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Effect of Drying Methods on the Chemical Quality Traits of Cocoa Raw Material

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Abstract: This study concerns the measurement of some chemical quality properties of raw cocoa dried by solar and heating methods. Sun drying method is considered as standard process. Drying trials were conducted in thin layer using natural sun light drying method, heating methods by exposition of the beans to hot air ventilated oven at 60ºC and in sun light consecutive artificial drying methods. Changes in volatile acidity on the drying method were not very clear. Only sun and mixed dried raw cocoa showed a high volatile acidity. Oven and mixed drying methods have caused higher free acidity and higher Ammonium Nitrogen content in raw cocoa than natural drying methods. Changes in Ammonium Nitrogen in fermented appeared significantly due to the fermentation. Also all studied drying processes did not influence the production of free fatty acids in raw cocoa. The results obtained from this study are essential in understanding and solving the problems associated with the final quality of raw cocoa material dependent on the drying methods. Better quality of raw cocoa material could be resulted from natural drying process than heating methods.

Key words: Chemical quality, cocoa, drying methods, fermentation

INTRODUCTION

Cocoa is consumed widely as chocolate. The application of cocoa can also be found in beverages, cosmetics, pharmaceuticals and toiletries products. The beans originate as seeds in fruit pods of the tree, *Theobroma cacao* L. (Ardhana and Fleet, 2003). Cocoa is cultivated in plantations in tropical regions throughout the world such as Ivory Coast, Ghana, Nigeria, Indonesia, Brazil, Venezuela and Malaysia (Beckett, 1994). World production of cocoa beans was about 3,888,000 t in 2006/07 crop year and nearly 40% of this quantity was produced in Côte d'Ivoire (World Cocoa Foundation, 2008). Fresh cocoa beans are embedded in a mass of mucilaginous pulp within the pod. The processing of cocoa beans consists of two major steps namely fermentation and drying (Hii *et al.*, 2009). Different methods of fermentation and drying are followed in the cocoa growing countries (Rohan, 1963; Wood and Lass, 1985). The beans and associated pulp are removed from the pod and subject to microbial fermentation which is generally conducted as traditional, indigenous processes and constitutes the first stage in preparation for chocolate production (Ardhana and Fleet, 2003) in certain cocoa producing countries prior drying (Lagunes-Gálvez *et al.*, 2007). Fresh cocoa beans are usually fermented using the heap or box methods for 5-7 days depending on the condition of the beans (Lagunes-Gálvez *et al.*, 2007; Hii *et al.*, 2009). The details of cocoa fermentation have been well reviewed (Roelofsen, 1958; Lehrian and Patterson, 1983; Lopez and Dimick, 1995; Schwan *et al.*, 1995; Thompson *et al.*, 2001). Fermented cocoa beans present generally moisture content between 55 and 60%. After fermentation, the beans are dried immediately to avoid over fermentation, which could lead to product deterioration. During this deterioration, a degradation of polyphenol compounds led to a high production of Nitrogen Ammonium and produced undesirable flavours. Cocoa beans within this moisture range have to be dried to reduce moisture contents ranged from 7 to 8%. In Tropical countries agricultural products like cocoa is harvested all the year round and the beans must be dried immediately to reduce mass losses and prevent mould spoilage. Drying can be carried out using natural or artificial hot air methods dependently on the quantity of cocoa beans and the climatic conditions (Ndukwu, 2009). Drying of fermented cocoa beans from 60 to 7% dry basis or less is immediately realized in order to achieve the formation of chocolate aroma and for safe storage (Cunha, 1990). Solar drying method involves spreading of the cocoa bean on the concrete floor or on a raised platform under the sun. These beans are

