as compare to their higher categories. The former often generates fines during winnowing, hence destroying the microstructure which are further disintegrated during roasting. This in turn destroys the membrane network of the oleosome through thermal activity. Lipid oxidation reactions occur when the cells exposed to oxygen causing spikes in iodine value in cocoa butter. (Afoakwa *et al.,* 2014). Processors have no option than to process smaller category of beans immediately it comes to the warehouse. Hording of such consignment easily undergo oxidation causing spikes in FFA and increasing the iodine number during production.

The iodine level of attachment depends on the number of bonds present. The more the double bond is attached by the iodine, the significant the iodine value which were more responsive, less stable,

softer and the more vulnerable to oxidation and rancidification of the fat or oil. There were level of correlation between the iodine value and free fatty acids from the test samples level. Long storage of lower categories is not the best option and that processors must devoid from such practices. The bean quality for such consignment is easily deteriorated when conditions in warehouses are not favourable. The impact of external forces or pressures like air or oxygen is greater in lower categories than lager size beans due to their size. This is because the surface area for smaller size categories are higher than the larger size beans hence the former would deteriorate faster under the same condition.

The iodine values from the various cocoa bean size categories were within the acceptable limits by the Codex Standard of 33-42 (Codex Standard 86, 1981). Work done by Biehl and Ziegleder (2003) also reported iodine values (36.5 g I/100 g) for cocoa butter extracted from Ghanaian cocoa beans to be within the Codex Standard. The iodine values observed in this research indicated that the cocoa butter were slightly soft and values were within the acceptable limit of the Codex Standard.

4.1.4 Peroxide value trend exhibited by the various categories

The trend for the peroxide values for all the categories were less significant as compared to the codex standard (figure 4). The minimum peroxide value was observed in super main crop (0.35 Meq O_2/kg) whereas the maximum peroxide value was found in small beans categories (1.53 Meq O_2/kg). The codex standard for peroxide value is 3.0 MeqO_2/kg. Figure 4 shows the effect of cocoa bean size on peroxide value and as the bean size decreases the peroxide value content increases.

The super main crop which had the largest bean sizes recorded the lowest peroxide value (PV).

The PV increases from 0.35 MeqO_2/kg <1.2 MeqO_2/kg <1.49 MeqO_2/kg < 1.50 MeqO_2/kg. < 1.53 MeqO_2/kg for super main crop, main crop, super light crop, light crop and small beans respectively. The bean sizes decreased in the order of the preceding categories.

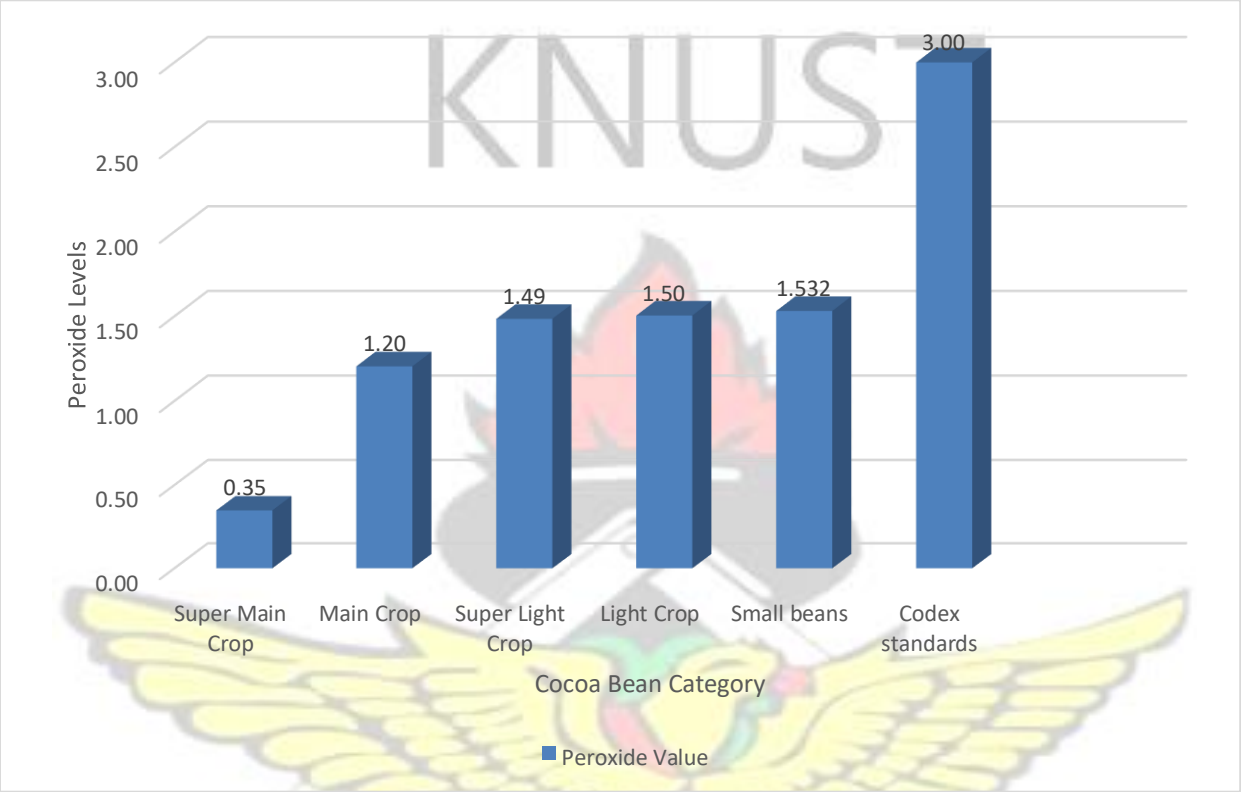

Figure 4 Peroxide values of the different bean categories in comparison to standard value

Peroxide value is a measure of oxidation during storage and the freshness of lipid matrix. The peroxide value for fresh oils is less than 10 MeqO_2/kg. High peroxide values are clear indication of fat rancidity nevertheless moderate values may be the result of depletion of peroxide after reaching high concentration. According to Chakrabary (2003), rancid taste is most noticeable with peroxide value between 30 and 40 MeqO_2/kg. Peroxide value signifies the extent to which the cocoa butter sample has undergone primary oxidation or the extent to which oil spoilage has deteriorated.

Determination of peroxide value provides evidence of onset of rancidity in unsaturated fats and oils. The degree of unsaturation identified in fats and oils play a key role in autoxidation process. Oils having a high degree of unsaturation are usually most vulnerable. Therefore the main reason why this analysis is conducted on the cocoa butter is to be able to determine the extent of its spoilage. The peroxide value often than not use serve as an indicator of emerging rancidity under mild condition (Choudhary, 2013). Most often than not, it is the measure of the primary lipid oxidation product. The freshness of lipid matrix as well as the oxidation during storage are detected by the peroxide value. The significant amount of peroxide value, the greater the rate of oxidation of the oil (Atinafu and Bedemo, 2011).

The greater the peroxide value, the more the rate of oxidation (Atinafu and Bedemo, 2011). It was observed that the peroxide for the larger size of beans increase significantly ($p < 0.05$) as compared to the codex standard. The highest percent increase once recorded in the small beans examined. The increase in the peroxide values might be due to increased aeration and diffusion of oxygen into the beans during fermentation, drying and storage which caused oxygen molecules to react with some of the double bonds (oleic and linoleic fatty acids) in the triacylglycerol molecules to form hydroperoxides The autoxidation is a mechanism that occurs in open air or where there is availability of oxygen which forms peroxides and hydroperoxides. Temperature controlled storage was one of numerous methods used to control lipid oxidation. (Afoakwa *et al.*, 2014). The level of peroxide value peaks and drops down during the foods life. The commencement of lipid oxidation as well as the free radical chain reaction, the whole cycle enters the monomolecular stage. There is a rapid uptake of oxygen in the bimolecular period which is the third stage. The rapid uptake of oxygen accumulate lots of hydroperoxides that causes spike in PV value.

Aldehydes, ketones and other non-radical compounds are produced as the PV climbs up and eventually drops down the PV. The flavor-aroma are termed rancid when oxidation occur and the reaction are said to be responsible by these aldehydes. Due to the hygroscopicity of cocoa it absorbs lots of water in humid ambient. That is to say changes in water content means contact with the air. The increase exposure to air often increases the oxidation rate which also means decrease in nutrient value and leads to discoloration of the surface and rancidity. Pressure is inversely proportional to area, hence the smaller the area the greater the rate of air transition or oxygen passage during storage. This instigates the action of lipid oxidation reactions leading to bean deterioration. The rancidity rate for smaller beans are comparatively greater under the same environment conditions which are positively skewed with the iodine number hence the trend in figure 3.

The shelf life is controlled by the product characteristics, the environment during distribution and lastly storage. That is controlling the moisture, temperature and oxygen preserves cocoa quality and shelf stability. Smaller categories are usually deteriorated for a short period compared to the larger categories when exposed to the same condition. The transition rate for air passage or oxygen uptake is greater in smaller categories and decreases as the size increases, which is transition rate per size is inversely proportional or negatively skewed on the graph. The impact is more severe in smaller beans than the lager sized beans when exposed under the same climatic conditions.

Although the test samples were cultivated within the same crop year (2014/2015). The variation of the trend for their PV could be the effect of differences in climatic conditions, storage conditions, the bean category and the rate of active passage of oxygen due to the size.

Cell aging may usually be instigated by lipid peroxidation process. Polyunsaturated fatty acids were usually attacked by oxygen species that triggered the peroxidative reaction. The aforementioned activity was commenced by propagation cycle of which the lipid and peroxyl radicals as well as lipid hydroperoxides are actively involved. The cell membrane are deteriorated and destabilized due to peroxidation and radical propagation cycle. Nonetheless as a result of nonenzymatic reaction or enzymatic inactivation of oxygen the propagation cycle are broken beans amidst free radical scavengers such as flavonoids as mentioned by Halliwell (1999). Simply by donating phenolic hydrogen and formation of a flavonoid radical, which then reacts with free radical, is influenced by the radical scavengers thus deteriorating the propagating cycle.

4.2. Shukoff's cooling curves trend exhibited by the various categories

The super main crop cocoa beans recorded the highest value of 0.16 (figure 5) followed by the main crop beans that recorded 0.14 and the order decreased from 0.12, 0.11 and 0.11 for super light crop, light crop and small beans respectively. The Q-factor obtained from the above listed categories (figure 5) and the results from table 8 in appendix A confirms that all the Q-factor values were significantly ($p < 0.05$) higher than the minimum allowable limit.

