Quality of traditionally processed shea (*Vitellaria paradoxa*) kernels and shea butter

Fernande Gbenato HONFO

Thesis committee

Promotors

Prof. Dr M.A.J.S. van Boekel
Professor of Product Design and Quality Management
Wageningen University

Prof. Dr M.M. Soumanou
Professor of Food Science and Biotechnology
University of Abomey-Calavi, Benin

Co-promotor

Dr A.R. Linnemann
Assistant professor, Food Quality and Design Group
Wageningen University

Other members

Prof. Dr O. van Kooten, Wageningen University

Prof. Dr B.E.E.A. de Meulenaer, Ghent University, Belgium

Dr M.J.R. Nout, Wageningen University

Dr P. Villeneuve, CIRAD-AMIS, Montpellier Cedex, France

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To

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Bruno and Béatrice

Abstract

The shea tree is an endogenous and multipurpose tree from the Savanah zone of Africa, mostly used for its fruits and the fat extracted from its kernels, commonly known as shea butter. The butter is used for cooking and medicinal purposes by local populations, and in cosmetic products as well as a cocoa butter substitute in chocolate in others areas of Africa and at the international level. The butter is generally extracted by traditional methods, which vary throughout the production zones but involve some common processing operations viz. boiling of the fresh nuts, sun drying, shelling, crushing, roasting, milling, churning, and heating. This thesis investigated the influence of traditional processing of shea on quality attributes of shea kernels and butter.

The results showed that 2 mains techniques (differing in the heat treatment applied to the fresh nuts) are used to process shea fruits after their collection: the boiling followed by sun drying technique and the smoking technique. Boiled and sundried kernels contained a higher fat content (48 % dw) and yielded more butter (30 % of kernel mass) than smoked kernels that had a fat content of 39 % dw. The butter extracted from the boiled kernels had a better quality than the butter from smoked kernels with respect to the unsaponifiable fraction (7 %), tocopherol compounds (125 mg/g), peroxide value (8 meq O_2/kg), and FFA (2 %). Some processing operations, namely the storage of fresh nuts as related to their boiling time and the roasting of kernels, were optimized using the response surface method to design the experiments. The conditions to obtain an optimal quality of kernels are to store the nuts for 3 days and boil them for 28 ± 3 min. Subsequently, optimal roasting conditions for kernels were found to be 15 min at 171 ^{o}C, which resulted in kernels with a fat content of 49 % dw, a butter yield of 32 %, and butter with a FFA of 1.2 %. The results also revealed that shea butter extracted from roasted kernels contained more volatile compounds (58) than that from unroasted kernels (27). Additionally, storage temperature and storage duration significantly affected some quality characteristics of shea butter, whereas the influence of local packaging materials was less pronounced.

Shea processors are advised to process shea fruits by integrating the optimal conditions of storage of fresh nuts, boiling and roasting found in this research, then pack the butter in clean and opaque plastic and store it in a relatively cool area to maintain the quality of the product during prolonged storage periods. Areas for future research were identified for further improvements of local shea processing.

Contents

Chapter 1

General introduction

1.1. Background information

To date, many people rely on indigenous plants to feed themselves. Forest trees are among these indigenous plants, meeting the needs of rural populations and small-scale farmers. These forest trees are wild resources present in different agro systems, and they are known under different names among which non-timber forest products (NTFPs) which is commonly used (Arnold and Ruiz Pérez 2001, IPGRI 2002). NTFPs are important for a number of reasons; among them: their valuable contribution to human diets, their social and economic importance, their availability on the market, the ease of access, the threats to which they are subjected in relation to their use and preservation, their extinction risks (IPGRI 2002). Among NTFPs, the shea tree (*Vitellaria paradoxa*) represents one of the top ten species selected to be conserved and domesticated in West Africa, including Benin (Eyog-Matig et al. 2002). Shea fruit constitutes a key economic species of which several parts are used daily in African savannah areas and it is one of the few economic commodities under the control of women (Kater et al. 1992, Boffa et al. 2000). Its importance, however, is mostly recognized through its kernels and butter, which are valuable export products (Ruyssen 1957, Boffa 1995, Hall et al. 1996).

In Benin, cotton has been, for a long time, the most important export crop, providing 90 % of the agricultural export value. However, due to national and international difficulties in cotton chains, the Beninese government decided to encourage the diversification of agricultural products for exportation. For this reason, different national development agencies have selected a number of crops and products to be promoted to increase production and export growth, among which shea kernels and shea butter (IMF 2007). Shea nuts represent the third export commodity after cotton and cashew nuts in Benin (Dah Dovonon and IdrissouYaya 2009). The tree plays a major role in local economies and the diet of the populations of the central and northern regions of the country, where the species contributes up to 46 % of households' income (Agbahungba and Depommier 1989, Gnanglè 2005, Dah Dovonon and IdrissouYaya 2009). The shea tree is an oleaginous plant and its products (*i.e.* kernels and butter) are usually processed by traditional ways, which are tedious. Therefore, efforts have been made to reduce the labour involved in processing and to improve the quality of the shea kernels and butter (Coulibaly et al. 2004, Kapseu et al. 2005, Womeni et al. 2006a, Womeni et al. 2006b).

1.2. The shea tree and its products

The shea tree (Figure 1.1) and its related species belong to the family of Sapotaceae. Formerly, known as *Butyrospermum paradoxum* or *Butyrospermum parkii*, it is nowadays called *Vitellaria paradoxa* C.F. Gaertner. **(**Hall et al. 1996, Boffa 1999). Many vernacular names are used for the shea tree in Benin: it is commonly named *kotoblè, limutin*, or *wugo* in Fon language; *akumolapa, emi*, or *emigidi* in Nago and Yoruba language; *tagan* in Goun language; and *sombu* in Bariba language (Dah-Dovonon and Gnanglè 2006).

Figure 1.1: The shea tree (*Vitellaria paradoxa* C.F. Gaertner)

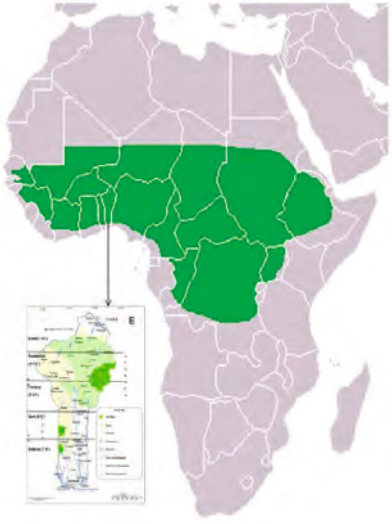

Figure 1.2: Shea tree distribution in Africa and Benin (adapted from image downloaded from Google image)

The tree is indigenous to the Savannah belt in sub-Saharan Africa (Figure 1.2), extending across 19-20 countries commonly referred to as the "Shea Belt", from western Senegal in the West to Ethiopia and Uganda in the East, viz. from 16 °W to 34 °E longitude and 1 °N to 15 °N latitude (Chevalier 1943, Sallé et al. 1991). Morphological and phenological traits of the tree are used to identify three main varieties: mangifolium, poissoni and niloticum, which occur in specific agro-ecological zones (Chevalier 1943, Bonkoungou 1987, Okullo et al. 2004, Sanou et al. 2006). The Mangifolium variety is found in the North-Soudanian zone including Mali, Côte d'Ivoire and Burkina Faso; the poissoni subspecies is present in Benin and

Ghana, while the niloticum subspecies is found in East Africa. The tree generally occurs in semi-arid to arid areas of the humid forest zone where annual rainfall ranges from 500 to 1200 mm (Sallé et al. 1991). It is commonly found around human habitations and may sometimes constitute more than 80 % of the woody biomass in farmers' fields (Lovett and Haq 2000a). The tree usually grows to a height of up to 20 m with a diameter at breast height of up to 1 m and a girth of 175 cm, exuberant branches and a thick waxy and fissured bark that makes it fire resistant. Sexual reproduction through insect pollination is the most common way for the shea tree to propagate, even though it is monoecious. Propagation is only done by seed; vegetative regeneration has failed so far (Hall et al. 1996, Okullo et al. 2004). The shea tree is characterized by its leaves, which persist more than 9 months per year and are useless for food purposes. The leaves and roots have various medicinal applications (Boffa et al. 2000). The wood is heavy and it is often used in construction works and in the production of household and farm implements. It is also used as a fire wood and in charcoal production (Schreckenberg 2004).

The shea tree begins to bear fruits (Figure 1.3a) after about 15 years and it can produce good quality fruits with a high fat content for up to 40 years (Hall et al. 1996). The fruit takes 4-6 months to develop, being subglobose to ovoid in shape, and resembling small avocado fruits with pulp when ripe; in Benin, fruit is available from May to August. The fruit weighs 10 to 57 g and its annual production is from 15 to 30 kg/tree (Agbahungba and Depommier 1989). The fruit is a berry and consists of a thin epicarp and a soft mesocarp enclosing 1 to 3 nuts (Figure 1.3b) (Ruyssen 1957, Hall et al. 1996). The sweet pulp of the fruit (45-65 % of fruit weight) plays an important role in the local diet and it is a source of sugars, proteins, calcium, ascorbic acid and iron (Hall et al. 1996, Maranz et al. 2004a). Shea fruits are available at the beginning of the rainy season, a period characterized by general food scarcity in Sub-Saharan regions (Ugese et al. 2008a, Maranz et al. 2004a). The pulp is also taken for its laxative properties (Soladoye et al. 1989).

Figure 1.3a: Shea fruits

Figure 1.3b: Shea nuts

The fresh shea nut is usually oval or fusiform and its production is 5 to 15 kg per tree per year depending on climate conditions (Lovett 2004, Diarassouba et al. 2008). Shea kernels (Figure 1.3c) are traditionally extracted from the boiled nuts after sun drying and shelling. Kernels contain 45 % up to 60 % of fat depending on the age of tree and its origin (Boffa 1995, Hall et al. 1996).

Figure 1.3c: Kernels

In shea production zones, shea kernels are processed into shea butter (Figure 1.3d) by grinding, roasting, milling, churning, washing, and heating (Kassamba 1997, Bruinsma 1998). The processing of shea butter generally falls into three main techniques: traditional, semi-mechanized and fully mechanized (Kapseu et al. 2002, Infocom 2004). The traditional processing is used to extract more than 60 % of all the crude butter produced in West Africa at an extraction rate of about 20-30 % of kernel

weight (Kassamba 1997, Infocom 2004, Elias and Carney 2004). This processing is fully done by rural women. The semi-mechanized technique uses appropriate technology to mechanize some of the unit operations such as milling, roasting, and churning of the traditional technique and its extraction rate amounts to 35-40 % of kernel weight (Djeumako et al. 2001, Yé et al. 2007). Fully mechanized processing is often based on automatic equipment and machines with extraction rates up to 52 % (Marchand 1988, Hall et al. 1996).

Data on shea kernel and butter yield vary a lot, but by using traditional processing, 20 kg of flesh fruits provides around 5 kg of dried nuts, which may give 4 kg of dried kernels from which 1 kg of butter is extracted (Bruinsma 1998, Kapseu et al. 2002, Lovett 2004). Shea butter is mainly composed of triglycerides and a large fraction (5-17 %) of unsaponifiable compounds (Kassamba 1997, Maranz and Wiesman 2004). Stearic fatty acid and oleic fatty acid represent 90 % of the total fatty acids (Maranz et al. 2004b). The unsaponifiable fraction of shea butter is mainly composed of triterpene alcohols, tocopherol, phenols, and sterols (Hall et al. 1996, Maranz et al. 2003).

Figure 1.3d: Shea butter

Shea products (*i.e.* kernels and butter) represent the second most important oleaginous export commodity in Africa after palm oil (Teklehaimanot 2001). About 650,000 tons of shea nuts are annually produced in the main producing countries, namely Ghana, Benin, Burkina Faso, Togo, Côte d'Ivoire, Mali and Nigeria, of which an estimated 10 % to 30 % is exported to Europe, Asia, and America (Lovett 2004, CNUCED 2006). Most West African countries (Benin, Burkina Faso, Mali and

Nigeria) export up to 93 % of their shea products as raw kernels due to the absence or poorly developed shea butter processing industry (Lovett 2004). In Benin, about 50,000 tons of nuts are annually collected from which 35,000 tons are exported as raw material and only 100 tons as butter (CNUCED 2006, USITC 2008). Moreover, due to the estimated number of fruit-bearing shea trees, the potential nut production of the region is considered much greater than the amount utilized and entering trade (Hall et al. 1996). Nearly half (48 %) of the shea harvest in producing countries remains uncollected (Lovett 2004).

1.3. Use of shea butter

Despite the cultivation of modern annual oil crops such as groundnut and cotton, soya, and the influx of palm oil from higher rainfall areas, shea butter is still the primary cooking and frying fat in areas where the tree occurs (Boffa et al. 1996). The butter is also locally used for various other purposes, for instance, as an illuminant, for body massage, as balm for sprains, for waterproofing house walls, to cure wounds and colds as well as for treating rheumatism and aching muscles (UNIFEM 1997, CNUCED 2006). Apart from this traditional utilization, shea butter is also used in locally produced soap and cosmetics (Hall et al. 1996, Alander 2004).

Shea butter is much appreciated as a raw material at international level. In 2000, the European Union has accepted and approved the substitution of up to 5 % of cocoa butter by other vegetable fats in chocolate products (Official Journal of the European Community 2000). This decision had boosted the trade of shea kernels and butter from African countries, and thus provided a valuable source of foreign exchange. Indeed, around 95 % of exported butter is used in food industries: for chocolate and confectionery products as cocoa butter substitute because of its high content of stearic-oleic-stearic triglyceride (16-45 %), in pastry for its high dough pliability as well as in other products usually containing plant fats (Lovett 2005, CNUCED 2006). The remaining 5 % is used for cosmetic and for pharmaceutical purposes viz. the treatment of hair, lips, burns, and multiple skin ailments due to the amount and composition of its unsaponifiable part of which 60-70 % are triterpene alcohols (Hall et al. 1996, Elias and Carney 2007).

1.4. Factors affecting the quality of butter

Quality characteristics of shea butter are linked to the quality of shea kernels and processing techniques. Shea butter is essentially composed of lipids (85-90 %). Therefore it might undergo hydrolytic and oxidative decomposition, which are the main causes of lipid degradation.

Fat hydrolysis is the process that breaks down the acyl groups of triglycerides, leading to the liberation of glycerol and fatty acids. Hydrolysis is influenced by the presence of water in the system, the interface between the oil and the water and alkaline materials (Akoh and Min 2002). Therefore, it is pronounced in water-containing lipid matrices, such as butter and virgin olive oils during processing (Kiritsakis and Tsipeli 1992). Hydrolysis may occur in two ways: chemical and enzymatic. Chemical hydrolysis especially occurs at high temperatures such as 180-220 °C *(*Adawiyah et al. 2012*)*. Lipases are responsible of enzymatic hydrolysis and are naturally present in some nuts, or produced by microorganisms such as fungi and bacteria (De Man 1999*)*. The activity of lipases is the cleaving of fatty acids from triacylglycerols, diacylglycerols and monoacylglycerols in decreasing rate of hydrolysis, respectively. Temperature, moisture, and pH are among the factors that control lipase activity (Akoh and Min 2002). The main consequence of hydrolysis is the negative effect on the quality of food by the release of free fatty acids and the production of off-flavours, mostly in fats containing relatively short chain fatty acids viz. C4-10 (Belitz et al. 2004).

Like hydrolysis, oxidation of lipids is an important reaction in fat degradation. According to Frankel (1985), unsaturated fatty acids and oxygen are the two major components involved in oxidation and they commonly interact by the mechanism of free radicals, which occurs in three main phases namely initiation, propagation and termination. Initiation arises when hydrogen is extracted from an unsaturated fatty acid, resulting in a lipid free radical, which in turn reacts with molecular oxygen to form a lipid peroxyl radical. The propagation phase is boosted by interactions of two lipids, where the lipid peroxyl radical isolates hydrogen from an adjacent molecule, leading to peroxide or hydroperoxide and a new lipid free radical. This interaction continues 10 to 100 times before two free radicals combine to terminate the process (Gutteridge and Halliwell 1990). The consequences of oxidation are the alteration of

the sensory and nutritional quality of foods and the production of toxic compounds; all of which make the foods less acceptable to the consumers and can reduce their shelf life (Min and Lee 1999). The rate of oxidation depends on several factors, including the nature of the lipid (*i.e.* unsaturated fatty acids are more susceptible to oxidation than saturated fatty acids), presence of inhibitors or catalysts (an enzyme, metallic ions, etc.), and external factors (temperature, light, pH, water activity) (Frankel 1985, Hsieh and Kinsella 1989).

1.5. Rationale of the study

Benin is a developing country, characterized by a high rate of rural poverty, problematic and unstable food security, and an unsustainable use of natural resources (UNDP 2008). Any attempt to find sustainable solutions to these problems should take into account some natural forest products available, well known, and used at locally level. Shea butter, also known as karité butter, represents an important export commodity and plays, together with the kernels, a significant role in poverty alleviation (Elias and Carney 2004). The exploitation and the processing of the shea products constitute an opportunity in general for Benin and for the farming women in particular, being a valuable source of income to achieve economic autonomy.

The traditional techniques to process the shea fruit into butter involve many operations, which vary throughout the regions where shea is produced, thus influencing the quality of the butter. Several authors have described the technologies to process shea butter (UNIFEM 1997, Kapseu et al. 2002, Elias and Carney 2004, CNUCED 2006, Mbaiguinam et al. 2007, Dandjouma et al. 2009). The traditional techniques can be described as having low efficiency, long processing time, high water consumption, high firewood consumption and high smoke production and finally are not standardized. Other authors have developed and proposed several labour-saving technologies in an attempt to remove or reduce the production bottlenecks in the traditional methods, and other problems faced by processors. For example, some equipment *viz*. shea kernels crusher, presser, mill, and roaster have been developed and adapted to the traditional processing (Hyman 1991, Bruinsma 1998, Olaoye and Babatunde 2001). Attempts were also made to improve both shea nut and butter qualities by assessing the influence of some processing operations *viz*. the storage, the cooking, the drying with various methods on their qualities (Kapseu

et al. 2005, Womeni et al. 2006b, Bup et al. 2011, Aculey et al. 2012). Those extractions methods have been explored like extraction by centrifugation (Coulibaly et al. 2004) and the use of some chemical solvents (Nkouam et al. 2007) in order to increase the butter yield and improve butter quality.

In spite of the results obtained so far, some quality constraints persist along the shea butter processing chain coupled with the inadequacy or no adaptation of certain innovations (mixer, solvents extraction,…). These include the following:

- the mode of collection of the shea fruits in the field by women, which results to the gathering of all fallen fruits under shea trees without any sorting, often leading to the collection of germinated and damaged fruits.
- the pre-treatments of the collected fruits namely storage conditions of fresh nuts and boiling practice. For instance, fresh shea nuts are generally stored for several days before processing. This practice often leads to the germination of the nuts and exposes the nuts to external agents such as microorganisms, moisture and insects attack that affect the quality of the final products (kernel and butter). Such germination leads to the reduction of butter yield and the bitterness of butter (Jacobsberg 1977). Boiling of nuts is one of shea processing stage for inactivation of enzymes responsible of triglycerides hydrolysis, (Lovett 2004, Womeni et al. 2006b). Excessive boiling can result in cellular damage, leading sometimes to discoloration of the shea nut (Aculey et al. 2012); while improper lipase inactivation may occur with insufficient boiling time leading to a high free fatty acid content in kernels (Bup et al. 2011).
- the storage practice including packaging, place, and duration of both dried nuts and kernels often leading to their exposition to external agents and affect the quality of derived butter;
- the roasting practice of shea kernels: roasting is one important stage in shea processing (Womeni 2004) for fat extraction easiness and sensory characteristics improvement. Even though it is a necessary step for butter extraction, it can affect the overall flavour and butter composition in a negative way if roasting is not done properly;
- the storage conditions of shea butter after its extraction should affect its quality and reduced its access to international market. For example in Benin,

the extracted butter stored in certain storage condition was sometimes high in free fatty acid percentage and peroxide values (Honfo et al. 2011). In addition, volatile compounds of shea butter could be altered during roasting step and storage of butter.

Consequences of all of these constraints are that customers' requirements for export are not fulfilled and the reduction of added value. In addition, major industrial importers of shea kernels are ready to import more shea butter directly from African producers, but they are often limited by the lack of products complying with norms and standards for quality attributes. Improvement of traditional processing and quality of added value products for a larger market are expected to increase the income of rural populations involved in this activity. A better knowledge about all of these different stages is necessary for shea processing improvement. Most importantly, optimizations of some processing operations based on local conditions are necessary to define the best way of improvement in order to attain the maximum potential in terms of yield and quality characteristics of kernels and butter and to guarantee the same quality of such products among shea processors. This research was therefore undertaken to investigate each part of the processing stage and by the way to optimize traditional processing of shea nuts within the boundaries of local production conditions.

1.6. Objective and research questions

This thesis aimed to study the impact of traditional processing on quality attributes of shea kernels and butter. To achieve this goal, the following specific objectives were:

a) to critically review the existing literature on the nutritional composition of shea products and chemical properties of shea butter;
b) to investigate the indigenous knowledge related to shea processing and shea products in Benin;
c) to characterize the quality of kernels and butters in relation to different processing techniques
d) to assess the effect of traditional processing operations on quality characteristics of shea products;
e) to study the quality degradation of shea butter during storage;

To reach these objectives, a number of specific research questions was formulated that address different activities along the production chain (Figure 1.4).

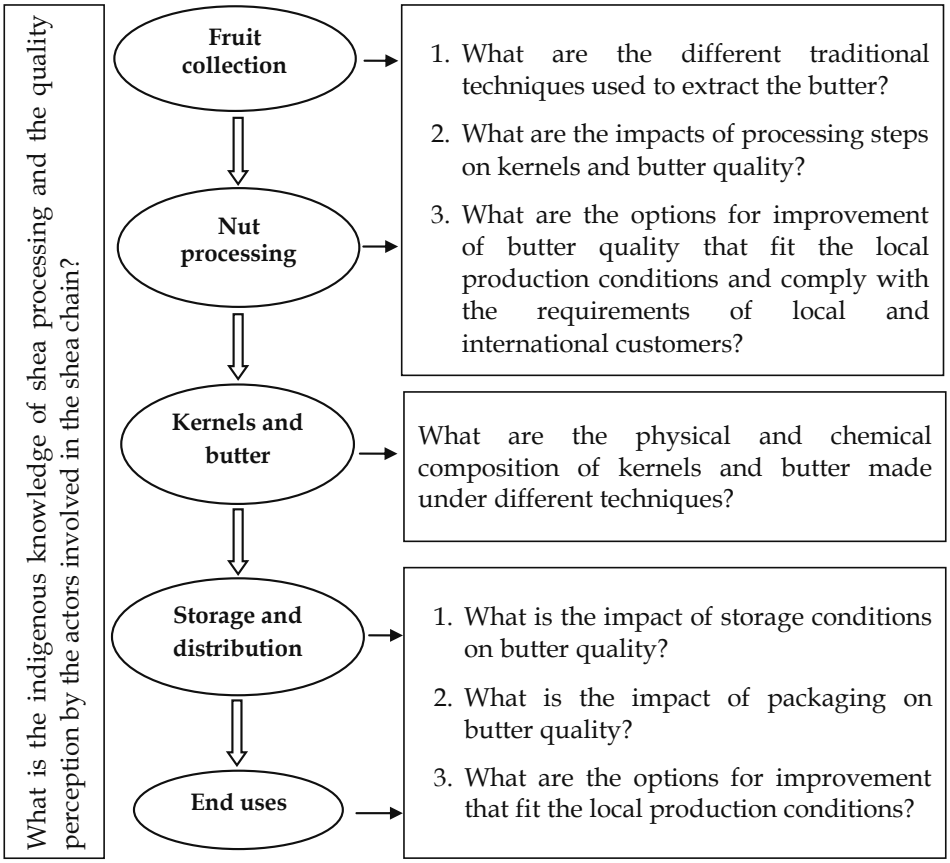

Figure 1.4: Flow chart of the shea chain and the research questions at each level of the chain

1.7. Thesis outline

After this general introduction, which provides general information about the shea tree and research issues related to shea products and their importance as well as the objectives of the thesis, chapter 2 presents a critical review of the nutritional composition of shea products and chemical properties of shea butter. In chapter 3, the indigenous knowledge of shea processing and quality perception of shea

products in Benin is described. Chapter 4 reports on the different techniques to process shea fruit in Benin and their influence on the quality characteristics of kernels and the extracted butter. Moreover, this chapter, in combination with chapter 2, gives areas for future research, some of which serve as the basis for the specific objectives for chapters 5 to 7 of this thesis. Specifically, chapter 5 studies the influence of the storage of fresh nuts and their boiling on some quality characteristics of kernels and butter while chapter 6 investigates the influence of roasting crushed kernels on volatile compounds and other quality attributes of shea butter. Subsequently, chapter 7 reports on the effects of butter storage conditions on volatile compounds and some quality characteristics of such butter. The final chapter, chapter 8, presents the general discussion of the main findings, together with concluding remarks on how far this thesis has achieved its objectives and some recommendations for further research.

Chapter 2

Nutritional composition of shea products and chemical properties of shea butter: a review

F.G. Honfo, N. Akissoe, A.R. Linnemann, M.M. Soumanou, M.A.J.S. Van Boekel
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Abstract

Increasing demand of shea products (kernels and butter) has led to the assessment of the state-of-the-art of these products. In this review, attention has been focused on macronutrients and micronutrients of pulp, kernels and butter of shea tree and also the physicochemical properties of shea butter. Browsing the literature revealed that the pulp is rich in vitamin C (196.1 mg/100 g); consumption of 50 g covers 332 % and 98 % of the Recommended Daily Intake (RDI) of children (4-8 years) and pregnant women, respectively. The kernels contain a high level of fat (17.4-59.1 g/100 g dry weights). Fat extraction is mainly done by traditional methods that involve roasting and milling of the kernels, churning the obtained paste with water, boiling, sieving and cooling. The fat (butter) is used in food preparation, medicinal, and cosmetics industries. Its biochemical properties indicate some antioxidant and anti-inflammatory activities. Large variations are observed in the reported values for the composition of shea products. Recommendations for future research are presented to improve the quality and the shelf-life of the butter. In addition, more attention should be given to the accuracy and precision in experimental analyses to obtain more reliable information about biological variation.

Keywords: Shea pulp, shea kernels, shea butter, nutrient composition, antioxidant properties

2.1. INTRODUCTION

The shea tree (*Vitellaria paradoxa* C.F. Gaertner, also classified as *Butyrospermum paradoxum* or *Butyrospermum parkii*; family Sapotaceae) is indigenous to the savanna belt in sub-Saharan Africa, extending across 19 countries, from Mali in the west to Ethiopia and Uganda in the east, viz. from 16 °W to 34 °E longitude and 1 °N to 15 °N latitude (Chevalier 1943, Master et al. 2004). The tree is generally found in semi-arid to arid areas north of the humid forest zone and it is characterized by its leaves that persist more than 9 months per year and are not used for feed or for food purposes. Its height reaches 15 m to 22 m and the trunk diameter varies from 0.5 m to 1 m. The shea tree begins to bear fruit after about 15 years and can produce good quality fruits with a high fat content for up to 30 years (Hall et al. 1996). The fruits are produced from May to August; being subglobose to ovoid in shape, and resembling small avocado fruits with delicious pulp when ripe. The fruit weighs from 10 g to 57 g and its annual production is from 15 kg to 30 kg/tree (Agbahungba and Depommier 1989). The fruit, which is a berry, consists of a thin epicarp and a soft mesocarp enclosing a single seed, sometimes two or more (Ruyssen 1957).

The importance of the shea tree was recognized centuries ago through the fruit, its kernels and butter (Ruyssen 1957, Hall et al. 1996, Boffa et al. 1995). The sweet pulp of the fruit is widely consumed in areas where the species occurs and is a rich source of sugars, proteins, calcium, ascorbic acid and iron (Maranz et al. 2004a). An additional benefit is that it becomes available at the beginning of the rainy season, which is a period characterized by general food scarcity in Sub-Saharan Africa (Ugese et al. 2008a, Maranz et al. 2004a). The kernels constitute a major commodity on the international market (Hall et al. 1996). The fat extracted from the kernels, also known as karité or shea butter, represents an important export commodity and plays, together with the kernels, a significant role in poverty alleviation (Elias and Carney 2004). The butter is widely used for cooking and as illuminant in rural areas of the savanna zone of West Africa (Chevalier 1946). Boffa et al. (1996) have reported that despite the cultivation of modern annual oil crops such as groundnut and cotton, and the influx of palm oil from higher rainfall areas, shea butter is still the primary cooking fat of the Sudanian savanna zone.

Shea butter is essentially composed of triglycerides with oleic, stearic, linoleic and palmitic fatty acids and unsaponifiable matter (Maranz et al. 2004b). Due to its

high percentage of unsaponifiables (viz. triterpenes, tocopherol, phenols, sterols), to which anti-inflammatory and antioxidant properties are ascribed, shea butter is highly demanded by international cosmetic industries (Alander 2004, Maranz and Wiesman 2004, Akihisa et al. 2010a). Some authors have also shown the usefulness of shea butter in European and Japanese food as well as its potential as a cocoa butter replacer in chocolate manufacture (Gasparri et al. 1992, Hall et al. 1996, CNUCED 2006).

A monograph by Hall et al. (1996) on the shea tree provides extensive information on taxonomy, distribution, properties, utilization, agronomy, and proximate composition of shea kernels and butter. In addition, there is a database on *Vitellaria* that was compiled by Maranz during 1999-2004, which is available on the website of Prokarité (http://www.prokarite.org/vitellaria-dbase-EN/index-EN.html). It presents information on the fat content, fatty acid profile, triglyceride content, unsaponifiable compounds, shea fruit composition and the nut quality parameters. All of the data on this website are derived from Maranz' own research on shea products in different locations in Africa. An omission of these two reviews is that they do not take all the existing data on shea products with their different analysis methods into account. Moreover, the data on shea products need to be updated to cover the research done in the past 10 years. The present review investigates the nutritional value of shea products (pulp, kernels and butter) and the quality properties of the butter based on data from various authors and critically evaluates the similarities and divergences of the values in relation to the research methods used. For each component, the reported values are, as much as possible, converted into the same unit, and their minimum, average, and maximum values are calculated and reported in Table 1. The review ends with recommendations for further research based on the analysis of the present state of knowledge.

2.2. NUTRITIONAL COMPOSITION OF SHEA PULP

2.2.1. Macronutrients

The moisture content of shea fruit pulp ranges from 67 % (Maranz et al. 2004a) to 80.3 % (Mbaiguinam et al. 2007) (Table 2.1). The energy value has been reported by Ugese et al. (2008a), who found it equal to 179.5 kcal/100 g dry weights (dw). Mbaiguinam et al. (2007) and Ugese et al. (2008a) reported carbohydrate contents of

8.1 and 37.2 g/100 g dw, respectively. Ugese et al. (2008a) have assessed the nutritional composition of shea fruit pulp across its major distribution zones in Nigeria and reported that the carbohydrate content decreased at higher latitude. They attributed this phenomenon to a more adequate water supply leading to improved photosynthesis at latitudes closer to the equator. The presence of sugars was mentioned by Maranz et al. (2004a), who found a total soluble sugar content of 13.3 g/100 g dw and glucose content of 1.6 g/100 g dw. Dako et al. (1974) reported glucose (1-2 g/100 g), fructose (1-1.9 g/100 g) and sucrose (0.7-1.7 g/100 g) in shea pulp from Ghana. The reported crude protein content varies from 4.4 g/100 g dw (Mbaiguinam et al. 2007) to 5.6 g/100 g dw (Maranz et al. 2004a). Crude lipid and crude fibre content were reported by Ugese et al. (2008a), who found them between 1.3 g/100 g and 42.2 g/100 g dw, respectively. Ash content ranges from 4.7 g/100 g dw (Mbaiguinam et al. 2007) to 5.4 g/100 g dw (Ugese et al. 2008a).

The variations in the reported values of the macronutrient composition of shea fruit pulp seem to be large even if the number of authors who investigated the macronutrient composition of shea fruit pulp is limited, although Maranz et al. (2004a) have evaluated the nutritional values and indigenous preferences for shea fruits in various African agroforestry parklands. Variations are more pronounced between data reported by Mbaiguinam et al. (2007), who collected the shea fruit in Tchad (West Africa), and those reported by Ugese et al. (2008a), who collected the shea fruit in Nigeria (West Africa). These differences seem to be primarily due to the methods of analysis used by the authors, specifically with respect to the determination of the carbohydrate content. Ugese et al. (2008a) determined the carbohydrate content by difference after using the methods of the Association of Official Analytical Chemists to assess fat content (determined by Soxhlet analysis), protein content (determined by the Kjeldahl method with a conversion factor of 6.25), ash content (determined by incineration) and fibre content. Mbaiguinam et al. (2007) assessed carbohydrate content by the colorimetric method described by Dubois et al. (1956). In this method the sample is first treated with a solution of phenol (80 %) and concentrated sulfuric acid (95 %). Next the mixture is shaken and placed for 10 - 20 minutes in a water bath at 25-30 °C before readings are taken. The absorbance of the colour is measured by a spectrophotometer. To determine crude fibre content, Ugese et al. (2008a) used the method of Weende; this method is based on the solubilization

of non-cellulosic compounds (protein, starch and other digestible carbohydrates and fat) by sulfuric acid and potassium hydroxide solutions.

2.2.2. Minerals

Shea fruit pulp is particularly rich in potassium (K) according to literature (Table 2.1). With an average of 830.4 mg/100 g dw, the highest value (1686 mg/100 g dw) was reported by Maranz et al. (2004a) and the lowest value (21.7 mg/100 g dw) by Mbaiguinam et al. (2007). The calcium (Ca) content of shea fruit pulp varies widely from 2.5 mg/100 g dw (Ugese et al. 2008b) to 426.0 mg/100 g dw (Maranz et al. 2004a) with an average of 117.3 mg/100 g dw. The reported magnesium (Mg) content ranges from 11.1 mg/100 g dw (Mbaiguinam et al. 2007) to 129 mg/100 g dw (Maranz et al. 2004a) with mean value of 57.2 mg/100 g dw. The phosphorus (P) content ranges greatly from 0.95 mg/100 g dw (Mbaiguinam et al. 2007) to 71.4 mg/100 g dw (Ugese et al. 2008b). Mbaiguinam et al. (2007) and Maranz et al. (2004a) reported an iron (Fe) content of 0.4 mg/100 g dw and 16 mg/100 g dw, respectively. The zinc (Zn) content varies from 0.5 mg/100 g dw (Eromosele et al. 1991) to 4 mg/100 g dw (Maranz et al. 2004a). Ugese et al. (2008b) reported that the sodium (Na) content is 19.3 mg/100 g dw. Copper (Cu) and manganese (Mn) contents are very low; the highest values were reported by Emorosele et al. (1991): 1.1 mg/100 g dw and 0.9 mg/100 g dw, respectively, while the lowest values were found by Maranz et al. (2004a): 0 mg/100 g dw and 0.3 mg/100 g dw, respectively.

Emorosele et al. (1991) and Maranz et al. (2004a) used atomic absorption spectrophotometry to determine all of the mineral elements. Ugese et al. (2008b) used this method too, except for Na and K which were determined by flame photometry. Mbaiguinam et al. (2007) used a flame spectrophotometer to determine K; while Fe, Ca and Mg were determined by an atomic spectrophotometer and a colorimeter was used to determine P.

2.2.3. Vitamins

Emorosele et al. (1991) have investigated the vitamin C content of shea fruit pulp and found that the pulp is particularly rich in vitamin C (196.1 mg/100 g) in comparison to oranges (50 mg/100 g) (Table 2.1). Vitamin content was determined by HPLC.

Table 2.1: Composition of shea pulp, kernels and butter

	Pulp				Kernels				Butter			
	Min	Average	Max	Reference	Min	Average	Max	References	Min	Average	Max	References
Macronutrients												
Moisture (%)	67.0	74.2	80.3	(Maranz et al. 2004a, Mbaiguinam et al. 2007)	5.0	6.8	8.1	(Busson 1965, Tallantire and Goode 1975, GRET 2007, Mbaiguinam et al. 2007)	0.1	1.4	4.9	(Greenwood 1929, Megnanou et al. 2007, Olaniyan and Oje 2007, Chukwu and Adigbizi 2008, Honfo et al. 2011)
Energy (kcal/100 g dw)		179.5		(Ugese et al. 2008a)								
Carbohydrates (g/100 g dw)	8.1	22.6	37.2	(Mbaiguinam et al. 2007, Ugese et al. 2008a)	25.0	30.9	34.8	(Greenwood 1929, Tallantire and Goode 1975, Duke and Atchley 1986, Tano-Debrah and Ohta 1994, GRET 2007)		22.3		(Chukwu and Adigbizi 2008)

Table 2.1 (*Continued*)

Crude protein (g/100 g dw)	4.2	5.2	5.6	(Maranz et al. 2004a, Mbaiguinam et al. 2007, Ugese et al. 2008a)	6.8	8.1	9.0	(Greenwood 1929, Busson 1965, Tallantire and Goode 1975, Duke and Atchley 1986, Tano-Debrah and Ohta 1994, GRET 2007)		
Crude lipid (g/100 g dw)		1.3		(Ugese et al. 2008a)	17.4	45.2	59.1	(Greenwood 1929, Busson 1965, Duke and Atchley 1986, Maranz and Wiesman 2003, Di Vincenzo et al. 2005, Mbaiguinam et al. 2007, Nkouam et al. 2007, Akihisa et al. 2010b)	75.0	(Chukwu and Adigbizi 2008)
Crude fibre (g/100 g dw)		42.2		(Ugese et al. 2008a)	3.2	9.1	20.4	(Greenwood 1929, Ruyssen 1957, Duke and Atchley 1986, Tano-Debrah and Ohta 1994)		

Table 2.1 (*Continued*)

Minerals (mg/100 g dw)											
Ca	2.5	117.3	426.0	(Eromosele et al. 1991, Maranz et al. 2004a, Mbaiguinam et al. 2007, Ugese et al. 2008b)	0.1	71.8	215.2	(Tallantire and Goode 1975, Duke and Atchley 1986, Megnanou et al. 2007, Alhassan et al. 2011)	0.2	9.6	34.1	(Megnanou et al. 2007)
Cu	0	0.1	1.1	(Eromosele et al. 1991, Maranz et al. 2004a)		0.3		Megnanou et al. 2007	0	0.8	1.5	(Megnanou et al. 2007)
Fe	0.4	8.5	16.0	(Eromosele et al. 1991, Maranz et al. 2004a, Ugese et al. 2008b)	0.01	1.6	3.1	(Duke and Atchley 1986, Megnanou et al. 2007)	0.5	3.6	6.7	(Megnanou et al. 2007)
K	21.7	830.3	1686.0	(Maranz et al. 2004a, Mbaiguinam et al. 2007, Ugese et al. 2008b)	0.1	0.1	0.2	(Alhassan et al., 2011)	0	2.2	4.5	(Megnanou et al. 2007)
Mg	11.1	57.2	129.0	(Eromosele et al. 1991, Maranz et al. 2004a, Mbaiguinam et al. 2007, Ugese et al. 2008b)		142.6		(Megnanou et al. 2007)	0	4.5	8.9	(Megnanou et al. 2007)

Table 2.1 (*Continued*)

Mn	0.3	0.6	0.9	(Eromosele et al. 1991, Maranz et al. 2004a)	0.1	0.4	0.7	(Alhassan et al. 2011)	0	0.006	0.14	(Alhassan et al. 2011)
P	1.0	39.8	71.4	(Eromosele et al. 1991, Maranz et al. 2004a, Mbaiguinam et al. 2007, Ugese et al. 2008b)		0.04		(Tallantire and Goode 1975, Duke and Atchley 1986)				
Zn	0.5	2.1	4.0	(Eromosele et al. 1991, Maranz et al. 2004a, Ugese et al. 2008b)		0.9		(Megnanou et al. 2007)	1.9	2.7	3.4	(Megnanou et al. 2007)
B		7.0		(Maranz et al. 2004a)								
Vitamins (mg/100 g)												
C		196.1		(Eromosele et al. 1991)								

2.2.4. Amino acids

The literature is limited on amino acid contents of the pulp; only Mbaiguinam et al. (2007) investigated the amino acids of shea fruit pulp (Table 2.2). They found that the pulp contains asparagine/aspartic acid (6.6 g/100 g protein); glutamine/glutamic acid (5.6 g/100 g protein); proline (3.9 g/100 g protein); leucine (3.1 g/100 g protein), and it is limited in cysteine (1.1 g/100 g protein) and methionine (0.1 g/100 g protein).

Table 2.2: Amino acids (g/100 g proteins) of shea fruit pulp

Amino Acid	Value	Amino Acid (*continued*)	Value
Asparagine/aspartic acid	6.6 ± 0.3	Methionine	0.1 ± 0.0
Threonine	1.7 ± 0.2	Isoleucine	2.0 ± 0.1
Serine	2.1 ± 0.2	Leucine	3.1 ± 0.1
Glutamine/Glutamic acid	5.6 ± 0.5	Tyrosine	1.7 ± 0.2
Proline	3.9 ± 0.2	Phenylalanine	1.5 ± 0.1
Glycine	2.2 ± 0.2	Lysine	1.8 ± 0.1
Alanine	2.4 ± 0.1	Histidine	1.2 ± 0.1
Valine	2.5 ± 0.2	Arginine	3.1 ± 0.14
Cysteine	1.1 ± 0.1		

Source: Mbaiguinam et al. 2007

2.3. NUTRITIONAL COMPOSITION OF SHEA KERNELS

After gathering/collecting, shea fruits are depulped, boiled for one or two hours and dried for 7-15 days to obtain the nuts. Throughout the shea butter producing areas in West Africa, producers employ different traditional methods for drying the shea nuts. Most use exposure to the sun while some use traditional ovens. After drying, the nuts are shelled by mortar, pestle or stick and the kernels are sundried for three to seven days. These traditional processes are common practice in the shea tree locations.

2.3.1. Macronutrients

The moisture content of dried shea kernels ranges from 5 % (Busson 1965) to 8.1 % (Mbaiguinam et al. 2007) with an average of 6.8 % (Table 2.1). The variation in the reported values for kernels is low compared with the variation in the reported values for the moisture content of the pulp. To our knowledge, no author has

investigated the energy content of shea kernels. Reported carbohydrate contents vary from 25 g/100 g dw (Busson 1965) to 34.8 g/100 g dw (Tano-Debrah and Ohta 1994). Crude protein values range from 6.8 g/100 g dw (Tallantire and Goode 1975) to 9 g/100 g dw (GRET 2007).