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stirred manually sometimes in order to provide even drying of the bean (Ndukwu, 2009). The disadvantage of this method lies in the need for intensive human labor, which in turn leads to poor operational performance. When the climatic conditions are not adequate or conducive, artificial drying method can be employed (Asiedu, 1989) consisting of mainly a motor, fan and heating element. When heat is added to the drying air, the rate of drying goes fast (Jayas and Sohkansanj, 1989). However artificial drying method reduces the dry matter and causes increase in energy cost (Arinze *et al.*, 1996) while quick drying prevents the chemical processes started during fermentation to be completed. Also the rate drying is critical to final quality of raw cocoa, according to Barel (1998), too rapid a drying rate results in excessively acid beans with case hardening. A high production of acidity in cocoa beans produces unsuitable raw cocoa for chocolate manufacture and leads to the reject of cocoa at the market. The flavour development process continues during drying and the browning process is the most important reaction occurring at this stage (Mc Donald *et al.*, 1981). This study aimed to evaluate the effect of different drying methods on some chemical quality traits of fermented raw cocoa material.

MATERIAL AND METHODS

This study was conducted from December to February 2005-09 in the experimental cocoa station of Centre National pour la Recherche Agronomique (CNRA) located at Bingerville region of South of Côte d'Ivoire, a moderate hot rainy region with an average of 28-29ºC during the harvest season, a low altitude, below 500 m, 70-80 mm/month rainfall. As major cocoa producing country in the world, Côte d'Ivoire is located in West of Africa.

Cocoa pod storage and opening: The ripe cocoa pods (*Theobroma cacao* L.) of mixed-hybrids were harvested by hand and then stored for 4 days at ambient temperature at the field before breaking using a piece of wood as a bludgeon as reported earlier (Meyer *et al.*, 1989). Pod opening using wooden billet involves one or two sharp blows with the edge of the billet. The distal portion of the pod falls away and the beans remain attached to the placenta from which they can be easily extracted. The beans were removed from placenta being careful to exclude any germinated, black or diseased beans or pieces of shell or placenta fragments.

Cocoa fermentation: One type of fermentation was studied as reported earlier by Lagunes-Gálvez *et al.* (2007) and Mounjouenpou *et al.* (2008): box fermentation, where the beans were putted in banana leaves placed in wooden boxes measuring $60 \times 60 \times 60 cm^3$. Fermentation was carried out in each experiment using 100 kg of fresh beans during 6 days without stirring. Wet cocoa beans were then covered in the box with fresh other banana leaves and other fresh banana leaves were used in order to insulate the top of box. Fermentation experimentations were conducted triplicate.

Drying processes: Fermented cocoa beans were fractioned into five same parts (about 20 kg). Beans of each fraction were dried according to a specific drying method. All drying methods processing were stopped when the moisture content of cocoa beans reached 7-8%. Natural or solar drying process consisting to expose cocoa beans from 9 am until to 6 pm during two weeks (C9) is considered as standard drying method. Characteristics of well-fermented dried beans resulted from all experiments were compared against to properties of unfermented cocoa beans for each drying method. The drying was made until obtaining 7% of moisture content.

Sun drying processes: For first experience, one batch of unfermented cocoa and one batch of fermented beans (about 20 Kg for each batch) were separately spread thinly on a meshed wooden tray with area about 30-90 cm and raised 1 m above ground level and sun-dried until they reached moisture content of about 7%. The beans were mixed every 1 h to ensure uniformity. Drying of the first batch was conducted from 9 am until 6 pm (C9). In the second experience two others batches of unfermented and fermented beans were dried from 2 pm until 6 pm daily (C14).

Artificial hot air drying process: Two batches of unfermented and fermented beans were artificially dried using an air-ventilated oven at temperature of 60ºC (EV34) as reported (Hii *et al.*, 2009). The beans were spread thinly in single layer (about 2 cm thick) on a meshed sample tray with square openings. Heat was generated by the heater integrated into the side walls of the oven and the hot air flowed through the samples. The exhaust air escaped through a ventilation hole (diameter 4 cm) at the back of the oven. The beans were mixed every 2 h to ensure uniformity. Drying was conducted for 8 h daily and the beans were left to temper at room temperature overnight. The tempering step is a common routine in cocoa drying and the purpose is to redistribute the internal moisture to the outer beans layer after each drying cycle.