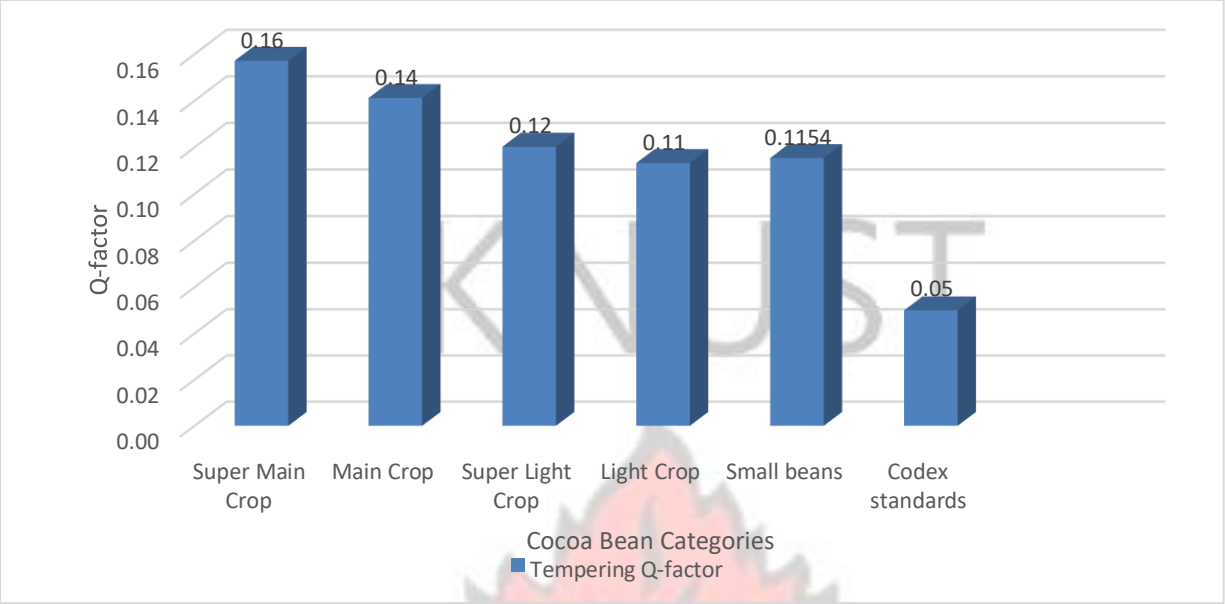

Figure 5 Effect of cocoa bean categories on shukoff's cooling curve with the Codex Standard (0.05 min).

The definition of the Q factor as the change in temperature over time during crystallization often than not gave a clue about how good or bad a butter. Q > 0.15 connotes a good or soft butter. This was clearly exhibited in the butter samples extracted from the super main crop beans. The Q-factor value less than 0.05 refers to bad or hard butter as ascribed in Exotherm 8000 manual of Shukoff. This was not recorded in any of the test samples. The cocoa butter is said to be good when Q-factor is greater than 0.15 (Q > 0.15) such cocoa butter are usually soft. On the other hand, anything below 0.05 is attributed as bad butter. In situation where the Q-factor appears to be lesser than 0.05 (Q < 0.05) is classified a non-acceptable cocoa butter. The butter quality has direct correlation to the seasonal changes, climatic conditions and the variety of the cocoa beans. The fat crystallization properties were controlled by experimentally measuring the Shukoff's tempering curve. The information on the fat compatibility and the purity of the cocoa butter were detected by this method. The cooling curve though indirectly related to the demoulding properties during cocoa

butter crystallization, usually has a correlation with the contraction of the chocolate hence used as predictive method.

The physical traits of the triglycerides are most influenced by the emulsifying action and its solubilizing effect which then interrupts the stable crystals. This makes the hardening or softening process impossible and most often takes longer time than usual. The minimum and maximum curve in the cooling curves connotes a prime –stay as a result of impurities like trisaturated triglycerides. The change in temperature gave a clue about the crystallization capacity and also connotes how hastily the fat mixture will solidify and presumably the difficulties to be expected the cooling tunnels of the moulding lines.

Light crop size beans and small beans were the least value recorded. The cooling curves gave an evidence on purity of cocoa butter as well as the compatibility of fat composites. The experiment had a direct correlation to butter crystallization and indirectly associated to the demoulding properties hence used as forecast method. Findings attributed to this experiment were that product quality, processing efficiency and the profitability improvements can be monitored by cooling curve.

4.2.1 Free fatty acids trend exhibited by the various categories

The free fatty acids as presented in figure 6 larger sized beans recorded the least Free Fatty Acid value of 0.89% for the super main crop and 1.23% as the highest recorded value for the small Beans Categories. Nonetheless the FFA values obtained in this study were far less significantly different from the codex standard of 1.75% ($P<0.05$) which is the maximum allowable limit (table

8). The FFA for super main crop beans had the lowest value followed by main crop, super light crop, light crop and the small beans.

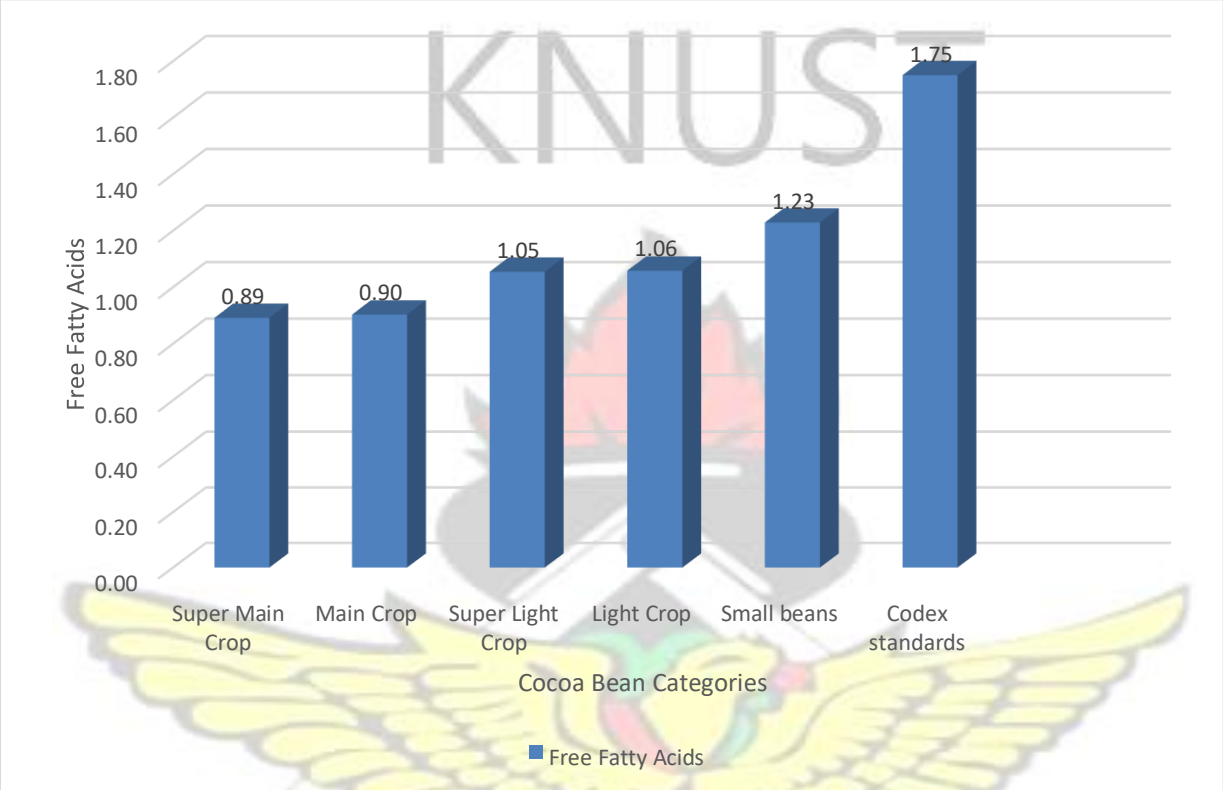

Figure 6 Effect of Cocoa Bean Category or size on Free Fatty Acid with the Codex Standard (1.75%).

The main crop beans are sold with high price due to its best quality as seen in the FFA results presented in figure 6, peroxide value (figure 4), iodine value (figure 3), considered to be the best grade cocoa. The triglycerides (fat) are a derivative from; oleic, palmitic and stearic acids. The thermal activity and enzymatic breakdown of the carboxylic acids unleashes the free fatty acids from the triglycerides. The resulted free fatty acids (FFA) means both the mono and the diglycerides are present with the triglycerides since the deterioration of the triglycerides are slower as compared to the oxidative attacks which are randomized. The butter and liquor crystallization

are greatly affected in the presence of the mono, di, and triglycerides together with the free fatty acids. Interruption of the crystals is usually triggered by the emulsifying action of the fat as well as its solubilizing effects. Most often than not production are retarded during butter or liquor tempering and the stacking becomes impossible. The hardening or softening of the butter becomes impossible or takes longer time and soils are visually seen on packaging materials under normal room temperature causing operational down times, decreasing glossiness and the organoleptic effect to the consumer.

Moldy beans are usually resulted from high moisture content. According to Wood and Lass (1955) the molds which are microflora are the root cause of free fatty acids (FFA) in stored beans. The enzymatic activities powered by lipase is naturally present in raw cocoa as confirmed by Minifie (1989) causes FFA spikes during storage. High temperature storage conditions of warehouses as well as the changes in the moisture content of the beans activate these enzymes. FFA is affected by humidity, moulds and exposure to oxygen. It was observed from figure 6 that cocoa beans with larger size were found to contain lower FFA levels than smaller size. Eatty acids in oil are usually in triglycerides form but are hydrolysed into free fatty acids during processing. The higher amount of free fatty acids interpret into decreased oil quality (Choudhary and Graver, 2013).

The trend was in agreement with earlier findings by Krysiak (2011) during cocoa roasting. The cocoa butter from the various categories cocoa categories had percentage free fatty acids content below the maximum industrial limit of 1.75% (Chaiseri and Dimick, 1989; Shukla, 2003; Krysiak, 2011) or 1.75% oleic acids.

4.2.2 Refractive Index trend exhibited by the various categories

Refractive index were observed to be the same for all the cocoa bean categories (figure 7). That is the super amin crop, main crop, super light crop, light crop and the small beans had a refractive index of 1.456 (figure 7). The refractive index often has a direct correlation to the purity of the butter.

