

Cocoa Butter and Its Alternatives: A Reveiw

Bindu Naik^{*a} and Vijay Kumar^b

^aDepartment of Farm Engineering, Institute of Agricultural Sciences, Banaras Hindu University, Varanasi, Uttarpradesh, India.

^bDepartment of Food Technology, Doon P.G. College of Agriculture Science and Technology, Selaqui, Dehradun, Uttarakhand, India-248011.

Abstract

Cocoa butter (CB) is the byproduct of cocoa bean processing industry and is obtained from the mature bean from the *Theobroma cacao* plant. It is an important ingredient in the chocolate and other confectionery industries. It's valued for its unique physicochemical properties which is given by its peculiar fatty acid composition. The major triacylglycerols (TAG) present in CB is symmetrical and contains very less amount of highly unsaturated fatty acid. The major fatty acids present in it are palmitic acid, stearic acid, oleic acid and linoleic acid, but low amounts of lauric acid and myristic acid. Increasing demand and shortage of supply for CB, poor quality of individual harvests, economic advantages and some technological benefits have induce for the development of its alternative called cocoa butter replacer (CBR). In the CBRs the TAG compositions are similar but are not identical to genuine CB. Most of them are produced by either modification of natural fat or by their blending in different proportion. However, it couldn't satisfy the consumer and fulfill the demand of confectionery industries. This review gives a brief idea about the processing of cocoa pod, the production of cocoa butter and its composition with fats that are commonly used as its Replacers.

*Corresponding Author:

Bindu Naik

Email : binnaik@gmail.com

Received: 13/02/2014

Revised: 05/03/2014

Accepted: 08/03/2014

Keywords: Cocoa butter, Cocoa butter replacers, *Theobroma cacao*, Interesterification.

1. Introduction

Cocoa bean (CB) is the fatty seed found inside a cocoa pod, fruit of the *Theobroma cacao* plant. It is small evergreen tree belong to the family *Malvaceae*. This plant is native to the deep tropical regions of Central and South America. After harvesting the cocoa fruit, it is opened to expose the seed, then fermented for a few days to separate pulp and seed. Pulp is used in distilleries and seed is used to prepare cocoa powder or chocolate and cocoa butter. The processing method of cocoa fruit is given in Fig 1. Cocoa butter is obtained by pressing of mature cocoa beans. CB is a valuable byproduct of the cocoa industry. It is a pale yellow liquid with a characteristic odor and the flavor of chocolate. It is an important and the only continuous fat phase found in chocolate, which help in the dispersion of the other ingredients also (Wang *et al.*, 2006). It is brittle at temperature below 25°C, soften in the hand and melts in the mouth having at a temperature of about 34C. This specific physio-chemical properties makes it is an important ingredient in confectionery industry. It is not greasy to touch. Cocoa butter contains a high proportion of saturated fat, derived from starch and palmitic acid and contains trace

amounts of caffeine and theobromine. It also contains fat soluble antioxidants such as vitamin E in the form of β -tocopherol, α -tocopherol and γ -tocopherol helps in its storage by increasing its therapeutic properties. CB can crystallize into several polymorphic forms, having α , γ , β' and β , crystals, with melting points of 17, 23, 26, and 35-37°C respectively. In the chocolate production, only β crystal is used because it has a high melting point. This crystal structure confers chocolate products an excellent quality in terms of sheen, snap, and smooth texture. It is also used in the formulation of cosmetics and soap due to its moisturizing and antioxidant properties which give it an anti ageing effect.

Due to the fact that about 30% of the world's coca crops are destroyed by pests and disease and is deteriorating due to climate change. With this the fat content of the cocoa bean is small in amounts as compared to the other fatty crops. It accounts for more than 50-58% of the cocoa beans. Less amount of fat content and is cultivated in few countries having a tropical climate, makes it availability unstable and expensive (Knapp, 2007). Other than this to overcome some technological problems like fat bloom, etc.