Combination of sun and artificial drying process: The unfermented and fermented cocoa beans (about 25 Kg for each sample) were dried by sun drying from 9 am to 6 pm daily until moisture content of about 25% and consecutively by artificial drying process using an air-ventilated oven (C9 EV18) until moisture content of

7%. The beans of the latest fractions were firstly sun dried from 2 pm to 6 pm daily until moisture content of 25% and then dried using an air-ventilated oven (C14 EV24) until moisture content of 7%.

Analytical methods:

Moisture content: The whole beans used in each experiment were weighed prior to mixing during drying by using an analytical balance. The moisture content (%) of the beans was determined with reference to the dry weight of the beans as early reported (Guehi *et al.*, 2007). The measurement was performed in triplicates.

Chemical acidities and pH: The methods used to quantify, free, total and volatile acidity, and ammonium nitrogen contents, and to determine pH were described by Pontillon and Cros (1998). Acidities were measured in triplicates on deshelled beans to check the good fermentation and conservation of the samples.

Free fatty acids content: About 15 g of deshelled dried cocoa beans were carefully shelled manually. Cocoa nibs were frozen in liquid nitrogen before finely grinding in a kitchen-scale coffee grinding (Moulinex, France) to the smallest particle (size < 500 μm). Ten grams of cocoa powder were putted in Whatman cartridge and soaked in 350 ml of petroleum ether (Prolabo Normapur, type 40-60ºC) for one night. Cocoa butter was extracted on a Soxhlet apparatus for 8 h. After eliminating of solvent in a rotary evaporator, FFA contents were quantified in triplicates by the official method 42-1993 (IOCCC, 1996) as reported earlier (Guehi *et al.*, 2008).

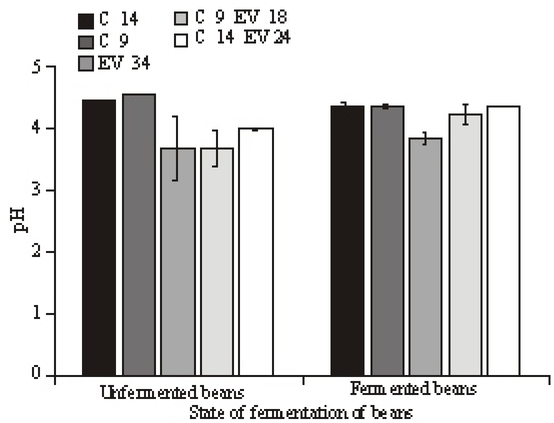

Fig. 1: Effect of drying processes on pH of coccoa beans

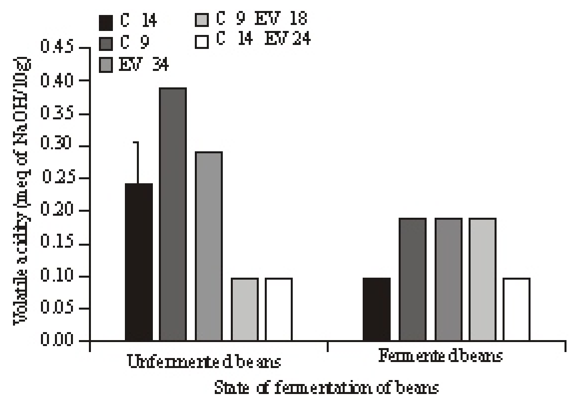

Fig. 2: Effect of drying processes on volatile acidity content of cocoa beans

RESULTS AND DISCUSSION

Effect of drying processes on pH of cocoa beans: Measurements of pH of cocoa beans dried by each drying method are presented in Fig. 1. The results show that whatever the drying process used, pH values of fermented cocoa beans are comprised roughly between 3.8 and 4.5. While natural drying processes (C9 and C14) and mixed drying methods (C9 EV18 and C14 EV24) produce less acidic cocoa beans with pH up to 4, artificial method (EV34) gives high acidic cocoa beans with pH is around 3.7