Many authors have investigated the fat content of shea kernels. Crude lipid contents of dried kernels vary greatly among the authors (Table 2.1). With an average of 45.2 g/100 g dw, the highest value (59.1 g/100 g dw) was found by Tano-Debrah and Ohta (1994), who extracted fat by Enzyme Assisted Aqueous Extraction. The lowest value (17.4 g/100 g dw) was reported by Nkouam et al. (2007) by using supercritical CO_2. They also used hexane to extract the fat from the kernels and found that the extraction yield varied from 44.9 g/100 g dw to 53.8 g/100 dw, compared with the yield of 17.4 to 39.6 g/100 g dw for extraction by supercritical CO_2. Mbaiguinam et al. (2007) used two different methods to extract the butter: hexane extraction and traditional manual extraction, as performed in the rural areas in which sundried kernels were ground, churned with water and heated to get the butter. They obtained different fat yields, namely 50 % by solvent extraction and 30 % by manual method, and concluded that a chemical solvent permits far better extraction, but also requires special equipment and chemical reagents, which are not available on the farms. Apart from differences caused by the use of different analytical methods, the variation in the fat content of shea kernels could also be attributed to environmental influences, geographical location, agronomic factors and genetic variation (Maranz and Wiesman 2003, Di Vicenzo et al. 2005). High altitude and cool temperatures (20-25 °C) are associated with high fat contents of shea kernels (Maranz and Wiesman 2003, Kapseu et al. 2007).

With an average of 9 g/100 g dw, the lowest fibre content (3.2 g/100 g dw) of shea kernels was reported by Greenwood (1929) and the highest value (20.4 g/100 g dw) by Tano-Debrah and Ohta (1994) who have used the method of Lee et al. (1992) with heat-stable α-amylase, α-glucosidase and a protease. Ash contents range from 1.8 g/100 g dw (Duke and Atchley 1986) to 3 g/100 g dw (Greenwood 1929), with an average of 2.5 g/100 g dw.

2.3.2. Minerals

Few authors have investigated the mineral contents of shea kernels (Table 2.1). The Ca content reported by Megnanou et al. (2007) is 215.2 mg/100 g dw but Tallantire and Goode (1975), Duke and Atchley (1986) and Alhassan et al. (2011) observed a value of 0.1 mg/100 g dw. This great variation is also observed for the Fe content, for which Megnanou et al. (2007) found 3.1 mg/100 g dw, while Duke and Atchley (1986) reported 0.003 mg/100 g dw. Except Alhassan et al. (2011) who used neutron activation analysis (it consist of the irradiation of the sample in one reactor) to determine the mineral contents, all of those authors used atomic absorption spectrophotometry. The variation in the reported data could be attributed to the environmental and genetic influences and also to the identification method. Megnanou et al. (2007) found 142.6 mg/100g dw for Mg; 73.9 mg/100 g dw for Na; 0.9 mg/100 g dw for Zn and 0.3 g/100 g dw for Cu and Alhassan et al. (2011) found 0.1 mg/100 g dw for K and 0.4 mg/100 g dw for Mn.

2.3.3. Vitamins

No author has investigated the vitamin content of shea kernels, to our knowledge.

2.4. NUTRITIONAL COMPOSITION OF SHEA BUTTER

The first stage of shea butter extraction by rural women after obtaining the kernels involves roasting and milling the kernel into a powdery material or flour, which is then mixed with warm or lukewarm water. The resulting semi-solid mixture is then stirred continuously or kneaded by hand until occurrence of the oily phase. This fat-rich fluid is collected and subsequently boiled until it is clear. The fat is then poured over a sieve into a basin where it is left to solidify.

2.4.1. Macronutrients

The reported moisture contents of shea butter vary from 0.1 % (Olaniyan and Oje 2007) to 4.9 % (Honfo et al. 2011) (Table 2.1). However, exceptional higher values of 8.4 % and 14.5 % were mentioned by Megnanou et al. (2007), who evaluated the physicochemical and microbiological characteristics of shea butter sold on markets in Côte d'Ivoire. However, the required moisture contents of shea butter destined for

cosmetic and food industries are 0.05 % and less than 0.2 %, respectively (Kassamba 1997). Carbohydrates and crude lipid contents were reported by Chukwu and Adigbizi (2008), who found 22.3 g/100 g dw and 75.0 g/100 g dw respectively. Reported ash content ranges from 1.3 g/100 g dw (Chukwu and Adigbizi 2008) to 3.2 g/100 g dw (Adomako 1985), with an average of 2.2 g/100 g dw.

All of the authors used the methods of the Association of Official Analytical Chemists to determine the different values.

2.4.2. Minerals

Some mineral contents of shea butter were assessed by Megnanou et al. (2007) by atomic absorption spectroscopy and Alhassan et al. (2011) by neutron activation analysis (Table 2.1). Ca value varies from 0.2 mg/100 g dw to 34.1 mg/100 g dw; Na reported is in the range of 0.7-9.6 mg/100 g dw; Fe level is 0.5-6.7 mg/100 g dw; Mg value is 0-8.9 mg/100 g dw; Mn content range is 0-0.14 mg/100 g dw; Zn level is 1.9-3.4 mg/100 g dw; Cu content is 0-1.5 mg/100 g dw and K value ranges from 0 to 4.5 mg/100 g dw.

2.4.3. Vitamins

No published reports on the vitamin contents of the shea butter were found because shea butter is a vegetable fat. However, the tocopherol content of shea butter was investigated by Maranz and Wiesman (2003), and more details are given next. However, shea butter should contain some vitamin A in view of its yellow colour.

2.5. PHYSICOCHEMICAL PROPERTIES OF SHEA BUTTER

Shea butter is mainly composed of triglycerides and a large fraction of unsaponifiable components, which are promising active ingredients for new functional cosmetic products (Akihisa et al. 2010a). As presented in Table 2.3, the average unsaponifiable content of shea butter is 8.1 %. It ranges from 1.2 % (Njoku et al. 2000) to 17.6 % (Megnanou et al. 2007). However, Adriaens (1943) found that the riper the fruit, the lower the quantity of unsaponifiable matter is, while Ruyssen (1957) reported that the amount of unsaponifiable matter varied from year to year and in accordance to the variation in rainfall. The values for unsaponifiable matter

reported by different authors are higher than those found in most vegetable oils (Anhwange et al. 2004, Dhellot et al. 2006, Tchobo et al. 2007).

The acid value of shea butter is a measure of the extent in which the glycerides in the butter have been decomposed by lipase or other actions such as heat and light. It is often used as a general indicator of the condition and edibility of the oil. The reported acid values of shea butter vary from 0 mg KOH/g (Womeni et al. 2006a) to 21.2 mg KOH/g (Nkouam et al. 2007), with an average of 8.1 mg KOH/g (Table 2.3). However, Nkouam et al. (2007) found the high acid value of 128.2 mg KOH/g in shea oil extracted by supercritical CO_2 in kernels that had been stored for 2 years. The required acid values for butter that is to be used for cosmetic and food applications are 0.3 mg KOH/g of oil and less than 9 mg KOH/g of oil, respectively (Kassamba 1997).

The decomposition of triglyceride is also measured by free fatty acid (FFA) percentage. The FFA values reported range from 1 % (Badifu 1989) to 10.7 % of oil (Badifu 1989) with an average of 5.3 % of oil (Table 2.3). The maximum tolerated amounts of FFA for cosmetic and food uses are 1 % and 3 %, respectively (Kassamba 1997, NB 04.02.001 2006). FFA produced irritation on the tongue and in the throat (Kirk and Sawyer 1991). Kapseu et al. (2005) reported that the acid value and FFA of the butter increase with the storage condition and duration of the shea fruits. They explained this increase by physiological activity of fruits; thus, during storage, the fatty acids are degraded to produce some energy and precursors for the synthesis of new molecules.

Kirk and Sawyer (1991) described peroxide as a first product of oxidation of unsaturated fats and oils. With an average of 7.6 meq O_2/kg, the reported peroxide value ranges from 0.5 meq O_2/kg (Njoku et al. 2000) to 29.5 meq O_2/kg (Dandjouma et al., 2009) (Table 2.3). Most of the authors found peroxide values below the average value reported here; the high value found by Dandjouma et al. (2009) is due to the kernels used for the butter extraction, which were fermented before the extraction. For use in the cosmetic and food industries, the required peroxide values of shea butter utilizations are 1 meq O_2/kg and less than 10 meq O_2/kg, respectively (Kassamba 1997). For this parameter, Kirk and Sawyer (1991) found that during fat storage, peroxide formation is slow at first, during an induction period (which may

vary from a few weeks to several months), depending on the particular oil and temperature.

The iodine value expresses the degree of saturation of oil. It is an indicator of the storability of the oil; the higher the iodine numbers, the higher the degree of unsaturation, and the shorter the shelf-life (Hui 1996). As presented in Table 2.3, the average reported iodine value is 51.4 g I_2/100 g. It ranges from 21.7 g I_2/100 g (Nkouam et al 2007) to 89.5 g I_2/100 g (Womeni et al. 2004). The low value reported by Nkouam et al. (2007) was found in butter extracted by supercritical CO_2.

Table 2.3: Physicochemical properties of shea butter

Parameter	Min	Average	Max	References
Unsaponifiable content (%)	1.2	8.1	17.6	(Greenwood 1929, Peers 1977, Gasparri et al. 1992, Tano-Debrah and Ohta 1994, Njoku et al. 2000, Kapseu et al. 2001, Alander and Andersson 2002, Letchamo et al. 2007, Mbaiguinam et al. 2007, Megnanou et al. 2007, Chukwu and Adgidzi 2008, Akihisa et al. 2010b)
Free fatty acid (%)	1.0	5.3	10.7	(Greenwood 1929, Badifu 1989, Renard 1990, Olaniyan and Oje 2007)
Iodine value (gI_2/100 g)	21.68	51.4	89.5	(Mital and Dove 1971, Renard 1990, Gasparri et al. 1992, Tano-Debrah and Ohta 1994, Njoku et al. 2000, Womeni et al. 2004, Mbaiguinam et al. 2007, Megnanou et al. 2007, Nkouam et al. 2007, Chukwu and Adgidzi 2008, Okullo et al. 2010, Honfo et al. 2011)
Saponification value (mg KOH/g)	132.0	180.9	207.5	(Mital and Dove 1971, Renard 1990, Ezema and Ogujiofor 1992, Gasparri et al. 1992, Tano-Debrah and Ohta 1994, Njoku et al. 2000, Womeni et al. 2004, Mbaiguinam et al. 2007, Megnanou et al. 2007; Chukwu and Adgidzi 2008)
Refractive index (40˚C)	1.45	1.5	1.5	(Renard 1990, Ezema and Ogujiofor 1992, Gasparri et al. 1992, Megnanou et al. 2007, Chukwu and Adgidzi 2008, Okullo et al. 2010)
Relative density (40˚C)	0.90	0.9	1.0	(Renard 1990, Chukwu and Adgidzi 2008)
Melting point (˚C)	25	35.9	45	(Mital and Dove 1971, Renard 1990, Ezema and Ogujiofor 1992, Gasparri et al. 1992, Tano-Debrah and Ohta 1994, Womeni et al. 2006a,

Table 2.3 (*Continued*)

				Megnanou et al. 2007, Chukwu and Adgidzi 2008)
Impurity (%)	0	0.9	3.5	(Greenwood 1929 GRET 2007)
Color	Yellow, yellow-orange, yellow-green, pale-yellow, orange, beige, ivory, grey, white, ivory-white, brown, cream, light grey, white			(Greenwood 1929, Letchamo et al. 2007, Megnanou et al. 2007, Okullo et al. 2010)

Literature data show a considerable range for the saponification values, but most fall between 132 mg KOH/g (Ezema and Ogujiofor 1992) and 207.5 mg KOH/g (Womeni et al. 2004), and the average is 180.9 mg KOH/g (Table 2.3).

Kirk and Sawyer (1991) define the refractive index of oil as the ratio of the incident angle to the refracted angle when light travels through the oil at a given wavelength. Fats/oils have specific refractive indices, which are used as a characteristic for identification and checking purity. Concerning this parameter, all authors reported values of about 1.46 at 40 °C (Table 2.3).

The relative density is a measure of the purity of a substance and it is the ratio of the density of a substance to the density of water (Kirk and Sawyer 1991). It changes with temperature. At 40 °C, the relative density found by most of the authors was closed to the average of 0.93 (Table 2.3).

The melting point is described by Letchamo et al. (2007) as an important aspect of traditional processing of shea butter. In many West African countries, women boil roots, grasses or branches together with shea nuts during shea butter preparation to enhance the melting point of butter. Hence, the degree of variation in melting point might not reflect the actual nature of shea butter. The reported melting points vary between 25 °C (Womeni et al. 2006a) and 45 °C (Gasparri et al. 1992), with an average of 35.9 °C (Table 2.3), depending on shea origin and processing method. Bonkoungou (1987) stated that a melting point close to body temperature is an attribute which makes the butter particularly suitable as a base for ointments and medicines.

The insoluble impurities of shea butter reflect the presence of unwanted components in the butter. Greenwood (1929) found that the insoluble impurities varied from 0.1 % to 0.4 % while the Group of Research Technology Exchange (GRET) reported in their bulletin of 2007 that the insoluble impurities ranged from 0 % to 3.5 % in shea butter extracted by a centrifugal process (Table 2.3). Cosmetic and food industries have set 0 % and less than 0.2 %, respectively, as maximum limits for insoluble impurities of shea butter (Kassamba 1997).

The colour of shea butter is reported to vary from white to gray with many nuances. Kar and Mital (1981) reported that the final shea butter colour is related to the quality of the kernels processed. The presence of fungal infection (visible as black nuts) increases the darkness of the butter; this can be prevented or reduced by more efficient drying and roasting techniques. Chukwu and Adgidzi (2008) found that the colour of shea butter varies, depending on the processing technique, in particular on the temperature used during processing. Some roots or bark of *Cochlospermum tinctorium* are often used to improve shea butter colour.

2.6. TRIGLYCERIDES AND FATTY ACIDS IN SHEA BUTTER

Kapseu et al. (2001) and Di Vincenzo et al. (2005) identified three groups of triglycerides in shea butter: polyunsaturated, di-unsaturated and mono-unsaturated; no saturated triglycerides were reported (Table 2.4). The main polyunsaturated triglyceride was OOO (10.8 %), while the principal di-unsaturated and mono-unsaturated were SOO (35.2 %) and SOS (40.4 %), respectively. Maranz et al. (2004b) assessed the variations in fat composition across the *Vitellaria* species distribution range and found that the main triglycerides in shea butter were SOS and SOO. SOS ranged from 13 % of total triglycerides in Ugandan shea butter to 45 % in Burkina Faso shea butter; while SOO was highest (28-30 %) in Uganda and some Malian shea butter. The SOS to SOO ratio is an important indicator for the melting point of a plant fat.

Kapseu et al. (2001) and Maranz et al. (2004b) used the equivalent carbon number procedure and HPLC analysis to determine triglyceride composition while Di Vincenzo et al. (2005) used a gas chromatograph to identify the triglycerides.

Table 2.4: Composition (%) in triglycerides of shea butter

Polyunsaturated									Di-unsaturated				Mono-unsaturated			References
SLiLi*	OOLi	POLi	OOO	SLiO	LiLiLi	OLiO	LiLnLi	PLiP	POO	PLiS	SOO	AOO	PPS	POS	SOS	
	2	2.6	7.8	10.5	-	-	-	-	2.5	-	35.2	-	0.5	8.5	32.6	Kapseu et al. 2001
0.6	-	-	10.8	5.2	1.7	1.6	0.3	0.1	3.1	1.5	26.7	1.2	-	5.3	40.4	Di Vincenzo et al. 2005

*S: Stearic, Li: Linoleic, O: Oleic, P: Palmitic, Ln: Linolenic, A: Arachidic

Fatty acid analysis shows great variability in shea butter among the reported values (Table 2.5). After screening 150 samples of shea kernels from different origins, Di Vincenzo et al. (2005) showed that shea butter fat is characterized by 16 saturated and unsaturated fatty acids, but five of them (oleic, stearic, palmitic, linoleic and arachidic) are the most dominant. The major fatty acid reported by different authors is oleic acid, which ranges from 37.2 % (Ugese et al. 2010) to 60.7 % (Akihisa et al. 2010b) with an average of 49.3 %. The second fatty acid is stearic acid, which varies from 29.5 % (Okullo et al. 2010) to 55.7 % (Akihisa et al. 2010b). Certain authors (Maranz et al. 2004b, Di Vincenzo et al. 2005, Akihisa et al. 2010b) found that oleic acid is dominant in butters from Uganda while stearic acid is dominant in samples of West Africa provenances. Concerning the palmitic acid content, the highest content (7.5 %) was reported by Okullo et al. (2010) and the lowest (3.4 %) by Di Vincenzo et al. (2005), the average is 4.4 %. The reported linoleic acid content ranges from 5.5 % (Mendez and Lope 1991) to 7.9 % (Mbaiguinam et al. 2007) with an average of 6.6 %. Maritz et al. (2006) reported that the linoleic acid is an essential fatty acid that is vital in nutrition because it intervenes in the fabrication of the cell membrane and cannot be synthesized by the body. According to Maranz and Wiesman (2004) the linoleic acid content of 6-8 % makes shea oil a moderate source of essential fatty acids in the human diet. As reported in Table 2.5, the content of arachidic acid varies from 0.6 %. (Mendez and Lope 1991) to 1.8 % (Akihisa et al. 2010b); and linolenic acid ranges from 0.2 % (Tholstrup et al. 1995) to 1.6 % (Tano-Debrah and Ohta 1994). Maranz and Wiesman (2004) reported that the large variability in fatty acid profiles indicates that shea butter is not a single uniform product across the continent. For example, Malian shea butter has more resemblance to cocoa butter while Ugandan shea is more comparable to olive oil, due to its high oleic content.

For all authors, fatty acid methyl esters were prepared by KOH methylation and fatty acid profiles were determined by gas chromatography.

Table 2.5: Main fatty acids content of the shea butter

Fatty acid	Min	Average	Max	References
	g fatty acid/100 g of fat			
Palmitic 16:00	3.3	4.4	7.5	(Tano-Debrah and Ohta 1994, Tholstrup et al. 1994, Alander and Andersson 2002, Maranz et al. 2004b, Di Vincenzo et al. 2005, Mbaiguinam et al. 2007, Letchamo et al. 2007, Womeni et al. 2007a, Akihisa et al. 2010b, Okullo et al. 2010, Ugese et al. 2010)
Stearic 18:00	29.5	40.4	55.7	(Kershaw and Hardwick 1981, Tano-Debrah and Ohta 1994, Tholstrup et al. 1994, Kapseu et al. 2001, Alander and Andersson 2002, Maranz et al. 2004b, Di Vincenzo et al. 2005, Mbaiguinam et al. 2007, Letchamo et al. 2007, Akihisa et al. 2010b, Okullo et al. 2010, Ugese et al. 2010)
Oleic 18:01	37.2	49.3	60.7	(Kershaw and Hardwick 1981, Tano-Debrah and Ohta 1994, Tholstrup et al. 1994, Kapseu et al. 2001, Alander and Andersson 2002; Maranz et al., 2004; Di Vincenzo et al. 2005, Mbaiguinam et al. 2007, Letchamo et al. 2007, Akihisa et al. 2010b, Okullo et al. 2010, Ugese et al. 2010)
Linoleic 18:02	4.3	6.6	8.0	(Mendez and Lope 1991, Tano-Debrah and Ohta 1994, Tholstrup et al. 1994, Kapseu et al. 2001, Alander and Andersson 2002, Maranz et al. 2004b, Di Vincenzo et al. 2005, Mbaiguinam et al. 2007, Letchamo et al. 2007, Akihisa et al. 2010b, Okullo et al. 2010, Ugese et al. 2010)
Linolenic 18:03	0.2	0.4	1.7	(Tano-Debrah and Ohta 1994, Tholstrup et al. 1994, Akihisa et al. 2010b)
Arachidic 20:00	0.8	1.3	1.8	(Kapseu et al. 2001, Maranz et al. 2004b, Di Vincenzo et al, 2005, Letchamo et al. 2007, Akihisa et al. 2010b, Okullo et al. 2010)

2.7. THE UNSAPONIFIABLE FRACTION OF SHEA KERNELS AND BUTTER

2.7.1. Triterpene alcohol compounds

The main components of the unsaponifiable fraction are triterpene alcohols. Peers (1977) reported that the most characteristic tritrepene alcohols of the unsaponifiable fraction of shea butter were α-amyrin (26.5 %), β-amyrin (10.2 %), lupeol (21.7 %) and butyrospermol (25 %), most of which occur as acetic acid and cinnamic acid ester (Table 2.6). According to Alander and Andersson (2002), the α-amyrin content was 40-50 %, the β-amyrin content 5-10 %, the lupeol content 10-20 % and the butyrospermol content 15-25 %. Akihisa et al. (2010a) assessed the triterpene alcohols in shea nuts from seven African countries and showed 4 triterpene acetates (α-amyrin acetate, β-amyrin acetate, lupeol acetate and butyrospermol acetate) and 4 triterpene cinnamates (α-amyrin cinnamate, β-amyrin cinnamate, lupeol cinnamate and butyrospermol cinnamate). Di Vincenzo et al. (2005) analyzed the percentages of acetyl and cinnamyl triterpene esters and showed strong regional affinity, with the highest values found in Nigerian provenances and the lowest values in Ugandan butters. Combination of these data suggests that West African provenances had significantly higher levels of both acetyl and cinnamyl triterpenes than shea butter from East Africa.

Table 2.6: Main compounds of Triterpene alcohols of shea butter

α-amyrin (%)	β-amyrin (%)	Lupeol (%)	Butyrospermol (%)	References
26.5	10.2	21.7	25	Peers 1977
40-50	5-10	10-20	15-25	Alander and Andersson 2002
31.3-41.1	8.2-13.2	17.5-25.1	14.9-26.3	Akihisa et al. 2010a

2.7.2. Tocopherol content

Maranz and Wiesman (2004) evaluated the tocopherol content of shea butters from 11 African countries by HPLC and found high variability between provenances and a significant effect of climate on the α-tocopherol levels. They found that the tocopherol content (α, β, γ, and δ) ranged from 29 to 805 μg/g; and the main

tocopherol was α-tocopherol with 64 % (112 µg/g), followed by γ-tocopherol (15 %), δ-tocopherol (14 %) and β-tocopherol (7 %). They stated that the α-tocopherol content appeared to be directly related to the temperature of the climatic zone from which the butter originated. The amount of both α-tocopherol and total tocopherols in shea butter increases with the temperature. Also, several factors linked to environmental conditions, storage period of the oil and genetic profile have been reported to cause variation in α-tocopherol. It has been reported that α-tocopherol always increases with temperature during seed maturation and also with drought (Kornsteiner et al. 2005).

2.7.3. Phenolic compounds

Maranz et al. (2003) identified and quantified eight catechin compounds in shea kernels from 40 shea tree provenances from 10 African countries by Liquid Chromatography and Mass Spectrometry. The mean kernel content of the eight catechin compounds was 4000 ppm (0.4 % of kernel in dry weight), with a 2100-9500 ppm range. They reported that among the six major phenolic compounds, gallic acid was the major phenolic compound, comprising an average of 27 % of the measured total phenols and exceeding 70 % in some populations (Figure 2.1). They found a wide variation of phenolic compound proportion across the countries, and they also reported that the amount of phenolic compounds followed a parabolic curve with high content occurring under both cool, wet and hot, dry conditions and low amount under unstressed, mesic growth conditions. Thus, the overall concentration of phenolic compounds in shea kernels may be linked to the level of environmental stress in the source population, with the highest phenolic concentrations occurring in *Vitellaria* trees at the upper and lower temperature limits of the species. This phenomenon has been reported in other species like olive (*Olea europaee*) (Patumi et al. 2002, Mulinacci et al. 2001). However, Shahidi and Alexander (1998) and Yang et al. (2001) reported that the compounds from the catechin family in shea kernels were similar to those found in green tea, which has gained wide attention recently as an antioxidant-rich and healthy beverage.

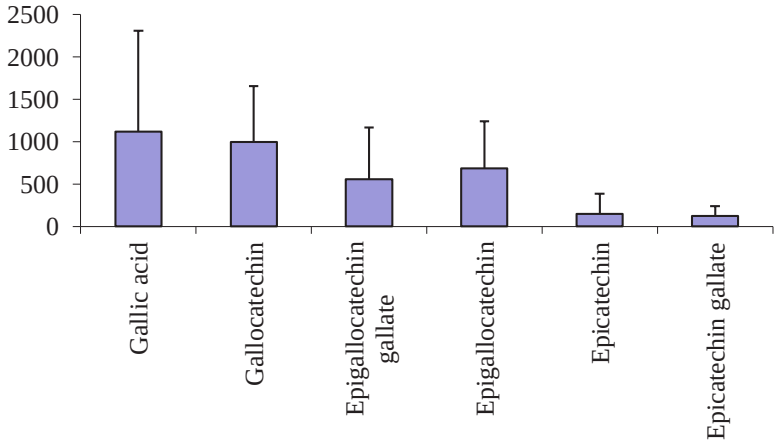

Figure 2.1: Concentrations (Parts per Million) of Phenolic compounds in shea kernels
Error bars represent standard deviation
Source: Maranz et al. 2003

In the same study, Maranz et al. (2004b) have extracted a total polyphenol in some samples of shea butter by colorimetric analysis using the Folin-Ciocalteu reagent method of Gutfinger (1981). The different samples of shea butter were extracted by hexane and the authors found an average of 97 ppm of total polyphenols, with the values for different provenances varying between 62 and 135 ppm. These values indicate that 90-98 % of the potential phenolic content of shea butter is lost in hexane extraction of shea kernels.

2.7.4. Sterol content

The unsaponifiable fraction of shea butter contains a small fraction of sterols, and few authors have investigated this aspect. Peers (1977) reported two sterol compounds in shea butter: stigmasterol and Δ7-stigmasterol. In addition to these compounds, Njoku et al. (2000) identified β-sitosterol and cholesterol (Table 2.7). According to Li and Sinclair (2002) *β*-sitosterol, campesterol, and stigmasterol are the main sterols in plants and constitute bioactive compounds that can decrease plasma/serum levels of lipids and lipoprotein lipids.

Table 2.7: Sterol contents of shea butter

Stigmasterol (mg/100 g)	β-Sitosterol (mg/100 g)	Δ7-Stigmasterol (mg/100 g)	Cholesterol (mg/100 g)	References
1.74	-	2.01		Peers 1977
0.5	0.4	-	0.2	Njoku et al. 2000

2.8. DISCUSSION

2.8.1. Variation in reported data

This review shows that the reported values of nutrient contents of shea products (pulp, kernels and butter) vary greatly. The causes of these variations are well known and most authors have worked on them. Variations are first due to the different provenances of the samples, the age of the sample, the climatic conditions, the genetic variation, and the soil structure and its chemical composition. Variation can also be attributed to the methods of analysis such as in the case of the determination of the carbohydrate content, which was determined by difference in one case and by a colorimetric method in the other case. In addition, another cause of variation is linked to shea butter composition and this is due to the wild nature of the shea tree and the wide range of its distribution as well as the different methods extracts the butter.

2.8.2. Antioxidant and anti-inflammatory effects of shea butter

The most valued product among the shea tree products is the shea butter extracted from the kernels. The majority of this fat is consumed directly at home as cooking oil and food accompaniment. This butter has been found to have high levels of tocopherols constituents, with significant regional variation in the content of α-tocopherol. In addition, shea butter contains some polyphenols and its concentration depends of the extraction technique. Then, in order to retain higher levels of phenolic compounds in shea butter, the extraction and refining processes will need to be modified. However, both of tocopherol and polyphenol constitute some anti-oxidants and consuming antioxidant-rich foods can contribute to the prevention of oxidation in the human cell, hence of some diseases. In general, antioxidants such as

α-tocopherol can be responsible for reducing degenerative diseases and also for mopping up free radicals responsible for oxidative damage of cell membranes, skin and causing of cancer. Since α-tocopherol is one of the groups of fat soluble vitamin E compounds that cannot be synthesized by animal cells, it must be obtained from plant sources through the diet (Kornsteiner et al. 2005). Because of their vital role in nutrition, the presence of α-tocopherol in shea butter makes it an important fat especially in human diet, nutrition and health.

The non-glyceride constituents of shea butter permit its use in skin care products and cosmetic product formulations. Most of the non-glyceride constituents are triterpene alcohols of cinnamates, which possess anti-inflammatory effects, especially lupeol and α/β amyrin in their esterified forms (Alander and Andersson 2002). Some anti-inflammatory activities against tetradecanoylphorbol acetate (TPA) induced inflammation in mice were reported by Akihisa et al. (2010a), who also noticed that the triterpene cinnamate isolated from shea fat could be valuable as chemopreventive agents in chemical carcinogenesis. Although these compounds can be found in other plants, shea kernels are a particularly attractive source due to their high levels of triterpene alcohols (up to 6.2 % of unsaponifiable of fat). In addition, triterpene alcohol esters are useful in high-performance skin care products such as sunscreen and suncare products because of the combination of its anti-inflammatory action and protease inhibiting effects (Alander 2004). With the findings of Di Vincenzo et al. (2005), the shea butter from West Africa had significantly higher levels of both acetyl and cinnamyl triterpenes than that of East Africa. Vissers (2000) and Maranz et al. (2003) reported that these results should be of significant interest to the cosmetic and pharmaceutical industries. The good stability and the inherently good formulating properties associated with shea butter in general open up a number of possibilities, extended by the variety of derived products that can be obtained from this well researched raw material.

2.8.3. Analysis of the main unit operations of shea butter processing

The traditional extraction techniques for shea butter have many unit operations which have an impact on the quality of the butter. The boiling of the depulped shea fruit is generally done during 15-60 minutes to inactivate the enzymes responsible for hydrolysis of the fatty acids, and facilitate shelling. If the boiling time is too short, shelling becomes difficult because latex appears on the kernels, binding

them to the shells, and enzymes are not inactivated. The direct exposure of the nuts/kernels to the sun for drying is one of the handicaps of shea butter production because it takes several days (7-15 days) and in the meantime the nuts are subjected to the prevailing climatic conditions with the risks of pollution and hydrolysis of fatty acids by lipases, which leads to increasing amounts of FFA in the product. Bup et al. (2008) showed that shea kernels dried without direct exposure to the sun yielded butter that was suitable for the standards for cosmetic and pharmaceutical uses. The storage of the kernels is not included directly in the shea butter extraction process, but considering the annual or seasonal gathering of the fruits, the storage of nuts/kernels is inevitable for butter extraction around the year. The kernels are usually stored for 1 to 12 months in bags or a granary before export or further use (Honfo et al. 2011). Most storage conditions that are used at present could lead to germination and infestation by microorganisms and birds. The germination of kernels is due to the bad drying of kernels before storage. According to processors, the roasting of the crushed kernels is generally done for 30-60 minutes to facilitate fat extraction and improve the sensory characteristics of the butter (Honfo et al. 2011). Failed to control this operation could lead to cumbersome volatile compounds in the product. Bail et al. (2009) compared the volatile profile of different shea butters and reported that processing steps including drying of kernels before producing the fat and additional roasting procedures influence shea butter volatile compounds significantly. Most of these volatile compounds investigated by Bail et al. (2009) are composed of fatty acids degradation products such as acetic and hexanoic acid; carbonyl compounds (hexanal, heptanal, trans-2-heptenal, 2,4-heptadienal), 2-pentylfurane; and processing compounds such as furfural as well as glycerol. Insufficient heating during the roasting may prevent the oil from attaining the maximum flow during extraction and, at a too high temperature, can also reduce the yield of oil. Finally, the storage of the shea butter is done under bad conditions; it is one of the key causes of its quality deterioration; for example, hydrolysis and oxidation of fatty acids. Some undesirable volatile/aroma compounds could also be produced in shea butter during different storage conditions.

2.8.4. Contribution of shea pulp to Recommended Daily Intake

In the following calculation, digestibility and bioavailability could not be taken into account, because of lack of data. Therefore, the values given should be seen as maximum values; in reality they will be lower.

The vitamin C content (196.1 mg/100 g) of the shea pulp has been reported by Emorosele et al. (1991). A comparison with the Recommended Daily Intake (RDI) for children (4–8 y) is presented in Table 2.8. Consumption of 50 g/day of pulp by a child (4–8 y) will cover 332 % of the RDI. On the other hand, the consumption of 15 g of shea pulp by children is enough to cover the RDI for vitamin C. Considering the lowest reported values for the macro and micronutrients, the consumption of 100 g of shea fruit pulp will cover 6.2 % of the RDI for carbohydrates; 23.1 % of the RDI for protein; 4.2 % of the RDI for Fe, 8.5 % of the RDI for Mg; and 0.3 % of the RDI for Ca.

Table 2.8: Shea pulp composition with the recommended daily intake (RDI) for children 4-8 years

Nutrients	Energy	Carbohydrates		Protein		Ca		Fe		Mg		Vit C
RDI for children (g/day)	1710 (kcal/day)	130	130	19	19	0.8	0.8	0.01	0.01	0.13	0.13	0.025
	kcal/100 g	Highest*	Lowest*	highest	Lowest	highest	Lowest	highest	Lowest	highest	Lowest	
Pulp composition (g/100 g)	179.5	37.2	8.1	5.6	4.4	0.43	0.003	0.016	0.0004	0.13	0.01	0.1661
% RDI covered by consumption of 50 g/d	5.2	14.3	3.1	14.7	11.5	26.6	0.2	80.0	2.1	49.6	4.3	332.2
% RDI covered by consumption of 80 g/d	8.4	22.9	4.9	23.6	18.4	42.6	0.3	128.0	3.4	79.4	6.8	531.5
% RDI covered by consumption of 100 g/d	10.5	28.6	6.2	29.5	23.1	53.3	0.3	160.0	4.2	99.2	8.5	664.4

Source: Recommended Daily Intakes for individuals for Energy: http://www.fnri.dost.gov.ph/reni/renitable1.htm , 03/11/2010.
Source: Over Recommended Daily Intakes for individuals: http://www.iom.edu/Global/News%20Announcements/~/media/Files/Activity%20Files/Nutrition/DRIs/DRISummaryListing2.ashx, 03/11/2010
*Highest and lowest values reported by different authors for nutrient composition of shea pulp

Similarly, the consumption of 50 to 100 g of shea pulp by a pregnant woman will cover 97.7 to 195.4 % of her RDI of vitamin C (Table 2.9). As mentioned for the children, the coverage of the macro and micronutrients will be possible when the lowest reported values are considered. Then, the consumption of 100 g of the pulp will cover 4.6 % of the RDI for carbohydrates; 6.2 % of the RDI for protein; 1.6 % of the RDI for Fe; 0.3 % of the RDI for Ca; and 3.2 % of the RDI for Mg.

Table 2.9: Shea pulp composition with the recommended daily intake (RDI) for pregnant women (19-30 years)

Nutrients	Energy (kcal/day)	Carbohydrates		Protein		Ca		Fe		Mg		Vit C
RDI for pregnant women (g/day)	2240	175	175	71	71	1	1	0.027	0.027	0.350	0.350	0.085
	kcal/100 g	Highest*	Lowest*	highest	Lowest	highest	Lowest	highest	Lowest	highest	Lowest	
Pulp composition (g/100g)	179.5	37.2	8.1	5.6	4.4	0.43	0.003	0.016	0.0004	0.13	0.01	0.1661
% RDI covered by consumption of 50 g/d	4.0	10.6	2.3	3.9	3.1	21.3	0.1	29.6	0.8	18.4	1.6	97.7
% RDI covered by consumption of 80 g/d	6.4	17.0	3.7	6.3	4.9	34.1	0.2	47.4	1.2	29.5	2.5	156.3
% RDI covered by consumption of 100 g/d	8.0	21.3	4.6	7.9	6.2	42.6	0.3	59.3	1.6	36.9	3.2	195.4

Source: Recommended Daily Intakes for individuals for Energy: http://www.fnri.dost.gov.ph/reni/renitable1.htm , 03/11/2010.
Source: Over Recommended Daily Intakes for individuals: http://www.iom.edu/Global/News%20Announcements/~/media/Files/Activity%20Files/Nutrition/DRIs/DRISummaryListing2.ashx , 03/11/2010.
*Highest and lowest values reported by different authors for nutrient composition of shea pulp

The energy content is low for the RDI for both children and pregnant women. The consumption of 50 g of shea pulp by children and pregnant women covers 5 % and 4 %, respectively, of their required energy intake.

2.9. CONCLUSIONS AND RECOMMENDATIONS

To date, research on *Vitellaria* products (fruit pulp, kernels and butter) has been fragmentary and undertaken mostly on a local and national basis. The literature review shows a wide variation of research on shea products with a fair number of investigations in a certain field such as the macro and micronutrient composition of shea pulp and butter, tocopherols and sterols contents of the non-glyceride part of shea butter. Despite this variability, the pulp is very rich in vitamin C and the kernels in fat (butter). The shea butter will have some antioxidant and anti-inflammatory activities even if most of this butter is extracted by traditional methods. Of greater interest is the very active level of research on the uses of shea butter in the medicinal, foods and cosmetics industries, as evidenced by a steady and current flow of research publications in these fields. Further research is necessary to improve the quality of the butter extracted by traditional techniques. Some of the possible solutions are highlighted below:

Further research is necessary to improve the sun drying and the storage conditions of the nuts/kernels, to enhance the processing and the quality of the butter in order to satisfy the international demand, to provide more information about the fruit pulp consumption. In addition, more attention should be given to the accuracy and precision in analyses in order to get more reliable information about biological variation of shea products.

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Chapter 3

Indigenous knowledge of shea processing and quality perception of shea products in Benin

F.G. Honfo, A.R. Linnemann, N. Akissoe, M.M. Soumanou, M.A.J.S. Van Boekel
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Abstract

A survey among 246 people belonging to 14 ethnic groups and living in 5 different parklands in Benin revealed different practices to process shea kernels (namely boiling followed by sun-drying and smoking) and extract shea butter. A relation between parklands, gathering period and sun-drying conditions was established. Moisture content and appearance of kernels were the selection criteria for users of shea kernels; colour was the main characteristic to buy butter. Constraints to be solved are long processing times, lack of milling equipment and high water requirements. Best practices for smoking, sun drying, and roasting operations need to be established for further improvement.

Keywords: karité, *Vitellaria paradoxa,* shea kernels, shea butter, Otamari, forest products

3.1. INTRODUCTION

In Africa, millions of poor people rely on a wide variety of forest products to sustain their livelihood. Among the forest tree species, the shea tree (*Vitellaria paradoxa*, Sapotaceae) has been identified as one of the top ten agroforestry tree species to be conserved and domesticated in West Africa (Eyog Matig et al. 2002), and it constitutes a key economic species used daily in African savannah areas (Kater et al. 1992, Boffa et al. 2000). The species is known to occupy a 5000 km stretch of African savannah from Senegal to Ethiopia and Uganda (Lovett and Haq 2000b). Shea trees commonly occur around human habitations and may sometimes constitute more than 80 % of the woody biomass in farmers' field (Lovett and Haq 2000a). The popularity of the shea tree among indigenous people is due to its various uses. The leaves and roots have various medicinal applications (Boffa et al. 2000). The wood is heavy and invaluable in construction works and in the production of household and farm implements. It is also used as a fire wood and its charcoal is particularly valued by blacksmiths (Schreckenberg 2004). Shea fruit pulp is taken for its laxative properties (Soladoye et al. 1989) aside from containing sugars, protein, calcium, ascorbic acid and iron (Maranz et al. 2004a).

The economic importance of the species is linked to the fat extracted from its kernels, which has a significant role in the local and national economy of the regions where the tree is encountered. About 650 000 tons of shea nuts are produced annually from the main producing countries of Ghana, Benin, Burkina Faso, Togo, Côte d'Ivoire, Mali and Nigeria (CNUCED 2006), of which an estimated 10 % to 30 % is exported specifically to Europe, Asia, and America (Lovett 2004). A major part of this fat is used in the food industry as cocoa butter substitute or improver because of its high content of stearic-oleic-stearic triglyceride (16-45 %), and another part is used for cosmetic and pharmaceutical purposes due to the high percentage (5-17 %) and composition of its unsaponifiable fraction, which consists of, among others, triterpenes, tocopherols, polyphenols, sterols, karitenes (Honfo et al. 2014). In African producer nations, shea fat is mostly extracted by the traditional way and it is used in cooking, as illuminant, as well as in soap and pomade preparations (Hall et al. 1996). Besides, cosmetic industries in these countries are also finding it invaluable in skin and hair cream formulations (Boffa et al. 1996).

The techniques to process the shea fruit into butter involve many operations, which vary throughout the regions where shea is produced and influence the quality of the butter. Several authors (UNIFEM 1997, Kapseu et al. 2002, Elias and Carney 2004, CNUCED 2006, Mbaiguinam et al. 2007, Dandjouma et al. 2009) have described technologies to process shea butter. Other authors (Hyman 1991, Bruinsma 1998, Olaoye and Babatunde 2001, Coulibaly et al. 2004) have developed and proposed several labour-saving technologies to facilitate some of the main operations. Moreover, enzyme-assisted aqueous extraction of shea butter was developed to increase fat extraction in rural shea kernel processing (Tano-Debrah and Ohta 1995). However, in spite of efforts to reduce the labour involved in processing and to improve the quality of the shea products, some problems persist. Improvement of traditional techniques and end products, and production of added value products for a larger market are expected to increase the income of rural, poor populations because of the existing market opportunities. The development of any technology to improve the quality of the main commercially interesting shea products (i.e. kernels and butter), has to take the indigenous practices into account to ensure dovetailing with local production circumstances. To date, no proper inventory of indigenous knowledge on processing of shea products in Benin and the quality of end products exists. The present study attempts to complete and update the existing data. Specifically, this research has (1) recorded the different traditional methods to process shea fruits in Benin, (2) assessed their constraints, and (3) analyzed the quality perception of shea products among the actors.

3.2. MATERIALS AND METHODS

3.2.1. Study area and sampling of respondents

Studies on shea tree, in particular those of Gnangle (2005) and Koumassa (2010), have identified five parklands in Benin, namely Bohicon, Save, Parakou, Bembereke and Kandi, and revealed that 3 %, 15 %, 27 %, 27 % and 28 %, respectively, of the population in these parklands is involved in production and processing of shea products. To determine the adequate size for sampling respondents for our survey among the shea actors per parkland, the following formula was used: $N_i = \frac{4P_i(1-P_i)}{d^2}$ where N_i is the total number of shea actors to be surveyed in parkland i, P_i is the proportion of shea actors found in previous studies

in parkland i, and d is the expected error margin in the conclusion, which was fixed at 0.1 (Dagnelli 1998).

According to this formula, 10 people were selected in Bohicon, 42 people in Save, 64 in Parakou, 64 in Bembereke, and 66 in Kandi, giving a total of 246 respondents.

Next, one location in the parkland of Bohicon and two locations in each of the four other parklands were chosen on the basis of the importance of shea fruit collection, butter processing and their socio-cultural diversity (Figure 3.1). The number of respondents needed in each location was calculated on the basis of its population size with the following formula: $T_j = \frac{N_j \times X_j}{\sum X}$ where T_j is the sample size in the location j, N_j is the total number of shea actors to be surveyed in parkland j, X_j is the population size in the location j, and $\sum X$ is the sum of the two population sizes selected in parkland j.