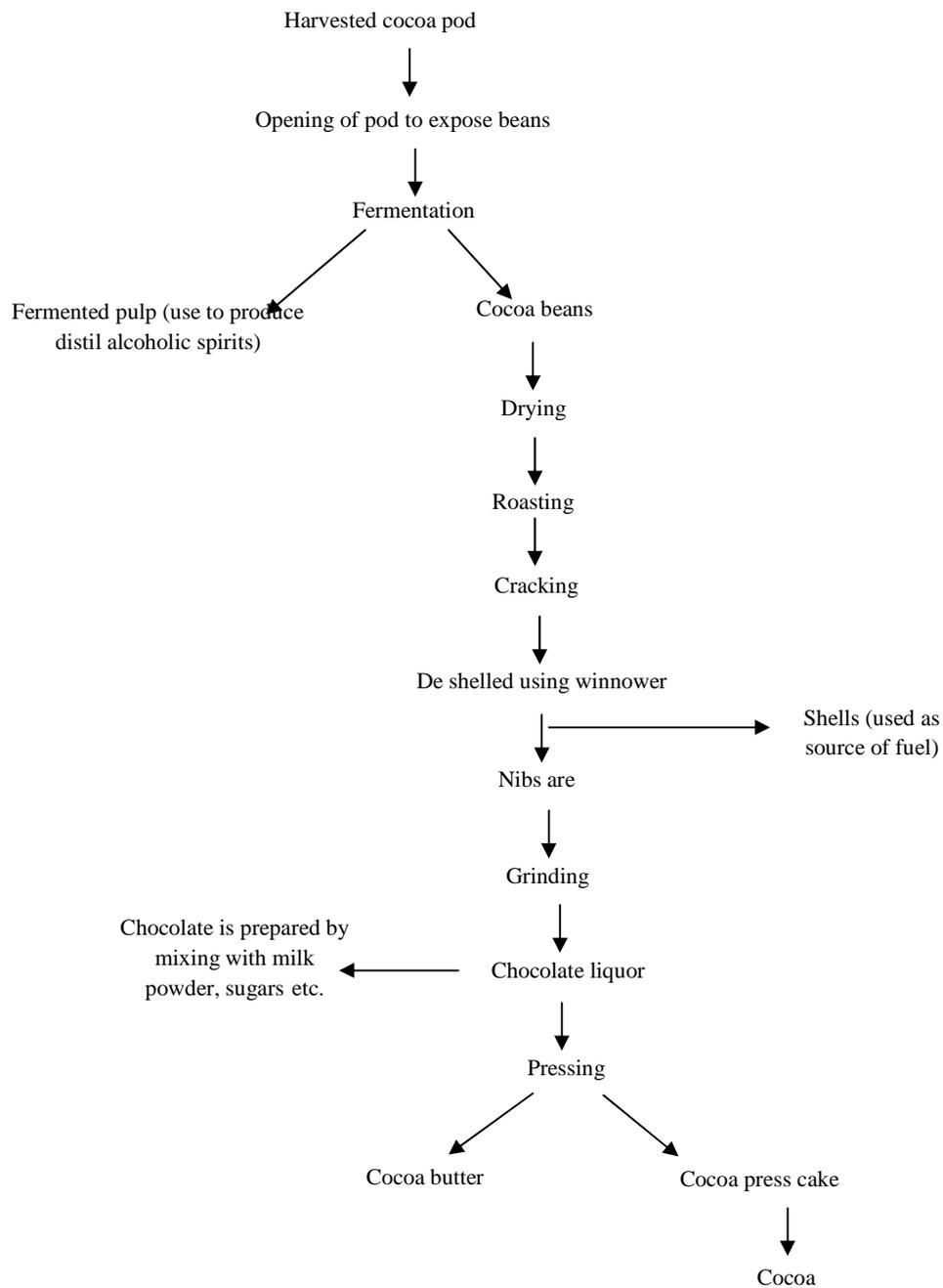


Fig 1: Processing of cocoa pod for production of CB, cocoa powder and chocolate.

during chocolate production it needs to design substitutes to use as CB alternatives (Hassan *et al.*, 1995; Moreton, 1988; Liu *et al.*, 2007). Vegetable oils are abundant in C18:1 acid, hence are very suitable to blend with cocoa butter replacer (CBR) and it is very good for confectionery fat due to its lower melting point. Most of the CBR are obtained from natural plant

fats or produced specifically by chemical or enzymatic fractionation from plant fats (Reddy and Prabhakar, 1989; Bloomer *et al.*, 1990; Chang *et al.*, 1990; Reddy and Prabhakar, 1990; Sridhar *et al.*, 1991; Chong *et al.*, 1992; Nesaretnam and Md. Ali, 1992; Mojovic *et al.*, 1993; Lipp and Anklam, 1998a). Interesterification of natural fats like palm kernel oil (PKO) and palm oil