Effect of drying processes on volatile acidity content of cocoa beans: Changes in volatile acidity of cocoa beans are shown in Fig. 2. Volatile acidity content of fermented cocoa beans was largely dependent on drying methods. All drying methods used reduced significantly the volatile acidity content to values ranged from 0.10 to 0.30 meq of NaOH.10^{-1}g while standard drying method increases it to 0.40 meq of NaOH.10^{-1}g. Artificial drying method (EV 34) and mixed drying method (C9 EV18) have the same effect on volatile acidity of cocoa beans than standard drying method increasing it 0.20 meq of NaOH.10^{-1}g while sun drying process (C14) and a combination of sun and artificial drying process (C14 EV24) reduce it sensitively in the same proportion from 0.20 to 0.10 meq of NaOH.10^{-1}g.

Efect of drying processes on free acidity content of cocoa beans: Free acidity contents resulted from each drying method are presented in Fig. 3. While the combination of sun and artificial drying process increased the free acidity content to 3.4 meq of NaOH.10^{-1} g, only solar drying (C14) and artificial drying (EV34) process had no effect on the free acidity content in comparison to the standard drying process.

Effect of drying processes on Ammonium Nitrogen content of cocoa beans: Figure 4 illustrates the influence of drying methods on Ammonium Nitrogen content of cocoa beans. Results show that all studied drying processes strongly increased the Ammonium Nitrogen content to about 600 ppm over.