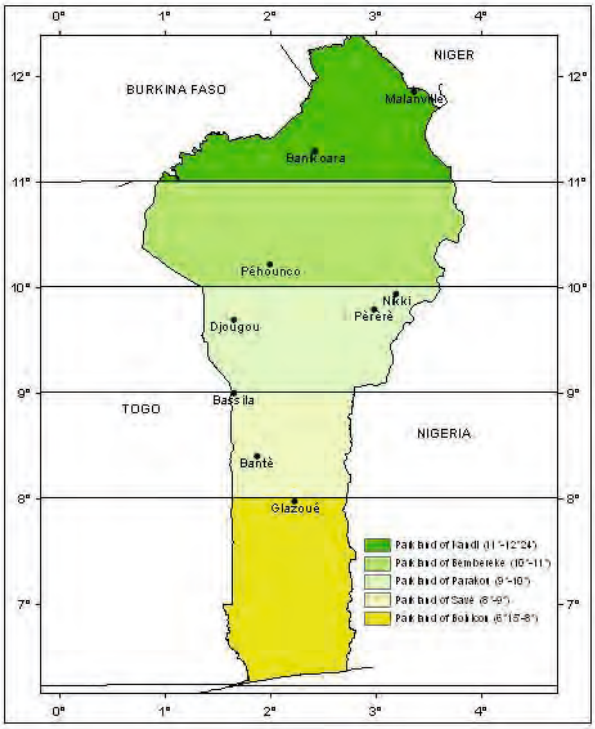

Figure 3.1: Map of Benin showing the parklands and study locations

Four types of actors involved in the shea chain were randomly selected in each location (i.e., gatherers of shea fruit in the field, processors of shea butter, traders of butter and users of butter). In summary, for all parklands, 64 gatherers, 66 processors, 60 traders and 56 users were interviewed.

3.2.2. Data collection

Surveys were conducted in August and September 2010. Respondents of both genders (234 women and 12 men) with various ages and diverse educational backgrounds were randomly selected and interviewed from 14 different ethnic groups (Bariba, Dendi, Gando, Gourmantche, Fulani, Lokpa, Mokole, Nagot, Peulh, Pilapila, Otamari, Taneka, Wama, Yom). One percent of the respondents were younger than 20 years and 27 % were older than 50 years; 80 % of respondents had no formal education and 17 % had finished primary school. Specific questionnaires were developed for each type of actor and tested before the survey.

The questionnaires included the following aspects:

- *At the gatherers' level*: Varieties of shea tree, periods and places of fruit gathering, parameters considered when gathering fruits, constraints in collecting fruits, processes to extract the kernels from the nuts, price variation of the kernels between years, characteristics of good quality of nuts, storage conditions of kernels, sales market of kernels, purchasers' preferences, different end uses of the butter.
- *At the processors' level (individual and group)*: Sources of the kernels, parameters considered when purchasing kernels, high and low availability periods of kernels, quality perception of kernels (drying degree, appearance, colour, size) characteristics of a kernel of good quality, processing techniques to extract the butter, frequency of butter production, constraints in butter production, storage conditions of butter, purchasers' preferences (colour, odour, texture), different end uses of the butter.
- *At the traders' level*: Places of purchase and sales of butter, periods of high and low availability, quality criteria of butter (colour, odour, texture), criteria to determine butter price, storage conditions of butter, purchasers' preferences, knowledge about the norms on shea butter, different end uses of the butter.

– *At the users' level*: Places of purchase, availability of butter, quality criteria for butter (colour, odour, texture), different end uses of butter and frequency of use.

Interviews were conducted in the language or dialect that was best understood by the respondents with translation when necessary.

3.2.3. Data analysis

Statistical analyses were performed using SAS 9.1 software. Principal Component Analysis (PCA) was performed to link processing techniques to parklands or ethnic groups. Only data provided by gatherers were used for PCA. Correlations were used to evaluate the relation between different variables such as ethnic group, parkland and unit operations to extract the kernels from the shea fruit.

3.3. RESULTS AND DISCUSSION

3.3.1. Shea products and their characteristics

Among the different ethnic groups involved in the gathering of shea fruits, the Fulani reported to know about trees producing fruits with sweet pulp. The sweet fruit pulp is consumed by the farmers in the fields. Besides, fruits with sweet pulp are often sold in piles of 10 fruits on the local markets. However, in most cases, the fruit pulp is just removed to get the nuts. Shea kernels are extracted from the nuts and their colour is often brown or dark brown, depending on the extraction method. The kernels are sold or stored for export or for further use. Shea butter is the cooking fat of the rural populations in all parklands except Bohicon. It results from the processing of the kernels and is shaped as a ball, in case of the Yom ethnic group; as an elongated form, in case of the Bariba ethnic group; and as a snail form, which is specific for the Fulani ethnic group (Figure 3.2). The butter is sold on the local and regional markets in the shapes that are specific for each ethnic group and at prices from 25 FCFA (€ 0.04) to 100 FCFA (€ 0.15), at average weights of 50 g and 150 g respectively. The price is standard throughout the year, but the weight of a single piece of butter increases in periods of abundance and decreases in periods of shortage.

Figure 3.2: Different forms of shea butter

3.3.2. Processing techniques of shea kernels and shea butter

- Gathering the shea fruits

All gatherers and processors interviewed were women. The ethnic groups that were most involved in the production of shea butter were the Bariba (29 % of gatherers/processors), Fulani (22 %), Yom (14 %), and Nagot (11 %). Gathering of shea fruits is generally done by women and children early in the morning (6-9 AM) between May and September depending on the parkland. In the parkland of Bohicon, the fruit is less valued and the harvest occurs from in May-July; it takes place in May-August in the parkland of Save, during June-August in the parklands of Parakou and Bembereke, and in June-September in Kandi. The period of abundance is June-July in most of the parklands. Women collect fruits from their personal or their husband's plots and the fields belonging to their family. The fruits are picked up from the ground and 92 % of the respondents picked up all of the fruits without sorting.

- **Preserving the nuts**

After gathering, the fruits are depulped in the field and brought back home where, depending on the quantity of the fruits and the availability of the women, they are stored for 3 to 15 days before giving the nuts a preservation treatment, either by boiling followed by sun drying or by smoking (Figure 3.3). The boiling of fresh

nuts is widespread in the shea areas and was done by 97 % of respondents. Boiling duration varied from 15-60 minutes. This operation is followed by sun drying for 7-21 days. Sun drying consists of spreading the nuts on the ground until the nuts are dried, so the nuts are subjected to the prevailing weather. Smoking was done for 36 to 48 hours in a traditional cylindrical oven built from sand and wood and is specific for the Otamari ethnic group. The women, who practise this technique, prefer it because the nuts do not need to be dried before shelling. However, there is no proper control of the heat during smoking, and this may cause the incidence of burned nuts, which subsequently could lead to a final product with a burnt smell.

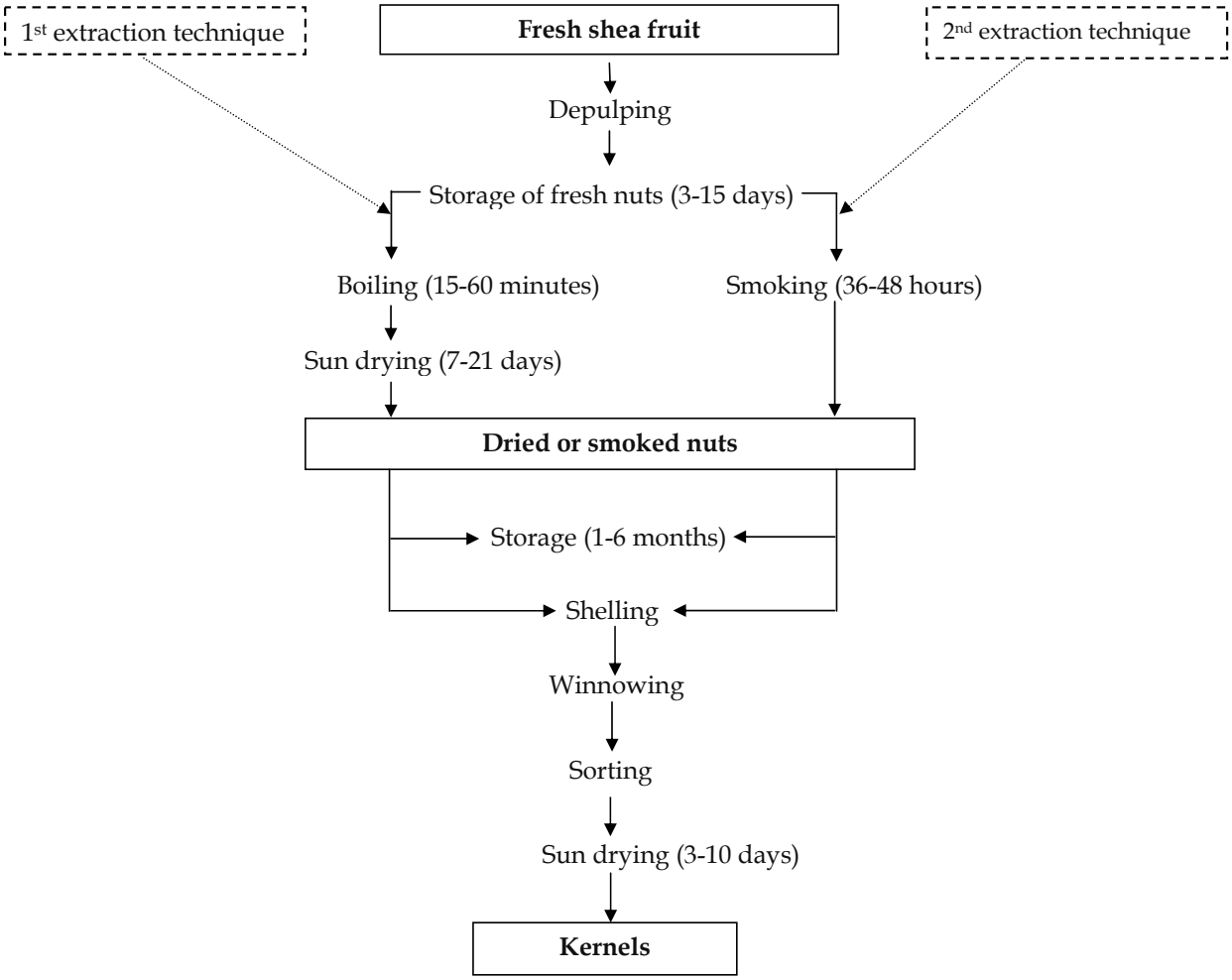

Figure 3.3: Flow chart for the local extraction of shea kernels

- **Shelling of the nuts and storage of the kernels**

The dried or smoked nuts are stored for 1 to 6 months by 20 % of the respondents, specifically in the Banikoara region (parkland of Kandi), or shelled in 80 % of the cases. Different methods are used to remove the shells, including pounding using a mortar and pestle, and cracking between two stones. Shells are also removed by trampling (Hall et al. 1996). Shelling is finished by a winnowing process. If the wind is strong enough, the pieces of shell will be blown away easily. If not, the

winnowing operation has to be repeated many times. The kernels obtained are spread on plastic or polyethylene bags or a cement platform for sun drying for 3 to 10 days before storage until further use or export. During this sun drying, the kernels are removed each night or before rainfall. Shea kernels thus obtained are stored for 1-3 months (22 % of respondents) to 9-12 months (12 %), but most commonly for 4-6 months (41 % of respondents). Most of the respondents (80 %) stored the kernels in polyethylene or jute bags, while the others used traditional baskets (9 %) or a granary (8 %). During storage, 13 % of the respondents sun dried the kernels at least once a trimester.

The different techniques to produce shea kernels involve several operations, which take place in poorly controlled conditions, leading to variation in the quality characteristics of the kernels. For instance, during the 3-15 days storage period of the fresh nuts, some physiological activities could take place, in particular hydrolysis of triglycerides, which leads to the production of free fatty acids, thereby increasing the acidity level. Guillaumin (1982) reported that during storage of oleaginous plants products at a high relative humidity, frequently an increase of the acidity of the lipid fraction is observed. According to the processors, boiling of the fresh shea nuts is generally done to inactivate the enzymes responsible for hydrolysis of the fatty acids, but also to facilitate shelling. Inadequate boiling could make the shelling difficult due to the occurrence of latex, a sticky substance which binds the shell to the kernels, and could also influence the inhibition of enzymes. The fact that drying of the nuts and the kernels is by direct exposure to the sun without removing at night, makes this operation a vulnerable step in the production chain: all gatherers interviewed found this a critical operation, essential for good kernel quality. The nuts are subjected to the prevailing weather conditions with the risks of germination and oxidation of fatty acids, which leads to an increased rancidity of the extracted fat. Bup et al. (2008) showed that shea kernels dried without direct exposure to the sun gave shea butter that meets the international standards for cosmetic and pharmaceutical uses. Drying without direct exposure is generally done in a greenhouse which offers protection against insects, rains and other contaminations. Most conditions to store the kernels at present could lead to germination and infestation by micro-organisms and birds.

- **Butter extraction**

According to the processors interviewed, most of them (91 % of respondents) gather the shea fruits, extract and store the kernels for butter processing. Processors (92 % of respondents) wash and sun-dry the kernels after storage for 4-8 hours before grinding or roasting (Figure 3.4). Two fundamentally different techniques to extract the butter were found. The first technique concerned 5 % of the processors and involved the roasting of whole kernels in ash or sand for 30-60 min, followed by pounding, and milling by a mill. The second technique implies the crushing of the kernels by a crusher (97 %) or their pounding (3 %), followed by roasting for 30-60 min and milling by a mill into a pasty material. The next stage is the mixing of the paste with warm water followed by manual churning in 98 % of the cases until the water and the fat separate. Subsequently the water is removed and the creamy fat layer is washed and heated for 1-2 hours until it is clear. The crude oil is then cooled in 74 % of the cases. In the other cases, water is added to the crude oil and the mixture is left for 1 h; the layer is separated by spoon and dehydrated by heating during 30 to 45 min. The resulting oil is clarified by sieving and cooled for 12-24 hours to get shea butter. The practice of adding water to the oil is generally done to reduce the impurities in the butter and done by women who have benefited from some training related to shea butter processing.

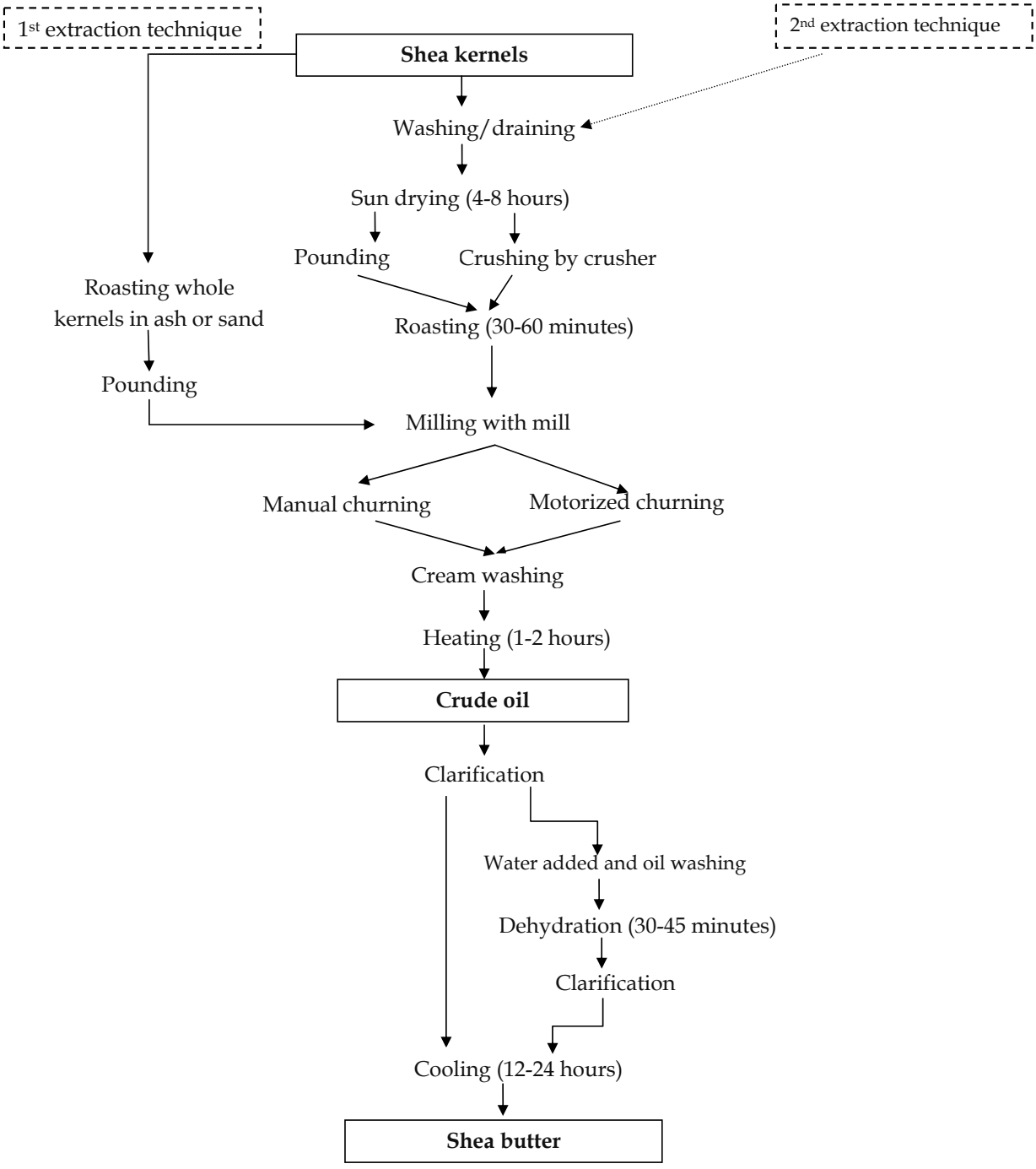

Figure 3.4: Flow chart for local processing shea butter

With respect to roasting the kernels, a practice to facilitate fat extraction and improve the sensory characteristics of the butter (Shimoda et al. 1996, Krist et al. 2006), it is known that insufficient heating may reduce the yield of oil (Krysiak and Motyl-Patelska 2005), and too high temperatures lead to undesirable volatile compounds (Krist et al. 2006). Bail et al. (2009) compared the volatile profile of different shea butters and reported that processing steps including drying of kernels before producing the fat and additional roasting procedures influence the volatile compounds in shea butter significantly.

- **Storage of shea butter**

The storage conditions of shea butter vary among the actors, with respect to packaging material as well as duration of storage (Table 3.1). Baskets lined with: teak (*Tectona grandis*) leaves, paper bags that previously contained cement or jute bags are used by 45 % of the processors and by 65 % of the traders as packaging material to store the butter, while plastic containers with a cover are used by 38 % of the processor, 23 % of the traders and the majority (66 %) of the users. Calabash containers with a cover are used to store the butter by the three types of actors; butter was also immersed in water by certain users during storage. The butter thus packaged is kept in a room or stored in market places. Traders exposed shea butter directly on their display to sell it in local markets. This presentation of shea butter was seen as a problem by some users because of the exposure to sun and dust.

Users stored shea butter for one week up to 6 months to have enough until the next production period. Most processors (77 %) store the butter for 1 to 4 weeks before selling it, and traders for 1-4 weeks (68 %) or for 2-3 months (28 %). When the butter is used as cooking fat, the storage duration is short; less than one month. However, when it is used as body or hair ointment, in soap making, and in traditional medicine, the butter is stored for 2 to 6 months.

Table 3.1: Packaging materials and duration for butter storage (as % of respondents)

		Processors (N = 66)	Traders (N = 60)	Users (N = 56)
Storage packaging	Aluminium container	3*	13	13
	Basket	45	65	0
	Calabash container	24	15	16
	Plastic container	38	23	66
	Water immersion	0	9	15
Storage duration	< 1 week	5	2	13
	1-4 weeks	77	68	39
	2-3 months	18	28	32
	4-6 months	0	2	9
	> 6 months	0	0	7

*Sum > 100 because several answers were possible for packaging materials

Quality degradation of shea butter was observed during storage. Honfo et al. (2011) found that colour, acid value, peroxide value, and iodine value of shea butter changed during storage; the colour of butter turned to white; acid and peroxide values were increased while iodine value decreased during storage; these observations were more pronounced when the storage duration was long; after 3 months for example. Undesirable volatile compounds can also be produced in shea butter during storage. Most of these volatile compounds in shea butter are degradation products of fatty acids, such as acetic and hexanoic acid; carbonyl compounds (hexanal, heptanal, trans-2-heptenal, 2,4-heptadienal), 2-pentylfurane; and processing compounds like furfural as well as glycerol (Bail et al. 2009b). Honfo et al. (2011) also reported that the degradation of shea butter quality was more pronounced in baskets lined with different materials. Plastic containers seemed to be the best packaging materials and this observation was corroborated by the respondents in the survey.

- **Use of butter**

The majority of users (84 % of respondents) of shea butter interviewed were women. Shea butter was used for cooking, skin/hair care, medicinal applications and soap making in the survey area. The use of shea butter as cooking fat for food preparation for the household or vending purposes (snacks and meals) was observed in 93 % of the cases. Some respondents used shea butter as skin/hair care (65 %) or as a medicinal ointment (43 %). Yellowish or yellow butter was frequently used for food preparation while white butter was generally used for skincare. Some consumers added onions, spices, or orange peels to shea butter to improve its smell and taste when used as cooking fat. Shea butter meant for skincare is often put into a small container and some perfumes or other body creams were added to improve the smell. Hard butter was commonly used for food preparation whereas soft butter is easy to smear on the skin. Only 7 % of respondents were non-food users, they used shea butter for medicinal purposes, as an ointment against rheumatic and joint pains and in case of dislocation, swelling, bruising or muscle ache. Besides, Pereira (1983) reported that shea butter is used to protect cowpeas (*Vigna* sp.) against insect (*Callosobruchus maculatus*) damage. He observed that a treatment with shea butter reduced the life span and fertility of the insects and hence the infestation rate.

3.3.3. Important quality criteria of kernels and butter

Quality criteria that are important in choosing shea kernels or butter are presented in Table 3.2. Drying degree of kernels and appearance are the major selection criteria mentioned by processors when they want to buy kernels. Drying degree is generally assessed by breaking the kernel and checking whether its interior does not contain any liquids. Appearance describes the integrity of kernel. Colour of kernels is another important quality characteristic for all processors, but in different degrees: 32 % of the respondents mentioned it as a very important characteristic while 29 % said it was moderately important. All respondents prefer a brown kernel colour. Kernel size and degree of boiling, assessed by the presence or absence of latex, are not the main concerns for most processors. However, 37 % of the respondents consider the degree of boiling as a quality attribute of a certain importance.

Table 3.2: Important quality criteria for processors of kernels and for traders and users of butter (as % of respondents)

	Attributes	Very important	Important	Moderately important	Not important
Shea kernels (N = 66)	Boiling degree	0	16	21	63
	Drying degree	96	5	0	0
	Appearance	70	26	5	0
	Colour	32	39	29	0
	Size	0	9	14	77
Shea butter (N = 116)	Colour	70	25	5	0
	Taste	0	7	5	88
	Odour	45	36	18	0
	Texture	8	49	17	25
	Shape	3	14	29	54

The colour of shea butter is the main quality criterion for traders and users. The colour varies from yellowish to white, which is considered to be the natural state of the butter. The majority of all respondents (61 %) preferred the yellowish or white colour (Table 3.3).

Table 3.3: Preferences with respect to butter colour (as % of respondents)

Actors	No preference	Yellowish	yellow	gray	white
Gatherers (N=64)	8	38	27	11	16
Processors (N=66)	12	35	12	9	32
Traders (N=60)	3	45	13	12	27
Users (N=56)	6	27	26	18	23
Total (246)	7	36	20	12	25

According to the traders, the yellow colour is more popular among end users. Certain respondents find yellow butter attractive. To satisfy their preferences, certain processors (12 %) used some roots or bark to get the yellow colour or to improve the butter colour. For this purpose, *Cochlospermum tinctorium* roots are usually used in the parklands of Parakou, Bembereke and Kandi by certain processors; the roots are dried and ground to powder, to be added during the boiling of shea cream. Gray butter is generally obtained during the rainy season, as the result of the darkness of kernels, when the nuts are not properly sundried. However, some buyers pointed out that the colour preference also depends on the end use by the consumers and on the availability of shea butter on the market. Odour is another important selection criterion when buying shea butter; 45 % of buyers judge it very important. The smell is a quick discriminating quality criterion that the buyers use for a rapid choice when they agree with the butter colour. Shea butter generally has a nutty smell and should be free from rancid odour. Another quality characteristic is the texture (hard or soft) of shea butter; 49% of buyers state that it is important to them. Hard butter is considered to have a low water content, which means better preservation and a higher fat content, whereas soft shea butter is chosen because it melts easily and is cheaper than hard butter. Certain buyers (25 %) do not consider the texture, and are more interested in external factors such as availability. All of the butter quality criteria depend on the way the butter has been processed, the processing period (rainy or dry season), and the storage conditions (Womeni et al. 2007a, Bup et al. 2008).

3.3.4. Relations between kernel and butter extraction, parklands and ethnic groups

Most practices to obtain the shea kernels from the fruits are similar throughout the parklands and among the ethnic groups. Principal Component Analysis (PCA) performed on the unit operations to extract shea kernels, parklands and ethnic groups showed 60.9 % of variation on the first three main axes (Figures 3.5a and 3.5b).

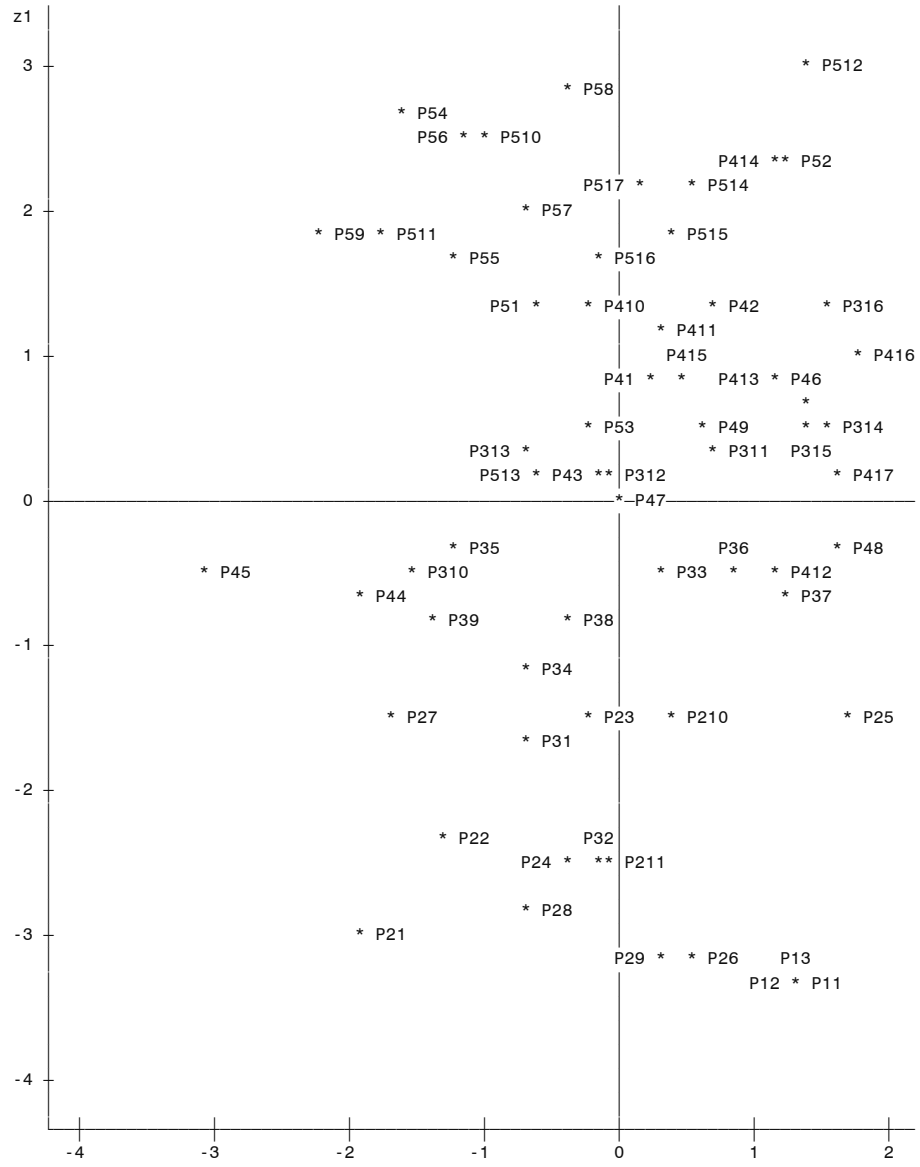

Figure 3.5a: Principal Component Analysis to reveal relations between shea parklands and unit operations of kernel extraction on axes 1 and 3.

The figure shows the relationships between the gathering period and unit operations (sun-drying conditions and kernel storage conditions) in five parklands. Parklands with similar gathering period and extraction technique are grouped together with respect to the two axes. Parklands with different gathering periods and sun-drying conditions are opposed.

Note: P = Parkland; P1 = Parkland of Bohicon; P2 = parkland of Save; P3 = Parkland of Parakou; P4 = parkland of Bembereke; P5 = parkland of Kandi; P11-P13=Number of respondents in P1; P21-P211=Number of respondents in P2; P31-P316=Number of respondents in P3; P41-P417= Number of respondents in P4; P51-P517=Number of respondents in P5

Axis 1 explained 29.4 % of the variation and mainly represented the relation between parkland, gathering period, duration of kernel sun-drying and sun-drying material (Table 3.4).

Table 3.4: Weight of main variables for each axis of PCA

Variable	Weight
Axis 1	
Parklands	0.89228
Gathering period	0.91452
Sun-drying of kernels	0.82860
Sun-drying material	0.66647
Axis 2	
Ethnic group	0.56874
Storage duration of fresh nuts	0.63949
Boiling duration of nuts	0.55030
Axis 3	
Sun-drying of nuts	0.50266
Storage duration of kernels	0.55004
Packaging material for kernels	0.46086

Note: only weight above 0.4 are reported here

The second axis (16.6 % of variation) concerns the relation between ethnic groups, storage conditions for fresh shea nuts and their boiling, while the third axis explained 14.9 % of the variation and mostly reflected the duration of sun drying of nuts and the storage conditions of the kernels. The variable related to the sun drying of nuts is present on axes 1 and 3; this variable is very important in the extraction of shea kernels.

Figure 3.5a represents the axes 1 and 3. It shows a gradual evolution of the parklands from the parkland of Bohicon (P1) to the parkland of Kandi (P5). All of the respondents of P1 are grouped at the bottom of the graph while the respondents of P5 are concentrated in the top of the graph. This means that when we move from the Centre of Benin to the North, the duration of certain units operations increases. This observation refers to the gathering period, the sun-drying of nuts and kernels, and the storage of the kernels, and is supported by positive correlations between

parkland and gathering period (*r=0.8904, p=0.0001*); parkland and duration of sun-drying of the nuts (*r=0.2976, p=0.0106*); and parkland and duration of sun-drying of the kernels (*r=0.7331, p=0.0001*).

Axes 2 and 3 in Figure 3.5b demonstrate that the Bariba, Fulani, Yom, and partially the Nagot have similar knowledge and habits with respect to certain unit operations to extract shea kernels, namely the storage of the fresh nuts, boiling, and sun-drying and storage of kernels. Most of these ethnic groups are found in all five parklands and dominate in producing shea products. They generally store shea fruits for 3-7 days, boil the nuts for 15-30 min, sun dry the kernels for 3-7 days and store the kernels in polyethylene or jute bags.

The Otamari ethnic group is totally isolated in the graph because of the specific technique used to extract the kernels from the fruits.

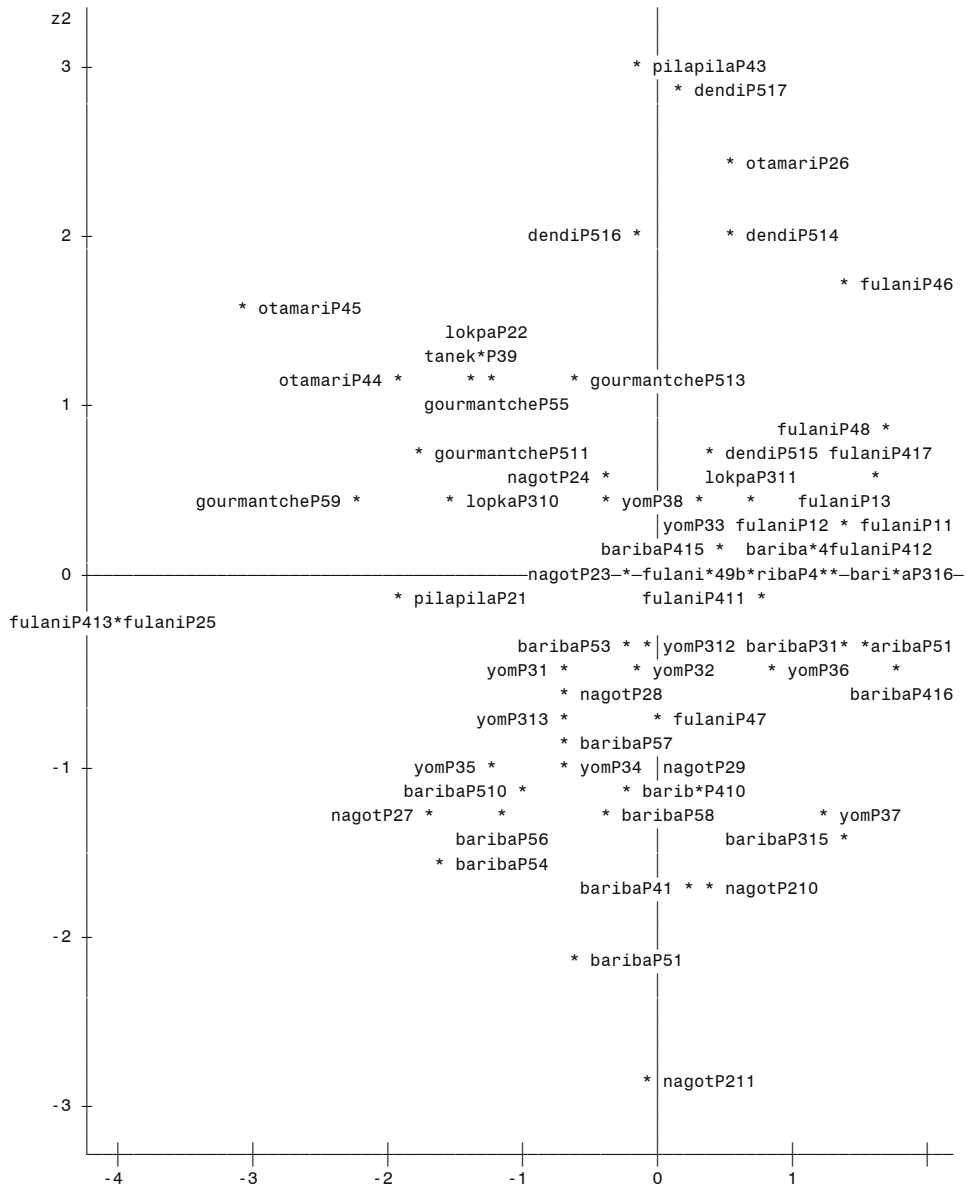

Figure 3.5b: Principal Component Analysis to reveal relations between ethnic groups and unit operations of kernel extraction on axes 2 and 3.

The figure shows the relationships between unit operations (storage duration of fresh nuts, boiling and storages conditions of dried kernels) and ethnic groups. Ethnic groups with similar boiling duration and storage conditions are grouped together with respect to the two axes. Ethnic groups with different boiling duration and storage conditions are opposed.

Note: P11-P13=Number of respondents in parkland of Bohicon; P21-P211=Number of respondents in parkland of Save; P31-P316=Number of respondents in parkland of Parakou; P41-P417= Number of respondents in parkland of Bembereke; P51-P517=Number of respondents in parkland of Kandi.

3.3.5. Constraints in shea kernels and butter processing operations

Traditional shea kernel and butter extraction operations were reported to be arduous, labour-intensive and time consuming (Kar and Mital 1981, Kapseu et al. 2002, Alonge and Olaniyan 2007). They also require large amounts of water and firewood, which are both scare and valuable commodities in the semi-arid and arid regions where the shea tree grows. From the collection of the shea fruits to the production of one kg of shea butter, 20-30 hours are spent by the processor and 8.5-10 kg of fire wood is used (Bruinsma 1998). Gatherers complain about gathering, sun-drying, and shelling. Women wake up early in the morning and trek up to 5-15 km, then carry loads of 20-30 kg back in head pans. They are exposed to hazards like scorpions and snakes, especially beyond the cultivated areas. Shelling is very tedious and when the gatherers use the stones as equipment, their hands sometimes get grazed by the stone. Some of the nuts are destroyed during the shelling process and this leads to losses of raw material for butter extraction. In addition, the shelling process includes a winnowing operation, which requires winds to blow away the pieces of shell and wind supply is not reliable.

Processors complain about pounding, milling, kneading and churning during butter extraction. To circumvent the constraints related to pounding and milling, most of the processors (97 %) use cereal mills to coarsely grind kernels. Millers often refuse grinding or leave the kernels during 2-3 days before grinding because of the undesired shea kernel colour on products milled later. Mills need to be cleaned thoroughly after milling shea kernels, and so the millers tend to charge extra to cover cleaning costs. Processors also complain about the time needed for extracting the butter and the low yield of butter. Shea kernels contain 40 %-57 % of fat (Di Vincenzo et al. 2005, CNUCED 2006); the traditional techniques extract about half of the fat of the kernel, namely 20 %-30 %. According to Olaoye and Babatunde (2001) the fat extraction yield of the artisanal method, including the use of some equipment such as a mill and press could be increased to 35 %-45 %.

Equipment like a crusher, mill, roaster and mixer have been developed for shea production, but several constraints are associated with the use of such equipment. For example, no processor uses a mixer for churning because of the high water consumption. According to the processors, the mixer utilizes 3-4 times the

quantity of water used for manual churning and the butter yield does not increase. Thus, they prefer the manual churning because of the water scarcity. During the manual churning, approximately two volumes of water are used for one volume of kernel paste. Other problems associated with the use of equipment are the constant fuel scarcity and the absence of financial resources to supports the installation of the equipment. In addition, the equipment is destined to women's associations; single processors, who are more numerous, usually have no access.

However, and irrespective all of the constraints, the production of shea kernels and butter remains traditional and unique, in that, they can be done only by women who possess knowledge of the location and history of the shea trees, the timing and process of harvesting. All of these aspects represent a knowledge that is passed through successive generations of women (Chalfin 2004). This system gives them a level of respect, authority, and control over resources that they do not possess in other sectors, as well as providing a source of cash income and fat for domestic use.

3.4. CONCLUSION

This study highlighted indigenous knowledge of shea production and processing in Benin. Many ethnic groups are involved in shea butter production, especially the Bariba, Fulani, Yom and Nagot. Apart from the Otamari ethnic group, who smoke the shea kernels before fat extraction, all other ethnic groups use boiling followed by sun-drying. Some constraints are linked to certain unit operations. Most of the butter extracted is used as kitchen fat and skin ointment in the production zones and as care pomade in all parklands. The degree of drying and kernel appearance are the most important quality criteria mentioned by the processors, while the colour of butter is the main quality criterion that traders and users utilize when buying the butter. With the exception of the use of a mill for crushing and milling the kernels, the processing operations remain traditional and variations in quality are often observed by the users. Research is advocated to reduce the arduousness and the constraints of processing by introducing reliable and adapted equipment, and also to improve the quality of shea products. As a follow-up to this survey, experimental research will be conducted to assess the quality characteristics of shea kernels and shea butter processed by the different technologies, with the

ultimate objective to determine in which way the quality of shea kernels and butter can be improved under local conditions.

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Chapter 4

Characteristics of traditionally processed shea kernels and butter

F.G. Honfo, A.R. Linnemann, N. Akissoe, M.M. Soumanou, M.A.J.S. Van Boekel
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Abstract

The traditional production of shea butter requires a heat treatment of the nuts. This study compared the end products derived by two commonly used heat treatments, namely smoking, and boiling followed by sun drying. Neither treatment influenced the moisture content of the kernels (8-10 %), but the boiling treatment resulted in more free fatty acids (FFA) (6 %) and a higher fat content (49 % dw) of kernels. A sensory panel preferred shea butter from boiled kernels because of its soft texture and intense smell. This butter also had the highest values for moisture content (2 %), unsaponifiable matter (8 %), tocopherol compounds (125 mg/g), peroxide value (8 meq O_2/kg), iodine value (53 g I_2/100 g), and FFA (2 %). Minor variations were noticed in the fatty acid profile. Aside from the use of butter from both boiled and smoked kernels for food purposes; the butter from boiled kernels will be more suitable for cosmetic

Keywords: shea butter, heat treatment, smoking, unsaponifiable matter, tocopherol

4.1. INTRODUCTION

The shea tree, also known as karité in the Francophone regions, is a tree from the African savanna zone with fruits containing a fat-rich kernel. Once extracted, this fat is locally used for various purposes, ranging from cooking, frying and soap processing to healthcare and medicinal uses (Hall et al. 1996, Alander 2004). Outside the production areas, shea butter is used for industrial applications: 95 % of exported butter is used for chocolate and confectionery products while the remaining 5 % is used for cosmetic and pharmaceutical purposes (Elias and Carney 2007, Hall et al. 1996). Consequently, shea products constitute a valuable source of income in the countries in which the tree occurs.

Shea kernels have a fat content of 40-57 % on wet weight depending on regions and species (Bup et al. 2012); the traditional extraction yield varies from 25 % to 35 % depending on the processing methods. The extraction efficiency, the quality of the end products as well as the potential use of the fat depend on the genetic diversity, the climatic conditions, but mostly on the processing conditions. As the butter is extracted from the shea kernel, the kernel quality ultimately determines the butter quality. To prevent quality defects due to different traditional methods used to extract the butter from the kernels, chocolate and food manufacturers prefer to buy the kernels than the butter. By procuring the kernels, manufacturers have full control as to the resulting products.

Shea kernels have to meet certain requirements if they are to be exported, for example, containing not more than 6 % of free fatty acid, a moisture content of no more than 7-8 % and a fat content of at least 42 % (Kassamba 1997). More specifically, in the manufacture of cocoa butter substitute for chocolate confectionary, the fat content and the quality are the most important quality attributes of shea kernels. Kernels with higher fat contents fetch higher prices in the world market and this is a premium for the exporters. In contrast, shea kernels with high moisture content (> 10 %) are not particularly suitable for butter extraction (Hall et al. 1996); they yield a butter that is less appreciated due to high enzyme activities that enhance the acidity and rancidity of the products. Acid value is one of the most important quality parameters for oil and fat. The acid value or free fatty acids (FFA) percentage is often used as a general indication of the condition and edibility of the oil (Kirk and Sawyer

1991). Fatty acids composition of a fat or oil influences their melting behaviour (Couvreur et al. 2006). One of the shea butter compounds is unsaponifiable to which antioxidant and anti-inflammatory properties are ascribed due to it tocopherol and phenolic content (Maranz and Wiesman 2004). Apart from chemical characteristics which are important for shea butter quality, sensory properties such as texture, colour and odour are also used to characterize the butter.