(PO) (Bloomer *et al.*, 1990; Calliauw *et al.*, 2005; Hashimoto *et al.*, 2001; Undurraga *et al.*, 2001; Zaidul *et al.*, 2007c), mango seed fat (Ali *et al.*, 1985; Jimenez-Bermudez *et al.*, 1995; Kaphueakngam *et al.*, 2009; Lakshminarayana *et al.*, 1983; Solis-Fuentes, 1998), kokum butter (Maheshwari and Reddy, 2005; Reddy and Prabhakar, 1994), Sal fat (Gunstone, 2011; Reddy and Prabhakar, 1989), Shea butter (Olajide *et al.*, 2000), illipe fat (Gunstone, 2011) etc. are conducted.

2. Processing of Cocoa Pod to Extract Cocoa Butter

Cocoa pod contains beans consists of about 85% nib and 15% shell. After harvesting pods are opened to expose beans and are used to remove pulp and cocoa beans with discarding rind. The rind separated pods are passed for sweating in heaps or trays where fermentation occurs. During this, pulp that surround the bean is liquefied by the application of natural liquefying enzymes present in pulp. Liquefaction of pulp helps in easy separation of beans from the pulp. The cacao fruit pulp is very sweet, hence liquefied fermented pulp is used in the distillery industries to produce distills alcoholic spirit. Separated beans are dried using conventional or unconventional heat source to remove extra moisture for storage or transportation process. Dried beans are cleaned to remove foreign materials and are roasted at controlled condition. After fermentation using this step proper chocolate flavor is developed. The roasted beans are cracked to remove shell. Cracked beans are deshelled using the light flow of air called winnowing process. It gives cleaned deshelled nibs which are ground to have cocoa mass or liquor. Cocoa liquor can be directly used or can mix with other required substances for chocolate making.

Cocoa liquors are used to extract cocoa butter. Several methods are employed for the extraction of cocoa butter from the cocoa mass. It includes hydraulic press, mechanical press, supercritical fluid extraction (SFE), and solvent extraction method (Asep *et al.*, 2008; Nair, 2010). From the above, supercritical carbon dioxide extraction (SFE) is best suitable for food grade applications. Butter extracted cakes called cocoa press cakes; give less fat containing cocoa powder. Products obtained from the processing of cocoa pod are useful in food, dairy, pharmaceutical and cosmetics industries.

3. Composition of Genuine Cocoa Butter

Cocoa butter can be characterized by sharp melting point and desirable physicochemical properties given by its fatty acid composition (Rao and Lokesh, 2003). It is rich in palmitic, stearic and oleic fatty acids. For more than 70% of its total TAG consist of

disaturated 1,3-distearoyl-2-oleoyl glycerol (SOS), 1(3)-stearoyl-2-oleoyl-3(1)-palmitoyl glycerol (SOP) and 1,3-dipalmitoyl-2-oleoyl glycerol (POP) with oleic acid in sn-2 position of glycerol backbone (Simoneau *et al.*, 1999; Liu *et al.*, 2007). This specific fatty acid composition and its arrangement give it a value crystallization and melting characteristics in the mouth with cooling effect in the mouth, and the typical mouth feeling which makes this fat the main base for chocolates and confectionery products (Shukla, 1995). The total saturated fatty acid present in CB consists of about 57-64% and unsaturated fatty acid about 36-43%. The saturated fatty acid present in CB is consists of palmitic acid, stearic acid, lauric acid and myristic acid, arachidic acid and in unsaturated fatty acid present are oleic acid, palmitoleic acid, linoleic acid and α -linolenic acid where palmitic acid, stearic acid, oleic acid are present in higher amount and lauric acid, myristic acid, palmitoleic acid, arachidic acid, linoleic acid in low amount. Cocoa butter triacylglycerols have saturated fatty acids at the 1, 3-positions and oleic acid at the 2-position with oleic, stearic and palmitic acid as the main fatty acids (Talbot, 1999). The typical fatty acid composition of cocoa butter with their percentage is given in Table 1. In CB natural antioxidant like vitamin E such as β -tocopherol, α -tocopherol and γ -tocopherol are present which help in its preservation. It contains β -tocopherol in higher amount followed by α -tocopherol and γ -tocopherol (Erickson *et al.*, 1983).