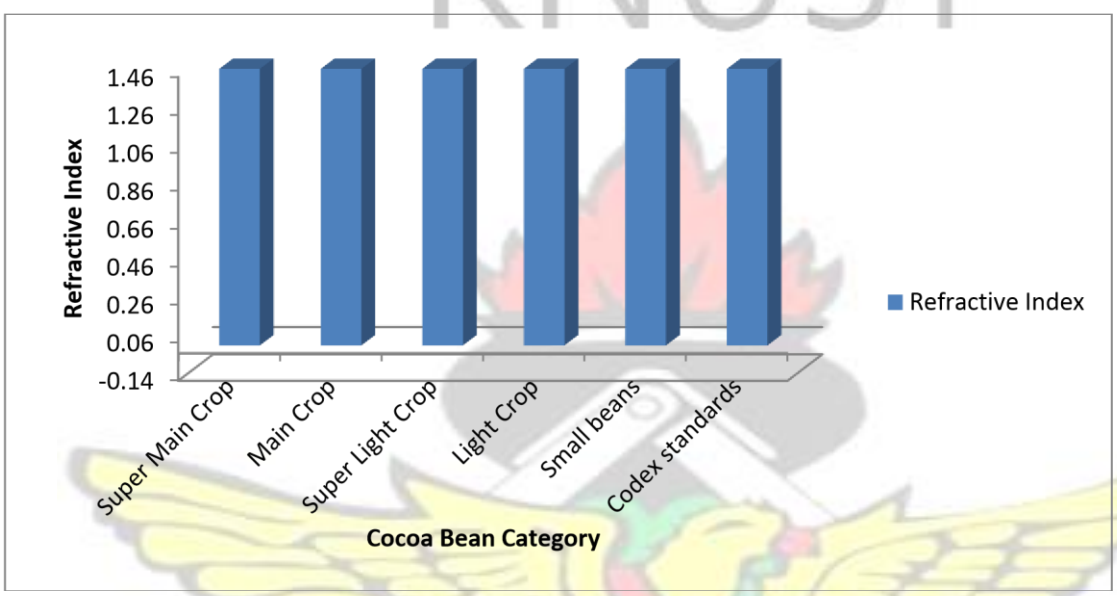

Figure 7 Effect of cocoa bean categories on Refractive Index values with the Codex Standard (1.456)

The rate of oxygen passage across the cells membrane is higher for smaller categories than the larger bean size. The severity of oxidative attack in smaller categories was usually greater due to its size. The categories were exposed to the same storage conditions with equal time; one would have expected the deterioration rate to be greater for the smaller sized beans. Cocoa beans are usually exposed to several forces or pressures during storage. The deteriorating effect is more severe to cocoa beans with smaller size. Cocoa beans with smaller size have smaller surface area. This is opposite in the case of larger sized beans. When the beans are equally exposed to the external conditions the impact are severe in the case of the smaller sized beans. That is pressure is inversely proportional to the area and directly proportional to force as proposed by Pascal. The

refractive index values were all the same for all bean categories and the codex standard. There were no significant differences in terms of the refractive index.

4.2.3 Fat trend exhibited by the various categories

The super main crop beans recorded the highest fat content of 55.24%, followed by main crop (54.71%), super light crop (53.01%), light crop (52.21%) and 52% for the small beans that recorded the lowest as shown in figure 8. The fat trend decreases as the bean sizes decreases. In other words the fat level is positively skewed by the bean size 9figure 8). The average fat levels for all the categories studied were above the minimum acceptable limit level according to the Federation of Cocoa Commerce.

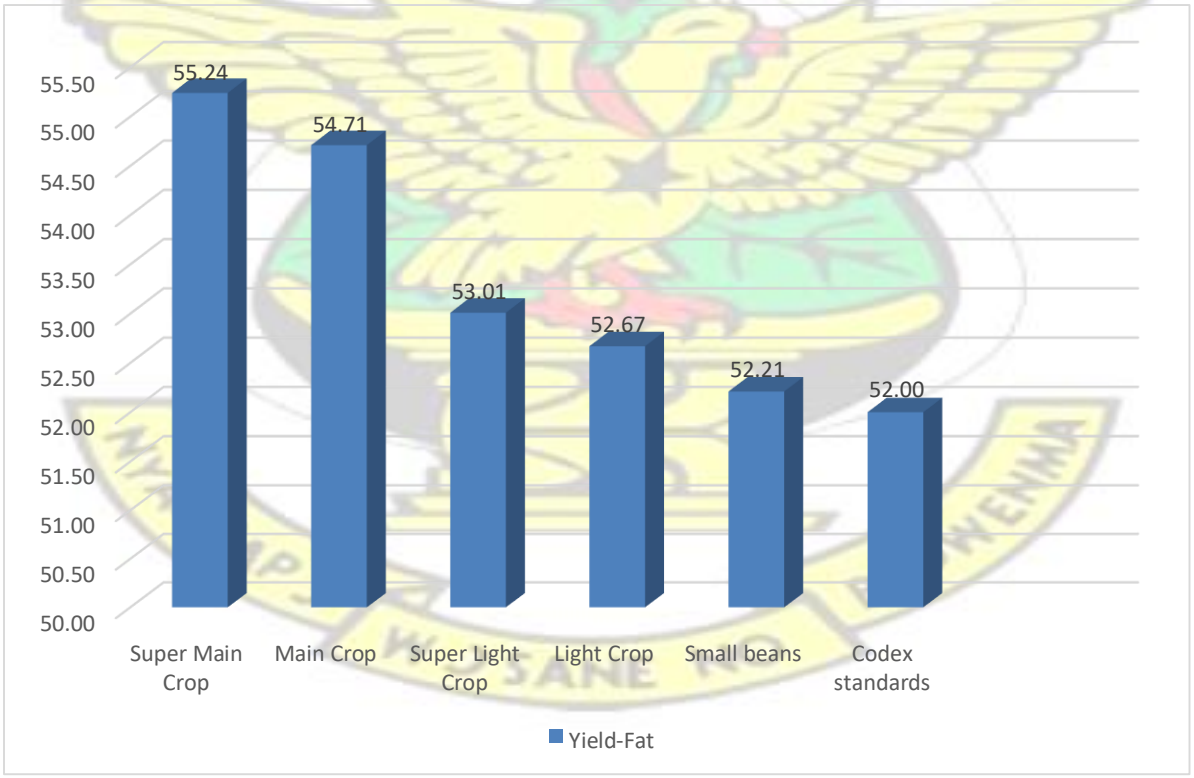

Figure 8 Effect of Bean Size or Categories on Fat values with Codex Standard by FCC rules

The fat content of cocoa is one of the key parameters for selling or buying cocoa liquor. Cocoa Liquor are usually traded with a minimum fat level of 52% by the Federation of Cocoa Commerce rule. Cocoa yield has a direct correlation to the cocoa bean size and inversely proportional to the bean count (Table 10). The yields are greatly affect by the amount of shell and moisture level present. Lesser shell content and lower moisture is likely to produce higher yield. The yield was represented mathematically as indicated in **Appendix B 6.** The amount moisture and shell has a direct correlation to the fat. That is more shell or more moisture means lesser yield. These two parameters are key in purchasing cocoa. Comparatively lower categories are noted for more or thicker shells. Depending on the recipe there is always retention of moisture content after liquor production. This moisture value differs from industry to industry when performing mild roasting, medium roasting and high roasting liquor. This recipe has a direct impact to the yield of fat.

The yield and fat content are directly proportional, which means the higher the yield, the higher the fat levels. Fat content for lower categories were observed to be lower because there are losses during production and most significantly the differences in their sizes. Most often than not lots of fines are generated which makes it impossible for shell separation. During roasting fat are easily moped off by shell's fines present. Contrary Larger sized beans do not generate much fines hence little or low fat mopping activities.

4.2.4 Slip melting point trend exhibited by the various categories

The slip melting point for the super main crop bean size recorded the highest value of 33.84 ˚C (figure 9). There were a steady drop for both main and the super light crop size beans each with less than a degree drop at 33.76 ˚C and 33.66 ˚C respectively. The light crop and the small bean

categories recorded 32.81 ˚C and 32.99 ˚C respectively. All the slip point values recorded were far less significantly different as compare to the Codex Standard (table 8).

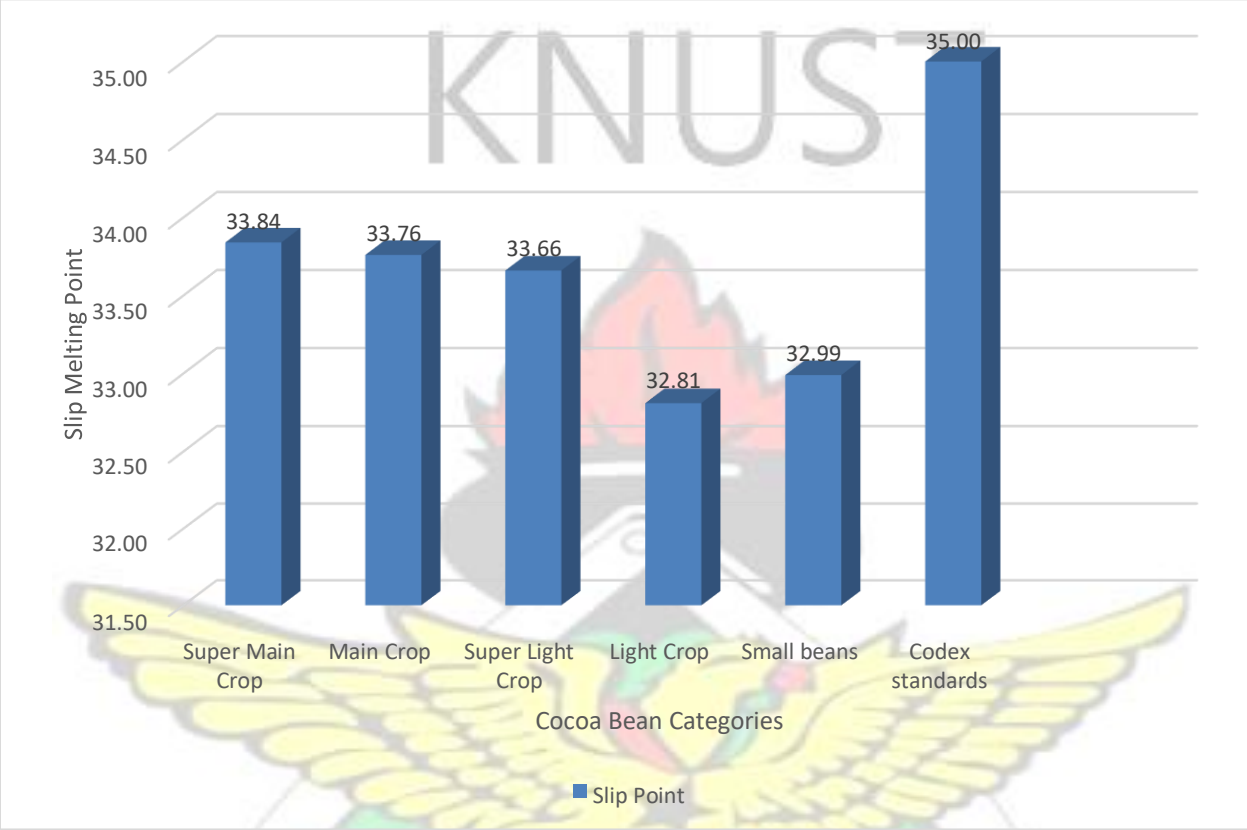

Figure 9 Effect of Cocoa Bean Categories on Slip melting point with the Codex Standard

All samples tested were far less significant ($p < 0$) to the codex standard of 35 ˚C. The irregularity of trend demonstrated were attributed to the fact that tempering temperatures were not regulated within the set limit hence the butter were tempered at different temperature. The slip melting value are usually affected when the butter tempering temperatures are not regulated within the set limit. According to IOCCC 41(1996), the slip point of fat is defined as the temperature at which the column of a fat solid begins to rise in the capillary tube due to floatation and the molten state of the fat. The abnormal trend of results observed in figure 9 could be attributed to irregular tempering temperatures. A replica of these anomalies was acknowledged by Berger *et al.* (1982). In his

experimented attributed the factors affecting slip melting point to the differences in the tempering temperatures, and also endorses the fact that the variation in tempering temperatures was dependent on the nature of the sample.