Over the years, various traditional methods have been developed to process fresh shea fruits into kernels and extract the butter throughout the regions where shea is produced (Kapseu et al. 2005, CNUCED 2006). In Benin, two methods that differ with respect to the kind of heat treatment are used to process the fresh nuts after gathering. This heat treatment is generally done to circumvent germination of the fresh nuts and consequently to prevent biochemical reactions that would influence the quality of butter (Kapseu et al. 2005). Depending on the type of heat treatment, sun drying is practiced to reduce the moisture content of the nuts and to facilitate the shelling operation. The practice of boiling the nuts, followed by sun drying, is widespread, whereas the practice of smoking the nuts is specific for the Otamari socio-cultural group (Honfo et al. 2012). The Otamari socio-cultural group is a minor community in Benin located in the regions where the shea tree occurs. To date, few scientific literature sources reported on the quality characteristics of shea kernels and shea butter resulting from traditional processing technologies in Benin. This study aims to fill that gap with respect to the influence that the different heat treatments might have on the quality of the kernels and the butter extracted from these kernels. The results from this research will contribute to the knowledge needed to improve current traditional processing practices and to select the best practices to produce kernels and butter for various purposes.

4.2. MATERIAL AND METHODS

4.2.1. Experimental design

Fresh shea fruits (40 kg) were gathered and depulped at Bassila (9°00 N and 1°40 E), located in the Donga Department in the North-Western part of Benin. Two different heat treatments, boiling followed by sun drying and smoking, traditionally used by the processors were used to process the fresh nuts. Two local processors for each type of heat treatment were chosen to perform the treatments. The fresh nuts

were divided into four batches. Two batches were processed by boiling during 30-45 min and sundried on a cement platform for 10-12 days before shelling (Figure 4.1). The resulting product was again sun-dried for 5 days and sorted. The sorting consists of selecting the intact kernels from the broken and damaged kernels. The other two batches were processed by smoking in a traditional oven for 48 hours at a temperature around 110-140 ^{o}C before shelling. The smoked nuts were sorted and sun-dried on a cement platform during 5 days and subsequently shelled to get kernels (Figure 4.1). For each batch, three samples of kernels (100 g) were randomly taken for quality assessment. The different batches of kernels were processed into butter by the selected processors, as follows: kernels were cleaned, sun-dried for four hours, sorted and crushed. The crushed kernels were roasted for 45-50 min, milled, mixed with water and churned. During the roasting, the temperature inside crushed kernels was around 110-130 ^{o}C. Next, the cream was transferred to a cooking pot, heated for 45-60 min and then an equal volume of water was added to the crude oil. The mixture was left for 20-30 min. Subsequently, the top layer was separated and dehydrated by heating during 20-30 min. The resulting oil was filtered and cooled for 24 hours to obtain the shea butter. The butters and the samples of the kernels were stored at 4 °C until analysis.

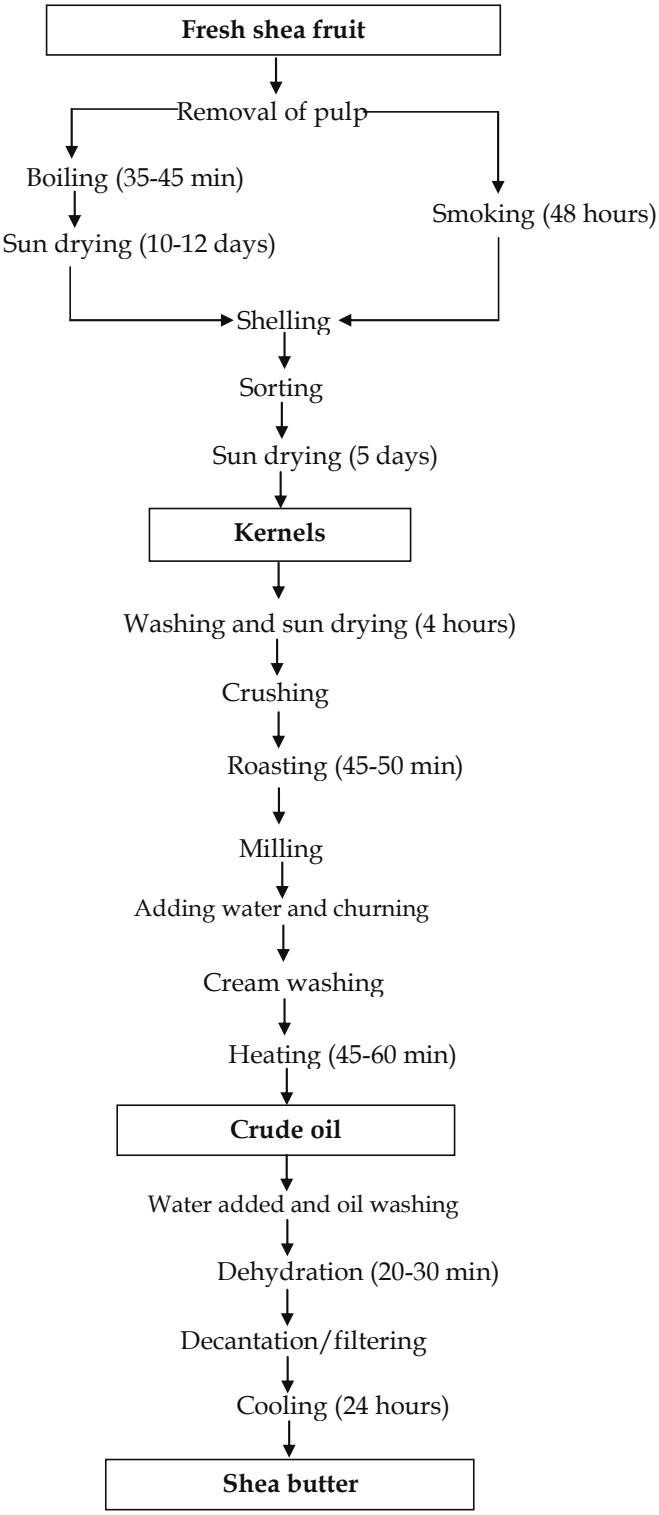

Figure 4.1: Flow sheet of traditional shea butter production

4.2.2. Characterization of shea kernels and butter

Shea kernels were characterized by the moisture content (AOAC 2002), colour parameters using a chromameter (Minolta CR210b), fat content using petroleum ether as a solvent and a Soxhlet apparatus for 4 hours at 70 °C (AOAC 2002), and FFA percentage by titration and calculated as the percentage of oleic acid (NB ISO 660 2006). The yield of shea butter was expressed on wet weight as the percentage of the mass of clear oil after filtering on the mass of the kernels used. Physical characteristics of the butter assessed were as follows: refractive index at 40°C determined with the refractive sensitive plane of the refractometer (NB ISO 6320 2006), and colour parameters (brightness and yellowness). Melting range was analyzed by DSC (Differential Scanning Calorimeter; Perkin-Elmer Corp., Norwalk, USA). The temperature range studied for this analysis was from 0 °C to 70 °C at a speed of 5 °C/min. The chemical characteristics of the butters were determined as follows: unsaponifiable matter after treatment with a solution of ethanolic potassium hydroxide and extraction by dietyhlether (NB ISO 3596 2006); the percentage of FFA (NB ISO 660 2006), iodine (NB ISO 3960 2006) and peroxide (NB ISO 3961 2006) indices assessed by titration respectively; fatty acid profiles using KOH methylation and determination by Gas Chromatography (Thermo Scientific) with helium as carrier gas (AOAC 2002). Tocopherol contents were quantitatively determined by the in-house method ANAL-10015 of the accredited CCL Nutricontrol Laboratorium in Veghel, the Netherlands (www.nutricontrol.nl). The digestion and extraction of the samples were done at 80 °C and separation was performed using HPLC (HP1100, Thermo Scientific (Thermo Separation Products), Waltham, MA, USA). Detection was done by fluorescence detector (LS40, PerkinElmer, Waltham, MA, USA). Each parameter was measured in triplicate.

4.2.3. Sensory evaluation of butter

The four shea butter samples were subjected to a sensory evaluation using a descriptive analysis by a panel of twelve students aged from 25 and 30 years selected and trained for this test (Watts et al. 1989). The training concerned the identification of the texture, the colour and the smell. The panelists scored the intensity of the following sensory attributes: whiteness, yellowness, smell intensity, and texture using a scale from 0 (whitish, pale-yellow, weak smell and soft texture) to 10 (white,

yellow, intense smell and hard texture), respectively. A 20 g sample of each type of shea butter was used for the evaluation procedure, which was carried out in triplicate.

4.2.4. Statistical analysis

Analysis of variance was used to determine the effect of the two processing techniques on the yield and quality characteristics of shea kernels and butter; the SNK (Student–Newman–Keuls) test, using SAS 9.1 software (SAS Institute Inc., Cart, NC, USA), was used to range the means of each parameter, except for the data on the tocopherol contents of the butters. Correlations between variables were also established. Analysis of variance was also used to analyse the sensory data.

4.3. RESULTS AND DISCUSSION

4.3.1. Characteristics of shea kernels

The moisture content of the shea kernels varied from 8 % to 10 % with no significant difference between the two heat treatments (Table 4.1). However, with moisture content close to 8 % the smoked kernels comply with the export requirements which are 7-8 % (Kassamba 1997). The fat content of the kernels ranged from 37 % to 50 % dw. Statistically, shea kernels processed by boiling followed by sun drying had a higher fat content ($p=0.0210$). A possible explanation is softening of the nuts due to boiling, leading to cell disruption and a better release of the oil. Some authors (Womeni et al. 2006b, Aviara et al 2005, Olaniyan 2002) stated that the boiling of shea nuts is necessary to allow efficient extraction of fat.

Smoked shea kernels had a significantly higher redness value (a*) than the ones treated by boiling followed by sun drying ($p=0.0001$). According to literature, the colour intensity of many smoked products is mainly linked to the tannins of the wood used for smoking (Ozdemir and Devres 2000, Kahyaoglu and Kaya 2006). If so, the long duration of the smoking (48 hours) may contribute to the intense red colour observed for the roasted kernels.

Table 4.1: Physico-chemical characteristics of shea kernels treated by boiling plus sun drying and smoking

	Boiled followed by sundried kernels		Smoked kernels	
	Sample 1	Sample 2	Sample 1	Sample 2
Moisture content (%)	10.1 ± 0.1[1]a	9.7 ± 0.5a	8.8 ± 0.4a	8.4 ± 0.1a
Fat content (% dw)	50.1 ± 0.1b	47.2 ± 0.1b	41.1 ± 0.3ab	37.4 ± 1.3a
a*(redness)	6.3 ± 0.1a	7.7 ± 0.1b	9.4 ± 0.1d	8.5 ± 0.2c
FFA (%)	6.2 ± 0.3c	5.9 ± 0.1bc	4.7 ± 0.1a	5.3 ± 0.1ab

[1]: Mean ± Standard error of mean; means with the same letters in a row are not significantly different at the 5% significance level

The FFA percentages were higher for the boiled kernels; this difference was significant for one of the two samples of smoked kernels (*p=0.0014*). All FFA percentages complied with the threshold value of a maximum of 6 % of FFA used as export criterion (Kassamba 1997). The storage of fresh nuts should be responsible for the values found for FFA. Indeed, Kapseu et al. (2005) reported that the acid value and FFA percentage of the butter are influenced by the storage conditions of the shea fruits and increase with the duration due to lipase activity.

4.3.2. Butter characteristics

- Sensory quality

Shea butter from boiled followed by sun-dried kernels had a soft texture and whitish colour (*p=0.0001*) according to the panel (Table 4.2). Shea butter from smoked kernels had a weak smell (*p=0.0032*) compared with the butter from boiled plus sun-dried kernels. No difference due to heat treatment was observed by the panel in the yellowness of the butter. Yellowness of shea butter should be attributed to the presence of ß-carotene pigments in the butter, which are nutritionally important. An earlier study indicated that shea butter with yellowish colour is preferred by 61 % of Beninese consumers while butter with weak smell is preferred by more than 45 % (Honfo et al. 2012).

Table 4.2: Mean of panel scores for sensory attributes* (colour, smell, and texture) of shea butters

	Boiled followed by sundried kernels		Smoked kernels	
Attributes	Sample 1	Sample 2	Sample 1	Sample 2
White colour	2.3[1]a	2.9a	3.7b	4.1b
Yellow colour	4.6a	4.2a	3.1a	3.4a
Smell	4.9b	5.2b	3.3a	3.6a
Texture	4.7a	4.9a	7.1b	7.5b

*: Attributes were scored on a scale of 10 points where 0 = (whitish, pale-yellow, weak smell, and soft texture) and 10 (white, yellow, intense smell, and hard texture);
[1]: Mean of 12 scores with the same letters in a row are not significantly different at the 5% significance level

- Physical characteristics

The yield of shea butter from boiled followed by sundried kernels was significantly (*p=0.0001*) higher than that from smoked kernels (Table 4.3). This result is corroborated by the crude fat content in the kernels. However, the yield of fat extracted (23-30 %) by the traditional methods (boiling followed by sun drying or smoking) was significantly lower than that after chemical extraction (37-50 %) using petroleum ether as a solvent. This observation is reported by many authors (Kar and Mital 1981, Mbaiguinam et al. 2007, Nkouam et al. 2007, Akihisa et al. 2010b).

The moisture content of shea butter extracted from the boiled followed by sundried kernels was significantly higher than that of butter from smoked kernels (*p=0.0130*) (Table 4.3). This result fits with the soft texture of the butter as observed by the panel during the sensory analysis. However, low moisture content is desirable in oils and fat to prevent oxidative rancidity and microbial growth. Thus, the relatively low moisture content found for all samples (< 2 %) of shea butter may indicate a low potential for rancidity.

Table 4.3: Physical characteristics of shea butters

	Boiled followed by sundried kernels		Smoked kernels	
Physical properties	Sample 1	Sample 2	Sample 1	Sample 2
Yield (%)	30.3 ± 0.0[1]b	29.0 ± 0.0b	23.2 ± 0.0a	22.8 ± 0.0a
Moisture content (%)	2.0 ± 0.2b	1.9 ± 0.3c	1.7 ± 0.1a	1.5 ± 0.1a
Refractive value at 40 °C	1.467 ± 0.0a	1.467 ± 0.0a	1.468 ± 0.0a	1.469 ± 0.0b
Brightness (L*)	69.9 ± 0.5a	70.6 ± 0.2a	72.65 ± 0.7b	73.8 ± 0.4b
Yellowness (b*)	24.6 ± 0.1a	24.40 ± 0.3a	23.7 ± 0.7a	24.4 ± 0.4a
Melting range (°C)	36-47	36-46	32-48	33-48

[1] Mean ± Standard error of mean; means with the same letters in a row are not statistically different at 5% significance level

According to Fashina and Ajibola (1989), the refractive index is used for rapid sorting of fats and oils to test their variety and purity. The refractive indexes at 40 °C of the different samples of shea butter were 1.467-1.469 (Table 4.3). A slightly higher value was observed for butter from smoked kernels (*p=0.0076*). This might be due to burning of the nuts during the smoking. However, the values obtained are in line with the values of different oil and fat of seeds (Chukwu and Adgidzi 2008, Anwer et al. 2006).

The brightness values (L*) were higher for butter from smoked kernels (*p=0.0137*) (Table 4.3). No significant difference was detected in the yellowness value (B*) and this result is in line with the observation of the sensory panel. A yellow colour corresponds to the natural colour of shea butter and when the butter is also bright, the butter is more attractive.

The melting interval was from 36 °C to 47 °C for butter extracted from boiled followed by sundried kernels and from 32 °C to 48 °C for butter from smoked kernels (Table 4.3). This difference might be due to a higher proportion of saturated fatty acids, specifically stearic acid, in the butter from smoked kernels (Table 4.4). Generally, the high amount of stearic acid with melting point of 69.6 °C in shea fat often leads to the solid consistency of the butter. The degree of its hardness is moderated by the presence of oleic acid, with a lower melting point (16.3 °C) (Bailey 1979). In addition, the saturation indices of butter from smoked kernels were higher than those of butter from boiled kernels (Table 4.4). Thus, butters from smoked

kernels could be considered as the hardest and this remark is in line with the firm texture of the butter from smoked kernels as observed by the sensory panel. The end points of the melting interval of the butters from both boiled kernels and smoked kernels indicate their suitability for use in the chocolate industry because chocolate has to be solid at ambient temperatures but melt in the mouth. Moreover, Bonkoungou (1987) stated that a melting point close to body temperature is an attribute that makes the butter particularly suitable as a base for ointments and medicines. However, with the same method to determine the melting interval, Womeni et al. (2006b) found that the melting interval of shea butter ranged from 25 ^{o}C to 45 ^{o}C. This difference might be due to the methods used to process the shea nuts. Indeed, Womeni et al. (2006b) combined different temperatures (120-180 °C) and times (0.4-11.6 min) to dry fresh shea nuts and assessed the melting properties of the fat obtained from these kernels.

- **Chemical characteristics**

The fatty acids in shea butter were similar to those mentioned in earlier studies (Kapseu et al. 2001, Maranz et al. 2004b, Di Vincenzo et al. 2005) (Table 4.4). The main fatty acid is oleic acid (45 %) followed by stearic acid (42-44 %); together they represent 87-89 % of the total fatty acids. Significant differences were found in fatty acid composition, specifically for stearic, linolenic, and arachidic concentrations, in relation to the processing method. Higher amounts of stearic acid ($p=0.0031$) were found for butter from smoked kernels while butters from boiled kernels had higher amounts of linolenic acid ($p=0.0001$) and arachidic acid ($p=0.0192$). Some traces of lignoceric acid (24:0) were found in butters from boiled followed by sun-dried kernels. These differences in fatty acid profile might be due to the starting material. Indeed, shea fruits were collected under many trees in one location, and the genotype and phenotype variations among these trees are unknown. However, the characteristic pattern of fatty acids explains the use of shea butter in some cosmetic and pharmaceutical preparations.

Table 4.4: Fatty acid composition of shea butters processed by two heat treatments

	Boiled followed by sundried kernels		Smoked kernels	
Fatty acid (%)	Sample 1	Sample 2	Sample 1	Sample 2
Myristic (14:0)	0	0	0	0.1 ± 0.0
Palmitic (16:0)	3.5 ± 0.1[1]a	4.0 ± 0.2a	4.2 ± 0.1a	3.8 ± 0.2a
Stearic (18:0)	42.7 ± 0.0a	42.5 ± 0.2a	43.2 ± 0.0b	43.8 ± 0.2c
Oleic (18:1)	45.9 ± 0.1b	45.2 ± 0.1a	45.1 ± 1a	45.2 ± 0.1a
Linoleic (18:2)	6.1 ± 0.1a	6.6 ± 0.4a	6.1 ± 0.1a	5.6 ± 0.1a
Linolenic (18:3)	0.1±0.0b	0.2 ± 0.2b	0.3 ± 0.0a	0.1 ± 0.0a
Arachidic (20:0)	1.4 ± 0.0b	1.3 ± 0.1b	1.1 ± 0.0a	1.3 ± 0.1b
Behenic (22:0)	0.2 ± 0.0a	0.2 ± 0.0a	0.2 ± 0.0a	0.2 ± 0.0a
Erucic (22:1)	0.1 ± 0.0a	0.1 ± 0.0a	0.1 ± 0.0a	0.1 ± 0.1a
Lignoceric (24:0)	0.10 ± 0.0b	0.1 ± 0.0b	0a	0a
SatFA	47.9	47.8	48.7	49.1
UnsatFA	52.1	52.3	51.3	50.9
Indexsat	0.92	0.91	0.95	0.96

SatFA: saturated fatty acid, UnsatFA: unsaturated fatty acid, indexsat: index of saturation;
[1] Mean ± Standard error of mean; means with the same letters in a row are not statistically different at 5% significance level

The total tocopherol content of the butters ranged from 106.7 to 128.9 mg/g (Table 4.5). Significant differences were found between the processing methods and the highest values were found for butters from boiled followed by sundried kernels ($p = 0.0121$). Irrespective of the heat treatment given to the nut before butter extraction, α-tocopherol represented the major type of tocopherol (76-80 % of the total tocopherols), followed by γ-tocopherol (17 %). Alpha-tocopherol was found to have the highest antioxidant activity among the tocopherols (Stocker et al. 2003). In addition, a smaller amount of δ-tocopherol was found (< 1 % of the total tocopherols). Bup et al. (2011) reported corresponding values of 53-80 %, 15-43 %, and 0.3-4 %, respectively, while Maranz and Wiesman (2004) reported values of 64 %, 15 %, and 14 %, respectively, for the same parameters.

Table 4.5: Tocopherol content (mg/g) of shea butters

	Boiled followed by sundried kernels		Smoked kernels	
Tocopherol compounds	Sample 1	Sample 2	Sample 1	Sample 2
α-tocopherol	97.5	98.1	93.2	83.8
β-tocopherol	3.7	6.7	3.8	3.8
γ-tocopherol	20.2	22.5	20.3	18.1
δ-tocopherol	0.9	0.9	0.95	0.97
Total	122.9	128.9	118.3	106.7

The unsaponifiable fraction represents a distinct characteristic of shea butter. The unsaponifiable fraction ranged from 5 % to 7 % for the samples of shea butter analysed (Table 4.6). The highest values were found for butters from boiled followed by sun-dried kernels; this difference was significant for one of the two samples of smoked kernels ($p=0.0042$). Butters with a high unsaponifiable fraction are preferred for cosmetic and medicinal purposes due to antioxidant and anti-inflammatory properties of certain compounds of the unsaponifiable such as tocopherols, phenols, and sterols (Maranz and Wiesman 2004).

The FFA percentages of butter from smoked kernels were lower than those for butters from boiled plus sun-dried kernels ($p=0.0001$) (Table 4.6). The difference observed might be explained by the same reasons as for the different FFA percentages of the kernels. All the FFA percentages were lower than the maximum value of 4 % that is tolerated for vegetable oil and the 3 % which is a maximum in the food industry (Codex Alimentarius 1992). However, all FFA values were higher than 1 %, which is the maximum for cosmetic purposes (Kassamba 1997, NB 04.02.001 2006).

The highest peroxide values were found for the butter from boiled followed by sundried kernels ($p=0.0021$) (Table 4.6). The sun drying of shea nuts could be responsible for the high peroxide values as the nuts are exposed to sun for a long time (10-15 days). Womeni et al. (2007) found that the long exposure (more than 8 days) of shea nuts to sun is favourable to the appearance of peroxides. Irrespective of the heat treatments used to process the nuts, the peroxide values in all samples were lower than the maximum value of 10 meq O_2/kg tolerated for cosmetic uses

(USAID/WATH 2005, NBF 01-005 2006). For food end uses, the values accepted are in the range of 10 meq O_2/kg (Codex Alimentarius 1992) to 50 meq O_2/kg after refining (USAID/WATH 2005, NBF 01-005 2006). Nevertheless, shea butter with a relatively high peroxide value (close to 50 meq O_2/kg) is susceptible to deterioration and inappropriate for human consumption. The FFA percentages and peroxide values obtained in this study are characteristic for many edible vegetable oils (Dhellot et al. 2006, Anhwange et al. 2004).

Table 4.6: Chemical characteristics of shea butters

	Boiled followed by sundried kernels		Smoked kernels	
Chemical properties	Sample 1	Sample 2	Sample 1	Sample 2
Unsaponifiable matter (%)	7.0 ± 0.1[1]c	6.3 ± 0.1b	5.4 ± 0.2a	5.9 ± 0.2ab
FFA (%)	1.9 ± 0.2b	2.1 ± 0.1b	1.4 ± 0.1a	1.3 ± 0.0a
Peroxide value (meq O_2 /kg)	7.6 ± 0.3c	8.2 ± 0.1d	6.1 ± 0.2b	4.7 ± 0.2a
Iodine value (g I_2/100 g)	55.2 ± 0.5d	51.8 ± 0.3c	49.6 ± 0.3b	46.8 ± 0.3a

[1] Mean ± standard error of mean; means with the same letters in a row are not statistically different at 5% significance level

Butters from smoked kernels had significantly (*p=0.0011*) lower iodine values than butters from boiled followed by sundried kernels (Table 4.6). Apparently, butters from smoked kernels were relatively more saturated than those from boiled followed by sundried kernels. This observation is supported by a negative correlation coefficient between the iodine values and the proportion of saturated fatty acids (*r= -0.844, p = 0.0081*) and by the percentage of saturated fatty acids found in butters from smoked kernels.

4.4. CONCLUSION

Processing methods of shea nuts had a significant effect on the colour of the kernels and their fat content. Some differences were also found in butter characteristics, namely in unsaponifiable matter, free fatty acid content, peroxide values, fatty acid profile, and iodine values. Apart from the moisture content that was slightly higher than the requirement for export, kernels processed by the two heat treatments can be easily exported. The findings from this study help to identify the processing techniques of butter which fit with quality demands for different

utilisations. Accordingly, the boiled followed by sundried kernels gave a butter that is more suitable for cosmetics and pharmaceutical purposes due to its higher unsaponifiable content and soft texture. Due to the importance of some units operations, namely boiling, sun drying, smoking, and roasting, in the different processing techniques, we recommend for further research in-depths studies of the effects of these operations on the yield and quality of the products (kernels or butter).

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Chapter 5

Effect of storage duration and boiling time of fresh shea nuts on physico-chemical characteristics of kernels and butter

F.G. Honfo, A.R. Linnemann, M.M. Soumanou, N. Akissoe, M.A.J.S. Van Boekel
(Submitted for publication)

Abstract

The primary objective of post-harvest processing of shea nuts is to produce dry kernels that will deliver a large amount of good quality butter. Two processing operations namely storage of fresh nuts and subsequent boiling were studied using the response surface methodology. Laser Scanning Confocal Microscopy (LSCM) was additionally used to visualize the microstructure of fresh kernels. With the increasing of storage duration and boiling time, kernel colour turned to darker with the increasing of a*, and others parameters *viz*. fat content (38-52 % dw), butter yield (24-36 %), FFA percentages (0.5-2 %) of butter and the decreasing of the brightness (L*) and yellowness (b*) of butter. Optimum storage duration of 3 days and boiling for 28 ± 3 min gave the best results, *i.e.* kernels with a moisture content of 7 % and a fat content of 50 % dw, resulting in a butter yield of 32 % having 0.8 % FFA, and 2.5 meq O_2/kg peroxide. The microstructure of fresh shea nuts showed large and small fat globules with some free spaces inside. Further studies need to be done on other critical processing operations (*viz*. roasting, churning) to standardize each step of the traditional technique and consequently to improve the yield and quality of butter.

Keywords: *Vitellaria paradoxa*, kernels, storage, boiling, physico-chemical characteristics, butter

5.1. INTRODUCTION

The shea tree (*Vitellaria paradoxa*) is a forest food resource with a significant contribution to the diet of local people in extensive parts of Africa. Its kernels are also an important export commodity at international level, although most nuts are locally used for fat extraction (Chalfin 2004). Shea butter is one of the most important vegetable fats due to its various uses: locally, the butter is used as cooking fat, in soap, pomade and traditional pharmacology. At international level it is in great demand among chocolate, cosmetic and pharmaceutical industries (Hall et al. 1996, Lovett 2005). Shea fat is the main component of the kernel. Its distribution and structure in the kernel are important in determining its physical and chemical properties as well as its extractability. Hence, knowledge of the microstructure, in relation to the macroscopic properties, may offer options to improve the existing processing methods and to design new ones (Heertje 1993).

The harvesting period of shea fruits often coincids with the begining of the rainy season, a period of many competing farm activities. Consequently, the processors, women only, have limited time, and therefore need to store the fresh nuts for several days (commonly 3 to 15 days) before further processing (Honfo et al. 2012). The storage conditions are also inappropriate and not adapted to keep the nuts fresh. All of these practices often lead to the germination of the nuts and exposes the nuts to external agents such as microorganisms, moisture and insects, which affects the quality of the final products (kernel and butter). Germination of nuts also leads to the reduction of butter yield and gives the butter a bitter taste (Jacobsberg 1977).

The preservation and processing of fresh shea nuts vary across shea regions and generally involve fruit gathering, depulping, and boiling of fresh nuts, followed by sun drying, shelling, roasting, milling, churning, and oil separation. Some processing steps, such as boiling and sun drying, have been reported as critical operations for kernel quality (Womeni 2004, Kapseu et al. 2007). The traditional boiling procedure facilitates the shelling of kernels and inactivates the enzymes, lipases, responsible for triglyceride hydrolysis (Lovett 2004, Womeni et al. 2006b). In Benin, boiling is traditionally done for 15-60 min and the end of this unit operation is generally determined by a colour change of the boiling water (Honfo et al. 2012). Variations in the duration of boiling can influence shea butter quality. For instance,

excessive boiling results in cellular damage, leading sometimes to discolouration of the shea nut (Aculey et al. 2012), while improper lipase inactivation may occur due to insufficient boiling, leading to a high free fatty acid (FFA) content in the kernels (Bup et al. 2011). In addition, mouldy kernels may come from nuts that have been boiled and were not dried well. Lovett (2004) recommended the optimisation of this process by establishing the right cooking time, thereby striking a balance between the advantages and disadvantages of the process.

Several studies on shea fruits assessed the impact of processing on quality indicators like the FFA, peroxide value, unsaponifiable fraction, and tocopherol content of kernels and butter (Womeni 2004, Kapseu et al. 2007, Bup et al. 2011, Aculey et al. 2012). To date, the impact of the storage duration of fresh shea nuts on kernel and butter quality characteristics is not well documented. Such an investigation combined with assessing the effect of the duration of boiling is important to determine how long the fresh nuts can be stored and how long they should be boiled to obtain shea products with optimal quality attributes. The main objective of this research was therefore to assess the effect of storage of fresh nuts and boiling time on some physico-chemical quality attributes of shea kernels and butter. Additionally, the microstructure of fat distribution in shea kernels was visualized for better understanding of the processes used for butter extraction.

5.2. MATERIAL AND METHODS

5.2.1. Experimental design

A central composite face-centered design (CCFD) with two factors was used to assess the simultaneous effect of storage duration (3-21 days) and boiling time (10-60 min) of fresh shea nuts on certain quality characteristics of derived kernels and butter and to determine the optimum roasting processing conditions. This design is usually used to study linear interactions and the quadratic effects between factors (Montogomery 2001). Ranges of storage duration and boiling time were chosen according to the processing practices in Benin (Honfo et al. 2012). The design generated 13 combinations (Table 5.1) and each of them was duplicated, giving a total of 26 combinations. For each parameter investigated, the design gave the following regression formula:

$Y = I + aX_1 + bX_2 + cX_1^2 + dX_2^2 + eX_1X_2$ [1]

Where: Y is the response, I is a constant; a and b are linear effect coefficients; c and d are quadratic effect coefficients; and e is an interaction effect coefficient. X_1 and X_2 are the variables storage duration and boiling time, respectively.

5.2.2. Experimental processing

Fresh shea fruits were collected from different shea trees in Arbonga village at Banikoara (11° 18'N and 2° 25'E), a location in Alibori Department, North-Benin. The fruits were depulped on the same day and the day after the fresh nuts were transported to the University of Abomey-Calavi, where the experiments took place. Three kilograms of fresh shea nuts were used for each treatment. The fresh shea nuts were stored in a room at 28 ± 1 °C with a relative humidity of 81 ± 2 %. The nuts were just piled on the floor until the end of storage according to treatment. Boiling was done in water that was three times the volume of the nuts (Honfo et al. 2012) and the time was chosen according to each treatment. At the end of the boiling time of each treatment, the nuts were placed in a basket for draining. The drained nuts were subsequently oven-dried at 38-40 °C for 5 days, within the temperature range commonly used for sun-drying in Benin. The dying duration allows reducing the moisture content of nuts 75 % to 10 % for easiness of the shelling operation. The dried nuts were shelled manually using a metal rod and the kernels were further oven dried at the same temperature for another 5 days. Next, the butter was extracted from the dried kernels according to the traditional process by grinding with electric grinder machine, roasting for 20 min at 130 °C in an oven, milling with an electric milling machine (Kenwood blender), manual churning and heating. The oil was washed and heated to remove particles and mucilage from the first stage of heating. The resulting oil was then filtered and left to cool. Samples of dried kernels and butters were packed in plastic containers and stored at 4°C until analysis. Each sample was tested in triplicate.

Table 5.1: Different combinations of storage duration and boiling time of shea nuts generated by the CCFD with the different responses

Treatment	Storage duration (day)	Boiling time (Minute)	Moisture content (%)	Kernel redness (a*)	Fat content (% dw)	Butter yield (%)	Butter brightness (L*)	Butter yellowness (b*)	FFA (%)	Peroxide (meq O_2/kg)
1	12	35	7.6±0	7.5±0.1	47.1±1.1	30.7±0.7	75.4±0.6	4.7±0.9	1.4±0	2.7±0.1
2	3	10	7.2±0.3	6.5±0.2	49.0±0.9	30.9±0.9	78.7±1.3	22.1±0.6	1.2±0.2	2.3±0.1
3	12	35	7.3±0.2	7.8±0.3	44.2±0.9	30.8±0.4	74.1±3.0	21.2±1.8	1.4±0.4	2.8±0.2
4	12	35	7.5±0.1	7.8±0.3	45.4±0.3	31.6±0.1	72.8±2.3	20.2±2.0	1.5±0	2.7±0.2
5	12	35	7.0±0.4	7.7±0	46.2±0.8	33.7±0.8	75.2±0.9	20.4±1.8	1.4±0	2.9±0.3
6	21	60	7.4±0.1	11.6±0.1	40.6±0.8	28.2±1.0	71.5±0	21.1±0.9	1.9±0.1	3.5±0.5
7	21	35	6.8±0.2	7.6±0.2	44.5±0.9	28.6±1.2	72.0±0.9	17.1±1.0	1.7±0.2	3.3±0.4
8	12	60	7.4±0.2	10.8±0.3	42.8±1.3	29.9±1.7	74.3±1.1	20.5±2.1	1.4±0	2.7±0
9	21	10	6.8±0.2	6.9±0.1	40.2±1.5	26.3±1.5	70.9±0	17.5±0	1.7±0	2.7±0.3
10	12	10	7.1±0.3	6.8±0.2	40.4±0.9	29.3±1.3	71.9±1.3	20.9±1.1	1.4±0	2.9±0.2
11	3	60	6.9±0.2	10.9±0.2	52.1±0.6	32.8±0.8	74.9±0.8	4.9±0.9	1.0±0.1	2.8±0.2
12	3	35	6.4±0.1	7.2±0.1	49.7±0.8	33.6±0.9	76.5±1.1	29.8±1.1	0.6±0.1	2.7±0.1
13	12	35	7.3±0	7.7±0.2	48.0±1.2	31.8±1.5	73.9±0.6	4.7±0.6	1.4±0.1	2.6±0.2

[1]: Mean ± Standard error of mean

5.2.3. Microstructural observation of shea kernels

Cross-sections of fresh kernels were studied using a Laser Scanning Confocal Microscopy (LSCM) (510 META Carl Zeiss Germany). The excitation wavelength was 543 nm, and the emission was recorded between 420 and 590 nm. For LSCM observations, pieces of fresh kernels (kernels that had not been treated) were cut into slices of 10 µm thickness by a Reichert-Jung cryostat (Microm) at -15 °C. The samples were then mounted on glass slides, coloured with deionized water containing lipid-soluble Nile Red to stain the fat and covered for observation. Samples were also directly observed under the lenses of the digital microscope (Nikon Eclipse 80i).

5.2.4. Physico-chemical characteristics of shea kernels and butter

Moisture contents of kernels were determined according to AOAC (AOAC 2002) as well as fat contents with a Soxhlet apparatus using petroleum ether as a solvent for 4 hours at 70°C (AOAC 2002). The yield of shea butter was expressed on wet weight as the percentage of the mass of filtered oil (butter) on the mass of the kernels used. Colour were determined using a chromameter (Konica Minolta CR 410) by measuring the Hunter parameters L*, a* and b* values. The parameter a* explains the redness of kernels while L* and b* express the brightness and the yellowness of butters. FFA percentage was calculated as the oleic acid percentage (NB ISO 660 2006), and the peroxide values of butter samples were determined by titration (NB ISO 3961 2006).

5.2.5. Statistical analyses

The experimental design and the different statistical analyses as well as the optimisation conditions were determined with Minitab 16.0 software as well as the different contour plots for each treatment. Analysis of variance (ANOVA) tables were generated and the effect of independent variables and regression coefficients of individual linear, quadratic and interaction terms were calculated. Based on sequential and lack-of-fit p-values the best fitting significant model ($p<0.05$) was selected.

5.3. RESULTS AND DISCUSSION

5.3.1. Microstructure of shea kernel

Figures 5.1a and 5.1b show the micrographs of non-oxidized and oxidized kernel sections taken by the digital microscope. Both figures show similar cell sizes and a regular shape of cell structures. However, some cells of the cross-section of the oxidized kernel are black, showing the absence of lipid inside. In the micrograph of the non-oxidized kernels, all cells contain lipid. Micrographs 5.1c and 5.1d indicate the fat structure of the periphery of the seed endosperm and figure 5.1e presented the endoplasmic reticulum containing lipid fraction in cells. As the figures illustrate, fat can be recognized under LSCM as oval, polygonal or irregular shapes with various sizes. The dark areas represent the serum pores including water, protein and others nutrients. Most fat globules were large with some free space inside; they were organized into aggregates. However, small fat globules were also dispersed in the serum pores. Lopez et al. (2007) found that small fat globules in milk had a higher stability against rupture of the milk fat globule membrane and a greater resistance to deformation and coalescence under pressure than large fat globules. A similar behaviour might occur in plant fat. In addition, rupture of the fat globule membrane to release fat could be enhanced by the closer proximity of the fat globules and may also depend on several parameters including the temperature and time during different processing operations (Lopez et al. 2007).

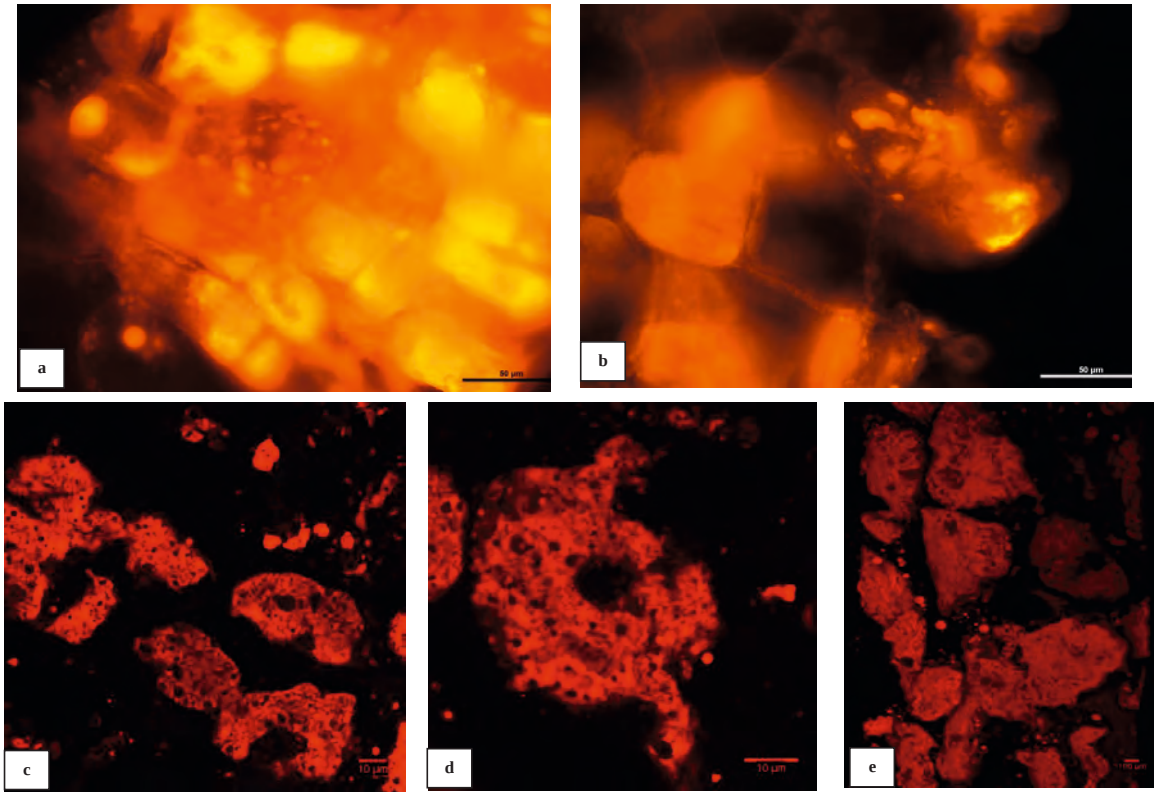


Figure 5.1: Micrographs of cross-section of fresh shea kernel
a: cross-section of non oxidized kernel; b: cross-section of oxidized kernel;
c, d and e: Laser Confocal Scanning micrograph of the flesh of shea kernel; c and d: micrographs showing the periphery of seed endosperm; e: micrograph of endomembrane localization, fat is stained with Nile Red

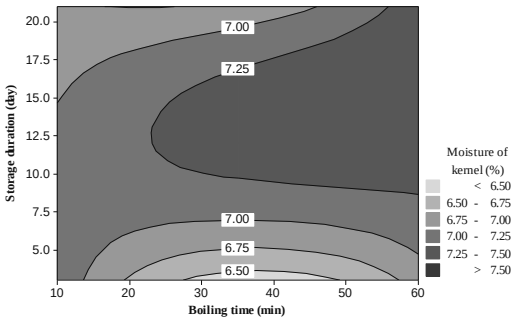
5.3.2. Moisture content and colour characteristics of shea kernels

The analysis of moisture content *(MC)* gave the following regression equations for the effect storage duration (X_1) and boiling time (X_2) of nuts:

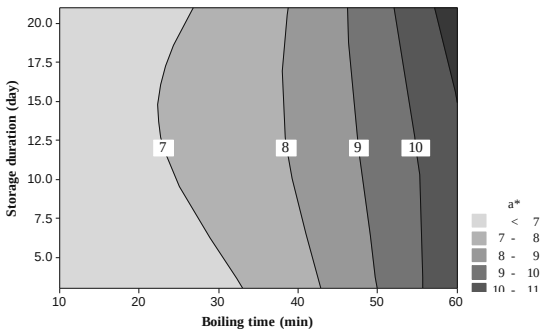
$$MC\ (\%) = 6.9117 + 0.113X_1 - 0.0254X_2 - 0.0058X_1^2 + 0.0003X_2^2 + 0.0012X_1X_2$$

This model explained only 36 % of the variation in moisture content (6.3-7.7 %) of shea kernels. Both factors did not significantly influence the moisture content of the kernels (Table 5.2). The linear term of the model had a positive value whereas its quadratic term expresses negative influence on moisture content.