Table 1: Fatty acid and triglycerides profile of genuine cocoa butter

Types of fatty acids	% of fatty acids
Saturated fatty acids	57-64
Palmitic acid (C16:0)	24.5-33.7
Stearic acid (C18:0)	33.7-40.2
Myristic acid (C14:0)	0-4
Arachidic acid (C20:0)	1
Lauric acid (C12:0)	0-1
Unsaturated fatty acids	36-43
Oleic acid (18:1)	26.3-35
Palmitoleic acid(C16:1)	0-4
Linoleic acid (18:2)	1.7-3
α -Linolenic acid	0-1
others	1.6
Triacylglycerol	$\geq 70\%$
1(3) palmitoyl-3(1) stearoyl-2-oleoglycerol (POS)	42.2
24.2% 1(3)-distearoyl-2-oleoylglycerol (SOS)	24.2
1,3-dipalmitoyl-2-oleoylglycerol (POP)	21.8

(Gunstone, 2011)

4. Properties of Cocoa Butter

Properties of cocoa butter are mainly dependent to its triglyceride composition. Cocoa butter has a sharp melting point ranges from 27 to 35°C. At room temperature, it is hard and brittle where its hardness depends on the solid fat content. However the nature of the crystalline lattice also affects the hardness of the cocoa butter. The physico-chemical properties of CB are given in Table 2. Iodine value indicates the degree of unsaturation and the cocoa butter having higher iodine value is softer than having a lower iodine value. The saponification value indicates the average chain length of fatty acids present in fat. If the saponification value of the fat is high, then the chain length of the fatty acid will be shorter, and vice versa. The acid value (AV) is defined as the weight in milligrams of potassium hydroxide necessary to neutralize the free fatty acid present in 1 g of fat and it is used to quantify the free fatty acids present in fats or oils. The cloud point (Cp) is related to the unsaturation of oil, that is, the unsaturation of oil is higher, when its Cp is low.

Table 2: Physico-chemical properties of cocoa butter
(ranges shows the variation from region to region)

Iodine value (g I ₂ /100g)	32-35
Saponification value (mg KOH/g)	192-199
Acid value (mg NaOH/g)	1.04-1.68
Peroxide value (meq O ₂ /kg)	1.00-1.10
Melting point	29-40°C

(Jahurul *et al.*, 2013)

5. Cocoa Butter Alternatives (CBAs)

Due to uncertainty in availability and higher price, industries are looking for alternatives to CB. Cocoa butter alternatives (CBAs) are fats that fulfilling the function of cocoa butter completely or in parts. On the basis of functional differences in the vegetable fats added to chocolate CBAs are to be distinguished and are labelled as cocoa butter replacer (CBRs), cocoa butter equivalents (CBEs) and as cocoa butter substitutes (CBSs) (Brinkmann, 1992; Bouscholte, 1994). All fats that are used in place of CB to replace it either partially or wholly in chocolate or other confectionary products are generally known as the CBRs (Kheiri, 1982).

A CBR is usually cheaper than CB and serves the purpose of CB. It can also be processed just like CB and meet specific country legal requirements such as use of non-animal and non-synthetic fats in chocolate products (McGinley, 1991). The fatty acid compositions of CBRs are similar to that of CB with more or less similar triglycerides structure. CBRs can be divided into two groups, namely cocoa butter equivalents (CBEs) and cocoa butter substitutes (CBSs).

CBEs are vegetable fats, which have similar physical and chemical characteristics like CB (Smith, 2001). Therefore, CBEs can be mixed with CB in any amount without altering the melting, rheological, and processing characteristics of final products like CB. CBE is designed to contain a glyceride composition similar to that of CB. Their properties are expected to be similar and compatible with CB in mixtures for chocolate manufacture. The major fatty acids contained in CBEs are palmitic acid, stearic acid and oleic acid, which are similar to that of CB. Most of CBE is prepared from blending of different mixtures of palm oil, palm oil fractions, shea, and illipe, sal and mango kernels fat etc. It contains approximately 40% 1-palmito, 2-olein, 3-sterin glycerol (POS), 27% of 1,3 distearinmonooleate glycerol (SOS) and 21% of 1,3 dipalmitin- 2-monooleato glycerol (POP) and minor amounts of other triglycerides (Undurraga *et al.*, 2001). CBEs are divided into two subgroups, namely cocoa butter extenders (CBEXs) and cocoa butter improvers (CBIs) (Lipp and Anklam, 1998a). CBEXs cannot be mixed with CB in every proportion, while CBIs are similar to CBEs, contain higher level of solid triglycerides, and because of this characteristic it is commonly used for improving soft cocoa butters.