The finding on his experiment on tempering temperature conducted for the palm oil and palm olein observed that the higher melting points were obtained when tempering at the higher temperatures in the range of 4 ^{0}C to 15 ^{0}C. For some soft strains however, lower melting points were obtained at the higher tempering temperatures.

Slip melting point analysis is an important way to test if the cocoa butter is pure. A pure material commonly have a melting range of one or two degrees. That is the difference between the temperature where the sample starts to melt and the temperature where melting complete was usually of one or two degrees for this experiment. Impurities and bad tempering temperatures depressed and extended the melting range. As expected the purified sample should have been smaller melting range than the original, impure sample, however there were anomalies in the trend that could be due to bad tempering. The range of slip melting point values for this work were within the acceptable range with earlier findings by Osborn (2002) and Zarringhalami (2012).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The quality of cocoa beans was greatly affected by the size categories. Among the five categories studied the super main crop registered the highest quality followed by main crop, super light crop, light crop, and small beans in that same order. The yield-fat decreased respectively in the order as

specified above; 55.24%, 54.71%, 53.01%, 52.67% , 52.21% just as the free fatty acids increased along the same other as 0.89%, 0.90%, 1.05%, 1.06%, 1.23%. Again the Q-factor from the Shukoff's cooling curves evaluated presented a similar order as 0.16, 0.14, 0.12, 0.11and 0.12. These values were above the minimum threshold of 0.05 below which the butter is unacceptable. The aforementioned trend clearly indicated the quality of the graded cocoa bean. All the other parameters studied showed similar trends. The IV, PV, SV and unsaponification values were significantly ($p<0.05$) lower compared to codex standards. The main crop beans recorded least traces of 0.35 $MeqO_2/kg$ whereas the smaller beans recorded 1.53 $MeqO_2/kg$ which was just a midway to the codex threshold of 3.00 $MeqO_2/kg$. Again the Iodine value for the five categories ranged between 31.67 $gI_2/100g$ to 33.13 $gI_2/100g$ which were far less significant to the allowable limit of 35 $gI_2/100g$. The unsaponification value detected ranged from 0.17% to 0.28% for the large size and small size cocoa respectively for the studies.

The trend exhibited from all the parameters evaluated in agreement with previous studies indicated that cocoa bean category or size has an effect on the product quality. The above standpoint appear that the marketers were indeed within their rights if cocoa beans are graded and marketed based on their sizes.

Also, the oil quality extracted from the five different categories endorses the fact that, the equipment design was able to handle cocoa beans that are larger than the smaller size beans.

5.20 Recommendations

1. Based on the results and conclusions the following recommendations have been made.

There were good trend of results obtain from the Shukoff's curves on the oil obtained from the different categories of beans studied and thus further work on the properties of finished products such as hardiness, viscosity, density of chocolate could be studied.

2. This study focused on five categories out of the seven major types in Ghana. It is recommended that the same study be replicated for the remaining two (type-4 and Remnant) cocoa bean types to offer a broader picture to the processor in their material balance ratio.

3. Low or medium roast is recommended when roasting cocoa beans with nib and shell fines to minimize chars that darkens oil colour and implicate hazards such poly aromatic hydrocarbons (PAH).

REFERENCES

Afoakwa, E. O., Ofosu-Ansah, E., Takrama, J.F., Budu, A.S. and Mensah-Brown, H. (2014): Changes in chemical quality of cocoa butter during roasting of pulp pre-conditioned and fermented cocoa (*Theobroma cacao*) beans. *International Food Research Journal 21(6):* 2221-2227.

Afoakwa, E. O. and Paterson, A. (2010): Cocoa Fermentation: Chocolate Flavour Quality. In: Encyclopedia of Biotechnology in Agriculture and Food. *Taylor and Francis Publishing Oxford, U.K.* 457 – 468.

Afoakwa, O. E. (2010): Chocolate science and technology. *Wiley-Blackwell publishing, UK. Pp 21-23.*

Amin, H.M**.,** McDonnell, T.J., Ma, Y., Lin, Q., Fujio, Y., Kunisada, K., Leventaki, V., Das, P., Rassidakis, G.Z., Cutler, C., Medeiros, L.J. and Lai, R. (2004): Selective Inhibition of STAT3 induces apoptosis and G (1) cell cycle arrest in ALK-positive anaplastic large cell lymphoma. *Journal of Oncogene Pubmed*. 23(32): 5426-5494

Archer, D.M. (2006): The De Zaan® Cocoa Manual. *Koog aan de Zaan, the Netherlands Publishers.*

AOAC, (2005): Official methods of analysis. *18th edition, Association of Official Analytical Chemists.* Washington, D.C -U.S.A.

Ardhana, M. M. and Fleet, G.H. (2003): The microbial ecology of cocoa bean fermentations in Indonesia. *International Journal of Food Microbiology.* 86, 87–99.

Atinafu, D.G. and Bedemo, B. (2011): Estimation of total free fatty acid and cholesterol content in some commercial edible oils in Ethiopia, Bahir DAR. *Journal of Cereals Oilseeds, 2,* 71-76.

Aydin, C. (2003): Physical properties of almond nut and kernel. J. *Food Engineering*. 60: 315-320.

Baryeh, A. (2001): Physical properties of Bambara groundnuts. *Journal of Food Engineering.* 47: 321-326.

Bart-Plange, A. and Baryeh, E.A. (2003): The Physical properties of category B cocoa beans. *Journal of Food Engineering, 60: 219-227.*

Bart-Plange, A., Addo, A. and Dzisi, K. A. (2005): Effect of Rewetting and Drying on Selected Physical Properties of '*Obatanpa*' Maize Variety. *Journal of the Ghana Institute of Engineers.* 3(1): 12-15.

Bart-Plange, A., Dzisi, A. K., Addo, A., Teye, E. and Kumi, F. (2012): A Comparative Study of Some Physical Properties of Large and Medium Size Cocoa Beans from Ghana, *ARPN Journal of Science and Technology,* 2(3): 135-140.

Beckett, S.T. (2008): The Science of Chocolate. Second edition. *Royal Society of Chemistry Paperbacks, London, UK.*

Belscak, A., Komes, D., Horzic, D., Kovacevic, K. and Karlovic, D. (2009): Comparative study of commercially available cocoa products in terms of their bioactive composition. *Food Research International*. 42:707–716

Berger, K.G., Siew, W.L and Flingoh, C.H. (1982): Factors Affecting Slip Melting Points of Palm Oil Products. Springer-Verlag. *Journal of the American Oil Chemists Society*. 5:244-249.

Biehl, B. and Voigt, J. (1996): Biochemistry of Chocolate Flavour Precursors. *12th International Cocoa Research Conference. Salvador, Brazil.* 17-23.

Biehl, B. and Ziegleder, G. (2003): Cocoa chemistry of processing. *Encyclopedia of food sciences and nutrition. Second Edition.* pp. 1436–1448.

Bharath, S. and Bowen-O'Connor, C. (2008): Assessing drying rates of cacao beans using small samples. *Annual Report 2007. Cocoa Research Unit, U.W.I. St. Augustine, Trinidad.* p. 52-58.

Bonvehi, J. S., and Coll, F. V. (2000): Evaluation of purine alkaloids and diketopiperazines contents in processed cocoa powder. *European Food Research and Technology*, 210(3), 189-195.

Borges, P.A.V., Lobo, J.M., Azevedo, E.B., Gaspar, C., Melo, C. and Nunes, V.L. (2006): Invasibility and species richness of island endemic arthropods: a general model Of endemic verses exotic species. *Journal of Biogeography,* 33: 169–187.

Burubai, W., Akor, A.J., Igoni, A.H. and Puyate, Y.T. (2007): Some physical properties of nutmeg, *International Agrophysics.* 21: 123-126.

Chaiseri, S. and Dimick, P. S. (1989): Lipid and hardness characterististics of cocoa butter from different geographic regions. *Journal of the American Oil Chemists Society* 66: 1771-1780.

Codex Standard. (1981): Codex Standard for Cocoa butters. Pp 1-6.

Chakrabarty, M.M. (2003): Chemistry and Technology of Oils and Fats. *Allied Publishers PVT. Limited.* pp 752.

Choudhary, M. and Glover K. (2013): Effect of Deep-Fat Frying on Physicochemical Properties of Rice Bran Oil Blends. *IOSR-Journal of Nursing and Health Science* India 1(4): 1-10

Counet, C., Ouwerx, C., Rosoux D. and Collin, S. (2004): Relationship between procyanidin and flavor contents of cocoa liquors from different origins. *Journal of Agricultural and Food Chemistry.* 52: 6243–6249.

Cruz, J. F. M., Leite, P. B., Soares, S. E., and Bispo, E. S. (2013): Assessment of the fermentative process from different cocoa cultivars produced in Southern Bahia, Brazil. *African Journal of Biotechnology*. 12(33). 5218-5225.

Dand, R. (2010): The International Cocoa Trade. *Elsevier Science Publishers,* 8:27-36

Davies, R. and EI-Okene, A.M.I. (2009): Moisture dependent physical properties of soybean. *International Agrophysics. 23(3):*299-303.

Davies, R, and Mohammed, U.S. (2013): Engineering Properties of Bitter Kola Nuts and Shell as Potentials for Development Processing Machines. *International Journal of Scientific Research in Environmental Sciences (IJSRES).* 1 (11), pp. 337-343,

Efraim, P., Alves, A.B., and Jardim, D.C.P. (2011): Polifenóis em cacau e derivados: teores, fatores de variação e efeitos na saúde. *Brazilian Journal of Food Technology*, 14(3):181-201.

Elwers, S., Zambrano, A., Rohsius, C. and Lieberei, R. (2009): Differences between the content of phenolic compounds in Criollo, Forastero and Trinitario cocoa seed (*Theobroma cacao*). *European Food Research and Technology*. 229(6), 937-948.

Firestone, D. (1994): Determination of the iodine value of oils and fat. *Association of Official Analytical Chemists International.* 3: 674-676

Fagunwa, O., Koya, A. and Faborode, M.O. (2009): "Development of an Intermittent Solar Dryer for Cocoa Beans". Agricultural Engineering International: *the CIGR Ejournal. Manuscript number* 1292. (6)

Guehi, **T.S. (2007):** Identification and Lipase-producing Abilities of Moulds Isolated From Ivorian Raw Cocoa Beans. In: "ECC eds", Directive 73/241/EEC by European Parliament and the European Council relating to cocoa and chocolate products intended for human consumption. *Official Journal of the European Communities L 228 of 16/08/1973, pp. 0023-003*5.

Guehi, T.S., Emile, M.D., Gérard, C., Guy, R.R, and Anne, C.V. (2008): Impact of cocoa processing technologies in free fatty acids formation in stored raw cocoa beans. *African Journal of Agricultural Research 3 (3),* pp. 174-179.

Halliwell, B. (1994): Free radicals, antioxidants and human disease: curiosity, cause of consequence? *Lancet 10:* 721-724

Hamid, A. and Lopez, A.S. (2000): Quality and weight changes in cocoa beans stored under two warehouses' conditions in East Malaysia. *The planter, Kuala Lumpur,* 76, 619–637.