The contour plots show the variations of moisture content with the storage duration and the boiling time (Figure 5.2a). These different variations could be due to the integrity of the nuts shell as well as their permeability to water. Some shells are sometimes cracked and this might facilitate the water absorption by kernel. However, the moisture content of shea kernels found complies with the export requirements for this parameter (7-8 %) (Kassamba 1997).



a: Moisture content (%) of kernels



b: Redness (a*) of kernels

Figure 5.2: Contour plots showing the effect of storage duration and the boiling time on moisture content and redness of kernels

Table 5.2: Regression coefficients (*RC*), constant (*I*), coefficient of determination (R^2) and lack-of-fit p-values (*P*) values describing relations between moisture content, redness, and fat content of shea kernels, yield of butter, FFA percentage and peroxide value of different butters according to the central composite design

	Moisture content (%)	Kernel redness (a*)	Fat content (% dw)	Butter yield (%)	Butter L*	Butter b*	FFA (%)	Peroxide value
Storage: X_1	0.1113	0.04454	-1.1479**	-0.1604	-0.5790*	-0.1333	0.0698*	-0.0306
Boiling: X_2	-0.0254	-0.06767*	0.4175**	0.2363**	0.0204	-0.1898	-0.0184	0.0062
X_1^2	-0.0058*	-0.00126	0.0345**	-0.0042	0.0050	-0.0102	-0.0016	0.0020
X_2^2	0.0003	0.00215**	-0.0048**	-0.0029**	-0.0012	0.0014	0.0002	-0.0001
X_1X_2	0.0012	0.00042	-0.0036	-0.0000	0.0048	0.007**	0.0004	0.0005
Constant	6.9117	6.84458	42.397	27.5162	79.1155	24.6282	1.0237	2.5049
R^2	35.6	97.3	84.6	71.5	61.5	42.5	74.1	48.4
Lack of fit	0.68	0.22	0.69	0.51	0.73	0.84	0.35	0.12

* Significant at $P < 0.05$; ** Significant at $P < 0.01$

Colour is one of the quality characteristics of shea kernels that is often taken into account during purchase, and the desired colour is brown (Honfo et al. 2012). Values of a* indicate the red colour of kernels. Values of a* were significantly influenced by the boiling time and the model explained 97 % of these variations (Table 5.2); they varied from 6.3 to 11.7 (Table 5.1). The contour plots of the variations of a* indicate an increase of a* values with increasing boiling time, irrespective of the storage duration (Figure 5.2b). Additionally, long boiling times resulted in darker nuts and kernels. The darker colour of nuts might be due to the release of tannins of the shell with the increasing of boiling time. However, it was noticed that a long storage duration of shea nuts resulted in more infested, black and germinated nuts (Figure 5.3), than when stored for short times.

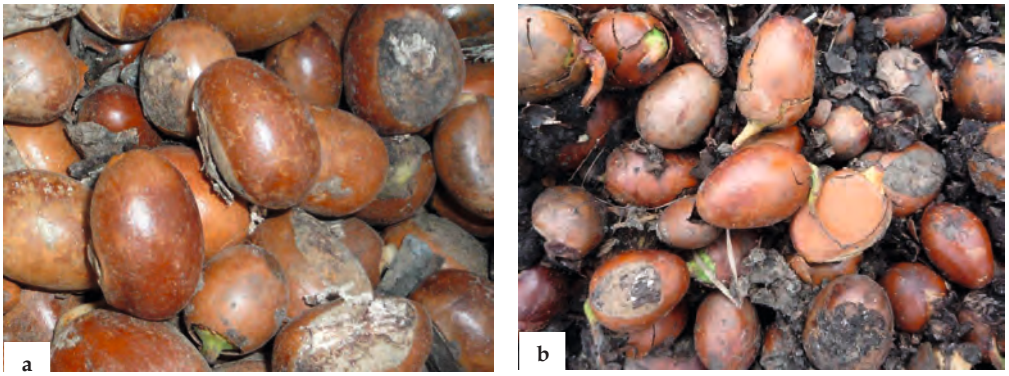
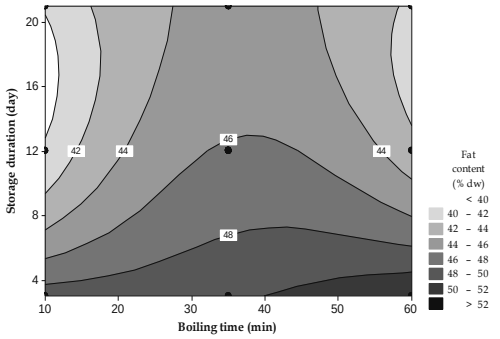


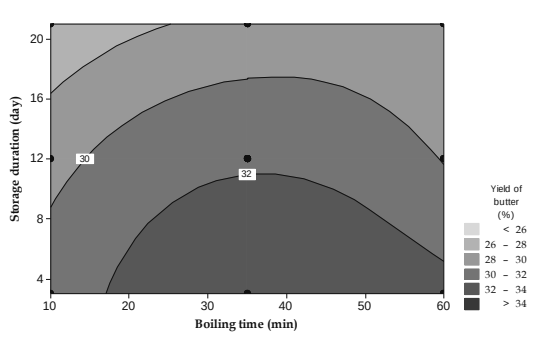
Figure 5.3: Fresh shea nuts after (a) 3 days and (b) 21 days of storage

5.3.3. Fat content of shea kernels and butter yield

Fat content of shea kernels ranged from 38 % to 52 % dw (Table 5.1). The regression model linked to these variations explained 85 %; the linear terms of both factors as well as their quadratic terms were significant for the fat contents of the shea kernels (Table 5.2). This effect can be described as a decrease in the fat content with increasing storage duration, which might be due to the germination occurring during prolonged storage (Figure 5.4a). However, as shown in figure 5.4a, fat content increased with boiling time until it reached a maximum of 48-52 % around 32 min after 3 days of storage. This could be caused by the rupture of the membranes of fat globules membrane to release fat with the increasing of boiling time and the size of the fat globules. During boiling, small fat globules coagulate, promoting fat release as it does in the case of milk (Lopez et al. 2002). Additionally, the coagulation of proteins during cooking, resulting in free space for the diffusion of oil, may increase the amount of oil extracted as cooking time increases (Norris 1982).



a: Fat content (% dw) of kernels



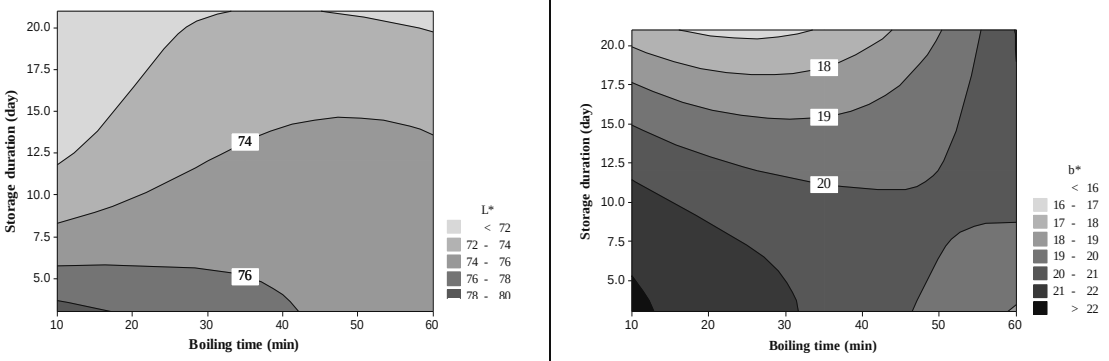
b: Yield (%) of butter

Figure 5.4: Contour plots showing the effect of storage duration and the boiling on fat content of shea kernel and yield of butter

The butter yield varied from 24 % to 36 % on wet weight of kernel mass; the highest values were obtained for nuts stored for 3 days and boiled for 30-35 min (Table 5.1). Compared with the yields (26-32 %) generally found for traditional processing (Kassamba 1997, Bruinsma 1998, Kapseu et al. 2002), most butter yields were relatively high. Butter yield was significantly and positively linked to the linear effect of boiling time; for its quadratic term, significant negative effects were also observed (Table 5.2). This result is corroborated by the variation in the crude fat content of the kernels. The linear and quadratic effects of storage duration as well as the interaction effect of the two factors were not significant. The regression model explained 73 % of the variation and the contour plots show the same trend as observed for the fat content (Figure 5.4b). Thus, irrespective of the boiling time, the butter yield decreases with increasing storage duration.

5.3.4. Colour characteristics of butter

Brightness (L*) values express the level of brilliance. L* values for the butter were significantly and negatively affected by the storage duration of nuts (Table 5.2). L* values varied from 70.5 to 80.1 and the regression model based on the storage duration and boiling time explained 62 % of the variation. The contour plots show a decrease of L* values due to the storage, irrespective of the boiling time (Figure 5.5a). This decrease might be due to the damage of fat by nut germination during the storage, resulting in a change of butter colour, in particular, the brilliance of butter.



a : **a**: Brightness (L*) **b**: Yellowness (b*)

Figure 5.5: Contour plots showing the effect of storage duration and the boiling time on colour parameters of shea butter

Yellowness (b*) was positively related to the interactive effect of both storage duration and boiling time (Table 5.2). The parameter b* expressed the intensity of the yellow colour of the butter and varied from 15.8 to 22.7 (Table 5.1). Only 43 % of the variation was explained by the regression model related to the two factors. The contour plots of the b* values show a decrease with an increasing storage duration from the beginning until 47 min of boiling (Figure 5.5b). A decrease of b* values was also noticed with an increase of the boiling time at the beginning of storage period.

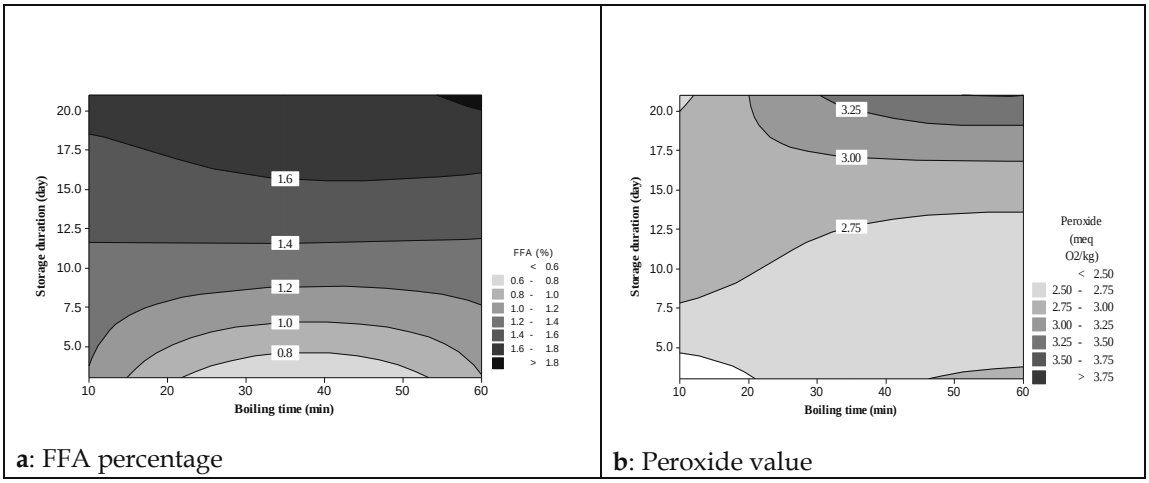
The highest values for L* and b* were found for the shortest storage period in combination with the shortest boiling treatment, namely 10 min. Colour in many food products including shea butter, is of great importance and appears as a key aspect in unprocessed and manufactured foods and an attribute for texture and flavour in regard with acceptance for consumers (Clydesdale 1998). A yellow colour corresponds to the natural state of shea butter, and when the butter is also bright, it is most attractive (Honfo et al. 2012).

5.3.5. FFA percentage and peroxide value of shea butter

The FFA percentages varied from 0.5 % to 2 % (Table 5.1) and were significantly and positively related to the linear effect of storage duration while the opposite was found for the boiling time (Table 5.2). The regression model explained 74 % of the variation. Low FFA values were found at the beginning of the storage

period. However, some of the FFA percentages were higher than the threshold of 1 % tolerated for cosmetic purposes (NB 04.02.001 2006), but all of them were lower than the maximum value of 3 % and 4 % approved by shea production countries for international trade and by the Codex Alimentarius respectively for food purposes (Codex Alimentarius 1992, NB 04.02.001 2006). The contour plots presented in Figure 5.6a show a gradual increase of the FFA percentage during the storage of nuts, irrespective of the boiling time. This increase may be due to the germination of the nuts during storage. Indeed, shea fruits fall from the tree and may start to germinate, which leads to the activation of the lipases, responsible for triglyceride hydrolysis (Guillaumin 1982). Furthermore, storage conditions may promote the growth of micro-organisms, for example fungi with a high lipolytic activity, increasing the amount of FFA (Greenwood 1929).

The different peroxide values obtained (2.3 to 3.8 meq O_2/kg) were lower than the maximum value of 10 meq O_2/kg set for cosmetic uses (NB 04.02.001 2006). The regression model of the peroxide values explained 48 % of the variation (Table 5.2). The effects of the two factors on the peroxide value were not significant. The contour plots show a gradual increase of the peroxide value with increasing storage duration and boiling time (Figure 5.6b). The increase of the amount of peroxide with the boiling time was also found by Womeni et al. (2006b), when they investigated the effect of cooking time and oven temperature on the peroxide value. The rise in the peroxide value during prolonged cooking of shea nuts may be due to the breakdown of water soluble anti-oxidants such as the monomers and polymers of catechins during the process (Maranz et al. 2004b). This action leads to the oxidation of fat inside the nuts and consequently, increases the peroxide value.



a: FFA percentage

b: Peroxide value

Figure 5.6: Contour plots showing the effect of storage duration and the boiling time on FFA percentage and peroxide value of shea butter

Since the models have shown non-significant lack of fit *p* values for all investigated parameters; the different regression equations sufficiently explained most of the variability of the responses. In general, a lack of fit is used to check the fitness of the regression models and a non-significant lack of fit *P* value is often linked to the adequacy of the model and the accuracy of the predictions (Montogomery 2001).

5.3.6. Optimisation of storage duration and boiling time

Optimum conditions for the storage duration and boiling time are predicted by the models. A condition is considered optimal if the desirability value associated to the response is 1 or close to 1. The desirability value is generally between 0 and 1 and explains the level of validity of the predicted optimum condition. From the results, optimum conditions were obtained for each parameter investigated. Since the desirability was not the same for all responses with a unique optimal condition to get kernels with low moisture and high fat content, and butter with low FFA and peroxide values, a range of desirability was then accepted, namely 0.8-1. This resulted in an optimum storage duration of 3 days and a boiling time of 28 ± 3 min at which the following values were obtained: a moisture content of the kernels of 7 %, a fat content of 50 % dw, a butter yield of 32 %; butter extracted from these kernels may have a FFA content of 0.8 % and a peroxide value of 2.5 meq O_2/kg and could

be used for cosmetic and food purposes without refining (USAID/WATH 2005, NB 04.02.001 2006). However, this predicted optimum treatment was not yet validated by experimental measurements.

5.4. CONCLUSION

In shea kernels, the fat is organized in large globules with some free spaces inside, and in small globules. The preservation of shea nuts for further use is very critical for end product quality. Handling alternatives of shea nuts such as storage and boiling applied separately or in combination had significant effects on colour and fat content of kernels and the FFA percentage of butter. Longer storage reduced the fat content of the kernels and increased the FFA percentage of the butter. Increasing the boiling time might allow the extraction of more fat from the kernels. The optimum value was found around 32 min. Based on the predicted optimal conditions, the storage of fresh nuts 3 days and their boiling for 28 ± 3 min should be recommended for shea nuts processing. In addition to this research, further investigations should be taken up on other critical processing operations (*viz.* roasting, churning) to upgrade each step of the traditional technique and consequently to improve the yield and quality of butter.

ACKNOWLEDGEMENTS

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Chapter 6

Influence of roasting of shea kernels on their fat content and some quality characteristics of shea butter

F.G. Honfo, A.R. Linnemann, M. Guo, N. Akissoe, M.M. Soumanou, M.A.J.S. Van Boekel (Submitted for publication)

Abstract

In shea production zones in Sub-Saharan Africa, shea butter is mostly produced by women using traditional methods. Improvement of their practices would allow them to obtain better monetary returns for their activities. Roasting of crushed shea kernels is a processing step that has a major influence on the quantity and quality of extracted shea butter. Using a Central Composite Face-Centered design (CCFD), the effect of roasting, specifically roasting time and temperature, was investigated. Both factors influenced fat content (44-53 % dw) of the crushed kernels; colour characteristics and free fatty acid (FFA) content (0.5-3 %) of the butter. In shea butter from differently roasted kernels, 58 volatile compounds were identified, of which 11 were quantitatively dominant, against 27 compounds in butter from unroasted kernels. The ideal practice according to the CCFD model is roasting at 171 ^{o}C for 15 min, which resulted in a fat content of 49 % dw of the kernels, a butter yield of 32 %, a FFA of 1.2 % of the butter, and a peroxide value of 3.2 meq O_2/kg. This optimum roasting time is appreciably shorter than the current practice, suggesting that the use of firewood during traditional processing can be reduced.

Keywords: roasting, volatile compounds, SPME-GC-MS, carbonyls, hexanal, FFA

6.1. INTRODUCTION

The economy of Benin is based on the agricultural sector, in which about 70 % of the population is involved. Cotton has been the most important export cash crop for a long time, providing 90 % of the agricultural export value. Due to national and international difficulties in cotton chains, the Beninese government decided to encourage diversification of agricultural export commodities. Among the selected products were the shea tree (*Vitellaria paradoxa*) products. In Benin, shea kernels represent the third export commodity after cotton and cashew nuts (Elias and Carney 2004). From the shea kernels, butter can be extracted, which to date is mostly done by traditional methods. Shea butter and shea kernels play a significant role in poverty alleviation (Elias and Carney 2004, Master et al. 2004), not only in Benin but also in other Sub-Saharan African countries where shea trees occur. A first step in the empowerment of local women and women's groups to produce shea-based products for the international market is to determine how local low-input production system impacts the quality of shea kernels and butter, and subsequently how local processing practices can be optimised.

Shea butter is used as cooking and frying fat in the production zones, while it is used for medical and cosmetic purposes as well as a cocoa butter substitute in chocolate at an international level. For the various purposes, different qualities of shea butter are used: as cooking fat, more flavourful butters are preferred by consumers (Alander and Andersson 2002). To substitute cocoa butter, shea butter without odour and with high palmitic and stearic acid contents is preferred due to crystallisation and melting characteristics, essential in chocolate confectionery (Lipp and Adam 1998). White or light coloured shea butter with a high amount of unsaponifiables is desired for personal care products (*i.e.* cosmetics, moisturisers, creams) (Di Vincenzo et al. 2005); a high unsaponifiable fraction is a characteristic that makes shea butter special due to its antioxidant and claimed anti-inflammatory properties (Maranz and Wiesman 2004). Apart from these desired attributes, and based on free fatty acids (FFA), peroxide value and moisture content, three shea butter grades are recognised and approved by shea production countries for international trade: the first grade refers to unrefined shea butter, obtained by manual or mechanical methods. It is the highest quality of shea butter, mainly used in the cosmetic industry; its FFA percentage has to be less than 1 %, the peroxide

value less than 10 meq O_2/kg and the moisture content less than 0.05 %. The second grade concerns unrefined shea butter used for food purposes and as edible oils; its FFA content must be between 1 % and 3 %, the peroxide value between 11 meq O_2/kg and 15 meq O_2/kg and the moisture content between 0.06 % and 0.5 %. The third grade of shea butter is mainly used in the soap industry or is refined (USAID/WATH 2005, NB 04.02.001 2006).

Among the traditional unit operations in shea kernel processing, roasting is reported to be critical for butter quality (Womeni 2004, Kapseu et al. 2007). Crushed shea kernels are commonly dry roasted for 30 - 60 min in a pot with direct heating by fire wood (Honfo et al. 2012). Roasting is performed to facilitate fat extraction and to improve sensory characteristics, such as smell, colour, taste, and flavour of butter (Honfo et al. 2012), although it may also affect the overall flavour in a negative way. Certain desirable aroma compounds may be lost and compounds that cause off flavours formed, when roasting is not done properly (Krysiak 2002). In other words, insufficient heating might reduce the yield of oil, and too high temperatures may lead to undesirable volatile compounds derived from peroxides or hydroperoxides (Nawar 1998, Frankel 1985, Krysiak 2002, Krysiak 2006). Most volatile compounds in shea butter can be characterised as fat degradation products, *viz.* ketones, aldehydes, hydrocarbons, and alcohols (Choe and Min 2006). Furthermore, sugars can condense with free amino acids, peptides, or proteins leading to the formation of brown Maillard reaction products (Krysiak and Motyl-Patelska 2006).

Previous studies on the processing of shea nuts into butter (Womeni 2004, Kapseu et al. 2007, Bup et al. 2011) have not assessed the relationship between roasting time and temperature during shea processing on the yield and quality of the butter. The main objective of this study was therefore to assess the impact of roasting conditions of shea kernels on fat yield, and on the FFA percentage, peroxide value and volatile compounds of the butter to optimize production practices in rural, low-input settings.

6.2. MATERIALS AND METHODS

6.2.1. Experimental design

Response surface methodology is a statistical method that uses quantitative data derived from an appropriate experimental design with quantitative factors to estimate the relationship between a response and the factors in order to optimize processes or products (Giovanni 1983). In this study, a central composite face-centered design (CCFD) with 2 factors (Montogomery 2001) was used to assess the simultaneous effect of roasting time (15-45 min) and roasting temperature (120-180 °C) of shea kernels on quality parameters of the resulting butter and to determine the optimum roasting processing conditions. Ranges of roasting time and temperatures were chosen to reflect the actual roasting practices of shea butter processors in most shea production zones including Benin (Honfo et al. 2012). Fat content of kernels, butter yield, FFA percentage, peroxide value and volatile compounds were the quality parameters measured. The design generated 13 combinations (Table 6.1) and each of them was duplicated, giving a total of 26 combinations.

Table 6.1: Different combinations of roasting time and roasting temperature of crushed kernels generated by the CCFD with the different responses

Treatment	Roasting time (Minute)	Roasting temperature (°C)	Fat content (% dw)	Butter yield (%)	Butter brightness (L*)	Butter yellowness (b*)	FFA (%)	Peroxide (meq O_2/kg)
1	30	150	49.1±0.3	31.0±0	1.4±0.1	3.5±0.1	75.4±1.1	18.0±0.3
2	15	150	47.7±0.7	28.5±0.5	1.2±0.1	3.0±0.2	78.1±1.2	18.4±0.9
3	45	120	48.2±0	29.0±0	3.0±0.1	3.4±0.1	73.7±0.8	17.3±0
4	15	120	43.8±0.8	27.5±05	1.2±0.1	2.9±0	77.2±0	18.6±0.2
5	30	120	47.5±0.1	30.0±0	2.2±0.1	3.0±0.1	77.0±0.6	18.6±0.1
6	15	180	52.5±0.2	29.5±0.5	0.7±0	3.2±0.1	57.4±0.7	11.9±0.1
7	30	150	46.3±0.3	32.0±0	1.4±0	3.4±0.1	73.6±0.9	18.7±0.3
8	45	150	49.9±0.1	30.0±0	0.5±0.1	3.7±0	73.3±0	17.9±0.8
9	30	150	49.1±2.6	31.5±0	1.4±0.1	3.2±0.2	74.7±1.2	18.7±0.4
10	30	180	52.8±0.2	32.5±0.5	0.8±0.1	3.7±0.1	66.4±1.8	12.5±1.1
11	30	150	48.5±0.1	32.0±0	1.4±0	3.1±0	75.3±0.3	19.0±0.2
12	45	180	52.3±0	33.0±0	0.6±0	3.9±0.1	67.0±1.2	14.1±0.9
13	30	150	48.5±0.1	31.5±0	1.3±0	3.3±0	75.0±0.3	18.8±0.2

[1]: Mean ± Standard error of mean

6.2.2. Experimental processing

Dried shea kernels processed by boiling followed the sun drying were bought at the local market of Bassila (9°00 N and 1°40 E), a location in Borgou Department, North-Benin. The characteristics of these kernels were: fat content (42-49 % dw), moisture content (7-9 %), and FFA percentage (6-7 %). The kernels were cleaned, sun-dried for 4 hours, sorted and crushed at the laboratory of the Nutrition and Food Science Department of the University of Abomey-Calavi, Benin. The crushed kernels were roasted according to experimental treatments. Once the oven had reached the desired temperature, 500 g of crushed kernels were spread on three trays (48 cm x 35 cm) and put in the oven. The time of roasting was measured from the moment when the temperature reached the desired temperature after putting the trays in the oven. Roasted kernels were cooled at room temperature before processing them into butter by milling with an electric milling machine (Kenwood blender) to get a paste which was churned with water (1 volume of paste against 4 volumes of water). The cream fatty layer after churning was washed three times and subsequent heated. The oil was washed and heated again to remove particles and mucilage from the first stage of heating. The resulting oil was then filtered and left to cool. Samples were taken from the roasted kernels and the butters. Samples were packed in plastic containers and stored at 4 °C until analysis. Two independent samples were prepared for each treatment.

6.2.3. Characterization of shea kernels and butter

Fat content of shea kernels was determined by extraction in a Soxhlet apparatus using petroleum ether as solvent (AOAC 2002). Yield of shea butter was expressed on wet weight as percentage of the mass of the filtered oil (butter) on the mass of kernels used. Colour parameters (brightness L* and yellowness b*) of the butter samples were measured with a Minolta CR-410 (Konica Minolta Optics, INC, Japan). FFA percentage was determined by titration and calculated as oleic acid percentage (NB ISO 660 2006). Titration was also used to determine peroxide values (NB ISO 3960 2006). Each parameter was tested in triplicate.

Volatile compounds in shea butter were assessed by Solid-Phase Micro-Extraction Gas-Chromatography and Mass-Spectrometry (SPME GC-MS) according

to Bail et al. (2009) and Krist et al. (2006). SPME sampling was done by putting two grams of shea butter in vials that were tightly closed with a septum by using a GC crimper and extracted isothermally for 10 h at room temperature using a preconditioned Supelco 57348 2 cm, 50/30 mm DVB/Carboxen/PDMS Stable-Flex fibre for analysing volatile compounds. After sampling, the SPME device was immediately placed into a splitless-mode injection port of a GC-MS instrument (Thermo Scientific DSQ II). Volatile compounds were separated using a Rxi-5ms GC column (60 m length x 0.25 mm inner diameter, 0.25 μm film thickness). The initial temperature of the oven was held for 1 min at 38 °C and then increased by 2.5 °C/min to 175 °C. From that point, the temperature was increased by 50 °C/min to a temperature of 220 °C, which was held for 2 min. The injector port temperature was 250 °C. After using splitless modes for 2 min, a split ratio of 1:40 was used to expurgate the system. A constant carrier gas (helium: 5.0) flow of 1 mL/min was applied. The transfer line temperature was 250 °C, which resulted in an ion source temperature of approximately 225 °C. The same GC was used to obtain the peak areas.The mass spectrometer was operated in electron impact (EI) mode with the ionization voltage set at 70 eV. The scan range was 32-250 amu.Compounds were identified by matching mass spectra with AMDIS and XcaliburQual Browser library of standard compounds. Relative quantifications of compounds were performed as % peak area using integration data.

6.2.4. Statistical analyses

The experimental design was set with Minitab 16.0 software, which was also used for the analyses of variance of the different responses. A polynomial model was proposed to establish the relationship between the responses (Y) and the variables (X) as follows:

$$Y = I + aX_1 + bX_2 + cX_1^2 + dX_2^2 + eX_1X_2 \qquad (1)$$

Where, I is a constant; a and b are linear effect coefficients; c and d are quadratic effect coefficients; and e is an interaction effect coefficient. X_1 and X_2 are the variables roasting time and roasting temperature. The fitted polynomial equations were expressed by different contour plots for each quality parameter in which the surface showed the response of such parameters. Tests for lack of fit and R^2 values were used to determine the adequacy of the models.

6.3. RESULTS AND DISCUSSION

6.3.1. Quality parameters

Analysis of the fat content of the kernels (*FC*) gave the following regression equations for the effect of roasting time (X_1) and roasting temperature (X_2):

$$FC\ (\%\ \text{dw}) = 49.2263 + 0.3822X_1 + 0.2250X_2 - 0.0012X_1^2 + 0.0012X_2^2 - 0.0017X_1X_2 \qquad (2)$$

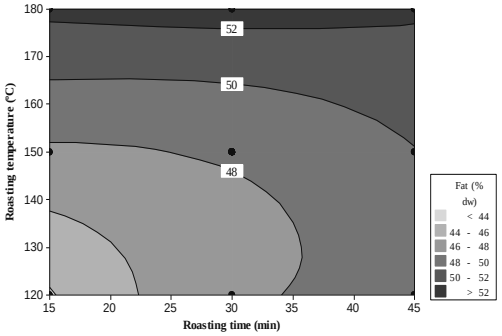
This model explains 94 % of the variation in the fat content of kernels, which ranged from 44 % to 53 % dw (Table 6.1). With a non-significant lack of fit with *P* value of 0.61 generated for fat content, the model could be effectively used to make accurate predictions. For instance a lack of fit is generally used to check the fitness of the regression models and a non-significant lack of fit *P* value is linked to the adequacy of the model and the accuracy of the predictions (Montogomery 2001). Unroasted kernels contained 42 ± 4 % dw of crude fat. Linear terms of the roasting time and roasting temperature influenced the fat content positively and significantly (Table 6.2). The interaction of both factors had a significant and negative influence on the fat content of shea kernels. Irrespective of the roasting time, the contour plots show a gradual increase of the fat content with increasing roasting temperature (Figure 6.1a). This observation might be explained by the reduction of the oil viscosity and the breakdown of cell walls and membranes of the plant material, both caused by heat (Akoh and Min 2008); making the fat present in the crushed kernels better extractable.

Table 6.2: Regression coefficients (RC), constant (*I*), coefficient of determination (R^2) and lack of fit *P* value for fat content of shea kernels, butter yield, L*, b*, FFA and peroxide values of shea butter obtained from kernels subjected to different roasting treatments

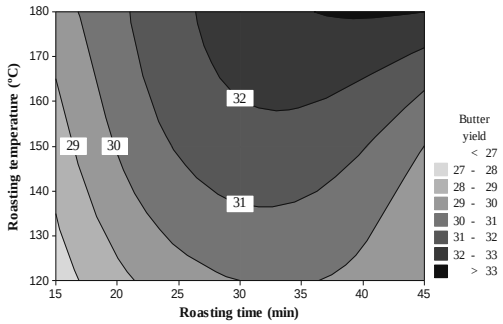
	Fat content (% dw)	Butter yield (%)	L*	b*	FFA (%)	Peroxide value
Roasting time: X_1	0.3822**	0.4228**	-0.8429*	-0.2124	0.2581**	0.0073
Roasting temperature: X_2	0.2250*	-0.0062	1.2181**	0.8180**	-0.1059*	-0.0039
X_1^2	-0.0012	-0.0086**	-0.0040	-0.0012	-0.0016*	0.0007
X_2^2	0.0012**	0.0001	-0.0055**	-0.0032**	0.0004*	0.0004
X_1X_2	-0.0017**	0.0011*	0.0073**	0.0019*	-0.0011**	0.0006
Constant	49.2263	20.9828	11.8046	-32.9767	7.0019	2.5221
R^2	0.94	0.93	0.87	0.86	0.84	0.78
Lack of fit	0.61	0.52	0.01	0.01	0.16	0.77

* Significant at $P < 0.05$; ** Significant at $P < 0.01$

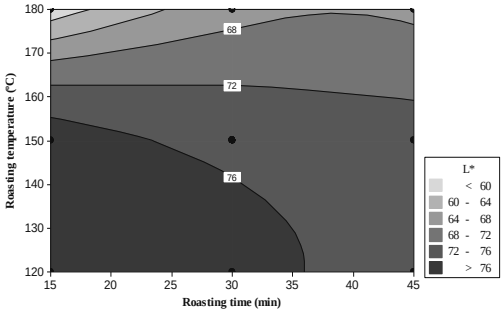
Butter yield increased with increasing roasting time and temperature (Figure 6.1b). Also, the linear and quadratic terms of roasting time as well as the interaction of the two factors had significant effects on butter yield (Table 6.2), which varied from 27 % to 34 % (Table 6.1). The regression model of butter yield explained 93 % of these variations with a non-significant lack of fit with *P* value of 0.52. Unroasted kernels yielded 23 ± 1 % of butter, significantly less than yields from roasted kernels. In general, shea butter extractions yield by traditional methods vary between 26 % and 32 % of kernels mass (Kassamba 1997, Bruinsma 1998, Kapseu et al. 2002); thus, most of the yield found in this study are in this range and some of them exceed the highest value of the range.



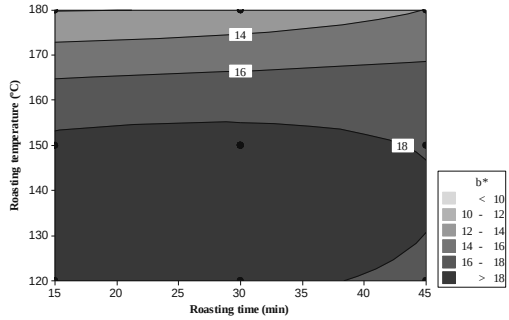
a: Fat content (% dw) of kernels



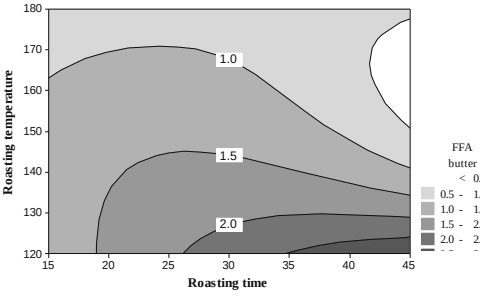
b: Yield (%) of butter



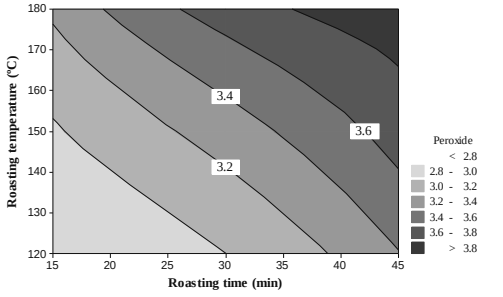
c: Brightness (L*) of butter



d: Yellowness (b*) of butter



e: FFA percentage of butter



f: Peroxide (meq O_2/kg) value of butter

Figure 6.1: Contour plots showing the effect of roasting time and temperature of shea kernels on some quality characteristics of shea butter

Color is one of the most important attributes used during shea butter purchasing. Brightness (L*) and yellowness (b*) were colour parameters taken into account for butter colour. The second order regression equation developed for L* was following:

$$L^* = 11.8046 - 0.8429\boldsymbol{X_1} + 1.2181\boldsymbol{X_2} - 0.004X_1^2 - 0.0055\boldsymbol{X_2^2} + 0.0073\boldsymbol{X_1X_2}$$

The regression equation for the L^* value of butter samples could explain 87 % of the variations of the brightness values which ranged from 57 to 80 (Table 6.1). The model had a significant lack of fit with P value of 0.01. The regression coefficients in Table 6.2 show that the linear terms of the two factors and the quadratic term of the roasting temperature as well as the interactions between the roasting time and the roasting temperature had significant influence on the L^* value. The contour plots show the gradual decrease of L* values with the increase of roasting temperature indicated that the brightness (Figure 6.1c); indicated that the colour of butter samples become darker when the roasting temperature of crushed kernels increased.

Yellowness (b*) of butter samples was also affected by roasting time and roasting temperature of kernels. The CCFD model developed for b* could explain 86 % of the variation of its values which varied from 10 to 19 and had a significant lack of fit with P value of 0.01. The linear and quadratic terms of roasting temperature significantly influenced the yellowness of butter samples (Table 6.2). It also observed that the interaction between the roasting time and temperature also significantly influenced the yellowness of butter. The contour plots developed for b* by the model show linear curves with roasting temperature of kernels irrespective of the roasting time (Figure 6.1d). During roasting, as the temperature increased, butter colour lost its yellowness with decreasing of b* values.

The FFA percentage is one of the most important quality parameters for oil and fat, which is often used as a general indication of oil conditions (Akoh and Min 2008). Linear terms, quadratic terms as well as the interaction of the two factors were found to have a significant effect on FFA percentages (Table 6.2). The regression model linked to FFA percentages was following:

$$FFA\ (\%) = 7.0019 + 0.2581X_1 - 0.1059X_2 - 0.0016X_1^2 + 0.0004X_2^2 - 0.0011X_1X_2$$

This model explained 84 % of the FFA percentage variations and since the model has shown a non-significant lack of fit (*P* value = 0.16), the regression equation explained the variation of the response. For the linear terms, a positive effect was found for the roasting time while a negative effect was observed for the roasting temperature. Therefore, an increase in FFA percentage coincided with an increase of roasting time, and lower values of FFA percentage were observed with an increase in roasting temperature. The decrease in acid value with roasting temperature might be probably linked to the denaturing of lipases at higher cooking temperatures. Fruit lipases are thermolabile and can denature at 80 °C after an hour or at 100 °C after 10 min (Ladurelle 1984). The variations of FFA percentage are illustrated by the contour plots that first show a decrease of the FFA percentage with increasing roasting temperature, irrespective of the roasting time; and second, an increase of the FFA value with increasing roasting time (Figure 6.1e). Most of FFA percentages (0.5-3 %) were higher than the value of 1 % tolerated for cosmetic purposes at international level (Codex Alimentarius 1992, NB 04.02.001. 2006), but lower than the maximum value of 4 % accepted by the Codex Alimentarius for food purposes (Codex Alimentarius 1992). Relatively low FFA values were found for the highest roasting temperature due to the total reduction of moisture in the kernels, preventing hydrolysis reaction.

No significant effects of roasting time and temperature were found on the peroxide values as well as the *P* value of the lack of fit of the model (Table 6.2). Nevertheless, a slight increase in peroxide values (from 2.8 meq O_2/kg to 3.8 meq O_2/kg) occurred with increasing roasting time and temperature (Figure 6.1f). As primary products of oxidation, peroxides might be decomposed during oxidation into secondary products viz. hydrocarbons, ketones, aldehydes, furans, which are among the identified volatile compounds (Frankel 1985, Akoh and Min 2008). This degradation might reduce the amount of peroxide, which would explain the non-significant effect of roasting conditions on peroxide values.

6.3.2. Volatile compounds

Twenty seven compounds were identified in the samples of shea butter from unroasted kernels while 58 compounds were detected in shea butter from different roasting treatments. These compounds were clustered in 11 groups, among which

carbonyls (14 compounds), hydrocarbons (14 compounds) and benzenoid hydrocarbons (8 compounds) were dominant in terms of the number of compounds (Table 6.3).

Table 6.3: Number of identified volatile compounds in shea butter obtained from kernels subjected to different roasting treatments

	Roasting treatments									Shea butter from unroasted kernel
	120 °C			150 °C			180 °C			
Volatile compounds	15 min	30 min	45 min	15 min	30 min	45 min	15 min	30 min	45 min	
Carbonyls	6[a]	9	9	5	11	11	5	12	10	7
Hydrocarbons	7	7	7	10	8	7	8	7	8	8
Benzenoid hydrocarbons	6	5	7	6	6	5	7	8	5	5
Furans	1	4	3	3	3	3	4	3	4	0
Acids	3	4	3	1	4	2	1	2	3	4
Alcohols	2	1	3	1	3	2	1	2	1	2
Ketones	2	3	4	3	3	3	4	4	3	0
Monoterpene hydrocarbons	1	1	1	1	1	1	1	1	2	1
Pyrazines	0	0	0	0	0	0	0	1	2	0
Esters	0	1	0	0	0	0	1	0	0	0
Phenols	0	0	0	0	0	0	0	0	1	0
In total	28	35	37	30	39	34	32	40	39	27

[a]Number of volatile compounds

Compounds in relatively high concentrations were 2-octene (0.1-9.2 %), furfural (0.6-7.1 %), acetic acid (1.4-6.7 %), 5-methyl 2-furancarboxaldehyde (0.5-4.7 %), and hexanal (0.3-2.6 %) (Table 6.4). Most compounds found were also detected by Krist et al. (2006) and Bail et al. (2009a) in shea butter from different regions and by Bail et al. (2009b) in several nut oils mainly used as food ingredients. Most of the identified compounds were generated by the roasting of the kernels, as apparent from the comparison of volatile components of shea butter from unroasted and roasted kernels: furans, ketones, pyrazines, esters, and phenols were absent in shea butter from unroasted kernels and consequently were generated during the roasting process (Jung et al. 1999). Roasting time significantly influenced the number of compounds ($p=0.001$); for instance, the number of compounds increased from 28 to 37 when the roasting time increased from 15 to 45 min at 120 °C. The highest number of volatile compounds was from butter obtained from kernels that were roasted at 180 °C for 30 min. Furthermore, the relative content of each volatile compound varied with roasting time and roasting temperature. For example, the relative content of acetic acid increased from 1.4 to 6.2 % when the roasting time increased from 15 to 45 min at 120 °C.