CBS are fats that be mixed with CB to a limited extent without significantly altering its melting, rheological, and processing properties. They do not necessarily have physico-chemical characteristics similar to CB. The amount of the CBS used depends on its degree of compatibility with CB and vegetable fat blends. This degree of compatibility determines the quality and the price of the cocoa butter extender (CBEX). CBSs contain lauric and myristic acid with some physical similarities to CB, but chemically they are completely different. Therefore, they are suitable for wholly replacement of CB. The subgroups of CBA and CBRs are given in Fig 2.

Vegetable fats are used as extenders in some countries where partial replacement of CB is permitted. Foreign fats having similar chemical and physical properties to those of CB are normally added to chocolate have into practice. Various components of CB have been targeted as indicators for the detection of CBAs other than CB added to chocolate. As the triglycerides account for more than 95% of CB, these can be determined as an indicator (Lipp and Anklam, 1998b; Zaidul *et al.*, 2006). CBRs of CBE or CBS can be produced by chemical or enzymatic fractionation of plant fats (Lipp and Anklam, 1998a; 1998b; Nesaretnam and Ali, 1992; Reddy and Prabhakar, 1990).

6. Fats Commonly Used as a Source of CBA

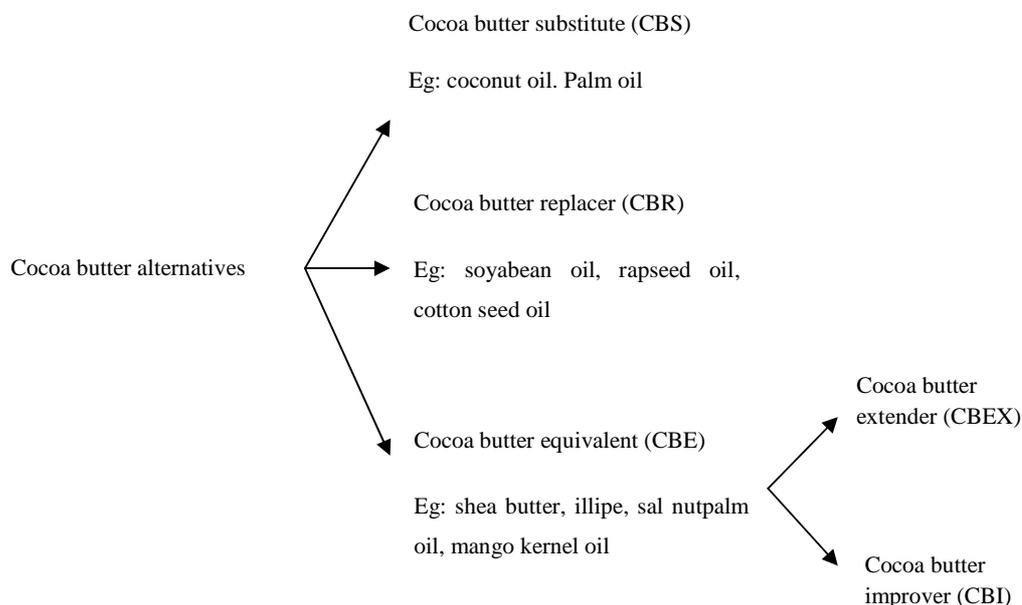


Fig 2: Subgroups of CBA and CBR (Lipp and Anklam, 1998a)

Palm kernel oil (PKO) is one of the majorly used edible oil to produce CBR. Its fatty acid composition consists of lauric acid in higher amount where as stearic acid and oleic acid constituents are relatively low as compared with cocoa butter. To produce CBR from PKO it needs to reduce the lauric acid content in oil while increasing the stearic and oleic acid content. PKO are fractionated using supercritical fluid to be used as a blending agent with CBR (Zaidul *et al.*, 2006). Palm kernel oil (PKO) could provide such a replacement as it is regarded as food-grade oil that is of high quality. It has high solid content and rapid melting point, which makes it particularly useful in confectionery products. In CB, the lauric and myristic fatty acid constituents are present as a trace or very low amounts, whereas the palmitic acid, stearic acid and oleic acid constituents are high (Kheiri, 1982; Pease, 1985).