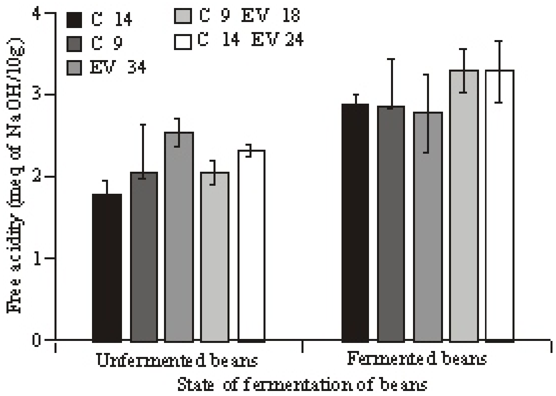

Fig. 3: Effect of drying processes on free acidity content of cocoa beans

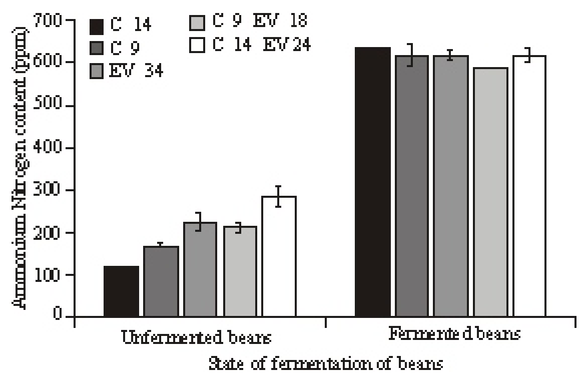

Fig. 4: Effect of drying processes on Ammonium Nitrogen content of cocoa beans

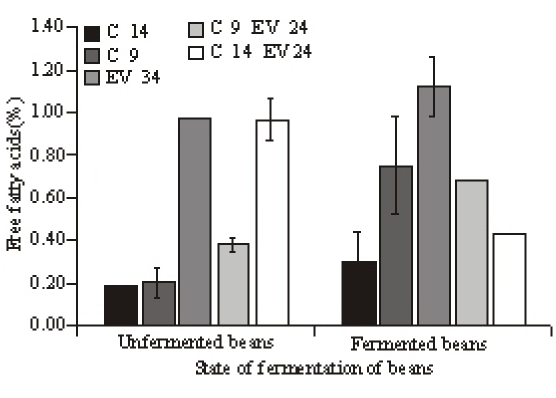

Fig. 5: Effect of drying processes on free fatty acids content of cocoa beans

Effect of drying processes on free fatty acids content of cocoa beans: The effect of drying methods on free fatty acids content of raw cocoa beans is illustrated by Fig. 5. Free fatty acids content of cocoa beans was generally low and bellow the critical value of 1.75% whatever the drying process used but it varied on the drying method used. While artificial drying method considerably increased free fatty acids content of cocoa beans compared to the other drying methods, final free fatty acids content remained below critical value of 1.75%.

DISCUSSION

The analysis of the drying curves illustrates that the removal of moisture from cocoa beans (results not shown) was slower in the natural method, and faster in the artificial and mixed drying methods (results not shown). The differences may be explained by several factors such as exposure time and temperature of dryng air, nature of drying airflow and the speed with which moisture migrated from the inner cocoa beans structures to their surface. These observations are in accordance with the studies obtained by Franke *et al.* (2008). The natural drying process was slower due to the limitations the method imposes, with little time needed for the cocoa beans to have their moisture reduced from about 60% to about 8%. Most studies have shown that removal of moisture from beans induce the increase of their acidities. In term of pH, the sun dried beans showed pH 4.6 while the pH of oven and mixed methods fermented dried beans ranged from 3.7 to 4.5. Generally, the fermented beans have registered higher pH values (4.7) than unfermented beans whatever the drying method. These results were similar with those obtained by Jinap *et al.* (1994). The pH of the sun-dried beans is different from the pH of the best-flavoured beans sourced generally from West Africa, which is around 5.5 (Franke *et al.*, 2008). However, our raw cocoa samples recorded a pH value, which was not different than the pH of greater raw cocoa according to the standard Malaysian, which fixed the pH between 4 and 4-4.7 (Nazaruddin *et al.*, 2006). After all, whatever the drying method, the pH of cocoa beans falls within the values reported for most dried cocoa beans, but the pH of sun dried beans is usually higher (less acidic) than artificially and mixed dried beans due to the slow and gentle drying process that enable the evaporation of more acetic acid during solar drying (Hii *et al.*, 2009).

According to Hii *et al.* (2009), low pHs are always associated with high acidic beans. Analyses of fermented beans showed that sun drying methods (C9), artificial method and mixed drying processes (C9 EV18) produce the same higher volatile acidity cocoa beans than other methods. This might be due to the fact that the loss of these volatile acidities during fermentation was induced by exudation of acidic liquid and not by chemical degradation. We can not conclude about these observations relating to the drying process because most studies have shown that generally acetic acid is removed as volatile acidity from fermented beans during a slow and gentle drying process as natural process. However, artificial drying process would dry faster and break the diffusion path of the acetic acid with moisture removal due to its high drying rate (Barel, 1987; Jinap *et al.,* 1994). Hence, artificial drying method cannot avoid retention of excessive acids and most of the acids remain inside the beans and cause excessive sourness note to the beans. For this reason Jinap *et al.* (1994) have recommended that drying of cocoa should be performed at temperature not exceeding 60ºC.