Table 6.4: Relative contents of volatile compounds identified in shea butter obtained from kernels subjected to different roasting treatments

		Roasting treatments									Shea butter from unroasted kernel
		120 °C			150 °C			180 °C			
Volatile compounds	vRI[a]	15 min	30 min	45 min	15 min	30 min	45 min	15 min	30 min	45 min	
Carbonyls											
Pentanal	710	0.04[b]	0.1	0.01	-[c]	0.01	0.01	-	-	0.02	0.1
Hexanal	799	-	0.5	-	-	2.6	0.5	0.3	2.2	1.1	1.9
Heptanal	908	0.04	0.05	0.03	0.01	0.03	0.02	0.04	0.03	0.02	0.5
2-Heptenal,(E)-	948	0.1	0.2	0.1	0.02	0.1	0.04	-	0.8	-	0.2
Benzaldehyde	968	-	0.3	0.2	-	0.3	0.2	-	0.2	0.1	-
Octanal	1017	-	0.01	0.005	-	0.8	0.4	-	1.0	-	-
Benzeneacetaldehyde	1052	0.1	0.1	0.3	0.04	0.1	0.03	-	-	-	-
Nonanal	1110	0.01	0.01	0.01	0.1	0.1	0.003	0.1	0.005	0.01	0.01
2-Nonenal,(E)-	1150	-	-	-	-	0.01	0.04	-	0.002	0.01	-
2-Decenal,(E)-	1201	0.05	0.002	0.001	0.001	0.1	0.0005	0.001	0.001	0.001	0.001
Decanal	1208	-	-	0.0001	-	0.002	0.0007	-	0.002	0.002	0.0005
2,4-Decadienal,(E,E)-	1319	-	-	-	-	-	-	-	0.0003	-	-
2,4-Decandienal	1328	-	-	-	-	-	-	-	0.0004	0.1	-

Table 6.4 (*Continued*)

2-Undecenal	1378	-	-	-	-	-	-	-	0.1	0.1	-
Total		0.4	1.3	0.6	0.2	4.0	1.2	0.5	4.3	1.5	2.6
Hydrocarbons											
Heptane,4-methyl-	782	-	0.1	0.05	-	0.1	0.1	0.4	1.2	0.03	-
Octane	811	0.6	0.4	0.3	0.5	0.6	0.1	0.2	0.2	0.1	1.2
2-Octene	828	3.6	-	-	4.7	-	-	-	-	-	9.2
2,4-Dimethyl-1-heptene	856	-	0.03	0.02	0.1	0.1	0.01	0.1	0.1	0.04	-
Nonane	900	2.8	-	-	1.3	-	-	-	-	-	2.6
1-Decene	991	-	-	-	1.0	-	-	-	-	-	2.5
Decane	1000	0.2	0.01	0.01	0.1	0.02	0.002	0.1	0.01	0.01	0.5
Limonene	1032	0.05	0.04	0.04	0.05	0.1	0.1	0.1	0.1	0.1	0.1
2-Undecene,(E)-	1087	-	-	-	-	0.04	-	0.004	-	-	-
Undecane	1100	0.0004	0.0004	0.001	0.0002	0.0003	0.0004	0.001	-	0.0003	0.0004
Dodecane	1200	-	0.0002	0.0001	0.0002	0.0001	0.0001	0.0001	0.0002	0.0001	0.0001
Undecane,2,6-dimethyl-	1210	-	-	-	-	-	-	0.2	0.1	0.03	-
Tridecane	1300	0.0001	-	-	0.0001	-	-	-	-	-	-
Naphthalene	1186	0.2	0.4	0.2	0.3	0.3	0.1	0.1	0.1	0.1	0.2
Total		7.5	1	0.6	7.9	1.3	0.4	1.2	1.7	0.3	16.2
Benzenoid hydrocarbons											
Ethylbenzene	871	0.3	0.7	-	-	-	-	-	0.9	-	0.4

Table 6.4 (*Continued*)

p-Xylene	887	0.2	0.3	0.1	0.01	0.1	0.1	0.1	0.1	0.1	0.2
Styrene	893	0.4	0.3	0.2	0.3	0.4	0.2	0.2	0.2	0.2	-
Benzene,(1-methylethyl)-	927	0.02	-	0.01	0.2	0.1	0.2	0.001	0.001	0.1	0.03
Benzene,propyl-	946	0.02	0.02	0.01	0.03	0.03	-	0.04	0.03	-	-
Benzene,1,2,3-trimethyl-	997	-	0.1	0.1	0.1	0.1	0.05	0.1	0.1	0.1	0.1
Benzene,1-methyl-4-(1-methylethyl)-	2228	0.002	-	0.002	0.001	0.002	0.001	0.001	0.001	0.001	0.002
Benzyl nitrile	2512	-	-	0.1	-	-	-	0.2	0.04	-	-
Total		1.0	1.5	0.6	0.6	0.8	0.5	0.6	1.3	0.4	0.8
Furans											
Furfural	849	-	2.0	7.1	0.6	1.0	0.7	0.9	1.4	1.3	-
2-Furanmethanol	1112	0.04	1.2	0.8	0.4	1.1	0.1	0.5	0.5	0.4	-
5-methyl, 2-Furancarboxaldehyde	1431	-	3.9	1.1	0.5	1.3	1.0	0.9	3.0	4.7	-
2,5-Furandione,3,4-dimethyl-	-	-	0.1	-	-	-	-	-	-	-	-
1H-Pyrrole,1-(2-furanylmethyl)-	-	-	-	-	-	-	-	0.3	-	0.6	-
Total		0.04	7.2	8.9	1.4	3.4	1.9	2.7	4.9	7.0	

Table 6.4 (*Continued*)

Acids											
Acetic acid	598	1.4	5.4	6.2	4.0	5.6	6.7	2.5	4.2	4.6	0.5
Hexanoic acid,2-ethyl-	971	-	0.0001	-	-	0.03	0.0003	-	-	-	0.00008
Octanoic Acid	1179	0.003	0.004	0.003	-	0.004	-	-	-	0.005	0.002
Nonanoic acid	1276	0.001	0.0006	0.0003	-	0.0004	-	-	0.0003	0.001	0.0001
Total		1.4	5.4	6.2	4.0	5.6	6.7	2.5	4.2	4.6	0.5
Alcohols											
1-Pentanol	1072	1.8	-	0.02	-	0.03	0.02	0.04	0.1	0.1	-
1-Octanol	1075	-	-	0.6	-	-	-	-	-	-	0.9
1-Octen-3-ol	1259	0.3	-	0.1	0.1	0.2	0.1	-	-	-	-
1,6-Octadien-3-ol,3,7-dimethyl-	1287	-	0.002	-	-	0.1	-	-	0.001	-	0.01
Total	-	2.1	0.002	0.6	0.1	0.4	0.1	0.04	0.1	0.1	0.9
Ketones											
Ethanone,1-(2-furanyl)-	909	-	0.1	0.1	0.1	0.2	0.1	0.1	0.3	0.4	-
Butyrolactone	918	0.05	0.1	0.1	0.3	0.5	0.6	0.1	0.5	1.4	-
Ethanone,1-(1H-pyrrol-2-yl)-	987	0.1	0.3	0.2	0.4	0.5	0.3	0.2	0.2	0.3	-
Acetophenone	1068	-	-	0.1	-	-	-	0.002	0.001	-	-
Total		0.1	0.5	0.5	0.8	1.1	1.0	0.4	1.0	2.1	

Table 6.4 (*Continued*)

Monoterpenes hydrocarbons											
Bicyclo[3,1,0]hexane,4-methylene-1-91-methylethyl	-	-	-	-	-	-	-	-	-	0.7	-
Total				0						0.7	
Pyrazines											
Pyrazien,methyl-	799	-	-	-	-	-	-	-	0.3	0.3	-
Pyrazine,ethyl-	915	-	-	-	-	-	-	-	-	0.7	-
Total									0.3	1.0	
Esthers											
1-Butanol,3-methyl-,acetate	1622	-	0.01	-	-	-	-	0.2	-	-	-
Total			0.01					0.2			
Phenols											
Phenol,2-methoxy-	2793	-	-	-	-	-	-	-	-	0.7	-
Total										0.7	

[a]RI calculated according to the formula: RIx = 100 n0 + 100 (RTx – RTn0) / (RTn1 – RTn0); wherex is the name of the target compound, n0 is identified volatile compound directly eluting before x, n1 is identified volatile compound directly eluting after x, RT is retention time (in min), (http://massfinder.com/wiki/Retention_index_guide)

[b]The relative content of each volatile compound was evaluated as % peak area using integration data (percentage related to the total level of volatiles)

[c]Not detectable

Independent of the processing steps, volatile compounds in shea butter mainly resulted from degradation of long chain and unsaturated fatty acids by hydrolysis and oxidation reactions. Indeed, at high temperature, hydroperoxides, which are the primary oxidation products of lipids, were decomposed into alkoxy radicals and formed aldehydes, ketones, acids, esters, alcohols, and short-chain hydrocarbons (Frankel 1985). As one of the degradation products of fatty acids, the relative content of acetic acid is an indicator of the quality of shea butter (Krist et al. 2006). Volatile compounds in shea butter may also result from the Maillard reaction, and typical Maillard products such as furans could be identified. The large numbers of volatile compounds are formed as minor products and many of them are responsible for off-flavours in fats, oils and other lipid-containing foods (Grosch 1982, Grosch and Ullrich 1987). Therefore, the detection of one or more of these compounds has often been used to indicate the early occurrence of oxidation or to obtain an objective assessment of the flavour changes. For example, pentanal, hexanal and 2,4-decadienal, which are formed during the autoxidation of linoleic acid, have been proposed as indicators for the development of off-flavours in vegetable oils (Frankel 1985, Grosch 1986).

Carbonyls

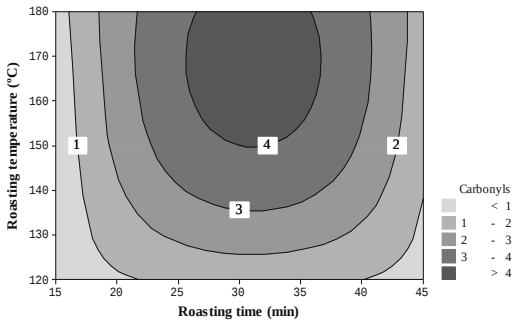
Carbonyls were the most important group of volatiles in shea butter with 14 compounds. Among them, hexanal dominated (Table 6.4). Roasting time and temperature significantly influenced the number of carbonyl compounds. The regression model generated by the two factors explained 91 % of variation in the relative contents of carbonyls. The contour plots of the total carbonyls in relation to roasting conditions show an increase of these compounds with increasing roasting time and temperature (Figure 6.2a). The lowest relative contents were found for the butter from kernels roasted at 150 °C and highest values for butter extracted from kernels roasted at 180 °C for 30 min. Therefore, most carbonyl compounds in shea butter were generated when the kernels were roasted at a high temperature for 30 min. As carbonyl compounds are considered to be indicators of oxidation and degradation of vegetable fats (Grosch 1982), roasting at high temperatures (150-180 °C) for long duration (> 30 min) is not recommended because of the higher number and relative contents of carbonyls in the butter derived from kernels roasted at these temperatures.

Hydrocarbons

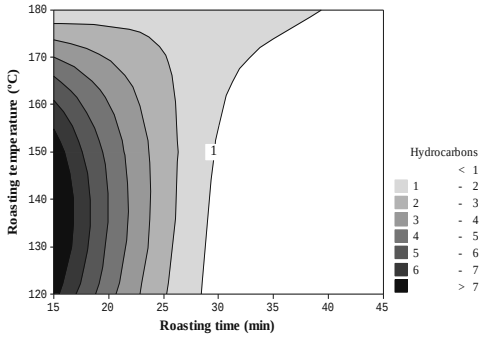
Hydrocarbons formed the second largest group of volatile compounds in shea butter made from roasted kernels. The roasting time and the interaction of roasting time and temperature had a significant influence on the relative contents and the number of hydrocarbons. The highest number of hydrocarbons (10 compounds) and their highest relative contents (7.6 %) were found in shea butter from kernels roasted at 150 °C for 10 min and the lowest contents (0.2 %) were obtained in butter from kernels roasted at 180 °C for 45 min (Table 6.4). The regression model linked to the two factors explained 84 % of the variation in the relative contents of hydrocarbons. The contour plots of the relative contents of hydrocarbons from the different treatments show first a decrease with increasing roasting time, irrespective of the roasting temperature (Figure 6.2b). Secondly, a decrease of the relative contents with increasing temperature after 150 °C and before 30 min of roasting time was apparent.

Benzenoid hydrocarbons

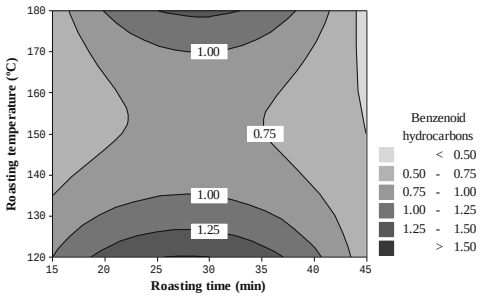
Among the 8 compounds in the benzenoid hydrocarbons group, ethylbenzene was the major compound in terms of its relative content, but this compound was not found in all treatments.The regression model of the relative contents of benzenoid hydrocarbons related to the roasting time and temperature explained 84 % of the variations in these compounds. The effects of the two factors on this group of compounds were significant as well as their interaction. Figure 6.2c shows the contour plots of the relative contents of the benzenoid hydrocarbons in shea butter in relation to roasting conditions. Irrespective of the roasting temperature, the relative content steadily increased from 15 min to 30 min, reaching its peak at 30 min, and then dropped at the highest roasting time (45 min). The highest relative content was obtained in butters from kernels roasted at 120 °C for 30 min and the lowest value in butter from kernels treated at 180 °C for 45 min.



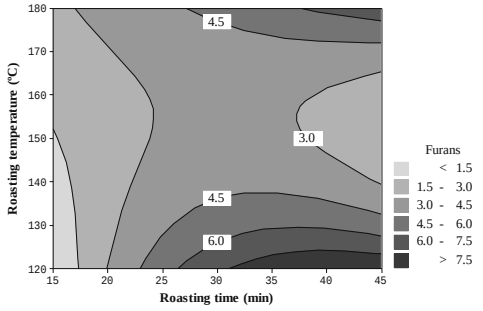
a: Carbonyls



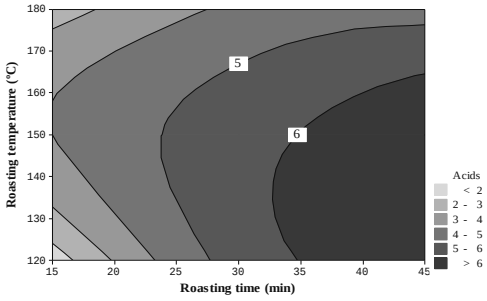
b: Hydrocarbons



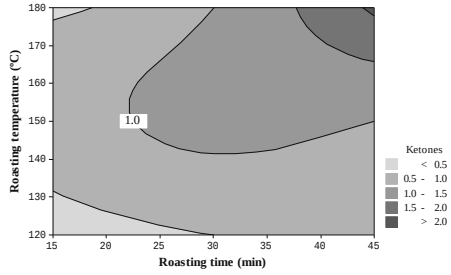
c: Benzoid hydrocarbons



d: Furans



e: Acids



f: Ketones

Figure 6.2: Contour plots showing the effect of roasting time and temperature of shea kernels on relative contents of different volatile compounds in shea butter

However, the hydrocarbons and benzenoid hydrocarbon compounds might not only have resulted from fat oxidation and the Maillard reaction (Farmer and Mottram 1990); they could also come from the surface used for the sun-drying of the kernels as this processing operation was generally done on the tar on roadsides, which is a known as source of hydrocarbons (Basha et al. 2009).

Furans

Furfural was the main compound among the 5 identified furans in different butter samples. Furan compounds are generally formed by the Maillard reaction during kernels roasting (Jung et al. 1999). The relative content of furans was significantly influenced by roasting time and temperature. The regression model linked to the relative content of this group of compounds explained 80 % of their variation. Contour plots of relative contents of furans in shea butter after roasting show an increase of these values with increasing roasting time at the lowest roasting temperature (120 °C), reaching the highest value of 8.9 % (Figure 6.2d). A similar trend was observed when shea kernels were roasted at 180 °C.

Acids

Acetic acid was the major acid among the 4 acid compounds found in different shea butter samples. Linear terms of roasting time and temperature and their interaction influenced positively, and significantly, the relative contents of acid compounds. The regression model explained 95 % of the variations in the relative contents of acidic compounds.The highest relative content (6.7 %) of acids was obtained for butter from kernels roasted at 150 °C for 45 min and the lowest value (0.5 %) in butter from unroasted kernels. Figure 6.2e shows how the relative content of acids in shea butter was affected by different roasting times and temperatures. This figure shows increasing relative contents of acids with increasing roasting time for all roasting temperatures. Therefore, a relatively long roasting time appears to generate more free acids by hydrolysis and oxidation of the fat.

When comparing the observed changes in acids to the FFA percentage of the same samples, differences were observed. These differences might be due to the nature of FFA in shea butter. Indeed, the FFA percentage is calculated as the

percentage of oleic acid and this fatty acid is not volatile due to its high molecular weight. Thus it is not present in the headspace fraction.

Ketones

Linear terms of roasting time and temperature and their interaction influenced positively, and significantly, the relative contents of ketones in shea butter. The regression model for this group of compounds explained 88 % of their variation. The contour plots of the relative contents of the ketones showed an increase with an increase of the roasting temperature when the kernels are roasted for 45 min (Figure 6.2f). As for many compounds found, ketones are often generated during lipid oxidation and also during the Maillard reaction when the fat contains phospholipids (Farmer and Mottram 1990).

6.3.3. Optimisation of roasting process conditions

Optimum conditions for the roasting time and roasting temperature are predicted by the CCFD models. A condition is considered optimal if the desirability value associated to the response is 1 or close to 1 (Minitab 16 guide). The desirability value is generally between 0 and 1 and explains the level of validity of the predicted optimum conditions. With the global desirability of 0.8 the RSM model generates the optimal conditions of roasting time of 15 min and roasting temperature of 171 ^{o}C to get a high fat content (49 % dw or 46 % wet weight) and butter yield (30 % wet weight of kernel mass) as well as low FFA percentage (0.8 %) and peroxide value (3.2 meq O_2/kg). Shea butter with these characteristics is classified as first grade according to the standards set by shea production countries for international trade, and so this butter would be suitable for all purposes, specifically for cosmetic purposes without refining (NB 04.02.001, 2006). An optimum roasting treatment with respect to the presence of volatile compounds cannot be given on the basis of this study as this requires an in-depth olfactory evaluation.

6.4. CONCLUSION

Roasting time and temperature applied separately or in combination had significant effects on all quality parameters investigated. Longer roasting at higher temperatures yielded more fat while a high roasting temperature resulted to shea

butter with low FFA percentage. However, it also generated more volatile compounds of which some may have some negative effects on butter flavour. Most of the compounds found were generated during roasting by hydrolysis, oxidation, and the Maillard reaction and some of them contributed to the aroma profile of shea butter. The optimum roasting conditions for shea processing according to the mathematical model during shea processing were to roast kernels for 15 min at a temperature of 171 ^{o}C. This optimum roasting time appears to be shorter than the current practice; therefore, it can reduce fire wood consumption during traditional processing. However, it is recommended to test the optimum roasting conditions under field conditions by using fire wood as well as the assessing of the effects of these conditions on the unsaponifiable fraction, on sensorial attributes such as colour, flavour, taste, smell and the nutritional value of shea butter.

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Chapter 7

Physico-chemical characteristics and volatile compounds of shea butter under different storage conditions

F.G. Honfo, A.R. Linnemann, N. Akissoe, M.M. Soumanou, M.A.J.S. Van Boekel

(Submitted for publication)

Abstract

Several quality characteristics (colour, free fatty acid percentage, peroxide value and volatile compounds) of shea butter stored under conditions as occurring in tropical production areas were studied. Three commonly used packaging materials were applied to store the butter for six months at ambient (28-30 ^{o}C) and low temperatures (4-7 ^{o}C). After 6 months of storage, all parameters investigated were significantly affected by storage conditions while the effects of the packaging materials were less pronounced. Most changes occurred at ambient conditions: after 6 months of storage, the increase of FFA of butter stored in a calabash at ambient conditions (FFA = 1.9 %) was three times higher than that stored in a refrigerator (FFA = 0.5 %). Also, the rate of oxidation reactions was two times higher at ambient temperatures. Black plastic containers seemed to be the better packaging materials for a long storage period.

Keywords: shea butter, storage conditions, calabash, black plastic, free fatty acid, volatile compounds.

7.1. INTRODUCTION

Vitellaria paradoxa, commonly known as the shea butter tree, is indigenous in the dry savannah woodlands of Africa (Boffa 1999). Its nuts contain up to 57 % of fat, which is traditionally extracted by local populations for purposes ranging from cooking to traditional pharmacology (Hall et al. 1996). Shea butter is also much appreciated for cosmetic and pharmaceutical purposes as well as being a fat replacer in chocolate manufacture at international level (Tano-Debrah and Ohta 1994, Hall et al. 1996, Alander 2004). Shea nuts are a seasonal product, which is generally available for 3 to 5 months annually, depending on the location. The dried nuts or kernels are stored for several months during which butter processing is performed regularly (Honfo et al. 2012). Storage of the butter after processing is also common practice; for a few days at processors' level before it is sold, up to several months at consumers' level during utilization (Honfo et al. 2012). In local conditions, shea butter is generally stored in a relatively cool area (28-30 ^{o}C) to avoid melting. Different packaging materials are used to store the butter and the most frequently used ones are calabashes, plastic containers, plastic bags, and aluminium containers (Honfo et al. 2012). All these packaging materials are always available in various sizes in the production zones. Calabashes are locally produced from the dry shells of the gourd plant. It is the cheapest packaging solution among the available packaging materials and the most popular one.

Proper storage conditions are essential to maintain the quality of shea butter for long duration. Indeed, packaging material, storage environment (*viz.* temperature, light, oxygen, relative humidity) and storage duration are critical factors in preserving the quality of foods (Gunstone 2002). Water activity (a_w) is an important parameter in predicting and controlling the shelf life of food products. Water acts in two ways in this respect: i) it can influence deteriorative chemical reaction rates because it acts as a reagent, ii) it is also a solvent for reactants and products; also microbiological activity depends on water activity (van Boekel 2009). Several changes caused by the different factors or chemical reactions during storage are reflected in many quality characteristics of fat *e.g.* rancid flavour, changes in colour, texture, changes in functional properties, a high percentage of free fatty acid (FFA) (Nawar 1998). A rancid flavour in fat is due to the presence of some volatile compounds, which are derived from peroxide and hydroperoxide formation during

fat oxidation reactions (Frankel 1985). FFA is produced during hydrolysis reactions in which mono-, di- or triglyceride molecules react with water (Kiritsakis and Tsipeli 1992). Lipases speed up this reaction enormously and are therefore generally responsible for fat hydrolysis if present (De Man 1999).

Some works on shea products, *viz.* kernels and butter, have been done to improve local processing (Olaniyan 2002, Womeni et al. 2006a,b, Kapseu et al. 2007, Bup et al. 2011); some research focused on the storage of the fresh nuts. Several researchers have also investigated changes in fat and shelf life. However, specific studies on storage of shea butter are limited. Thus, keeping in mind that shea butter has to be stored and handled with care after its production for further use, it is necessary to test packaging materials used for their suitability to assure quality during storage in different environments. In addition, shea butter for export has to meet the requirements for different uses. The aim of this work was to investigate the effect of (1) traditional packaging materials, (2) storage duration and (3) storage temperature on relevant quality characteristics of shea butter, namely FFA percentage, peroxide value and volatile compounds responsible for butter flavour. The hypothesis underlying this objective was that quality changes of shea butter during storage are due to chemical reactions influenced by storage conditions and packaging.

7.2. MATERIALS AND METHODS

7.2.1. Sample preparation and storage

Shea kernels were bought at the local market of Bassila (9°00 N and 1°40 E), located in Donga Department, in the north-western part of Benin. The kernels were processed into butter: kernels were cleaned, sun-dried for 4 h on a cement platform, sorted and crushed. The sorting consisted of selecting the intact kernels from the broken and damaged kernels. The crushed kernels were roasted for 20 min at 130 °C in an oven, milled, mixed with three volumes of water and churned manually before washing. Next, the cream was transferred to a cooking pot, heated for 45-60 min around 100 °C and left for 20-30 min. An equal volume of water was added to the crude oil and subsequently the top layer was separated and dehydrated by heating. The resulting oil was filtered and cooled for 24 hours to obtain the shea butter. The butter was packed in three packaging materials, namely black plastic containers with

a lid, transparent plastic containers with a lid, and calabashes with a cover made from calabashes as well, and stored for 6 months at either ambient conditions (28-30 °C, relative humidity: 81 ± 3 %) with exposure to daylight, or cool and dark conditions in a refrigerator (4-7 °C). Each packaging material was duplicated. A butter sample was taken at the begining of the storage period. Thereafter, monthly, 2 samples were taken from each packaging material.

7.2.2. Characterization of shea butter

The most important colour parameter for shea butter is its yellowness value (b*); thus, this was measured using a chromameter (Minolta CR210b). The FFA percentage was determined by titration and calculated as oleic acid percentage (NB ISO 660 2006). Titration was also used to determine peroxide values (NB ISO 3960 2006). Water activity (a_w) was assessed for each sample by a thermo-hygrometer recorder (hygrolab 2 rotronic 8303 Bassersdorf, USA). Each parameter was measured in triplicate.

Volatile compounds in shea butter were assessed by Solid-Phase Micro-Extraction Gas-Chromatography and Mass-Spectrometry (SPME GC-MS) according to Bail et al. (2009) and Krist et al. (2006). SPME sampling was done by putting two grams of shea butter in vials that were tightly closed with a septum by using a GC crimper and extracted isothermally for 10 h at room temperature using a preconditioned Supelco 57348 2 cm, 50/30 mm DVB/Carboxen/PDMS Stable-Flex fibre for analysing volatile compounds. After sampling, the SPME device was immediately placed into a splitless-mode injection port of a GC-MS instrument (Thermo Scientific DSQ II). Volatile compounds were separated using an Rxi-5ms GC column (60 m length x 0.25 mm inner diameter, 0.25 µm film thickness). The initial temperature of the oven was held for 1 min at 38 °C and then increased by 2.5 °C/min to 175 °C. From that point, the temperature was increased by 50 °C/min to a temperature of 220 °C, which was held for 2 min. The injector port temperature was 250 °C. After using splitless mode for 2 min, a split ratio of 1:40 was used to expurgate the system. A constant carrier gas (helium: 5.0) flow of 1 mL/min was applied. The transfer line temperature was 250 °C, which resulted in an ion source temperature of approximately 225 °C. The mass spectrometer was operated in electron impact (EI) mode with the ionization voltage set at 70 eV. The scan range

was 32-250 amu. Compounds were identified by matching mass spectra with AMDIS and Xcalibur Qual Browser library of standard compounds. Relative quantification of compounds was done as % peak area using integration data.

7.2.3. Statistical analysis

Analysis of variance was used to determine the effect of the three factors (*i.e.* storage duration, packaging material and storage temperature) on the quality characteristics (b*, FFA percentage, and peroxide value). Correlations between the three factors and different variables were also established. *P* values < 0.05 were considered significant. Data of volatile compounds were described qualitatively and quantitatively. All of these analyses were performed using SAS 9.1 software (SAS Institute Inc., Cary, NC, USA).

7.3. RESULTS AND DISCUSSION

7.3.1. Effect of storage conditions on quality characteristics of shea butter

The values of the colour characteristic b* of butter were found to be significantly affected by storage duration, storage temperature and packaging material (Table 7.1). As storage time increased, butter lost its yellowness with decreasing b* values and became more pale, irrespective of the packaging material. These observations were confirmed by negative correlations between b* with storage duration (r=-0.653, *p=0.000*) and between b* with storage temperature (r=-0.497, *p=0.000*). Significant differences were also noticed between the two storage temperatures, irrespective of the packaging material and the storage duration. The higher the storage temperature, the faster the colour of the butter changed; thus, the rate of the decrease of b* values was less pronounced during storage at low temperatures (Figure 7.1b). At ambient conditions, some differences were also noticed among the tested packaging materials. For example, the colour of butter stored in transparent plastic was more affected than the butters stored in the other types of packaging; the mean values of b* ranged from 28.4 at the beginning of the storage period to 25.2 after 6 months of storage. This observation can be explained by the fact that light can enter the product in the case of transparent material, and that colour changes of fat during storage are initiated or accelerated by light (Kim et al. 2002). Additionally, the yellow colour of shea butter is caused by carotenoids and the

main cause of the degradation of carotenoids is oxidation, which is also accelerated by light (Clydesdale 1998). Thus, plastic packaging for shea butter ought to be opaque in order to protect from the pro-oxidative action of light.

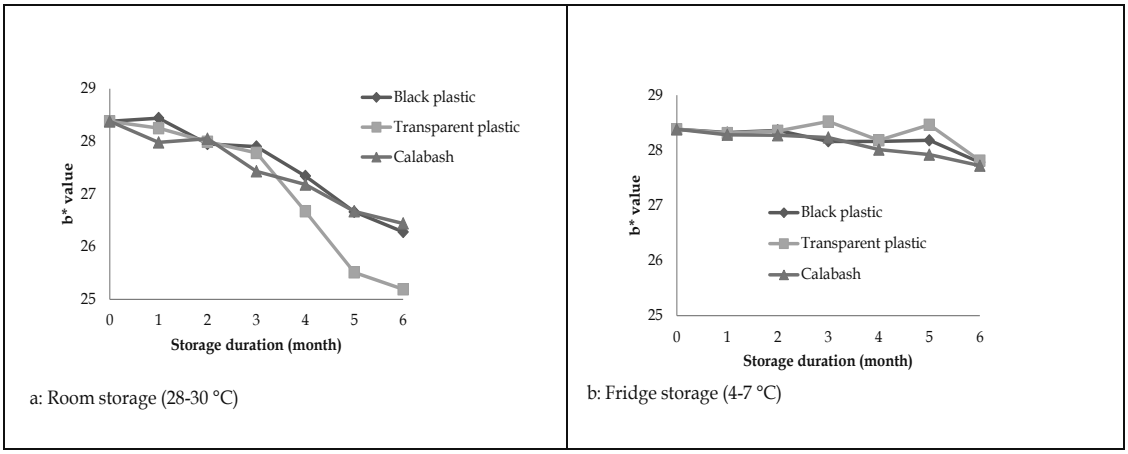


Figure 7.1: Change of yellowness of shea butter during storage in different packaging at room (a) and refrigerator (b) temperature

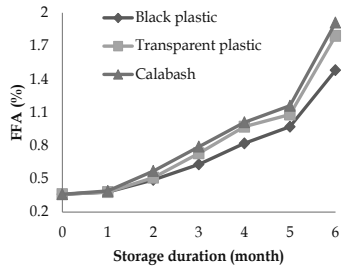
Significant effects of storage duration (r = 0.635, *p=0.000*) and storage temperature (r = 0.509, *p=0.000*) on FFA percentage were observed while no significant effect was observed for packaging materials. These effects, however, were more pronounced at ambient conditions (28-30 °C) (Table 7.1). In fact, the FFA percentage increased from 0.36 % to 1.48 % in butter packaged in black plastic after 6 months of storage at room temperature while the increase was less pronounced (from 0.36 % to 0.53 %) for butter packaged in the same container and kept in the refrigerator (Figure 7.2). The same trend was also observed for butter packaged in transparent plastic and in calabashes. At room temperature, butter stored in calabashes had the highest percentage (1.91 %) of FFA after 6 months of storage. Considering the FFA requirements for cosmetic purposes (less than 1 %) and for food utilization (less than 3-4 %) (USAID/WATH 2005, NB 04.02.001 2006), butter stored in the refrigerator could still be used for cosmetic purposes, while butter stored at room conditions was still suitable for food purposes after 6 months of storage. Regarding the FFA percentages in samples stored at different temperatures, it can be concluded that the hydrolysis rate is 2-3 times higher at ambient conditions (28-30

°C) than refrigerator conditions (4-7 °C). Obviously, the activity of lipase increases with temperature (unless the enzyme becomes inactivated) (Akoh and Min 2002). Additionally, the negative correlation between the yellowness factor b* and the FFA percentage (r=-0.903, *p=0.000*) indicates a relation between the FFA percentage and the colour change of the butter. This observation was also noticed in cocoa butter. Indeed, Akaki et al. (2013) found that low acidity was related to cocoa butter with desired yellowness.

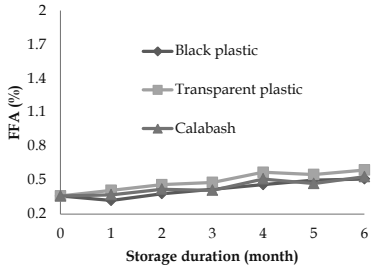
Table 7.1: Quality parameters of shea butter samples before and after 6 months of storage

		Quality parameters		
	Packaging materials	b*	FFA (%)	Peroxide (meq O_2/kg)
Before storage		28.4 ± 0.1[1a]	0.4±0.2[c]	2.6±0.1[c]
After storage at 28-30 °C	Black plastic	26.3 ± 0.4[c]	1.5 ± 0.3[b]	4.5 ± 0.4[ab]
	Transparent plastic	25.2 ± 0.2[d]	1.7 ± 0.3[a]	4.9 ± 0.3[a]
	Calabash	26.4 ± 0.4[b]	1.9 ± 0.3[a]	5.0 ± 0.3[a]
After storage at 4-7 °C	Black plastic	27.8 ± 0.3[a]	0.5 ± 0.4[c]	3.4 ± 0.3[b]
	Transparent plastic	27.8 ± 0.2[a]	0.6 ± 0.3[c]	3.6 ± 0.2[bc]
	Calabash	27.7 ± 0.3[ab]	0.5 ± 0.4[c]	3.5 ± 0.2[b]

Mean ± standard error of mean; means with different letters in a column are statistically different at 5% significance level



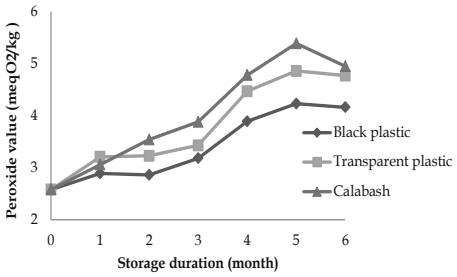
a: Room storage (28-30 °C)



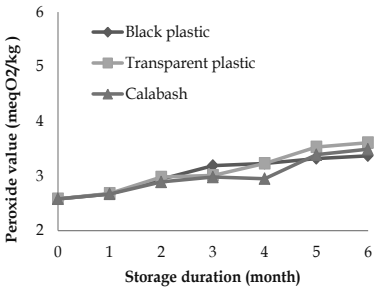
b: Fridge storage (4-7 °C)

Figure 7.2: Evolution of FFA percentage of shea butter during storage in different packaging at room (a) and refrigerator (b) temperature

Significant and positive effects of storage duration (r=0.697, *p=0.000*) and storage temperature (r=-0.483, *p=0.000*) were found on peroxide values. The rate of this reaction was two times higher at room temperature than at refrigerator temperature, giving peroxide values ranging from 2.6 meq O_2/kg to 5.4 meq O_2/kg at room temperature and from 2.6 meq O_2/kg to 3.5 meq O_2/kg at refrigerator temperature (Figure 7.3). With respect to peroxide formation, Berger and Hamilton (1995) noticed that during storage peroxide formation is slow at first during a period called induction period, which may vary from a few weeks to several months depending upon the type of fat or oil. However, the type of packaging material used also influenced the peroxide value during storage. Relatively higher peroxide values were found for the samples packaged in calabashes. Butter in calabashes appeared to be more susceptible to oxidation than butter in the other packaging materials, probably since the cover did not fit the container properly, allowing air to get into contact with the sample. Kirk and Sawyer (1991) reported that the rancid state of fats begins to be noticeable when the peroxide value is between 20 and 40 meq O_2/kg. Thus, even though peroxide values increased in butter kept at room temperature, the increase was probably not too high to cause noticeable rancidity. In addition, peroxide values of all butter samples were lower than the thresholds of 10 meq/kg and 15 meq/kg tolerated for cosmetic and food purposes, respectively. However, a low peroxide value does not necessarily indicate that fat or oil is not oxidized. As reported in the literature (Frankel 1985, Choe and Min 2006, Kim and Min 2008), a combined index of primary and secondary oxidation products may indicate the state of oxidation of products better. A positive correlation (r=0.842, *p=0.000*) was found between the peroxide value and the FFA percentage, showing the influence of hydrolysis reactions on oxidation. FFAs are known to enhance the picking up of trace metals from equipment or storage tanks, thereby increasing the rate of oxidation (Nawar 1998).



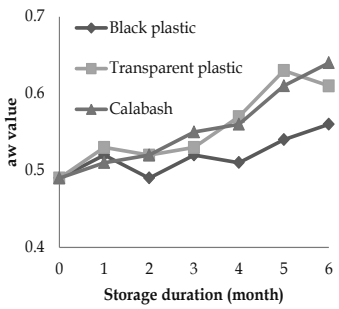
a: Ambient storage (28-30 °C)



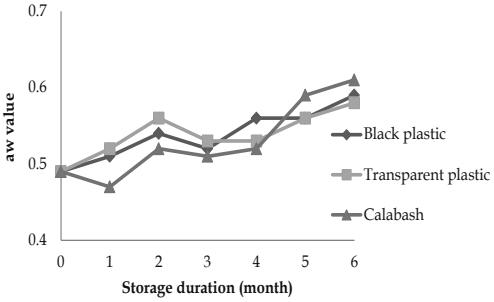
b: Fridge storage (4-7 °C)

Figure 7.3: Evolution of peroxide values (meq O_2/kg) of shea butter during storage in different packaging at room (a) and refrigerator (b) temperature

However, chemical reaction rates concerning oxidation and hydrolysis may be influenced by water activity. For instance, lipid oxidation is strongly promoted at very low water activity and decreases with increasing water activity, while hydrolysis increases with water activity as water is a reagent in hydrolysis (van Boekel 2009). During the 6 months of storage of the experiment, a_w varied from 0.5 to 0.6 in the samples of shea butter (Figure 7.4); thus water activity did not change drastically and thus will not have influenced chemical reactions in shea butter substantially. Lipid oxidation has a minimum rate at about a_w = 0.2 to 0.3 (Rockland and Nishi 1980); therefore, the rate of this reaction in shea butter may not have been noticeably influenced by the water activity. Water activity is a function of temperature; thus, storage temperature can change the effect of a_w on the microbial, chemical, and physical properties of foods (Le Meste et al. 2001). Yet in this case, a similar trend in a_w was noticed during storage under the two conditions, so it is not likely that the storage temperature had an effect on reaction rates via the a_w. Another important conclusion to be drawn from the a_w results is that microbial spoilage can be excluded at a_w between 0.5 and 0.6. Compared to butter made from cow's milk and margarine, the a_w of shea butter is much lower. Unsalted butter and margarine have an a_w of about 0.99 while salted butter or margarine has an a_w of about 0.91 (Welti-Chanes et al 2007). In this respect shea butter is similar to cocoa butter.



a: Room storage (28-30 °C)



b: Fridge storage (4-7 °C)

Figure 7.4: Evolution of water activity of shea butter during storage in different packaging at room (a) and refrigerator (b) temperature

7.3.2. Effects of storage conditions on volatile compounds of shea butter

After 6 months of storage, the number of volatile compounds in shea butter increased from 42 to 54 at room temperature and from 42 to 47 compounds at refrigerator temperature (Table 7.2). Apparently, the number of compounds increases with the storage duration, whatever the storage temperature and packaging material. The production rate of volatile compounds increased with increasing storage temperature and this observation is understood as most of the volatile compounds are generated by oxidation reactions, which were two times faster in ambient conditions than in refrigerator conditions. Most of the compounds found were identified by Krist et al. (2006) and Bail et al. (2009) in shea butter from different regions. Independent of the processing steps, the composition of volatile compounds in shea butter mainly results from degradation of long chain fatty acids by hydrolysis due to enzymatic activity as well as oxidation (Bail et al. 2009). For instance, a variety of compounds, such as hydrocarbons, alcohols, furans, aldehydes, ketones, and acid compounds, are formed during oxidation as peroxide or hydroperoxide degradation products. Volatile compounds might also result from the Maillard reaction as shea butter is derived from a roasted product. Most of these volatile compounds are responsible for the off-flavour in oxidized edible oils (Min and Bradley 1992). Comparing the results for the different packaging materials, a similar number of compounds was identified at the same storage temperature, but different compounds

were detected (Table 7.2). Most of the volatile compounds occurred in small quantities, but this observation does not mean that they were not important. The 10-15 quantitatively most dominant compounds in the different packaging materials are discussed next.

Table 7.2: Number of identified volatile compounds in shea butter before and after storage

Volatile compounds	Before storage	After storage at 28-30 °C			After storage at 4-7 °C		
		Black plastic	Transparent plastic	Calabash	Black plastic	Transparent plastic	Calabash
Carbonyls	10	12	12	12	11	11	12
Hydrocarbons	7	9	9	9	8	8	9
Benzenoid hydrocarbons	7	8	10	10	6	7	7
Furans	2	3	2	2	2	2	1
Acids	5	5	5	5	5	5	5
Alcohols	4	6	6	6	5	5	6
Ketones	5	5	5	5	5	4	5
Monoterpene hydrocarbons	1	1	1	1	1	1	1
Esters	1	1	1	1	1	1	0
Phenols	2	2	3	3	2	2	3
Total	42	52	54	54	46	47	47

Storage in black plastic. The dominant volatile compounds of samples stored in black plastic at ambient temperature were dodecane, pentanal, decane, furan 2-pentyl and phenylethyl alcohol (Figure 7.5a). A gradual increase of dodecane (1-21 % of total amount) and decane (1-18 %) was observed throughout the storage period. Both compounds are hydrocarbons with an undesired petrolic or tarry odour (Umano and Shibamoto 1987); their increase during storage may affect the butter flavour. A sharp decrease of furan, 2-pentyl (from 21 % to 1 %) was observed after 2 months of storage till the end of storage. In terms of odour profile, this corresponds with a shift from a fruity, flowery and sweet odour (Fors 1983) to a more tarry/oily, fruity odour (Umano and Shibamoto 1987, Chung et al. 1994, Adams 2007). During storage in the refrigerator, the dominant compounds of samples packed in black plastic were pentanal, furan, 2-pentyl, phenylethyl alcohol, limonene, and acid acetic (Figure 7.5b). A gradual increase (3-28 % of total amount) of pentanal was noticed throughout storage. Furan, 2-pentyl showed a peak (41 %) at 2 months of storage before its rapid decrease (4 %) from the third month onwards until the end of storage. Acetic acid was the main free acid dominant in shea butter; its content was higher during refrigerator storage, ranging from 2 % to 12 %. Thus, during refrigerated storage, the flavour of butter changed towards compounds with a more pungent, green, and fruity profile (Sumitami et al. 1994, Qian and Reineccius 2003).