Hii, C.L., Rahman, R.A., Jinap, S. and Che-Man, Y.B. (2006); Quality of cocoa beans dried using a direct solar dryer at different loadings. *Journal of the Science of Food and Agriculture,* 86: 1237–1243.

Hii, S.W., Tam, J.S., Thompson, B.R. and Naughton, M.T. (2008): Bullous lung disease due to marijuana. *Respirology,* 13: 122-127.

Hii, C.L., Law, C.L., Cloke, M. and Suzannah, S. (2009): Thin layer drying kinetics of cocoa and dried product quality. *Biosystems Engineering,* 102: 153–161.

Howell, A.B., Reed, J.D., Krueger, C.G., Winterbottom, R., Cunningham, D.G., Leahy M., (2005): A-type cranberry proanthocyanidins and uropathogenic bacterial anti-adhesion activity. *Phytochemistry.* 66(18):2281-91.

IOCCC, (1996): Determination of free fatty acids content of cocoa fat as a measure of cocoa nib acidity. In: "Mohos, F. eds", Analytical Method International Office of Cocoa, Chocolate and Sugar Confection. pp 42-199

Jay, J. M., Loessner, M. J., & Golden, D. A. (2005). Radiation protection of foods, and nature of microbial radiation resistance. *Modern Food Microbiology*, 371-394.

Jia, Z.S., Tang, M.C. and Wu, J. (1999): The determination of flavonoid contents in mulberry and their scavenging effects on superoxide radicals. *Food Chemistry*, 64: 555–559.

Jonfia-Essien, W. A. (2004): Cocoa West Africa (Ghana). In: "Hodges, R. and Farrell, G. (Eds)", Crop Post Harvest: Science and Technology. *Blackwell Publishing, Oxford, UK.* 2: 216-245.

Krysiak, W. (2011): Effects of convective and microwave roasting on the physicochemical properties of cocoa beans and cocoa butter extracted from this material. *Grasasy Aceites* 62(4): 467-478. *Liendo.*

Kyi, T.M., Daud, W.R.W., Mohammad, A.B., Samsudin, W.M., Kadhum, A.A.H. and Talib, M.Z.M. (2005): The kinetics of polyphenol degradation during the drying of Malaysian cocoa beans. *International Journal of Food Science and Technology,* 40: 323–331.

Lasisi, D. (2014): A Comparative Study of Effects of Drying Methods on Quality of Cocoa Beans. *International Journal of Engineering Research & Technology (IJERT)*, 3 (1): 991-996.

Leite, P. B., Cruz, J. F. M., Soares, S. E. and Bispo, E. S. (2013): Assessment of the fermentative process from different cocoa cultivars produced in Southern Bahia, Brazil. *African Journal of Biotechnology*, 12(33): 5218-5225.

Lee, K.W., Kim, Y.J., Lee, H.J. and Lee, C.Y. (2003): Cocoa has more phenolic phytochemicals and a higher antioxidant capacity than teas and red wine. *Journal of Agricultural and Food Chemistry,* 51: 7292–7295.

Leo, M.L. and Fidel, T. (2011): Handbook of Analysis of Edible Animal by Products. *CRC Press. Technology and Engineering.*

Liendo, R., Padilla, C.F. and Quintana, A. (1997): Characterization of cocoa butter extracted from Criollo cultivars of Theobroma cacao L. *Food Research International* 30(9): 727- 731.

Lipp, M. and Anklam, E. (1997): Review of cocoa butter and alternative fats for use in chocolate, *Commission of the European Union, DG Joint Research Centre, Environment Institute, Food and Drug Analysis/Consumer Protection Unit,I*-21020 *Ispra, Italy.*

Lopez, A. S. (1986): Chemical changes occurring during the processing of cacao. In Proceedings of the Symposium Cacao Biotechnology, *Pennsylvania (pp. 19-54). Pennsylvania: University Park, The Pennsylvania State University.*

Lopez, A.S. and Dimick, P.S. (1995): Cocoa fermentation. In: Enzymes, Biomass, Food and Feed. *2nd edition (Edited by G. Reed and T.W. Nagodawithana).* Pp. 561–577. *Weinheim: VCH.*

Martin, M., Granado-Serrano, A., Ramos, S., Izquierdo-Pulido, M., Bravo, L. and Goya, L. (2009): Cocoa flavonoids up-regulate antioxidant enzyme activity via the ERK1/2 pathway to protect against oxidative stress-induced apoptosis in HepG2 cells. *Journal Nutrients Biochemistry.* 5(8): 2955–2968.

McDonald, C.R., Lass, R.A. and Lopez, A.S. (1981): Cocoa drying – a review. Growers' *Bulletin,* 31: 5-41.

Mert, S., Dandik, L. and Aksoy, H.A. (1995): Production of glycerides from glycerol and fatty acids by native lipase of Nigella sativa seed. *Applied Biochemistry and Biotechnology.* 3: 333-342**.**

Meyer, B., Biehl, B., Said, M.B. and Samarakoddy, R.J. (1989): Post-harvest pod storage: a method of pulp preconditioning to impair strong nib acidification during cocoa fermentation in Malaysia. *Journal of the Science of Food and Agriculture.* 48: 285–304.

Minifie, B. W. (1989): Chocolate, Cocoa and Confectionery: Science and Technology. *Springer Science and Business Media.* pp 904.

Mounjouenpou, P., Gueule, D., Fontana-Tachon, A., Guyot, B., Tondje, P.R. and Guiraud, J.P. (2008): Filamentous fungi producing Ochratoxin A during cocoa processing in Cameroon. *International Journal of Food Microbiology,* 121: 234–241.

Muhammad, N., Bamishaiye E., Bamishaiye, O., Usman, L., Salawu, M., Nafiu, M., and Oloyede, O., (2011): Physicochemical properties and fatty acid composition of cyperus esculentus (Tiger Nut) Tuber Oil". *Bioresearch Bulletin, 5*: 51-54.

Nazaruddin, R., Seng, L.K., Hassan, O. and Said, M. (2006a): Effect of pulp preconditioning on the content of polyphenols in cocoa beans **(***Theobroma cacao***)** during fermentation. *Industrial Crops and Products,* 24: 87–94.

Ndukwu, M.C. (2009): Effect of drying temperature and drying air velocity on the drying rate and drying constant of cocoa beans. *Agricultural Engineering International**:** CIGR Ejournal**.** Manuscript,* 11: 1091.

Noor-Soffalina, S.S., Jinap, S., Nazamid, S. and Nazimah, A.H. (2009): Quantitative Model Studies on the Formation of Aroma-Active Aldehydes and Acids by Strecker-Type Reactions. *International Journal of Food Science & Technology.* 44 (1), 168-180

Nsiah, E. K., Adu-Ampomah, Y. and Lockwood, G. (2009): Selecting high yielding clones in the presence of Phytophthora megakarya: *Improving the Sustainability of Cocoa Production in Ghana,*

Ogunjimi, L.A.O., Aviara, N.A. and Aregbesola, O.A. (2002): Some physical engineering properties of locust bean seed. *Journal of Food Engineering,* 55: 95- 99.

Oke, D.O. and Omotayo, K.F. (2012): Effect of forced-air artificial intermittent drying on cocoa beans in South-Western Nigeria. *Journal of Cereals and Oil seeds,* 3(1): 1 –5.

Opeke, L.K. (2012): Effect of forced-air artificial intermittent drying on cocoa beans in South-Western Nigeria. In: "Duncan**,** R. J., Godfrey, E.G., Yap, T.N., Pettipher, G.L. and Tharu-marajah, T., eds", Improvement of Malaysian cocoa bean flavour by modification of harvesting, fermentation and drying method. *Journal of Cereals and Oil seeds,* 3:1-5

Opoku-Ameyaw, F. Baah, V., Anchirinah, H.K., Dzahini-Obiatey, R.A., Cudjoe, S. and Acquaye, Y.S. (2010): Cocoa Manual-A Source Book for Sustainable Cocoa Production, *Cocoa Research Institute of Ghana, Tafo.*

Osborn, H.T. and Akoh, C.C. (2002):"Enzymatically Modified Beef Tallow as a Substitute for Cocoa Butter," *Journal of Food Science*, 67(7): 2480-2485.

Ory, R.L., Saint-Ange, A.J. and Altschu, A.M. (1962): The acid lipase of castor, properties and substrate specificity. *Journal of Agricultural Research* 3: 99-105.

Otunola, A.G., Adebayo, G.B. and Olufemi, O.G. (2009): Evaluation of some physicochemical parameters of selected brands of vegetable oils sold in Ilorin metropolis. International Journal of Physical Sciences, 4, 327-329.

Pontillon, J. (1998): Le beurre de cacao et les matières grasses en chocolaterie. In: "Pontillon, J. (ed)", Cacao, chocolat, production, utilisation, caractéristiques. *Techniques et documentation, Lavoisier, Paris.* 257-269.

Quarmine, W., Haagsma, R., Sakyi-Dawson, O., Asante, F., Huis, V.A. and Obeng-Ofori, D. (2012): Incentives for cocoa bean production in Ghana: Does quality matter? *Journal of Life Sciences. NJAS – Wageningen.* 63:7–14

Raghavendra, M.P. and Prakash, V. (2002): Phenylboronic acid- a potent inhibitor of lipase from *Oryzae sativa*. *J. Agricultural. Food Chemistry.* 50: 6037-6041.

Razari, M.A., Emadzadeh, B., Rafe, A. and Mohammed, A.A. (2007): The physical properties of pistachio nut and its kernel as a function of moisture content and variety, part 1 Geometric properties. *Journal of Food Engineering, 81: 209-217.*

Ramiro-Puig, E., Perez-Cano F.J. and Ramirez-Santana, C. (2007): Spleen lymphocyte function modulated by a cocoa enriched diet. *Clinical Experimental Immunology* 149: 535– 542.

Ramiro-Puig, E., Urpi-Sarda, M. and Perez-Cano, F.J. (2007): Cocoa-enriched diet enhances antioxidant enzyme activity and modulates lymphocyte composition in thymus from young rats. *Journal Agricultural Food Chemistry* 55, 6431–6438.

Ramos, S. (2008): Cancer chemoprevention and chemotherapy: dietary phenols and Signaling pathways. *Molecular Nutrition and Food Research.* 52, 507-526.

Redovnikovic, I.R., Delonga, K., Mazor, S., Dragovic-uzelac, V., Caric, M. and Vorkapic-furac, J. (2009): Polyphenolic content and composition and antioxidative activity of different cocoa liquors. *Czech Journal of Food Science,* 27: 330–337.

Saldana, M.D.A., Mohamed, R. S. and Mazzafera, P. (2002): Extraction of cocoa butter from Brazilian cocoa beans using supercritical CO_2 and ethane. *Journal of Fluid Phase Equilibria.* 194-197: 885-894

Selamat, J., Hamid M.A, Mohamed, S. and Man, C.Y. (1996): Physical and chemical characteristics of Malaysian cocoa butter. In "Selamat J, Lian BC, Lai TK, Ishak W.R.W.and Mansor, M. (eds)", *Proceeding of the Malaysian international cocoa conference Kuala Lumpur.* 351-357.