Higher free acidity content of fermented cocoa beans dried by mixed drying methods may be explained mainly by the presence of lactic acid produced during fermentation. Indeed, during fermentation conducted without turning beans, the low aeration of cocoa mass led to the growth of lacitic acid bacteria after declining of yeasts. Lactic acid bacteria produced lactic acid from ethanol initially produced by yeasts favoured by the anaerobic environment (Lagunes-Gálvez *et al*., 2007). Adhering pulp becomes liquid and under anaerobic conditions. Cell liquids move across cell walls and are spread all over the cocoa nib (Schwan *et al*., 1995). Although considerable acidity due to both acetic and lactic acids is turned out during fermentation, acetic acid is removed as volatile acidity from beans while the lactic acids inside of beans cannot be evaporated off since it is not a volatile compound (Nazaruddin *et al.*, 2006). In general, too high drying rate was not recommended for cocoa drying as this will retain most of the acids inside the beans and cause excessive acidity in the finished chocolate products (Mc Donald *et al.*, 1981; Barel, 1987; Jinap *et al.*, 1994). Excessive bean acidity will cause improper flavour development during roasting and the sour note cannot be removed even in the subsequent chocolate conching process.

In term of acidity, the analysed beans presented high values both of pH and free acidity content. This contrast confirms that titratable acidity is a better indicator of acidity than pH for cocoa beans as previously indicated by Nazaruddin *et al.* (2006).

Results from the study of the effect of drying methods on Ammonium Nitrogen content of cocoa beans show that fermented beans contain high Ammonium Nitrogen content ranged from 590 to 630 ppm. Oven and mixed drying methods produce higher Ammonium Nitrogen content in cocoa beans than natural drying methods. These results may be explained by the fact that Ammonium Nitrogen is not a volatile compound and also due to the fact that slow and gentle drying process such as natural method is not enabling to induce the evaporation of Ammonium Nitrogen. Drastically high Ammonium Nitrogen content was observed in fermented cocoa beans. Ammonium Nitrogen contents of fermented cocoa beans were similar for raw cocoa, whatever the drying method. These observations demonstrate clearly that Ammonium Nitrogen might result from the conversion of cocoa beans Nitrogen compound such as total polyphenol, flavonoids, epicatechin and catechin during fermentation process. Whatever the drying method employed, raw cocoa beans resulted presented the putrid odour mainly due to the production of Ammonium nitrogen through amino acid oxidase enzyme (Jinap *et al.*, 1994) which coul be originated from microbial growth such us *Bacillus subtillus* (Hashim *et al.*, 1998; Hansen *et al.*, 1998) and cocoa beans are dark appearance probably due to the presence of tanning-containing macromolecules and quinone-amino acid adducts.

Free fatty acids content of beans was low and ranged from 0.3 to 1.5% for fermented cocoa beans irrespective the drying methods. The free fatty acids contents of no sample analyzed reached the critical value of 1.75% as recommended the UE directives (EEC, 1973). These results show that the drying methods have no effect on the hydrolysis of triglycerids, which constitute cocoa butter as previously conclude Guehi *et al.*, (2008). Also, these observations confirm the results obtained by Guehi *et al.* (2008) who conclude that the formation and the accumulation of free fatty acids in cocoa raw beans are due to lipasic enzyme produced by micro flora.

The information obtained from this study are essential in understanding and solving the problems associated with the quality of cocoa raw material according to the drying methods. Further research is needed to determine the impact of fermentation duration and the pod storage time on physical, chemical and microbial quality properties of raw cocoa beans.

CONCLUSION

Overall results showed that drying methods determine the chemical quality of raw cocoa. The sun dried cocoa beans are globally higher (less acidic) than artificially and mixed dried cocoa beans. However, while highest free acidity content was associated to only mixed dried cocoa beans, raw cocoa beans resulted from drying processes using sun showed the same higher volatile acidity than cocoa beans sourced from other methods. In terms of Ammonium Nitrogen formation, oven and mixed drying methods produced higher Ammonium Nitrogen content in cocoa beans than only natural drying methods. But, the drying methods have no effect on the production of free fatty acids in cocoa. Among all processes of drying studied sun and mixed drying methods could be recommended for the production of better chemical quality raw cocoa. As the biochemical process in which Ammonium Nitrogen is produced has never been fully elucidated, further research may be needed to determine the origins and the process of formation of Ammonium Nitrogen founded in fermented raw cocoa beans.

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