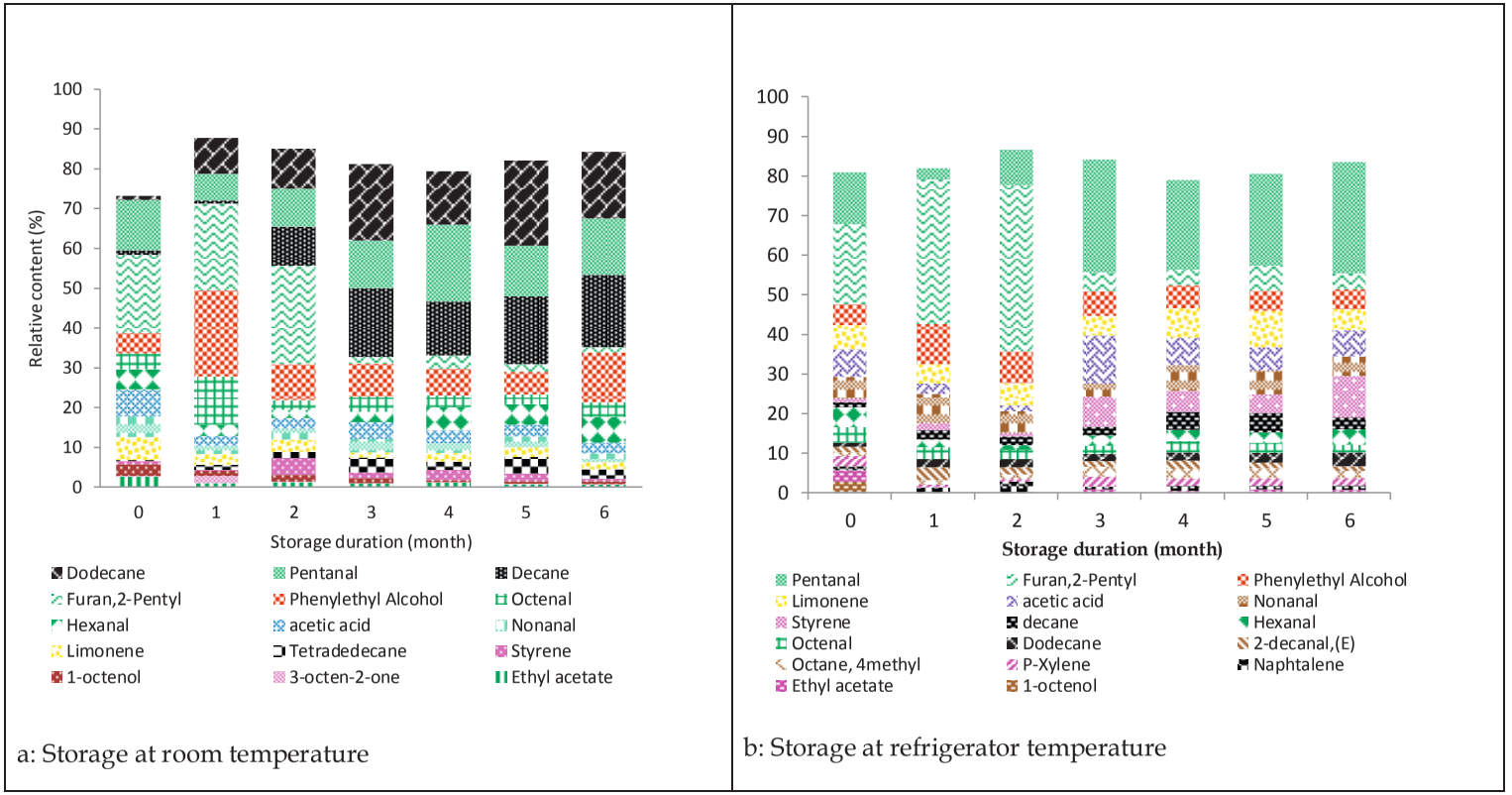
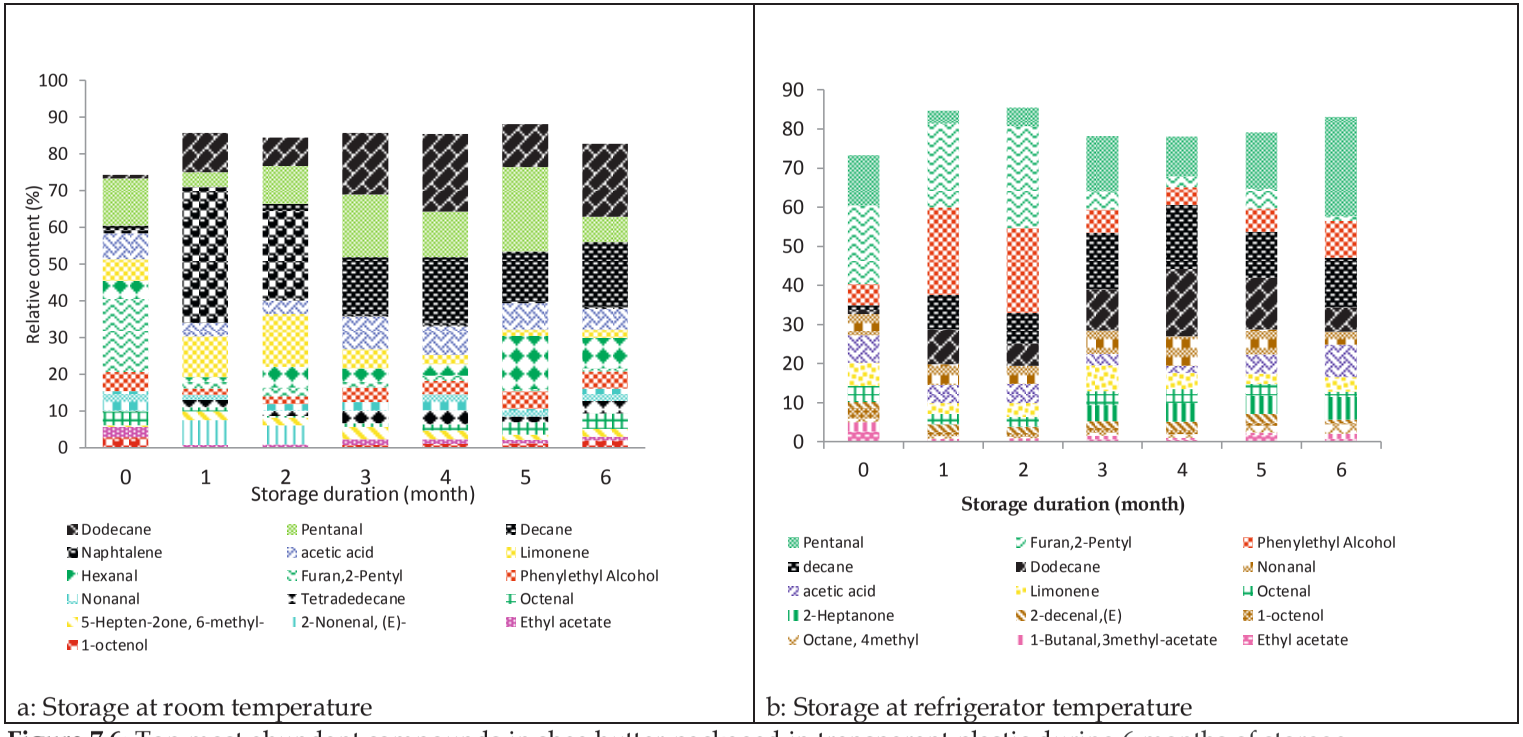


Figure 7.5: Top most abundant compounds in shea butter packaged in black plastic during 6 months of storage
The colour black represents tarry oily odours, green: fruity green odours, red: floral odours, brown: meaty mushroom-like odours, pink: sweet turquoise: fatty, nutty, cucumber (http://www.flavornet.org/flavornet.html / http://www.odour.org.uk/cgi-bin/)

***Storage in transparent plastic*:** At storage under ambient conditions, dodecane, pentanal, naphthalene, decane, acetic acid, and hexanal were dominant (Figure 7.6a). Among them, naphthalene was the main compound (25-35 %) during the first two months. Gradual increases of the relative contents of dodecane (1-21 %), pentanal (4-23 %), and decane (2-18 %) were noticed throughout the storage period. These compounds, as well as naphthalene, belong to hydrocarbons group and are generally generated by oxidation and fuel. As with all plastic containers, an increase of the relative content of the alkanes was noticed. Based on the odour profiles of these compounds, the butter odour may change from a coal tar and fatty green citrus profile to a more tarry oil and fruity profile during storagein this container (Umano and Shibamoto 1987, Gasser and Grosch 1988, Chung et al. 1994). During refrigerated storage, the amounts of decane (1-16%) and dodecane (1-17 %) increased, changing the odour to a more tarry and oily profile (Figure 7.6b).



a: Storage at room temperature

b: Storage at refrigerator temperature

Figure 7.6: Top most abundant compounds in shea butter packaged in transparent plastic during 6 months of storage
The colour black represents tarry oily odours, green: fruity green odours, red: floral odours, brown: meaty mushroom-like odours, pink: sweet turquoise: fatty, nutty, cucumber (http://www.flavornet.org/flavornet.html / http://www.odour.org.uk/cgi-bin/)

Storage in calabash: During the first two months of ambient storage, furan, 2-pentyl was the dominant volatile (45 %) among the major compounds found in butter packed in calabashes (Figure 7.7a). A gradual increase (14 to 52 %) of pentanal was noticed throughout the storage period. After 6 months the odour profile was dominated by pentanal and furan, 2-pentyl, which could give a pungent, fruity and green odour (Sumitami et al. 1994, Qian and Reineccius 2003). Apart from these two compounds, phenylethyl alcohol, acetic acid, and hexanal were also dominant with relative contents of about 10 % for each of them. A similar trend, but less pronounced, was observed during refrigerated storage (Figure 7.7b). Additionally, the content of each compound changed during storage. Furan, 2-pentyl was dominant at the beginning, while pentanal was present in a larger proportion at the end of the storage. Another noticeable change was the absence of hexanal during refrigerated storage and the occurrence of new compounds, *viz.* limonene and decane, which may impact the odour profile of the butter.

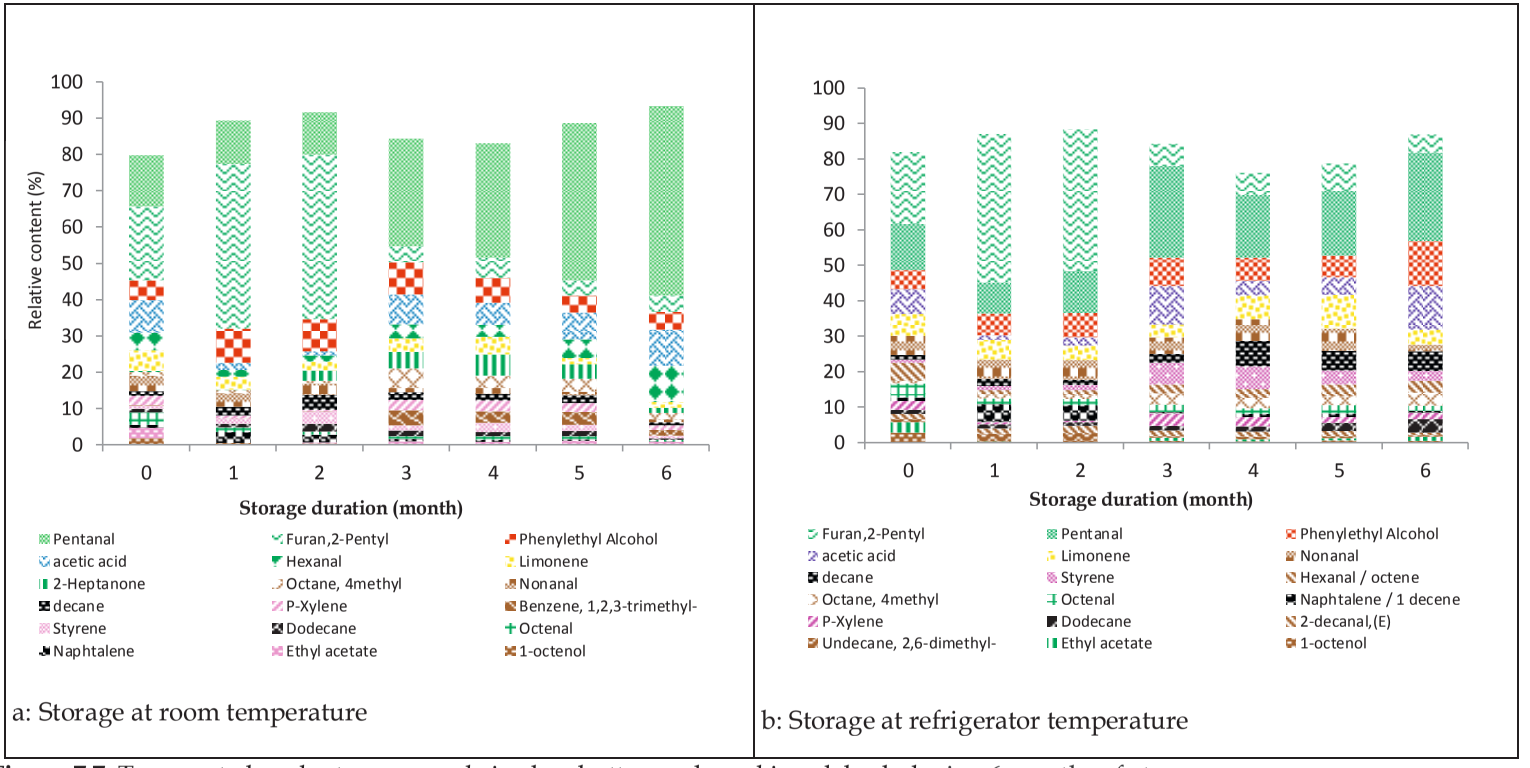


Figure 7.7: Top most abundant compounds in shea butter packaged in calabash during 6 months of storage
The colour black represents tarry oily odours, green: fruity green odours, red: floral odours, brown: meaty mushroom-like odours, pink: sweet turquoise: fatty, nutty, cucumber (http://www.flavornet.org/flavornet.html / http://www.odour.org.uk/cgi-bin/)

7.4. CONCLUSION

Shea butter stored at ambient conditions for a period of six months showed a change of colour, an increase in the FFA percentage, peroxide value and number of volatile compounds. Storage temperature and storage duration significantly affected the quality attributes of shea butter, essentially the chemical properties with impact on colour and odour, and presumably also on taste. Shea butter stored at ambient conditions was affected most during storage, even though the changes observed would not impede its use for food purposes. After storage, butter samples stored in the refrigerator can still be used in cosmetic and pharmaceutic industries. For shorter periods (1-3 months), all of the three packaging materials studied can be used. The increase in the rate of chemical reactions at ambient conditions is in accordance with the hypothesis that the quality changes of shea butter during storage are caused by chemical reactions. However, the plastic containers, notably the black ones were the best option as demonstrated by the small changes during storage. In the absence of possibilities to store butter at low temperatures, it is recommended to keep shea butter in a relatively cool area to maintain the quality of the product. However, as plastic containers vary in their permeability to oxygen, light and water due to their composition, further studies could focus on assessing the plastic packaging material that will be most appropriate for shea butter storage.

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Chapter 8

General discussion

8.1. INTRODUCTION

This study investigated the quality of shea kernels and butter produced in Benin by analysing processing under local conditions with the aim to analyse and optimise traditional processing and improve the quality of the resulting products. To achieve this objective, investigations on shea products were reviewed and indigenous knowledge related to shea processing was explored as entry points. Next, the influence of certain processing operations (*i.e.* storage and boiling of fresh nuts, roasting of kernels) was assessed to find the optimum conditions for high quality kernels and butter, *viz.* maximum yield, butter with a low percentage of free fatty acids (FFA) and a low peroxide value. Additionally, volatile compounds of shea butter were identified and quantified. Prior to this, the characteristics of shea kernels and butter made by different processing methods were investigated. The last investigation assessed quality degradation of shea butter under different storage conditions.

This chapter summarizes the main findings of the research and discusses the progress made in relation to the research questions. In addition, it debates remaining methodological questions about the quality of the studies in a prospective view. The chapter ends with suggestions for future research and recommendations for the improvement of shea processing.

8.2. MAIN FINDINGS IN RELATION TO THE RESEARCH OBJECTIVES

This thesis was design-oriented and tackled specific research questions along the production chain of shea kernels and butter (Figure 1.4 in chapter 1). First of all, the state of the art in the shea products domain has been critically assessed. The review (chapter 2) revealed that most research had focused on shea kernels and butter and that shea pulp had been neglected (Figure 8.1), whereas in the production areas, the shea fruit is actually much appreciated by local populations for its sweet pulp (45-60 % of the fruit weight), which is rich in proteins (2.4-10.3 g/100 g dw), carbohydrates (4-33.9 g/100 g dw), iron (1-17.6 mg/100 g dw), zinc (1-16 mg/100 g dw), and calcium (72-1103 mg/100 g dw) (Maranz et al. 2004a). Apparently, the widely recognized dietary and socio-economic value of shea butter has reduced research efforts on shea fruit pulp. More focus on the nutritional value of shea pulp and its potential role in the diet of local populations with its possible processing to

other products, *viz.* jams, conserves, or dry fruit would be useful for its valorization. Shea kernels and butter are often processed by traditional methods and large variations were observed in the reported values on the composition of shea kernels and butter. Aside from the variations linked to processing, provenance of the sample, impact of soil, climate and harvesting period as identified by several authors, different analytical methods might also have contributed to the variability in the outcomes. Therefore, more attention should be given to the sampling method as well as the accuracy and precision of experimental analyses. Several recommendations were also given for further research for improving the traditional processing operations and, consequently, the quality of kernels and butter for larger markets at international level. They were: the investigation of the physico-chemical composition of shea kernels and butter derived from different processing techniques, and the assessment of the influence of some critical processing operations on the quality characteristics of shea kernels and butter.

Figure 8.1: Pulp of shea fruits (fruit size 45 ± 11 mm)

However, the development of any technology to improve the quality of the main commercially interesting shea products has to take the indigenous practices into account to ensure dovetailing with local production circumstances. In this respect, three research questions were formulated:

1. *What is the indigenous knowledge on shea processing?*
2. *What are the traditional techniques used to extract the butter*?
3. *What is the quality perception of kernels and butter by the different actors involved in the shea production chain?*

To answer these questions, a survey was conducted to record the traditional methods to process shea fruits in Benin, to assess their constraints, and to analyze the quality perception of shea products among the actors (chapter 3). Two main processing techniques were found for producing shea kernels and butter. The first technique consisted of boiling followed by sun drying of fresh nuts and was most common, while the second technique was related to the smoking of the nuts and was restricted to the Otamari ethnic group (3 % of respondents). The main difference between the two techniques is the amount of butter extracted from the nuts. Boiling followed by sun-drying of shea nuts is the processing technique generally encountered and promoted in all shea production zones of Africa due to the yield of butter and its quality characteristics (Kapseu and Ngongang 2004). However, processors of the Otamari ethnic group do not want to change their practice since their elders used this method to process shea nuts, even if they know that the yield of butter is significantly lower when the nuts are smoked instead of boiled followed by sundried. Hence, it belongs to their culture and they want to maintain and cherish this practice. Shea nut processing is an activity that provides a source of cash income and fat for domestic use, thus it contributes to the improvement of livelihood of processors' families. In this respect and even though Otamari processors want to maintain their culture, they could consider the use of the boiling followed by sun drying method to process shea nuts to produce butter for trade and use the smoking method to produce butter for their own consumption. In this case, they not only preserve their culture and pass this knowledge to the next generation, but they also increase their income. Furthermore, they would benefit from training related to the improvement of the boiling followed by the sun drying method. The survey also revealed that sun drying and shelling represent the bottleneck in shea kernel processing in terms of the materials used and time spent for these operations, while grinding and milling are the processing operations that butter processors complain most about in the absence of an appropriate mill. In locations close to national roads, shea nuts and kernels are sometimes dried on the tar along the roadsides, which is an

inappropriate practice due to the hydrocarbon compounds present in the tar (Basha et al. 2009) and the risk of contamination by other toxic substances and micro-organisms. Besides, current shelling practices cause a lot of damage to the kernels; as reported by Mensah (2010) more than 50 % of shea kernels were visibly bruised after shelling. These processing operations represent some key constraints that need to be improved to support the shea processing activities in which more than 3 million African rural women are involved (USAID/WATH 2013). The investigation also showed that processors or buyers who want to purchase kernels evaluate quality aspects such as the degree of drying by visual inspection, whereas the colour and odour are important to determine butter quality during purchase. The degree of drying is subjectively assessed by buyers who break the kernel and check whether its interior does not contain any liquid. However, sometimes well-dried kernels can contain oxidized fat, which influences the quality of the extracted butter. Figure 8.2 shows the cross-sections of two dried kernels. The one on the right (b) has a dark colour inside, which points at fat oxidation, while in the kernel on the left (a), the colour is bright and uniform, which reflects the non-oxidized status of the fat present. Apart from the drying degree, additional visual assessment like appearance of the whole kernel and its colour should also be taken into account to be sure that the kernel is of good quality. Moreover, due to the use of *Cochlospermum tinctorium* roots to improve the yellow colour of the butter in certain shea production zones, it is recommended to local purchasers in these production zones, to no more focus on the colour when purchasing because this might not be the real colour of the butter in certain cases.

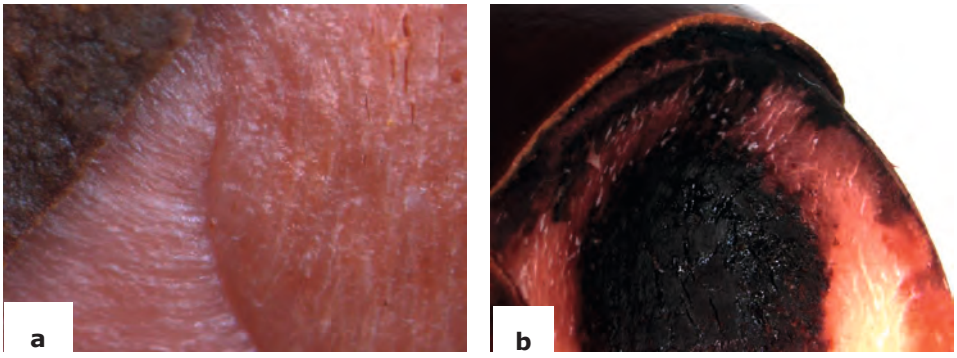

Figure 8.2: Cross section of dried shea kernels. a: Non oxidized kernel; scale 25x; b: Oxidized kernel; scale: 8x

Next, to characterize the shea kernels and shea butter resulting from the two traditional processing techniques, the following research question was investigated:

What is the physico-chemical composition of shea kernels and butter made by different processing techniques?

The quality characteristics of shea kernels (*i.e.* moisture content, fat content and FFA percentage) and shea butter (*i.e.* colour, moisture content, FFA percentage, and peroxide value) taken into consideration throughout this thesis are the most important ones, used for export or for human consumption and industrial purposes (USAID/WATH 2005, NB 04.02.001 2006). In chapter 4, the assessment of these quality characteristics of kernels produced using the two processing techniques showed that boiled kernels followed by sun-drying had a high FFA percentage (6 %) and fat content (49 % on dry weight or 46 % on wet weight) and could be exported easily as they comply to the standards of a maximum FFA percentage of 7 % and minimum fat percentage of 45 % on wet weight required for export (USAID/WATH 2005, NB 04.02.001 2006). Butter extracted from these kernels had a high unsaponifiable fraction (8 %), tocopherol content (125 mg/g), and iodine value (53 mg I_2/100 g) compared to butter from smoked kernels. Apart from these positive quality parameters, the butter extracted from boiled and sundried kernels also had higher content of moisture, FFA, and a higher peroxide value than butter from smoked kernels, even more than the standards used for cosmetic purposes (Kassamba 1997). Such quality parameters need to be improved by the upgrading and the optimisation of some processing operations, like storage of shea fresh nuts, boiling, roasting, and churning. According to a report of West Africa Trade Hub (USAID/WATH 2005), butter extracted from smoked kernels might contain Polycyclic Aromatic Hydrocarbons (PAHs), organic compounds forming during various processes including smoking. These compounds are considered to be carcinogenic when the content exceeds 30 µg/kg, the threshold tolerated in the European Union (European Food Safety Authority 2008). Hence, at international level, the export of smoked kernels and butter derived from these kernels is not allowed. Therefore, recommendations are given for further studies to assess the PAHs content of kernels and butter produced by the different techniques to be sure that their content do not exceed the threshold accepted.

Increasing the yield of butter and improvement of some quality characteristics, *viz.* the FFA percentage and fat content of shea kernels and the FFA percentage and peroxide value of butter, are attractive options to increase the price of kernels and butter and this might be an incentive for processors to invest in new techniques. For this, the development of efficient extraction processes or improving the existing technique is required. Two research questions were then formulated to investigate whether traditional processing can be improved:

1. *What are the effects of processing operations on kernel and butter quality?*
2. *What are the options for improvement of kernel and butter quality that fit local production conditions?*

Chapters 5 and 6 addressed these questions by investigating the effects of three critical processing operations, namely storage of fresh nuts, boiling of nuts, and roasting of kernels, on the physico-chemical characteristics of kernels and butter. These processing operations are critical because of their influence on the quality of final products. For instance, current storage practices of fresh nuts storage often lead to the germination of nuts and expose the nuts to external agents such as micro-organisms, moisture and insects. The boiling is done to facilitate the shelling of nuts and to inactivate the enzymes with lipase activity, responsible for the hydrolysis of triglycerides (Lovett 2004, Womeni et al. 2006b), while the roasting is performed to facilitate fat extraction and to improve the sensory characteristics of butter. The investigation allowed determining the optimum conditions of these processing operations to get a maximum yield of butter, with a low FFA percentage and peroxide value of the extracted butter. As shown in chapter 5, the storage duration of fresh nuts and boiling time significantly affected some quality characteristics of kernels and butter. Longer storage can reduce the fat content of kernels and increase the FFA percentage of butter. Optimum conditions to obtain the best quality of kernels with a moisture content of 7 % and a fat content of 50 % dw are to store the fresh nuts for 3 days and boil them for 28 ± 3 min. Processing these kernels in the traditional way resulted in a butter yield of 32 % on wet weight of kernel mass and butter with 0.9 % of FFA, and a peroxide value of 2.5 meq O_2/kg. With these quality

characteristics, the butter could be used for cosmetic and food purposes without refining (USAID/WATH 2005, NB 04.02.001 2006).

The roasting experiment (chapter 6) revealed that roasting time and roasting temperature, applied separately or in combination, had significant effects on all quality parameters investigated. Roasting crushed kernels at 171 ^{o}C for 15 min proved suitable to obtain a fat content of 49 % dw of kernels, a butter yield of 32 % on wet weight, and butter with FFA percentage of 1.2 %, and a peroxide value of 3.2 meq O_2/kg, thus, good for food purposes without refining (NB 04.02.001 2006). The optimum roasting time is appreciably shorter than the current practice, suggesting that the use of firewood during traditional processing can be reduced. Twenty seven volatile compounds were detected in shea butter from unroasted kernels against 58 compounds (clustered in 11 groups) in butter extracted from different roasted kernels. This observation shows the importance of roasting in the production of volatile compounds, and consequently, in the development of butter flavour. This experiment also showed that roasting time and roasting temperature significantly influenced the number of compounds, which confirms the findings of Krist et al. (2006), who stated that the variations in processing conditions of shea butter resulted in considerable differences in the composition of volatile compounds. Most of the compounds found were identified by Krist et al. (2006) and Bail et al. (2009) in shea butter from different production regions. Some of the compounds were generated by the degradation of fatty acids, *i.e.*, acetic acid and some carbonyl compounds (*viz.* hexanal, heptanal); compounds such as furfural and some hydrocarbon compounds resulted from processing steps including sun drying and milling. Many of these compounds (*i.e.* pentanal, hexanal and 2,4-decadienal) are responsible for off-flavours in fats, oils and other lipid-containing foods (Grosch 1982, Frankel 1985, Ullrich and Grosch 1988). Acetic acid, hexanal, and furfural were quantitatively dominating among the 58 compounds, while the carbonyl group was the most dominant group among the eleven groups of compounds identified in shea butter. Based on the specific flavour characteristics of each compound, shea butter flavour might be sour, pungent, grassy, tallowy, leafy, fatty, green, sweet, brown, and woody (Lee et al. 1991, Shiratsuchi et al. 1993, Jirovetz et al. 2003, Adam 2007). In this experiment, shea kernels were roasted in an oven in which the heat was transferred by convection while in traditional roasting (*i.e.* with the use of fire wood), heat is transferred by conduction. Thus, it is recommended to mimic the real roasting

procedure by using fire wood to roast the kernels for different periods of time to assess the influence on butter yield and quality characteristics of shea butter. This experiment also did not include a sensory evaluation of different butters from roasted kernels and since the roasting contributed to butter flavour, furthers studies should look at this aspect. Most importantly, the unsaponifiable fraction is one of the characteristics of shea butter that make it special due to its putative antioxidant and anti-inflammatory properties which are promising active ingredients for new functional cosmetic products (Maranz et al. 2003, Maranz and Wiesman 2004, Akihisa et al. 2010a) and our investigation did not measure the effects of different processing operations on the amount and composition of this unsaponifiable fraction. Therefore, another recommendation is to study this aspect, especially if the butter is to be used for cosmetic purposes.

After production, shea butter is usually stored for later use or export in conditions that can affect its quality characteristics. These conditions are mainly related to moisture content of the fat, the storage temperature, and the effectiveness of packaging materials used to maintain the quality of fat (Chinachoti 1998). In general, processors or users in Benin store shea butter in a cool place in their room and prevent exposure of the butter to the sun (Honfo et al. 2011). The following research questions linked to shea butter storage were addressed to assess the storability of shea butter:

1. *What are the effects of storage conditions and packaging on butter quality?*
2. *What are the options for shea storage improvement that fit the local production conditions?*

The effects of three factors, namely *(1)* packaging materials that are often used in shea production zones (*i.e.* calabash, black plastic and transparent plastic), *(2)* storage temperatures (28-30 ^{o}C and 4-7 ^{o}C) and *(3)* storage duration (from 0 up to 6 months) on physico-chemical characteristics of shea butter were investigated (chapter 7). Butter colour (*i.e.* yellowness), FFA percentage, peroxide value, and number of volatile compounds were significantly affected by storage temperature and storage duration. More alterations were noticed at room temperature conditions

(28-30 °C); for instance, regarding the FFA percentages and peroxide values in samples stored at different temperatures, it can be noticed that the hydrolysis rate is 2-3 times higher and the oxidation rate two times higher in room conditions (28-30 °C) than refrigerator conditions (4-7 °C). However, the changes observed during the period of storage did not affect the suitability of butter for food purposes. During room storage and based on volatile compounds identified, flavour and odour of butter might change from fruity and flowery (Fors 1983) to a more tarry oil and pungent odour (Umano and Shibamoto1987, Gasser and Grosch 1988, Chung et al. 1994, Sumitami et al. 1994, Qian and Reineccius 2003, Adams 2007). Minor differences were noticed during the storage with respect to packaging materials. The findings proved that shea butter can be stored for a long time in a cool place (4-7 °C); storage in local conditions without electricity can be done in clean and cool areas as already done by most processors. Of the packaging materials tested, a calabash could be used for temporary storage (1-3 months), while a plastic container (mostly black plastic) seems to be the best packaging for longer periods of storage. Transparent plastic is more susceptible to light than the black one; thus some physical and chemical characteristics (*i.e.* colour, peroxide value) of shea butter stored in transparent plastic could be more affected than that stored in other plastics. However, plastic containers vary in their permeability to oxygen, light, and moisture. Indeed, the Farm Implements and Tools (FIT) Programme, reporting on food packaging options appropriate for rural women in Ghana (FIT 1994), state that plastics from Low Density Poly Ethylene (LDPE) and from High Density Poly Ethylene (HDPE) have a poor barrier against oxygen and CO_2, which can cause discoloration of shea butter. In contrast, plastics from Poly Vinyl Chloride (PVC) and from Poly Propylene (PP) provide better protection, although attention should be given to the sealing process because sometimes the cover does not fit the container well. During storage of shea butter at room temperature conditions, the samples were exposed to day light, which was not measured. As light is one of the factors that mainly influence oxidation (Franckel 1998), the measurement or control of light intensity during storage will yield more information about the changes in chemical properties induced by oxidation of the butter.

8.3. METHODOLOGICAL LIMITATIONS

During this research, sample collection was a challenge because the shea tree is endogenous, thus, many varieties can be found in the same location (Maranz and Wiesman 2003, Fontaine et al. 2004, Sanou et al. 2005). Additionally, shea nuts are a seasonal product; the fresh fruit is available for 3-5 months a year, depending on the location. For example in Benin, shea fruit is available for 4 months, during which continuous processing of shea nuts into kernels is taking place. Certain processors store the kernels resulting from these processing operations in the same container throughout the year until the next year. Therefore, the same container may contain kernels with lower and higher fat contents. Moreover, shea fruits are gathered and all fallen fruits are collected except the germinated fruits in those cases when the gatherers have benefited from training from NGOs or public programmes involved in food processing improvement; thus, some fruits can be fresher than others. Consequently, the homogeneity and the quality of the kernels are not ensured. In some of our experiments (roasting and butter storage experiments), these limitations will have had an effect on the results, since kernel samples were collected from processors or bought at local markets. To improve this, we recommend to process shea fruits into kernels the same day of their gathering. Moreover, kernels derived from continuous processing should be stored in separate packaging to avoid the mixture of their quality.

The experiment related to the characterization of kernels derived from the two heat treatments and the butter extracted from these kernels (chapter 4) was duplicated. It would be valuable if more than two replications could be done to validate the findings. Additionally, for each treatment, kernel and butter production, as well as their replication, might have been done by one processor to reduce the variations within the same treatment.

The methods used to identify and quantify the volatile compounds were also used by other researchers (Krist et al. 2006, Bail et al. 2009a) and are based on Solid Phase Micro Extraction (SPME). SPME is a head-space adsorption technique, usually used in the field of environmental chemistry and toxicology (Belardi and Pawliszyn 1989, Arthur et al. 1992), and nowadays in lipid chemistry to identify volatile compounds (Chin et al. 1996, Kim and Min 2008). The detection limit and the number

of identified compounds by SPME depend on the amount and the type of the adsorbent applied for the extraction of the volatile materials (Pawliszyn 1997, Doleschall et al. 2003) and conditions can be set to extract either highly volatile compounds (Pérès et al. 2001) or fatty acids (Tomaino et al. 2001), but only a relatively narrow range of compounds is extracted. The method developed by Krist et al. (2006) for the volatile compounds in shea fat was time consuming due to a long extraction time (10 hours). In addition, **t**he quantification of identified compounds was difficult due to the large number of volatile compounds and not totally accurate because the area of some identified compounds was so small and sometimes not taken into account during the calculation as the quantification is based on percentage of **p**eak area with the total integrated peak area set at 100 %. In the future and in order to facilitate the quantification of all volatile compounds, methods of quantification need to be reviewed and standardized.

8.4. ANALYSIS OF SHEA CHAIN PRODUCTION

In Benin around 50 000 tons of nuts are annually collected of which 35 000 tons are exported as kernels and only 100 tons as butter (CNUCED 2006). Shea products contribute for 40 –50 % to the income of local populations (producers and traders) in the production zones and the butter provides fat for more than 80 % of these populations (Dah Dovonon and Idrissou Yaya 2009). The exploitation of shea products is therefore an important economic activity. However, to date a number of constraints limit the shea value chain from reaching its full potential namely: (1) variability in quality of the kernels and processed butter, (2) low access to appropriate equipment and the lack of adequate mechanization for butter processing, (3) insufficient availability of essential logistical products and services (*i.e.* packaging and storage infrastructure), (4) lack of organization at the producers' and processors' levels, (5) limited access to market and export information for women gatherers and processors, and (6) ageing of shea trees and lack of organized shea plantations. In addition, statistical data on the different actors along shea value chains are missing, which impedes the ability of the government and private sector to strategically plan for the sector's growth (FINTRAC 2013).

Most of these constraints contribute to the low kernel and butter production. Moreover, Benin has a potential to harvest annually 80 000 tons of shea kernels,

which is 30 000 tons of nuts more than collected at present (CNUCED 2006). Therefore, nearly half of the shea harvest remains uncollected and unused. Each year, the quantity collected also diminishes due to the yields of the nearby trees in the personal and/or husband's plots which are getting lower because of the older of trees. Consequently, the harvest areas (lands and forests) become far (5-10 km) from gatherers' homes. Additionally, individual processors have no access to equipment and training. All of gatherers and some butter processors work individually and thus lack the support provided by associations. All of these circumstances do not stimulate the women to devote themselves totally to the production of shea butter. This thesis research has tackled the constraint linked to the variability and quality of kernels and butter; some parts of this constraint are then left out.

Furthermore, the dominant players (wholesalers, intermediate traders, exporters) along the chain control the market at the cost of individual women gatherers and processors. Domestic markets represent the largest market for shea kernels and butter and are largely informal. Small-scale traders, mostly women, have little ability to negotiate or fix the price, which is usually set by the buyers. Additionally, poor knowledge of the market and its requirements in terms of product quality and the various marketing intermediaries also reduce the profit for these women. Also, as the majority of butter processors are not belong to any association, they lacks of distribution chain to sell their products in good price.

In the area of chain governance and support services, the Beninese government recognizes the importance of shea products as a national resource but has few controls during their trade apart from the delivery of some administrative documents necessary for export. NGOs and the government give technical support to the actors along the chain. Sometimes such interventions did not reach their objectives due to a lack of understanding of the shea actors' needs, especially with regards to the allocation of credits. Many actors (wholesalers and exporters) tried to obtain credits from banks but the procedure is so long that the actors were discouraged and disappointed. Therefore, finance is a major constraint to extending shea production and exports.

To sum up, providing stronger economic incentives to women gatherers and processors could expand available supply in the short run, even with possible rural

labor shortages during collection periods. Also, organizing women gatherers in associations may motivate them to travel farther for collection. The use of mass media by relevant government ministry such as rural radio to share market information (kernels or butter price at national level for example) may also increase the production level. In addition, as the proportion of inhabitants having a mobile phone in Benin particularly in rural area is in continuous increasing, the concept of the use of mobile phone to supply and receive market information could be adapted to shea production chain. This kind of communication tools for sharing information and promoting quality and market access in developing countries in used in some agri-foods supply chains *viz* pineapple chain in Ghana to overcome information asymmetry in the pineapple supply chain and to allow farmers to have more information and therefore more bargaining power in their transactions with traders (Arinloye et al. 2013).

8.5. IMPLICATIONS FOR FURTHER STUDIES

Based on the findings of this study, the following research areas should be explored:

- It would be interesting to assess the butter quality made by traditional method by local processors using a batch they have selected themselves and a batch that would be critically selected. For instance, through this research, the remark is that local processors are not critical enough during the selection of fresh nuts in field and during kernels purchasing for further processing and as the quality of the starting material (nuts or kernels) has a large impact on the produced butter, this investigation will confirm or annul the assumption that the traditional processing of the butter is not the most critical for the quality of kernels and butter, but the starting material.

- Research along the production chain should be carried out to determine the processing operations that affect the unsaponifiable fraction of shea butter and how this fraction can be maximised in order to increase the butter price at international level as this is the characteristic that cosmetic and pharmaceutic industries are looking for. thus, within the stabilization of this fraction during traditional processing, shea butter exporters will be willing to pay an additional price to butter cost, as for shea kernels, the exporters are willing to pay the premium of 5-20 % of

the real purchased price when the kernels fit the international requirements (fat content ≥ 45 % dw, moisture content ≤ 7-8 %, and FFA ≤ 7 %) (FINTRAC 2013).

- The genetic diversity of shea tree should be assessed to enable the selection and promotion of trees that bear fruits with a high fat content. It is then of interest to look for varieties of shea trees in the different parklands of Benin and their impact on the quality characteristics of the derived products (*i.e.* kernels and butter).

- Apart from kernels and butter, shea pulp is usually consumed in shea production zones. The dietary and socio-economic value of the shea nut and butter seem to have diminished the attention given to the usefulness of the shea fruit pulp, which becomes available at the beginning of the rainy season; thus investigating its consumption level across the shea zone will be useful in relation to food security. Besides, most of the pulp is thrown away during processing; however, due to its high contents of sugar and vitamin C and it perishability, it is recommended to investigate preservation, for example by processing into other products such as jams, conserves, dry fruit.

- It would be useful for buyer and users to build kinetic models to predict the shelf life of kernels and butter during storage because proper storage conditions are essential to maintain product quality for prolonged periods of time. For this, some quality attributes *viz.* physical aspects, fat content, and FFA percentage of shea kernels and colour, FFA percentage, and peroxide value of shea butter will be targeted. Thus, further experiments related to kernels and butter storage are recommended.

- In addition to the technological aspects (*viz.* processing techniques), some social and financial issues need to be taken into account for shea kernel and butter production in relation to quality improvement. For instance, the government and NGOs involved in the development of agricultural food chains on the one hand and actors along the shea chain on the other hand, need to take up several issues to expand and boost shea butter production to meet the increasing demand on local and international markets:

- Relevant government ministries and NGOs should foster shea butter processors to organize themselves into associations. Most of them work individually

and there is no access to equipment or training for individual processors. By organizing themselves, they will be recognizable and this will also enhance their chances to get training and other necessary support.

- Support services (government and NGOs) should also provide more information and technical support to such associations or cooperatives that seek funding support from financial institutions. This will facilitate the procurement of loans and equipment needed.

- Furthermore, water availability is very important for shea processing and it is one of the resources that are scarce in shea production zones. To exclude or reduce this impediment, support services are needed to improve access to water in locations where shea activity is well developed. Alternatively, the development of efficient churning equipment and washing equipment due to the high water use during both processing operations and their use might also reduce water consumption during the processing.

8.6. CONCLUDING REMARKS

Shea processing remains traditional, despite the contribution of shea kernels and shea butter to Benin's GNP. This research showed that improvement of certain processing operations, namely storage of fresh nuts, boiling and roasting of kernels, may increase the yield of butter, improve some quality characteristics of kernels and butter, and reduce the fire wood consumption during traditional processing. For instance, by storing fresh shea nuts no longer than 3 days after their gathering followed by boiling for about 28 min, the kernel colour can be improved with an increase of butter yield. Furthermore, some quality characteristics of the derived butter might be improved. In the same way, roasting crushed shea kernels at 171 ^{o}C for 15 min during processing can also increase the butter yield as well as some characteristics of butter, like butter flavour. Improving processing operations can be achieved locally, apart from the oven for roasting, which could be substituted by roasting equipment used by some processor associations. Thus, with necessary financial support for the procurement of equipment and training support on improving processing, local processors can efficiently reduce fire wood consumption during processing and produce shea kernels and butter that fit the standard requirements to enable them to sustain their livelihoods.

The knowledge on improved shea processing practices can be transferred to local producers through different organisations involved in the development of agricultural food chains. For instance, the results of this study will be given to National Research and extension services, which are responsible to organize the training of trainers (*viz.* relevant local NGOs and public sector) on the improvement brought to traditional processing. After that, these organisations could assist local producers by providing training at their level. These actions will be possible because of the growing interest of the government and local NGOs in promoting high quality shea products and organizing the chain for better added value.

Regarding the goal of a PhD project like this one, which is to help in training and educating rural populations by using the results of the scientific work, we can say that our research is in accordance with this objective by tackling a practical problem in shea production zones. For instance, this thesis is focused on the improvement of current traditional shea processing by using some scientific skills. The role of shea production is to increase the cash income and livelihood of local populations involved in this activity. The findings of this research have then solved some parts of shea production bottlenecks which may influence its development. Most importantly, the PhD goal is also to increase our scientific knowledge related to shea processing and in that sense, this research provides insight in the characterization of derived butter from different traditional processing, and the effect of storage, boiling and roasting on the final product. This kind of research is mostly needed in developing countries where many food production processes are still indigenous and need to be optimized for better understanding and the way for their improvement for better life of populations. Yet, the outcome of our study are not only useful for local populations to efficiently produce the kernels and butter by traditional methods, but it also gave a basis for further investigation aimed at shea processing improvement.