Sessiz, R.E., Esgile, O. and Kizls, A. (2005): Moisture dependent physical properties of caper (capparis) fruit. *Journal of Food Engineering,* 79: 1426-1431.

Shepherd, H. and Bhardwaj, R.K. (1986): Moisture dependent Physical properties of pigeon pea. *Journal of Agricultural Engineering Research*, 35: 227-234.

Stabling, J., Gajapathy, V. and Lowdell, C. (2013): Chocolate: delicious beauty or harmful beast? *The Lancet Oncology*. 14, 457-458.

Sukha, D.A. (2003): Potential value added products from Trinidad and Tobago cocoa, in: Revitalisation of the Trinidad and Tobago cocoa industry-Targets, Problems and Options, *the Association of Professional Agricultural Scientists of Trinidad and Tobago,Trinidad and Tobago.* 5: 69-73.

Tabatabaefa, A. (2003): Moisture-dependent physical properties of wheat. *International Agrophysics,* 12: 207- 211.

Tafuri, A., Ferracane, R. and Ritieni, A. O. (2004): Ochratoxin A in Italian marketed cocoa products. *Food Chemistry elseivier* 88: 487–494.

Tamzid, H.M., Alam M.T. and Islam, M.A.U. (2007): Physico-chemical and nutritional studies of Terminalia belerica roxb. Seed oil and seed kernel. *Journal of Biosciences, 15*, 117-126 .

Thomas, A. (2002): fat and oils Ullmann's Encyclopedia of Industrial Chemistry. *Weinhem: Wiley-VCA:*10.1002/14356007.a10-173.

Wahyudi, T. (2008): The world scenario of cocoa production and consumption. *Second International Plantation Industry Conference and Exhibition (IPiCEX), UiTM Shah Alam, Selangor, Malaysia.*

Vitaglione, P., Morisco, F. and Caporaso, V. (2004): Dietary antioxidant compounds and liver health. *Critical Reviews in Food Science and Nutrition.* 44:575-586.

Varnamkhasti, M. G., Mobli, H., Jafari, A., Rafiee, S., Soltanabadi, M. H. and Kheiralipour, K. (2007): some engineering properties of paddy (var. sazandegi). *International Journal of Agriculture and Biology*.

Wanasundara, P.D., Wanasundara, U.N. and Shahidi, F. (2001): Lipolytic activity of enzymes from germinating seeds of sesame (*Sesamum incidcum*). *Journal of Food Lipids.* 8: 75-84.

Whitefield, R. (2005): Making chocolates in the factory. *Kenedy's Publications Limited, London*.

Warra, A.A., Wawata, I.G., Gunu S.Y. and Aujara, K.M. (2011): Extraction and Physicochemical Analysis of some selected Northern Nigerian Industrial oils, *pp 53 Nigerian Journal of Nutritional Sciences.*

Wood, G.A.R. and Lass, R.A. (1985): Cocoa, 4th edition. *Longman Group, London.*

Wood, G.A.R. and Lass, R.A. (1986): Cocoa. Tropical Agricultural Series. Longman's Scientific and Technical. *Co-published with John Wiley and Sons, Inc. New York, pp. 445 – 503, 544.*

Yamagishi, M., Natsume, M., Nagaki, A., Adachi, T., Osakabe, N., Takizawa, T., Kumon, H. and Osawa, T. (2000): Antimutagenic activity of cacao: inhibitory effect of cacao liquor polyphenols on the mutagenic action of heterocyclic amines. *Journal of Agricultural and Food Chemistry*, 48, 5074–5078.

Yamagishi, M., Natsume, M., Osakabe, N., Nakamura, H., Furukawa, F. and Imazawa, T. (2002): Effects of cacao liquor proanthocyanidins on PhIP-induced mutagenesis *in vitro,* and *in vivo* mammary and pancreatic tumorigenesis in female Sprague- Dawley rat. *National Institutes of Health* 185: 123-130.

Yamagishi, M., Natsume, M., Osakabe, N., Okazaki, K., Furukawa, F. and Imazawa, T. (2003): Chemoprevention of lung carcinogenesis by cacao liquor proanthocyanidins in a male rat multi-organ carcinogenesis model. *Medical Lancet.* 191: 49-57.

Zarringhalami, S., Sahari, M. A., Barzegar, M**.,** Hamidi-Esfehani, Z. (2012): Production of Cocoa Butter Replacer by Dry Fractionation, Partial Hydrogenation, Chemical and Enzymatic Interesterification of Tea Seed Oil. *Journal of Food and Nutrition Sciences*, 3, 184-189

APPENDIX A
TABLE OF RESULTS

Table 3 Butter Characterization Results from Super Main Crop Bean Categories.

	PARAMETERS												
											SHUKOFF CURVE		
	FFA	Moisture	Turbidity	Saponification value	Unsap matter	Refractive Index	Slip point	Iodine value	Peroxide value	Colour	Q-factor	∂T-30	Temp.
1	1.07	0.10	1.88	190	0.17	1.456	34.1	33.04	1.52	20Y+ 1.1R	0.143	0:45:40	4.5
2	0.70	0.11	1.09	190	0.17	1.457	34.1	32.53	0.20	30Y+ 3.0R	0.148	0:39:05	4.55
3	0.80	0.12	1.43	190	0.17	1.456	34.1	33.06	0.20	30Y+ 1.1R	0.163	0:44:15	4.99
4	0.71	0.13	1.20	190	0.17	1.456	34.1	31.54	0.20	30Y+ 1.2R	0.157	0:42:10	4.85
5	0.74	0.12	0.93	190	0.17	1.456	34.1	31.54	0.25	30Y+ 1.3R	0.161	0:40:45	4.86
6	0.82	0.09	2.89	190	0.17	1.456	34.1	31.54	0.25	30Y+ 3.1R	0.162	0:42:50	4.92
7	0.85	0.13	1.57	190	0.17	1.456	34.1	31.54	0.25	30Y+ 2.3R	0.153	0:42:40	4.70
8	0.96	0.10	0.93	190	0.21	1.456	34.1	31.54	0.30	31Y+ 2.3R	0.157	0:45:25	4.78
9	0.98	0.11	1.20	189	0.21	1.455	33.46	31.54	0.30	30Y+ 2.0R	0.169	0:41:40	4.77
10	0.97	0.23	1.13	189	0.21	1.456	33.46	31.54	0.26	30Y+ 2.0R	0.162	0:47:05	4.36
11	0.92	0.11	1.88	189	0.15	1.456	33.46	31.54	0.26	30Y+ 2.0R	0.164	0:44:25	4.84
12	0.92	0.10	1.19	189	0.15	1.456	33.46	32.06	0.26	30Y+ 2.2R	0.165	0:45:15	4.86
13	0.90	0.12	1.21	189	0.15	1.456	33.46	33.06	0.26	30Y+ 2.2R	0.158	0:46:30	4.82
14	0.91	0.09	0.89	189	0.15	1.456	33.46	33.06	0.30	30Y+ 2.0R	0.158	0:46:25	4.78
15	0.78	0.13	1.18	189	0.18	1.456	33.46	33.06	0.30	30Y+ 2.0R	0.163	0:43:35	4.88
16	0.89	0.13	1.24	189	0.17	1.456	33.60	32.59	0.30	30Y+ 2.0R	0.150	0:45:45	4.62
17	0.89	0.10	1.01	189	0.17	1.457	35.00	31.01	0.30	30Y+ 2.1R	0.156	0:43:40	4.83
18	0.84	0.16	1.04	189	0.17	1.456	34.90	31.01	0.30	30Y+ 2.2R	0.141	0:42:55	4.58
19	0.75	0.10	1.40	189	0.17	1.456	34.20	31.01	0.30	30Y+ 2.0R	0.162	0:43:50	4.76
20	0.90	0.08	1.51	189	0.17	1.457	33.60	31.01	0.30	30Y+ 3.0R	0.155	0:43:30	4.69
21	0.94	0.14	1.27	189	0.17	1.457	32.89	31.01	0.27	30Y+ 2.3R	0.155	0:43:30	4.69
22	0.93	0.16	1.01	189	0.17	1.456	33.48	31.01	0.27	30Y+ 2.1R	0.155	0:47:30	4.23
23	0.89	0.16	0.90	189	0.17	1.457	33.90	31.01	0.27	31Y+ 2.2R	0.155	0:42:50	4.62

24	0.94	0.09	0.93	189	0.17	1.457	34.30	31.24	0.27	30Y+ 2.1R	0.151	0:44:20	4.62
25	1.05	0.13	1.14	190	0.17	1.456	34.29	31.24	0.27	30Y+ 3.0R	0.158	0:44:50	4.75
26	0.85	0.13	2.68	190	0.17	1.456	33.89	31.24	0.27	30Y+ 4.0R	0.151	0:47:55	4.73
27	0.95	0.10	0.97	190	0.17	1.456	33.80	31.24	1.59	30Y+ 2.0R	0.161	0:46:35	4.9
28	0.92	0.12	2.76	190	0.21	1.456	33.40	31.24	0.24	30Y+ 2.0R	0.161	0:43:40	4.79
29	0.96	0.14	1.21	190	0.21	1.457	33.40	31.24	0.28	30Y+ 2.0R	0.167	0:46:40	4.92
30	1.02	0.09	0.91	190	0.15	1.456	33.80	31.24	0.24	30Y+ 2.0R	0.154	0:45:30	4.80
31	0.88	0.15	1.87	190	0.15	1.457	33.50	31.24	0.20	30Y+ 2.1R	0.157	0:46:10	4.76
Average	0.89	0.12	1.37	189.48	0.17	1.46	33.84	31.67	0.35	30Y + 2.2R	0.16	0.03	4.73

Table

4 Butter Characterization results obtained from Main Crop Bean Categories.

Sample	PARAMETERS												
	FFA	Moisture	Turbidity	Saponification value	Unsap Value	Refractive Index	Slip point	Iodine value	Peroxide value	Colour	SHUKOFF CURVE		
											Q-factor	∂T-30	TEMP.
1	1.07	0.10	1.88	190	0.17	1.456	33.40	32.41	0.2	20Y+ 1.1R	0.143	0:45:40	4.5
2	0.80	0.11	2.95	190	0.17	1.456	33.40	32.41	0.2	30Y+ 1.3R	0.134	0:42:25	4.33
3	0.70	0.11	1.09	190	0.17	1.457	33.30	32.41	0.2	30Y+ 3.0R	0.148	0:39:05	4.55
4	0.78	0.17	3.01	190	0.20	1.456	33.00	32.41	0.2	30Y+ 2.2R	0.138	0:46:10	4.43
5	0.83	0.11	0.95	190	0.20	1.456	34.20	32.1	0.3	30Y+ 2.2R	0.147	0:43:40	4.60
6	0.92	0.11	1.88	189	0.20	1.456	33.80	33.46	0.3	30Y+ 2.0R	0.164	0:44:25	4.84
7	0.80	0.12	1.12	189	0.20	1.457	33.20	32.46	1.99	30Y+ 2.0R	0.148	0:45:40	4.71
8	0.81	0.12	0.91	189	0.20	1.457	33.20	32.46	1.99	30Y+ 2.1R	0.142	0:44:50	4.53
9	0.11	0.90	1.25	196	0.21	1.457	34.20	31.06	1.79	30Y+ 2.2R	0.123	0:46:30	4.09
10	1.03	0.10	3.97	190	0.21	1.457	34.10	31.11	1.59	30Y+ 2.3R	0.14	0:46:55	4.54
11	0.97	0.13	0.89	190	0.21	1.456	34.80	31.11	1.59	30Y+ 2.1R	0.134	0:46:25	4.36
12	1.03	0.15	0.89	190	0.19	1.456	34.60	31.11	1.59	30Y+ 2.3R	0.127	0:46:35	4.23
13	1.09	0.10	0.99	190	0.19	1.457	33.50	31.11	1.59	30Y+ 2.2R	0.145	0:46:05	4.55
14	1.14	0.11	0.94	190	0.19	1.457	33.90	31.11	1.59	30Y+ 2.2R	0.126	0:49:20	4.23
15	1.06	0.11	1.09	190	0.19	1.456	33.82	31.11	1.59	30Y+ 2.0R	0.137	0:46:45	4.46
16	0.95	0.15	1.73	190	0.19	1.457	34.38	31.11	1.59	30Y+ 3.0R	0.143	0:46:45	4.54
17	1.06	0.13	1.06	195	0.19	1.457	33.40	33.46	1.69	30Y+ 2.0R	0.145	0:45:35	4.58
18	1.10	0.15	1.87	195	0.19	1.457	33.50	33.46	1.69	30Y+ 2.1R	0.157	0:46:10	4.76
average	0.90	0.17	1.58	190.72	0.19	1.46	33.76	31.99	1.20	30Y + 2.1R	0.141	0.03	4.49

Table

5 Butter Characterization results obtained from Super Light Crop Bean Categories.

Sample	PARAMETERS												
	FFA	Moisture	Turbidity	Saponification value	Unsap Value	Refractive Index	Slip point	Iodine value	Peroxide value	Colour	SHUKOFF CURVE		
											Q-factor	∂T-30	TEMP.
1	1.25	0.17	1.62	192	0.21	1.456	33.50	32.2	1.39	30Y+ 3.2R	0.11	0:49:50	3.75
2	1.21	0.12	2.37	195	0.21	1.456	34.20	32.2	1.39	30Y+ 2.0R	0.12	0:46:45	3.84
3	1.24	0.17	1.31	195	0.25	1.456	34.50	32.2	1.39	30Y+ 3.0R	0.12	0:48:50	3.92
4	1.15	0.11	1.47	195	0.25	1.456	33.90	32.2	1.39	30Y+ 2.9R	0.12	0:49:45	3.88
5	1.01	0.18	1.63	195	0.25	1.456	33.40	32.2	1.39	30Y+ 3.0R	0.120	0:47:40	4.07
6	1.05	0.12	1.57	195	0.25	1.457	33.00	32.2	1.39	30Y+ 3.0R	0.12	0:47:45	4.10
7	0.98	0.16	2.18	195	0.25	1.456	33.80	33.1	1.39	30Y+ 2.0R	0.11	0:46:30	3.94
8	0.98	0.17	1.17	195	0.24	1.456	33.60	33.1	1.39	30Y+ 1.4R	0.13	0:45:15	4.14
9	1.09	0.14	2.45	188	0.24	1.456	32.90	33.1	1.58	30Y+ 3.2R	0.13	0:45:20	4.17
10	1.04	0.11	1.70	188	0.24	1.456	33.00	31.4	1.58	30Y+ 4.0R	0.13	0:45:35	4.19
11	0.98	0.10	1.01	188	0.26	1.456	32.79	31.4	1.58	30Y+ 4.3R	0.13	0:46:15	4.19
12	0.97	0.16	1.41	188	0.26	1.455	33.20	31.1	1.58	30Y+ 1.4R	0.13	0:45:20	4.25
13	0.90	0.13	0.89	188	0.26	1.456	33.90	31.1	1.58	30Y+ 1.5R	0.130	0:44:25	4.27
14	0.95	0.09	4.47	188	0.3	1.456	34.10	31.9	1.58	30Y+ 1.5R	0.110	0:46:45	3.90
15	0.88	0.14	2.18	188	0.27	1.456	34.10	31.9	1.58	30Y+ 4.0R	0.12	0:44:35	3.95
16	1.19	0.15	1.42	188	0.26	1.456	34.60	33.5	1.58	30Y+ 4.0R	0.110	0:47:40	3.93
Average	1.05	0.14	1.80	191.31	0.25	1.46	33.66	32.17	1.49	30 Y + 2.8R	0.12	0.03	4.03

Table

6 Butter Characterization results obtained from Light Crop Bean Categories.

Sample	PARAMETERS												
	FFA	Moisture	Turbidity	Saponification value	Unsap Value	Refractive Index	Slip point	Iodine value	Peroxide value	Colour	SHUKOFF CURVE		
											Q-factor	∂T-30	TEMP.
1	1.24	0.18	1.68	191.71	0.34	1.457	33.60	30.93	1.56	30Y+2.5 R	0.119	0:44:20	4.11
2	1.17	0.19	1.96	191.71	0.34	1.457	33.70	30.93	1.56	30Y+2.4 R	0.117	0:43:20	4.07
3	1.12	0.16	2.58	191.71	0.34	1.456	33.90	30.93	1.56	30Y+2.3 R	0.119	0:42:25	4.08
4	1.22	0.12	1.48	191.71	0.34	1.457	33.90	30.93	1.56	30Y+2.2 R	0.111	0:42:55	3.94
5	1.10	0.19	1.43	191.71	0.34	1.457	33.90	30.93	1.56	30Y+ 3.0R	0.119	0:43:20	4.09
6	1.34	0.16	1.47	188.87	0.32	1.456	34.00	34.24	2.26	30Y+ 3.0R	0.118	0:43:40	4.07
7	1.00	0.19	1.55	188.87	0.32	1.457	33.80	34.24	2.26	30Y+ 3.0R	0.116	0:45:30	4.03
8	0.96	0.13	1.41	188.87	0.32	1.457	34.00	34.24	1.27	30Y+ 3.0R	0.111	0:43:10	4.03
9	0.94	0.19	1.18	188.87	0.32	1.457	33.90	34.24	1.27	30Y+ 3.0R	0.115	0:40:50	3.99
10	1.03	0.17	1.45	188.87	0.32	1.456	33.90	34.24	1.27	30Y+2.5 R	0.115	0:41:45	4.00
11	1.59	0.15	1.20	188.87		1.457	34.00	34.24	1.27	30Y+2.4 R	0.114	0:42:50	4.01
12	1.05	0.14	1.28	188.87		1.456	34.00	34.24	1.27	30Y+2.3 R	0.114	0:44:25	4.12
13	0.91	0.25	5.07	195.00		1.457	33.00	30.14	1.27	30Y+2.4 R	0.115	0:46:50	4.11
14	1.02	0.23	5.75	195.00		1.457	34.00	30.14	1.27	30Y+2.2 R	0.112	0:45:25	4.03
15	0.96	0.18	2.86	195.00	0.32	1.456	33.90	30.14	1.27	30Y+2.6 R	0.115	0:45:05	4.12
16	1.03	0.20	1.59	195.00	0.32	1.457	33.50	30.14	1.27	30Y+2.3 R	0.115	0:44:40	4.03
17	0.92	0.21	2.05	195.00	0.30 0.30 0.30 0.30 0.30	1.456	34.00	30.14	2.19	30Y+2.5 R	0.118	0:42:30	4.05
18	1.01	0.20	1.45	195.00	0.30	1.457	34.00	30.14	2.19	30Y+2.5 R	0.117	0:41:50	4.03
19	0.98	0.11	1.54	192.00	0.30	1.457	33.00	32.19	1.56	30Y+2.5 R	0.114	0:45:50	4.00
20	1.07	0.19	1.40	192.00	0.30	1.457	34.00	32.19	1.56	30Y+2.6 R	0..110	0:40:10	3.73
21	1.08	0.12	1.05	192.00	0.30	1.456	34.00	32.19	1.56	30Y+2.4 R	0.126	0:43:10	4.17
22	1.07	0.10	1.26	192.00	0.30	1.457	33.00	32.19	1.56	30Y+2.3 R	0.125	0:41:20	3.99

Table

23	0.94	0.20	1.09	192.00	0.30	1.457	33.80	32.19	1.56	30Y+2.4 R	0.123	0:43:10	4.19
24	1.01	0.18	1.45	192.00	0.30	1.456	34.00	32.19	1.56	30Y+2.5 R	0.110	0:42:50	3.95
25	1.00	0.19	1.76	192.00	0.30	1.457	33.90	32.19	1.56	30Y+ 3.0R	0.116	0:42:40	4.02
26	1.05	0.19	1.08	192.00	0.30	1.457	33.90	32.19	1.56	25Y+ 3.0R	0.118	0:41:20	4.05
27	0.96	0.14	1.25	194.00	0.18	1.457	33.80	33.3	1.59	31Y+ 3.0R	0.118	0:42:15	4.07
28	1.02	0.16	1.24	194.00		1.456	34.00	33.3	1.59	30Y+ 3.0R	0.123	0:42:30	4.15
29	0.99	0.19	1.18	194.00		1.457	34.10	33.3	1.59	28.5Y+ 2.8R	0.110	0:45:15	3.83
30	0.99	0.19	1.03	194.00	0.18	1.456	33.70	33.3	1.59	28.6Y+ 2.6R	0.119	0:43:20	4.15
31	0.93	0.13	1.58	194.00	0.18 0.18 0.18	1.456	33.60	33.3	1.59	30Y+ 2.6R	0.114	0:41:50	4.04
32	1.03	0.13	1.46	194.00	0.18	1.456	33.90	33.3	1.59	30Y+ 2.7R	0.112	0:42:35	3.82
33	1.21	0.19	1.63	194.00		1.456	34.30	33.3	1.59	30Y+ 2.5R	0.097	0:45:20	3.68
34	1.22	0.78	6.19	194.00	0.18	1.456	34.30	33.3	1.59	30Y+ 2.5R	0.097	0:45:20	3.68
35	1.14	0.20	2.72	193	0.18 0.24	1.456	34.80	34.46	1.74	30Y+ 3.0R	0.105	0:43:05	3.84
36	0.99	0.24	2.75	191	0.19	1.456	33.7	31.6	1.21	30Y+ 3.0R	0.114	0:43:25	3.99
37	0.97	0.28	3.64	191		1.456	33.4	31.6	1.21	30Y+ 3.0R	0.107	0:42:50	3.81
38	1.00	0.33	8.02	191	0.19	1.457	33.6	31.6	1.21	30Y+ 3.0R	0.100	0:44:50	3.86
39	0.85	0.27	2.74	191	0.19 0.19	1.456	33.3	31.6	1.21	30Y+ 3.0R	0.111	0:46:30	3.98
40	1.01	0.21	1.69	191	0.19	1.457	33.0	31.6	1.21	30Y+ 3.0R	0.115	0:46:55	4.13
41	1.27	0.21	1.57	191	0.19	1.457	33.6	31.6	1.21	30Y+ 3.0R	0.100	0:45:30	3.73
42	1.20	0.31	2.46	190	0.19	1.456	34.8	34.24	1.19	30Y+ 2.3R	0.100	0:45:15	3.79
43	0.91	0.19	1.67	190	0.19	1.456	33.4	34.24	1.19	30Y+ 3.0R	0.103	0:43:25	3.78
Average	1.06	0.20	2.11	192.04	0.26	1.46	33.81	32.36	1.50	30Y + 2.7R	0.11	0.03	3.98

Table 7 Butter Characterization results obtained from Small Bean Categories.