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Summaries in English, Dutch, and French

Summary

Shea (*Vitellaria paradoxa* C.F. Gaertner) is an indigenous tree generally found in semi-arid to arid regions in sub-Saharan Africa covering around 19 countries forming the shea belt. The tree is highly appreciated at national and international levels, mainly for the fat extracted, commonly known as shea butter, from the nuts of its fruit. The butter is used as cooking fat, in soap making and in traditional medicine by local populations. It is useful in the cosmetic, and pharmaceutical industry, as well as the chocolate industry as cocoa butter equivalent. The exploitation and processing of the shea tree offers an opportunity in general for shea production countries and for the farming women in particular, to alleviate poverty and achieve economic autonomy.

Shea nut is often processed by women by traditional methods at the village level, which can be described as having low efficiency, long processing time with many critical processing operations, as well as the variability of the quality of the end products. Despites of the research efforts to reduce the hardness of traditional processing and improve the quality of kernels and butter, some quality constraints persist along the shea butter processing chain. Consequently, the kernels and butter sometimes do not satisfy the standard requirements for exportation. The main objective of this thesis was, therefore, to assess the impact of some traditional processing operations of shea nuts on quality characteristics of shea kernels and butter. Specifically, this thesis i) critically reviewed the existing literature on the nutritional composition of shea products and chemical properties of shea butter; ii) investigated the indigenous knowledge related to shea processing and shea products in Benin; iii) characterized the quality of kernels and butters in relation to different processing techniques; iv) studied the effect of certain traditional processing operations on quality characteristics of shea products; and v) assessed the quality degradation of shea butter during storage.

Chapter 2 reviewed the literature on shea products and found that the pulp usually consumed by local population is rich in carbohydrate (8.1-37.2 g/100 g dry weight: dw), fibre (42.2 g/100 g dw), and vitamin C (196.1 mg/100 g). The kernels contain a high level of crude lipid (17.4-59.1 g/100 g dw). Fat is extracted from kernels mainly by traditional methods that involve crushing, roasting, milling, churning, heating, filtration, and cooling. The fat (butter) is composed of triglycerides and a large fraction of unsaponifiable components (1.2 % to 17.6 %, with an average of 8.1 %), which are promising active ingredients because of their supposed antioxidant and anti-inflammatory activities for new functional cosmetic products.

Shea butter is composed of 16 fatty acids with four dominant (oleic: 49 %, stearic: 40 %, linoleic: 7 %, and palmitic: 4 %). The main triglycerides are SOS (40 %), SOO (35 %), and OOO (11 %). Large variations are observed in the reported values for the composition of shea products. The causes of variations were the provenances of the samples, the age of trees, the climatic conditions, the genetic variation, the soil structure and its chemical composition. Variations were also attributed to the methods used to analyze the samples. Recommendations are given to pay more attention to the accuracy and precision in experimental analyses with the clear description of sampling and methods used. Additionally, recommendations for future research on shea processing were formulated: (1) improving butter yield and its quality by optimizing some processing operations; (2) assessing the storability of butter with respect to its quality.

A survey among 246 people living in shea parklands of Benin described in **chapter 3** was done next, first to record the different traditional shea processing techniques, second, to assess their constraints, and lastly to analyse the quality perception of shea products among the actors along the shea chain production. The survey revealed that many ethnic groups are involved in shea butter production, especially Bariba, Fulani, Yom, Nagot, and Otamari. They use two main practices to process shea nuts distinct from each other by the heat treatment (first: boiling followed by sun drying; second: smoking) applied to fresh nuts. Two techniques were also recorded to extract the fat from kernels: roasting of the whole kernels in the sand and roasting of crushed kernels. Apart from the Otamari ethnic group (3 % of the total processors surveyed), who smoked the shea nuts before fat extraction, all other ethnic groups boiled and sundried the fresh nuts during shea processing. The survey also showed that the degree of drying and appearance of kernels were the most important quality criteria taken into account during kernel purchasing; while the color of butter is the main quality attribute that buyers use when purchasing the butter. Some constraints are linked to certain processing operations, *viz.* long processing times, lack of milling equipment and high water requirements. Recommendations were given to reduce the arduousness and the constraints of processing by introducing reliable and adapted equipment, in order to improve the quality of shea products.

In **chapter 4**, the assessment of quality characteristics of kernels produced by the two methods (boiling followed by sun drying, and smoking) revealed by the survey as well as the composition of the derived butters were investigated. Results showed that boiling followed by sun drying treatment resulted in more free fatty acids (FFA, 6 %) and a higher fat content (48 % dw) of kernels and yielded more butter (30 % ww of kernel mass)

compared to smoked kernels with FFA of 5 %, fat content of 39 % dw and yield of 23 %. The colour of smoked kernels were more intense in redness with value of a* (expressed the level of redness colour) of 9 than the colour of boiled kernels (a* value = 7). With a melting range of 36 to 47 °C, butters derived from boiled kernels had the highest values of moisture content (2 %), unsaponifiable fraction (7 %), tocopherol compounds (125 mg/g), peroxide value (8 meq O_2 /kg), iodine value (53 g I_2 100/g) and FFA percentage (2 %) as well as low value of brightness (L* = 70) (L* expressed the level of brightness or lightness of product). Minor variations were noticed in the fatty acid profile of different butters. A sensory panel preferred shea butters from boiled followed by sundried kernels due to their soft texture and intense smell. Apart from the moisture content that was slightly higher than the requirement for export, kernels processed by the two heat treatments can be easily exported as far as quality standards are concerned. The findings from this study help to identify the processing techniques of butter that fit with quality demands for different utilizations. For instance, although butters from both boiled and smoked kernels can be used for different purposes, butter from boiled kernels is more suitable for cosmetics and pharmaceutical purposes due to its higher unsaponifiable content and soft texture, while butter from smoked nuts will be more appropriate for food purposes. Best practices for smoking, boiling, and roasting operations need to be established for further improvement.

Chapter 5 presented the findings about the experiment on two processing operations, namely storage of fresh shea nuts and their boiling. By using the central composite face-centered design (CCFD), fresh nuts were stored for 3 to 21 days and boiled for 10 to 60 min in order to assess the influence of the storage and boiling operations on fat content and colour of kernels and on colour, FFA, and peroxide values of butter. Results were used to define the optimum storage duration and boiling time. Results showed that storage duration and boiling time applied separately or in combination significantly influenced kernels characteristics *viz*. fat content (38-52 % dw), yield (24-36 % ww of kernels mass), and colour, as well as butter characteristics, namely brightness (70-80), yellowness (16-23), and FFA percentages (0.5-2 %) of butter. Longer storage can reduce the fat content of kernel and increase the FFA percentage of butter. Increasing boiling time might increase the fat content and the highest value was found after 32 min boiling. Optimum conditions to obtain the best quality of kernels with a moisture content of 7 % and a fat content of 50 % on dry weight are to store the fresh nuts for 3 days and boil them for 28 ± 3 min. Processing these kernels in the traditional way resulted in a butter yield of 32 % on wet weight of kernel mass and butter with 0.9 % of FFA, and a peroxide value of 2.5 meq O_2/kg. With these quality characteristics,

the butter could be used for cosmetic and food purposes without refining. The microstructure of fresh shea nuts, also studied with Laser Scanning Confocal Microscopy, showed large and small fat globules with some free spaces inside. Other critical processing operations of traditional shea butter processing also need to be optimised to increase the yield and improve the quality of butter to meet international trade standards.

In the same way, the experiment related to the traditional roasting operation of shea kernels was undertaken in **chapter 6** to evaluate the effect of roasting time (15-45 min) and roasting temperature (120-180 °C) of crushed shea kernels on some quality attributes of derived butter and its volatile compounds. Roasting time and temperature influenced fat content of kernels (44-53 % dw), FFA of butter (0.5-3 %), as well as the number and the relative content of volatiles in relation to butter flavour compounds. Longer roasting at higher temperatures yielded more fat and a high roasting temperature also resulted in a low FFA percentage in shea butter. In total, 27 volatile compounds in butter from unroasted shea kernels against 58 volatile compounds (clustered in 12 groups) in butters from roasted kernels were identified, of which 11 compounds were quantitatively dominant. Most of the compounds found were generated during roasting by oxidation and hydrolysis. Roasting around 171 ^{o}C for 15 min proved to be the optimum condition predicted by the CCFD model, as it resulted in a fat content of 49 % dw of the kernels, a butter yield of 32 %, a FFA of 1.2 % of the butter, and a peroxide value of 3.2 meq O_2/kg. This kind of shea butter is suitable for food purpose without refining.

Chapter 7 focused on the changes in the chemical properties of shea butter under different storage conditions and packaging materials. Three packaging materials (*i.e.* calabash, black plastic, and transparent plastic), often used to store shea butter in the production zones, were used to store the butter for six months at ambient conditions (temperature: 28-30 ^{o}C, relative humidity: 81 ± 3 %) and in a refrigerator (4-7 ^{o}C). Colour, water activity, FFA, peroxide and volatile compounds were assessed after each month till the end of storage. After 6 months of storage, all parameters investigated were significantly affected by storage conditions and storage duration while the effects of the packaging materials were less pronounced compared to those factors. At ambient conditions, changes were more pronounced than at low temperatures. The temperature coefficient of the changes was in accordance with that expected for chemical reactions. For instance, after 6 months of storage, the increase of FFA of butter stored in a calabash was three times higher than that stored in refrigerator (1.9 % at ambient conditions against 0.53 % in refrigerator). Plastic containers seemed to be the better packaging materials for a long storage period. In the

absence of possibilities to store butter at low temperatures, it is recommended to keep shea butter in relatively cool area to maintain the quality of the product during prolonged storage periods.

In **chapter 8**, the main results of this thesis were discussed. These were the upgrading of some traditional processing operations and preservation techniques in order to improve the butter yield and the quality of kernels and butter. This chapter ends with recommendations for future research and advices are given to shea processors; the implementation of which should probably be done through relevant government ministries and NGOs involved in the development of agricultural food chains.

Samenvatting

Shea (*Vitellaria paradoxa* C.F. Gaertner) is een inheemse boom die over het algemeen te vinden is in halfdroge tot droge gebieden in Afrika bezuiden de Sahara in een gebied dat ongeveer 19 landen beslaat. De boom wordt zeer gewaardeerd op nationaal en internationaal niveau, met name vanwege het geëxtraheerde vet, algemeen bekend als shea boter, uit de noten van zijn vruchten. De boter wordt gebruikt bij het koken, voor het maken van zeep en in de traditionele geneeskunde door de lokale bevolking. De boter wordt toegepast in de cosmetische en farmaceutische industrie, alsook als vervanger van cacaoboter in de chocolade-industrie. De exploitatie en verwerking van de shea vruchten bieden in het algemeen een kans voor de landen waarin shea wordt geproduceerd, en in het bijzonder voor de boerinnen, om armoede te verlichten en economische zelfstandigheid te bereiken.

De shea noot wordt meestal verwerkt door vrouwen op traditionele wijze op dorpsniveau, hetgeen wordt gekenmerkt door lage opbrengsten, lange verwerkingstijden met vele kritieke bewerkingen, alsook een grote variabiliteit in de kwaliteit van de eindproducten. Ondanks onderzoeksinspanningen om de traditionele verwerking te vereenvoudigen en de kwaliteit van de noten en de boter te verbeteren, zijn er problemen met de kwaliteit blijven bestaan in de verwerkingsketen van shea boter. Bijgevolg voldoen de noten en boter soms niet aan de exportnormen. De belangrijkste doelstelling van dit proefschrift was dan ook om de impact te bepalen van een aantal traditionele verwerkingsprocessen op kwaliteitskenmerken van shea noten en boter. Dit proefschrift omhelst met name i) een kritische evaluatie van de bestaande literatuur over de voedingskundige samenstelling van shea producten en de chemische eigenschappen van shea boter; ii) een onderzoek naar de inheemse kennis met betrekking tot shea verwerking en shea producten in Benin; iii) een karakterisering van de kwaliteit van noten en boters met betrekking tot verschillende verwerkingstechnieken; iv) een studie naar het effect van bepaalde traditionele verwerkingstechnieken op kwaliteitskenmerken van shea producten; en v) een analyse van de kwaliteitsachteruitgang van shea boter tijdens bewaring.

Hoofdstuk 2 geeft een overzicht over de literatuur over shea producten en beschrijft dat het vruchtvlees dat gewoonlijk door de lokale bevolking wordt geconsumeerd, rijk is aan koolhydraten (8,1 - 37,2 g / 100 g droge stof: d.s.), vezels (42,2 g / 100 g d.s.) en vitamine C (196,1 mg / 100 g). De noten bevatten een hoog gehalte aan ruw vet (17,4 - 59,1 g / 100 g d.s.). Vet wordt hoofdzakelijk uit de noten gewonnen met traditionele methoden, die bestaan uit

het verkleinen, roosteren, malen, roeren, verwarmen, filtreren en afkoelen. Het vet (de boter) bestaat uit triglyceriden en een groot deel onverzeepbare bestanddelen (1,2 % tot 17,6 %, met een gemiddelde van 8,1 %), die als veelbelovende werkzame stoffen worden gezien voor nieuwe functionele cosmetische producten vanwege hun veronderstelde antioxidant en anti-inflammatoire eigenschappen. Shea boter is samengesteld uit 16 vetzuren waarvan er vier kwantitatief de belangrijkste zijn, namelijk oliezuur met 49 %, stearine met 40%, linolzuur met 7 %, en palmitinezuur met 4 %. De belangrijkste triglyceriden zijn SOS (40%), SOO (35%) en OOO (11%). In de gerapporteerde waarden voor de samenstelling van shea producten komen grote variaties voor. De oorzaken van deze variaties zijn de verschillende herkomsten van de monsters, de leeftijd van de bomen, de klimatologische omstandigheden, de genetische variatie, de bodemstructuur en zijn chemische samenstelling. Variaties kunnen ook zijn veroorzaakt door de gebruikte analysemethoden. Aanbevolen wordt om meer aandacht te besteden aan de nauwkeurigheid en precisie van de experimentele analyses en de omschrijving van de bemonstering en de gebruikte methoden. Daarnaast worden de volgende aanbevelingen gedaan voor toekomstig onderzoek naar de verwerking van shea: 1) het verbeteren van boter opbrengst en de kwaliteit ervan door het optimaliseren van een aantal verwerkingsprocessen; 2) het bepalen van de houdbaarheid van boter in relatie tot kwaliteit.

In onderzoek onder 246 mensen die leven in verschillende shea parklandschappen van Benin, zoals beschreven in **hoofdstuk 3,** werden eerst de verschillende traditionele shea verwerkingstechnieken in kaart gebracht, ten tweede de beperkingen daarvan, en ten slotte de kwaliteitsbeleving van shea producten onder de actoren in de shea productieketen. Uit het onderzoek blijkt dat veel etnische groepen zich bezig houden met de productie van shea boter, vooral de Bariba, Fulani, Yom, Nagot en Otamari. Zij maken gebruik van twee belangrijke praktijken om shea te verwerken, die van elkaar verschillen in de toegepaste warmtebehandeling van de verse noten, namelijk koken gevolgd door drogen in de zon, of roken. Twee verschillende technieken werden ook gevonden voor het extraheren van het vet uit de noten: het roosteren van hele noten in zand en het roosteren van vermalen noten. Afgezien van de Otamari (3% van de ondervraagde verwerkers van shea), die de shea roken voor de vetextractie, maken alle andere etnische groepen gebruik van koken gevolgd door zondrogen voor het verwerken van verse shea noten. Het onderzoek toonde ook aan dat de mate van droging en het uiterlijk van de noten de belangrijkste kwaliteitscriteria waren waarmee tijdens het inkopen van noten rekening werd gehouden, terwijl kleur de belangrijkste kwaliteitseigenschap was die kopers gebruikten bij de aankoop van boter.

Sommige beperkingen zijn gekoppeld aan bepaalde verwerkingsstappen, nl. lange doorlooptijden, gebrek aan apparatuur om te malen en een groot watergebruik. Aanbevelingen zijn om de verwerking lichamelijk minder zwaar te maken en de beperkingen van de verwerkingstechnieken te adresseren door het introduceren van betrouwbare en aangepaste apparatuur, teneinde de kwaliteit van de shea producten te verbeteren.

Hoofdstuk 4 doet verslag van onderzoek naar verschillen in kwaliteitskenmerken van noten verkregen volgens de twee methoden (koken gevolgd door zondrogen en roken) die naar voren waren gekomen uit het onderzoek beschreven in hoofdstuk 3, alsmede naar de samenstelling van de verkregen boters. De resultaten tonen aan dat koken gevolgd door zondrogen resulteerde in meer vrije vetzuren (FFA, 6 %) en een hoger vetgehalte (48 % d.s.) van noten en een hogere boteropbrengst (30 % van het versgewicht van de noten) dan het roken van noten; gerookte noten hadden een FFA van 5 % en een vetgehalte van 39 % d.s. en gaven een boteropbrengst van 23 %. De kleur van gerookte noten was intenser in roodheid met een a* waarde (een maat voor roodheid) van 9 dan de kleur van gekookte noten (a* waarde = 7). Met een smelttraject van 36 tot 47 °C hadden boters op basis van gekookte noten de hoogste waarden voor het vochtgehalte (2 %), de onverzeepbare fractie (7 %), tocoferol verbindingen (125 mg/g), het peroxidegetal (8 meq O_2/kg), het joodgetal (53 g I_2 / 100 g) en het FFA percentage (2 %) en een lage score voor helderheid (L* = 70) (L* is een maat voor de helderheid van een product). Kleine verschillen werden gevonden in het vetzuurprofiel van de verschillende boters. Een sensorisch panel gaf de voorkeur aan shea boters op basis van gekookte en zongedroogde noten vanwege hun zachte textuur en intense geur. Afgezien van het vochtgehalte dat iets boven de vereiste norm voor export lag, voldeden de noten verkregen met beide warmtebehandelingen aan de kwaliteitsnormen voor export. De bevindingen uit dit onderzoek helpen om de technieken voor de productie van boter te identificeren die passen bij de kwaliteitseisen voor verschillende toepassingen. Hoewel bijvoorbeeld boters op basis van gekookte en gerookte noten beide voor verschillende doeleinden kunnen worden gebruikt, is boter uit gekookte noten beter geschikt voor cosmetische en farmaceutische doeleinden vanwege het hogere gehalte aan onverzeepbare bestanddelen en de zachte textuur, terwijl boter uit gerookte noten beter geschikt is voor voedingsdoeleinden. Best practices voor het roken, koken en roosteren moeten worden vastgesteld voor verdere verbetering.

Hoofdstuk 5 presenteert de bevindingen van onderzoek naar twee verwerkingsstappen, namelijk de bewaring en het koken van verse shea noten. Op grond

van een zogeheten 'central composite face-centered design' (CCFD) werden verse noten gedurende 3 tot 21 dagen bewaard en gedurende 10 tot 60 minuten gekookt om de invloed van deze operaties te bepalen op het vetgehalte en de kleur van noten en de kleur, het FFA percentage en het peroxidegetal van boter. De resultaten werden gebruikt om de optimale bewaar- en kooktijd vast te stellen. De resultaten toonden aan dat de opslagduur en de kooktijd afzonderlijk en in combinatie een significante invloed hadden op kenmerken van de noten, te weten het vetgehalte (38-52 % d.s.), de boteropbrengst (24-36 % op basis van het versgewicht van de noten) en kleur, evenals op kenmerken van de boter, namelijk helderheid (70-80), geelheid (16-23), en FFA percentages (0,5-2 %). Langere opslag kan het vetgehalte van noten en het FFA percentage van boter verlagen. Een langere kooktijd kan het vetgehalte verhogen en de hoogste waarde werd gevonden na 32 min. koken. Optimale omstandigheden voor het verkrijgen van de beste kwaliteit noten met een vochtgehalte van 7 % en een vetgehalte van 50 % op droge stof basis zijn het bewaren van verse noten gedurende 3 dagen gevolgd door 28 ± 3 minuten koken. Verwerking van deze noten op traditionele wijze resulteerde in een boteropbrengst van 32 % op basis van het versgewicht van de noten en boter met 0,9 % FFA en een peroxidegetal van 2,5 meq O_2/kg. Met deze kwaliteitskenmerken kon de boter worden gebruikt voor cosmetische en voedingsdoeleinden zonder raffinage. De microstructuur van verse shea, bestudeerd met laser scanning confocale microscopie, toonde grote en kleine vetbolletjes met een aantal vrije ruimten. Andere kritieke verwerkingsstappen van traditionele shea boter verwerking moeten ook worden geoptimaliseerd om de opbrengst te verhogen en de kwaliteit van de boter te verbeteren om aan de internationale handelsnormen te voldoen.

Op dezelfde wijze zoals beschreven in **hoofdstuk 6,** werd de traditionele manier van het roosteren van shea noten onderzocht om het effect van de duur (15-45 min) en de temperatuur (120-180 °C) van het roosteren van fijngemalen shea noten te evalueren op kwaliteitskenmerken van de geproduceerde boter en het ontstaan van vluchtige verbindingen. Zowel de duur als de temperatuur van het roosteren beïnvloedden het vetgehalte van de noten (44-53 % d.s.), het FFA gehalte van de boter (0.5-3 %), alsmede het aantal en het relatieve gehalte aan vluchtige stoffen in de vorm van geurstoffen van de boter. Langer roosteren bij hogere temperaturen leverde meer vet op en een hoge temperatuur resulteerde ook in een lager FFA percentage in shea boter. In totaal werden er 27 vluchtige verbindingen aangetroffen in boter uit ongeroosterde shea noten tegen 58 vluchtige verbindingen (geclusterd in 12 groepen) in boters uit geroosterde noten, waarvan 11 verbindingen kwantitatief domineerden. Het merendeel van de verbindingen werd

gegenereerd tijdens het roosteren door oxidatie en hydrolyse. Roosteren bij 171 ° C gedurende 15 minuten was de optimale behandeling volgens het CCFD model, die resulteerde in een vetgehalte van 49 % in de noten, een boter opbrengst van 32 %, een FFA gehalte van 1,2 % in de boter, en een peroxidegetal van 3,2 meq O_2/kg. Dergelijke shea boter is geschikt voor gebruik als voedsel zonder voorafgaande raffinage.

Hoofdstuk 7 richt zich op de veranderingen in de chemische eigenschappen van shea boter tijdens verschillende opslagomstandigheden en verpakt in diverse verpakkingsmaterialen. Drie verpakkingsmaterialen (namelijk kalebassen, zwart plastic en doorzichtig plastic), vaak gebruikt in de productiegebieden om shea boter in te bewaren, werden toegepast om de boter op te slaan gedurende zes maanden bij omgevingsomstandigheden (temperatuur: 28-30 °C, relatieve vochtigheid: 81 ± 3 %) en in een koelkast (4-7 °C). Kleur, wateractiviteit, FFA gehalte, peroxide en vluchtige verbindingen werden bepaald na elke maand tot het einde van de opslag. Na 6 maanden opslag werden alle onderzochte parameters significant beïnvloed door opslagomstandigheden en opslagduur, terwijl de effecten van het verpakkingsmateriaal veel minder uitgesproken waren. Bij omgevingsomstandigheden waren de veranderingen groter dan bij lage temperaturen. De temperatuurcoëfficiënt van de veranderingen was overeenkomstig de verwachting voor chemische reacties. Bijvoorbeeld, na 6 maanden opslag was de toename van het FFA percentage in de boter die was opgeslagen in een kalebas drie maal hoger dan van boter die in de koelkast was bewaard, namelijk respectievelijk 1,9 % en 0,53 %. Plastic containers bleken de beste verpakkingsmaterialen voor een lange opslagduur te zijn. Bij het ontbreken van mogelijkheden voor het opslaan van boter bij lage temperaturen is het raadzaam om shea boter op een relatief koele plaats te bewaren om de kwaliteit van het product gedurende langere tijd goed te houden.

In **hoofdstuk 8** worden de belangrijkste resultaten van dit proefschrift besproken. Dit waren de verbeteringen van een aantal traditionele verwerkings- en bewaringstechnieken om de boter opbrengst en de kwaliteit van de noten en boter te verbeteren. Het hoofdstuk eindigt met aanbevelingen voor toekomstig onderzoek en adviezen aan shea verwerkers; de uitvoering daarvan zou moeten worden opgepakt door de relevante ministeries en niet-gouvernementele organisaties (NGO's) die betrokken zijn bij de ontwikkeling van agrarische voedselketens.

Résumé

Le karité (*Vitellaria paradoxa* C.F. Gaertner) est un oléagineux qui pousse à l'état sauvage dans les zones semi-arides et arides de l'Afriques sub-Saharienne, présent dans 19 pays sur une bande de 5000 km connue sous le nom de "la ceinture du karité". L'arbre est apprécié pour la matière grasse communément appelée beurre de karité, extrait de ses amandes. Ce beurre est utilisé comme huile de cuisine, en cosmétique et dans la médecine traditionnelle par la population locale et sur le plan international, il est utilisé comme un ingrédient dans les produits alimentaires, dans la cosmétique et dans la pharmacologie. L'exploitation et la production du beurre de karité contribuent à la croissance économique des pays producteurs en général, et en particulier à la réduction de la pauvreté au niveau des femmes productrices.

Le beurre de karité est généralement extrait de façon traditionnelle selon les zones de production d'où la variation par rapport à sa qualité. Ces techniques traditionnelles sont consommatrices de temps, d'eau et d'énergie avec une faible efficacité, et ne sont pas souvent standardisées. Cependant, en dépit des nombreuses études effectuées en vue d'améliorer le rendement et la qualité des amandes et du beurre, les problèmes de qualité persistent toujours tout au long de la chaine de production. La présente étude a donc évalué l'impact des procédés traditionnels de production du beurre de karité sur la qualité des amandes et du beurre. De façon spécifique, cette étude a i) effectué une synthèse bibliographique sur la production et la composition nutritionnelle des produits de karité, ii) capitalisé les connaissances endogènes relatives à la production du beurre de karité, iii) caractérisé sur le plan physicochimique les amandes et le beurre issus des différentes méthodes traditionnelles, iv) évalué l'influence de certaines opérations de production sur la qualité des amandes et du beurre, et enfin, v) évalué l'effet des conditions de stockage sur la qualité du beurre.

Dans le **chapitre 2**, une revue critique de la littérature existante a montré que la pulpe du fruit de karité largement consommée par la population locales est riche en carbohydrates (8,1-37,2 g/100 g base sèche: bs), en fibre (42,2 g/100 g bs), et en vitamine C (196,1 mg/100 g). La teneur en matière grasse de l'amande varie de 17,4 g/100 g à 59,1 g/100 g bs et est souvent extraite de manière traditionnelle. Cette matière grasse est composée de triglycérides et une large fraction de matière insaponifiable (1,2 % à 17,6 %, avec une moyenne de 8,1 %) ayant des fonctions antioxydants et anti-inflammatoires. Le beurre de karité est composé de

16 acides gras dont 4 sont dominants (acide oléique: 49 %, acide stéarique: 40 %, acide linoléique: 7 %, acide palmitique: 4 %). Une large variation a été notée au niveau des différentes données reportées sur les produits de karité. Selon certains auteurs, ces variations sont dues à la provenance des échantillons, le degré de maturité des fruits de karité, les variations génétiques, les conditions climatiques, le type de sol et leur composition chimique. Les variations provenaient également des méthodes d'échantillonnage et d'analyses de laboratoire. Les recommandations ont été faites pour que plus d'attentions soient accordées à la précision des méthodes d'échantillonnage et d'analyses. Les axes de recherche pour l'amélioration des procédés de transformations des produits de karité ont été également identifies à l'issu de cette synthèse bibliographique; il s'agit de: 1) entreprendre des recherches pour l'optimisation de certaines opérations critiques du procédé traditionnel en vue de l'amélioration du rendement et de la qualité du beurre; 2) évaluer l'effet des conditions de stockage du beurre sur sa qualité.

L**e chapitre 3** a présenté les résultats d'une enquête réalisée sur 246 acteurs de la chaîne de production du beurre de karité vivant dans les 5 parcs à karité du Bénin. Cette enquête a révélé que plusieurs groupes ethniques dont les Bariba, les Fulani, les Yom, les Nagot, et les Otamari sont impliqués dans la production du beurre de karité. Deux techniques traditionnelles de production d'amandes de karité ont été identifiées: la technique de cuisson à l'eau des noix fraiches suivie de leur séchage au soleil et la technique du fumage des noix fraiches. Le fumage des noix est l'apanage des transformatrices Otamaris. Deux techniques d'extraction du beurre ont été également identifiées: la technique de torréfaction des amandes entières dans de la cendre et la technique de la torréfaction des amandes concassées. L'enquête a aussi révélé que le dégrée de séchage et l'apparence (aspect) des amandes sont les critères les plus importants sur lesquels les acheteurs se basent au cours de l'achat des amandes, alors que la couleur du beurre est le plus important critère lors de l'achat du beurre. Aussi, des contraintes liées à la production (longue durée de production, manque d'équipements de base tels que le moulin pour la mouture, manque de point d'eau) ont-elles été soulevées par les transformatrices comme des freins pour une meilleure production en plus des contraintes intrinsèques aux procédés de transformation. Les recommandations ont été données en vue de réduire la pénibilité de certaines opérations de production par l'introduction des équipements pratiques et fiables au niveau de la chaîne de production.

La caractérisation des amandes issues des deux techniques de production a montré que les amandes issues des noix bouillies et séchées au soleil ont un pourcentage élevé en AGL (6 %) et une teneur en matière grasse élevée (48 % bs) de même que le rendement en beurre comparé aux amandes issues des noix fumées dont la teneur en AGL est 5 % et la teneur en matière grasse est de 39 % bs (**chapitre 4**). Par contre, les amandes issues des noix fumées ont une couleur brune plus intense (a* = 9) que celles issues des noix bouillies et séchées. Avec un intervalle de point de fusion de 36-47 °C, les beurres extraits des noix bouillies et séchées ont des teneurs élevées en: eau (2 %), insaponifiable (7 %), tocophérols totaux (125 mg/g), peroxyde (8 meq O_2/kg), iode (53 g I_2/100 g) et AGL (2 %) comparées à ceux obtenus à partir des noix fumées. Une variation mineure a été observée au niveau des profils d'acide gras des différents beurres extraits des deux types d'amandes. L'analyse sensorielle effectuée sur ces beurres avec un panel de 12 personnes a révélé que les beurres extraits des amandes bouillies et séchées ont une texture plus molle avec une odeur plus intense comparés à ceux issus des noix fumées. Avec une teneur en eau de 10 %, légèrement au-dessus des 7- 8 % exigées sur le plan international lors de l'exportation, les amandes issues des noix bouillies et séchées peuvent être exportées de même que les amandes issues des noix fumées. Les résultats ont montré que malgré que les beurres issus des deux types d'amandes peuvent être utilisés dans différents domaines, les beurres issus des noix bouillies et séchées sont plus adaptées pour l'usage cosmétique et pharmaceutique à cause de la teneur élevée en matière insaponifiable et en tocophérols; tandis que ceux issus des noix fumées seront plus adaptés à l'usage alimentaire. Par ailleurs, une optimisation de certaines opérations unitaires telles que le fumage, la cuisson, la torréfaction est nécessaire pour l'amélioration du rendement et la conformité de la qualité des produits.

Dans le **chapitre 5,** les résultats relatifs à l'influence de la durée du stockage (3-21 jours) des noix fraiches et du temps de leur cuisson (10-60 minutes) sur les caractéristiques physicochimiques des amandes et du beurre ont été présentés. Le plan expérimental utilisé est la méthode de surface de réponse avec un dispositif expérimental composite centré. Les résultats ont montré que les deux facteurs pris séparément ou combinés ont des effets significatifs sur les caractéristiques d'une part des amandes telles que la teneur en matière grasse (38-52 % bs), la couleur et le rendement en beurre (24-36 % du poids des amandes), et d'autre part du beurre extrait dont la brillance (L* = 70-80), la saturation en jaune (b* = 16-23), et le pourcentage d'AGL (0,5-2 %). Un stockage plus long entraine une réduction de la teneur en matière grasse et augmente le pourcentage d'AGL du beurre; par contre, une augmentation du temps de cuisson des noix entraine une augmentation de la teneur en

matière grasse et la valeur maximale est trouvée autour de 32 minutes. Les conditions optimales données par le model pour obtenir une beurre de bonne qualité est de stocker les noix fraiches pour une durée inférieure ou égale à 3 jours et ensuite de cuire ces noix pendant 28 ± 3 minutes. Avec ces conditions, les amandes ont une teneur en eau de 7 % et une teneur en matière grasse de 50 % bs avec un rendement en beurre de 32 %. Le beurre extrait de ces amandes aura un pourcentage d'AGL de 0,8 % avec un indice de peroxyde de 2,5 meq O_2/100 g. avec ces caractéristiques, le beurre pourrait être utilisé en cosmétique et alimentation sans raffinage. Les suggestions ont été faites pour qu'au cours de la transformation, s'il y a lieu de stocker les noix de ne pas dépasser 3 jours et que le temps de cuisson soit autour de 28 minutes.

Dans le **chapitre 6**, l'influence du temps (15-45 minutes) et de la température (120-180 °C) de torréfaction des amandes concassées de karité sur les caractéristiques physicochimiques et les composés volatiles du beurre de karité a été évaluée en grâce à la même méthode de surface de réponse. Les résultats ont montré que le temps et la température de torréfaction ont un effet significatif sur la teneur en matière grasse de l'amande (44-53 % bs), sur le pourcentage d'AGL du beurre (0,5-3 %), et sur le nombre des composés volatiles du beurre et par conséquent sur l'odeur du beurre. Une longue durée de torréfaction à une température élevée entrainerait un meilleur rendement en beurre. Au total, 27 composés volatiles ont été identifiés dans le beurre extrait des amandes non torréfiées contre 58 composés identifiés (rangés en 12 groupes) dans les beurres extraits des amandes torréfiées. Parmi ces composés, 11 sont quantitativement dominants. La plupart des composés ont été générés par l'oxydation, l'hydrolyse et certains par la réaction de Maillard. Les conditions optimales de torréfaction identifiées par le model expérimental est la torréfaction des amandes à une température de 171 °C pendant 15 minutes. Avec ces conditions, la teneur en matière grasse des amandes sera de 49 % bs avec un rendement en beurre de 32 %. Le beurre extrait aura un taux d'AGL de 1,2 % et un indice de peroxyde de 3,2 meq O_2/kg. La recommandation a été faite donc de torréfier les amandes avec ces conditions et d'évaluer leur impact sur la teneur en matière insaponifiable des beurres extraits.

Le **chapitre 7** a évalué les changements physicochimiques du beurre de karité au cours du stockage. Pour cela, les échantillons du beurre ont été conditionnés dans des matériels tels que la calebasse traditionnelle, le plastique noir et le plastique transparent et stockés pendant 6 mois en salle (température: 28-30 °C, humidité relative: 81 ± 3 %) et au

réfrigérateur (4-7 °C). La couleur, l'activité de l'eau, le taux d'AGL, l'indice de peroxyde, et les composés volatiles ont été évalués au début et à chaque mois jusqu'à la fin du stockage. Tous les paramètres évalués ont été significativement affectés par le milieu et la durée de stockage tandis que l'effet des emballages a été moindre. L'altération a été beaucoup plus prononcée au cours du stockage en salle. Ainsi, le stockage en salle a entrainé un changement de couleur du beurre avec une augmentation du taux d'AGL et du peroxyde. Par exemple, à la fin du stockage, le taux d'AGL des échantillons stockés en salle dans les calebasses est trois fois supérieur à celui des échantillons stockés dans le réfrigérateur (1,91 % en salle contre 0,53 % au réfrigérateur). Egalement, la plupart des composés volatiles ont été détectés au cours du stockage en salle. La calebasse peut être utilisée comme emballage temporaire pour le stockage du beurre tandis que pour le stockage de longue durée, les emballages en plastique opaques sont conseillés. Aussi, en absence d'un réfrigérateur, le stockage du beurre doit-il se faire dans un milieu relativement frais afin d'éviter les réactions d'altération de sa qualité.

Dans le **chapitre 8**, les principaux résultats obtenus ont été discutés sur la base de la documentation existante. Ses principaux résultats ont été surtout l'optimisation de certaines opérations unitaires du procédé traditionnel et la préservation du beurre après extraction. Des suggestions ont été données pour les recherches futures pour l'amélioration de toute la chaîne de production des produits du karité et surtout pour que les productrices puissent avoir accès à ces résultats à travers les structures étatiques appropriées et les organisations non gouvernementales impliquées dans le développement de la chaîne des valeurs des produits agricoles.

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About the author

List of publications and reports

Full papers

2007 – Honfo, F.G., Kayodé, A.P.P., Coulibaly O. and Tenkouano, A. Relative contribution of banana and plantain products to the nutritional requirements for iron, zinc and vitamin A of infants and mothers in Cameroon. *Fruits*, **62** (5) 267-277.

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Submitted papers

1. Honfo, F.G., Linnemann, A., Meng Guo, Akissoe, N., Soumanou, M., and van Boekel, M.A.J.S. Influence of roasting on volatile compounds and other quality characteristics of shea butter.
2. Honfo, F.G., Linnemann, A., Akissoe, N., Soumanou, M., and van Boekel, M.A.J.S. Effect of storage and boiling of fresh shea nuts on quality characteristics of kernels and butter
3. Honfo, F.G., Linnemann, A., Soumanou, M., Akissoe, N., and van Boekel, M.A.J.S. Physico-chemical characteristics and volatile compounds of shea butter under different storage conditions

Proceeding

1. Honfo, F.G., Linnemann, A., Akissoe, N., Soumanou, M., and van Boekel, M.A.J.S. Connaissances endogènes et perception de qualité pour la valorisation des produits de karité au Bénin. "Etat des lieux des recherches récentes sur les filières ananas, karité, anacarde et crevette au Bénin." *Cotonou, Benin,* August 2011
2. Honfo, F.G., Linnemann, A., Akissoe, N., Soumanou, M., and van Boekel, M.A.J.S. Quality of shea kernel and shea butter processed in Benin. "Toward the development of a framework for agrifoods value chains in Benin." *Cotonou, Benin*, March 2012
3. Honfo, F.G., Linnemann, A., Akissoe, N., Soumanou, M., and van Boekel, M.A.J.S. "Influence des procédés traditionnels de production du beurre de karité sur la qualité des amandes et du beurre. Atelier scientifique national: 8e édition. " *Cotonou, Benin*, December 2014

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1. Fernande G. Honfo, Kerstin Hell, Ousmane Coulibaly, Abdou Tenkouano. Ion, zinc, and vitamin A contents of banana and plantain and their consumption by children and mothers in Cameroon. "Banana and Plantain in Africa: Harnessing International Partnerships to Increase Research Impact." *Mombassa, Kenya,* October 2008.
2. Fernande G. Honfo, Kerstin Hell, Ousmane Coulibaly, Pascal Fandohan, Guy A. Mensah. Effet des conditions de stockage sur les qualités sanitaires et physicochimiques du beurre de karité. "Présentation des résultats du projet

Amélioration de la qualité des produits agricoles au Bénin: Cas de l'anacarde et du karité." *Cotonou, Benin*, Novembre 2009.

3. Fernande G. Honfo, Anita R. Linnemann, Noel Akissoe, Mohamed M. Soumanou, Martinus A. J. S. van Boekel. Characteristics of traditionally processed shea kernels and butter in Benin. EFFoST Annual. "A lunch box for tomorrow: An interactive combination of integrated analysis and specialized knowledge of food." *Montpellier, France*, November 2012.

Biography

Fernande Gbenato Honfo was born on June 5th 1975 in Porto-Novo, Republic of Benin. She attended primary and secondary school in Porto-Novo and graduated from the secondary school in 1996. In October of the same year, she joined the Faculty of Agronomic Sciences of the University of Abomey-Calavi (FSA/UAC) and graduated in 2001 as "Ingénieur Agronome" with a specialization in Nutrition and Food Science. From 2002 to 2004, she worked as a research assistant in the Department of Food Science and Nutrition at The University of Abomey-Calavi. In 2005, she joined the International Institute of Tropical Agriculture (IITA) Benin station where she worked as associate researcher in nutrition. In between she was involved in research at IITA, she pursued her postgraduate studies in Nutrition and Food Science at the Faculty of Agronomic Sciences of the University of Abomey-Calavi (FSA/UAC) where she obtained in 2009 the degree as "Diplome d'Etudes Approfondies". She was granted a PhD fellowship under the project NPT/BEN/263 (funded by the Foundation for International Cooperation, NUFFIC) to undertake PhD research at Wageningen University, The Netherlands. She carried out the research presented in this thesis from April 2010 to March 2015, alternately in Benin and at Wageningen University. She can be contacted on fernandehonfo@gmail.com.

Overview of completed training activities

DISCIPLINE SPECIFIC ACTIVITIES		
Courses	Graduate School/Institute	Year
Sensory perception and Food preference	VLAG, Wageningen	2011
Formation sur la rédaction et la recherche de financement des projets de recherche en sécurité alimentaire et la valorisation des produits agricoles d'exportations prioritaires et de pêche	Projet NPT 263 et GVAL, Benin	2011
Formation á l'écriture scientifique dans le domaine de la sécurité alimentaire	Projet GVAL, Benin	2012
Course on food systems : from agronomy to nutrition and health with focus on Neglected and Underutilized Species (NUS) of plants	Bioversity International, Benin	2012
Reaction kinetics in food sciences	VLAG, Wageningen	2012
Workshop/Symposia/Colloquia		
Amélioration de la qualité des produits agricoles au Benin : Cas de l'anacarde et du karité	IITA-Cotonou, Benin	2010
Genre et Recherche des projets NPT"	UAC, Benin	2010
Agriculture-Nutrition linkages	CDI, Wageningen	2011
Workshop on Globalizations in a nutshell	WUR, Wageningen	2011
Etat des lieux des recherches récentes sur les filières ananas, karité, anacarde et crevette au Bénin	Projet NPT 263, Benin	2011
Le karité et ses dérivés: une nouvelle opportunité pour l'économie nationale	ABePEC, Bénin	2012
Conference and meetings		
EFFoST conference, Poster presentation	EFFoST, France	2012
UAC annual conference, Poster presentation	UAC, Benin	2013
Atelier scientifique national: 8e edition : Oral presentation	SNRA, Benin	2014
GENERAL COURSES AND WORKSHOPS		
Searching for Science on the Web	WGS, Wageningen	2010

Information Literacy for PhD Including Endnote Introduction	WGS, Wageningen	2010
EndNote X2 Advanced	WGS, Wageningen	2010
VLAG PhD week	VLAG, Wageningen	2011
Write a world class paper	VLAG, Wageningen	2011
Linear Model	PERC, Wageningen	2011
Advanced Course to Scientific Artwork	WGS, Wageningen	2012
Scientific publishing	WGS, Wageningen	2012
Techniques for writing and presenting a scientific paper	WGS, Wageningen	2013
Communication with the media and the general public	WGS, Wageningen	2013
OPTIONAL COURSES AND ACTIVITIES		
Preparation, submission and approval of research proposals	VLAG, Wageningen	2010
PDQ colloquia	PDQ, Wageningen	2011
Participating in PhD excursion to England	PDQ, Wageningen	2012
DNSA colloquia	FSA/UAC, Benin	2013

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