Sample	PARAMETERS												
	FFA	Moisture	Turbidity	Saponification value	Unsap Value	Refractive Index	Slip point	Iodine value	Peroxide value	Colour	SHUKOFF CURVE		
											Q-factor	∂T-30	TEMP.
1	1.30	0.16	1.52	196	0.31	1.457	32.4	33.04	1.39	30Y+ 2.8R	0.09	0:43:35	3.92
2	1.20	0.17	1.11	196	0.31	1.457	32.4	32.53	1.39	30Y+ 3.0R	0.121	0:45:25	4.4
3	1.33	0.14	1.89	194	0.31	1.456	32.9	33.06	1.90	30Y+ 3.0R	0.133	0:44:40	4.07
4	1.38	0.18	1.26	194	0.32	1.456	32.4	33.06	1.90	30Y+ 3.0R	0.132	0:45:25	4.04
5	1.31	0.15	1.94	194	0.33	1.456	33.2	33.06	1.90	30Y+ 3.0R	0.09	0:45:35	4.03
6	1.23	0.19	1.07	194	0.31	1.456	32.4	33.06	1.90	20Y+ 3.0R	0.100	0:44:10	4.04
7	1.22	0.16	1.06	194	0.34	1.456	33.4	33.45	1.90	20Y+ 3.0R	0.12	0:44:10	4.1
8	1.19	0.19	1.85	194	0.34	1.456	33.4	33.45	1.90	30Y+ 3.0R	0.112	0:44:15	4.11
9	1.14	0.22	5.45	194	0.21	1.456	33.0	33.45	1.90	20Y+ 3.0R	0.132	0:41:25	4.09
10	1.15	0.18	2.88	194	0.24	1.456	33.2	33.45	1.90	20Y+ 3.0R	0.117	0:43:20	3.89
11	1.18	0.22	1.26	194	0.2	1.457	33.0	33.06	1.00	30Y+ 3.0R	0.118	0:44:45	4.03
12	1.20	0.17	1.86	194	0.21	1.456	33.0	33.06	1.00	20Y+ 3.0R	0.11	0:44:25	3.97
13	1.16	0.19	1.55	194	0.27	1.456	33.6	33.06	1.00	28Y+ 2.1R	0.111	0:43:30	3.95
14	1.23	0.18	2.39	194	0.27	1.457	33.0	33.06	1.00	20Y+ 3.0R	0.123	0:43:25	3.97
15	1.21	0.12	2.06	194	0.21	1.457	33.6	33.06	1.00	30Y+ 2.3R	0.122	0:46:20	3.95
Average	1.23	0.17	1.94	194.27	0.28	1.46	32.99	33.13	1.53	25Y + 2.9R	0.12	0.03	4.04

Table 8 Different Cocoa Bean Categories and their Responses.

		Super Main Crop	Main Crop	Super Light Crop	Light Crop	Small beans	Codex standards
Response	Saponification Value	189.48	190.72	191.31	192.04	194.27	197.00
		Super Main Crop	Main Crop	Super Light Crop	Light Crop	Small beans	Codex standards
Response	Unsaponification Value	0.17	0.19	0.25	0.26	0.28	0.35
		Super Main Crop	Main Crop	Super Light Crop	Light Crop	Small beans	Codex standards
Response	Iodine Value	31.67	31.99	32.17	32.36	33.13	35.00
		Super Main Crop	Main Crop	Super Light Crop	Light Crop	Small beans	Codex standards
Response	Peroxide Value	0.35	1.20	1.49	1.50	1.53	3.00
		Super Main Crop	Main Crop	Super Light Crop	Light Crop	Small beans	Codex standards
Response	Tempering Q-factor	0.16	0.14	0.12	0.11	0.12	0.15
		Super Main Crop	Main Crop	Super Light Crop	Light Crop	Small beans	Codex standards
Response	Free Fatty Acids	0.89	0.90	1.05	1.06	1.23	1.75
		Super Main Crop	Main Crop	Super Light Crop	Light Crop	Small beans	Codex standards
Response	Refractive Index	1.46	1.46	1.46	1.46	1.46	1.46

Table 9 Yield-Fat content of Cocoa Liquor from different Cocoa Bean Categories.

Super Main Crop	Main crop	Super Light Crop	Light Crop	Small beans
54.97	54.44	53.22	52.81	52.11
55.10	54.75	53.44	52.93	52.01
55.02	54.85	53.24	52.80	52.22
54.88	54.75	53.62	52.87	52.47
55.62	54.84	53.01	52.48	52.34
55.23	54.49	53.41	52.43	52.01
55.68	54.99	52.88	52.82	52.28
55.01	54.70	52.97	52.64	52.06
54.97	54.46	52.68	52.84	52.31
55.21	54.85	52.65	52.68	52.13

55.66	54.71	53.21	52.29	52.18
55.48	54.03	53.11	52.81	52.03
55.54	54.97	52.84	52.58	52.18
54.87	54.49	52.76	52.30	52.11
54.91	54.92	52.97	52.95	52.16
54.93	54.44	52.68	52.90	52.32
55.47	54.91	52.97	52.70	52.27
55.34	54.52	53.13	52.52	52.30
55.28	54.72	52.72	52.55	52.15
55.61	54.89	53.00	52.87	52.11
55.21	54.91	52.84	52.60	52.34
55.31	55.03	52.93	52.39	52.51
55.24	**54.71**	**53.01**	**52.67**	**52.21**

Table 10 Mean Values and P-Values for the response for all categories with the Codex Standard.

Experimental Parameters	Statistical Parameters	Super Main Crop	Main Crop	Super Light Crop	Light Crop	Small Beans

FFA	Mean Value	0.891	0.903	1.054	1.058	1.229
	P-Value	0.000	0.000	0.000	0.000	0.000
MOISTURE	Mean Value	0.122	0.166	0.139	0.202	0.175
	P-value	1.000	0.925	1.00	1.000	1.000
IODINE	Mean Value	31.670	31.993	32.169	32.363	33.127
	P-Value	0.000	0.000	0.000	0.000	0.000
PEROXIDE	Mean Value	0.348	1.204	1.485	1.505	1.532
	P-Value	0.000	0.000	0.000	0.000	0.000
SAPONIFICATION VALUE	Mean Value	189.484	190.722	191.313	192.038	194.267
	P-Value	0.000	0.000	0.000	0.000	0.000
UNSAPONIFIABLE MATTER	Mean Value	0.171	0.193	0.250	0.2640	0.2787
	P-Value	0.000	0.000	0.000	0.000	0.000
SLIP POINT	Mean Value	33.838	33.761	33.656	33.812	32.993
	P-Value	0.000	0.000	0.000	0.000	0.000
REFRACTIVE INDEX	Mean Value	1.456	1.457	1.456	1.457	1.456
	P-Value	0.000	0.000	0.000	0.000	0.000
FAT YIELD	Mean Value	55.241	54.712	53.013	52.671	52.209
	P-Value	0.000	0.000	0.000	0.000	0.000
Q-FACTOR	Mean Value	0.16	0.14	0.12	0.11	0.11
	P-Value	0.000	0. 000	0.000	0.000	0.000

APPENDIX B
FORMULATION OF PARAMETERS STUDIED.

Appendix B 1: Saponification Value (SV)

$$S V = \frac{[(B - S) \times C] \times 56.1}{m}$$

Where: B = ml 0.5N HCl required to titrate blank, S = ml 0.5N HCl required to titrate sample, C = concentration of HCl; C= 0.5M, m = weight of sample, Mr (KOH) = 56.1/gmol

Appendix B 2: Unsaponification value (USV)

$$USV = \frac{(W_2 - W_1)}{m} \times 100$$

Where: W_1 = weight of empty and conditioned flask, W_2 = Weight of flask with unsaponifiable sample after the experiment and m = weight of sample.

Appendix B 3: Iodine Value (IV)

$$\% (IV) = \frac{12.69 \times T \times (V_2 - V_1)}{m}$$

Where V_1= ml of standardized sodium thiosulfate solution used for the blank determination V_2= ml of standardized sodium thiosulfate solution used for the colour butter samples. T= the exact Normality of the sodium thiosulfate and m= the mass in g of the cocoa butter samples.

Appendix B: 4 Peroxide Value (PV)

$$(PV) = \frac{(S - B)\, C}{m} \times 100$$

Where: B =Volume in ml of $Na_2S_2O_3$for the blank, S = Volume in ml of $Na_2S_2O_3$ used for the sample determination, C = Concentration in moles per litreof$Na_2S_2O_3$, m = mass of sample.

Appendix B: 5 Percentage Fat Content

$$Fat = \frac{(W_3 - W_2) \times 100}{W_1}$$

Where W_1= weight of sample/g, W_2= weight of empty round bottom flask/g, W_3= weight of round bottom flask with fat/g.

Appendix B: 6 Determination of Q-factor in Shukoff's tempering cooling curve

$$\text{Q-factor} = \Delta T/\Delta t$$

Where; Δt = t max-t min, ΔT = Tmax-Tmin also the ΔT provided information about the crystallization capacity. That is the high value of ΔT testifies that a large amount of Cocoa Butter was crystallized and the Δt also means the crystallization time. The Q factor (ΔT/Δt) is related to the setting rate. Averages of the ΔT, Δt and the Q factor (ΔT/Δt) were calculated and recorded.

Appendix B: 7 Determination of yield of cocoa

% Yield = 100 – [% Average Moisture + % Average Shell – 1.5 %].

The 1.5 % represent the amount of moisture retained after processing cocoa beans in to cocoa masse (cocoa solids and butter).

APPENDIX C
CHEMICAL EQUATIONS.

Appendix C 1: Chemical Equation of Iodine

$2I + H_2O + HOOH \rightarrow HOH + 2OH^- + I_2$

Iodine formation by reacting peroxides formed in fat or oil with iodine ion

Appendix C 2: Chemical Equation of Thiosulfate with Iodine

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I$

Note that the base produced in this reaction is taken up by the excess of acetic acid

Appendix C 3: Chemical Equation involve in the assessment of Iodine released

$I_2 + Na_2S_2O_3 \longrightarrow Na_2S_40_6 + 2NaI$ ……Equation 2

The determination of iodine released by titrating against a standardized solution of sodium thiosulfate ($Na_2S_20_3$) using a starch indicator (Equation 2)