Kokum kernel is a byproduct of agro-processing industry, it contains about 40-50% fat, which has the potential to be used as cocoa butter alternative (CBA). However, inefficient extraction techniques that are practiced at cottage level restrict its industrial applications (Vidhate and Singhal, 2013). Kokum kernel fat is a light yellow hard solid with a faint odor, an iodine value of 35-37, and a saponification value of 189 (Raju and Reni, 2001). It has a melting point of 39-

42°C with major fatty acids being stearic (50-60%) and oleic (36-40%); the major triacylglycerols are 2-oleodistearin (SOS), present to the extent of about 70% suggesting its potential to become a worthy CBE (Reddy and Prabhakar, 1994). Kokum fat with high in stearic acid and low in palmitic acid is less atherogenic than other CBA containing higher palmitic acid, and can be a healthy source of CBA in chocolate and confectionery products. Reddy and Prabhakar (1994) produced cocoa butter extenders with different melting profiles by blending of both middle fraction of Kokum fat with phulwara butter in different proportion and reported blend with higher levels of Kokum fat are harder than cocoa butter and have short melting ranges.

Fractionated high stearic-high oleic sunflower oil can be used as a CBE. It contains disaturated triacylglycerols typically present in CBEs, albeit at a lower concentration than that required to produce a solid fat. Joaquín *et al.* (2011) have assessed and optimized a means to fractionate high stearic-high oleic sunflower oil in order to produce solid fractions that can be used as stearic acid-rich butters appropriate for CBE formulation (Joaquín *et al.*, 2011).

Sal fat (*Shorea robusta*) is obtained from the seed kernel of sal trees, widely grown in India, Malaysia, Borneo, Java, and Philippines. Gunstone (2011) reported that fractionation of sal fat is necessary

for making cocoa butter resembles triglycerides, which is a valuable ingredient for CBEs. Reddy and Prabhakar (1989) produced cocoa butter extenders by blending of stearins of sal fat with phulwara butter in different ratios. Their results showed that the solidification properties and solid fat indices of blends containing 75-85% of sal fat stearin and 15-25% of phulwara butter stearin closer to CB. Cocoa butter extenders were made by decreasing the sal fat stearin to 50-67% in the blend. They also reported that a series of cocoa butter extenders can be made by changing the sal fat and phulwara butter stearin ratios in the blends which show similar chemical and physical properties like CB.

Shea butter is obtained from the shea kernel which contain about 40-55% oil. It is an African and sub-Saharan African edible vegetable fat. Based on the triglyceride compositions; shea butter is used as cocoa butter substitutes in the chocolate and confectionery industry in Europe (Olajide *et al.*, 2000).

Illipe butter (*Shorea stenoptera*) is obtained from the seed kernel of Illipe tree widely grown in Sarawak, Malaysia, Java, Indonesia, the Philippines and the other parts of Borneo. It is also called Borneo tallow. The ripe Illipe nuts contain about 40 to 60% valuable edible fats. The fatty acid compositions of Illipe butter resemble that of cocoa butter. Recently, Gunstone (2011) reported that Illipe butter can be used directly as cocoa butter equivalent without further processing. Physicochemical properties of different fats commonly used as replacer of CB are given in Table 4.

7. Production of Cocoa Butter Analog Through Enzymatic Interesterification

Procedures for chemical interesterification of cheap fats and oils to produce analogs have been developed for years and are found to be practical to industries (Liu *et al.*, 1997). Recently, preparation of CBE through 1, 3-specific lipase-catalyzed interesterification has received much attention because lipases offer certain advantages over other chemical catalysts (Chang *et al.*, 1990). The purpose of interesterification is to incorporate selectively stearic residues into triglycerides in positions 1 and 3 until a composition resembling CB composition is obtained. The stearate donor could be either free stearic acid or an ester of stearic acid, however, for practical applications stearic acid is preferred due to its availability and low cost. For that purpose, the enzyme used should be 1, 3-regiospecific, exchanging triglyceride residues only at positions *sn*-1 and *sn*-3, and preferably immobilized because in this form it is easily separated from the products and is also more thermostable than the free enzyme. The interesterification reaction can be carried out in a

system containing triglycerides and stearic acid only that is in a solvent free system or the mixture could be diluted with some suitable non-polar solvent. There are distinct advantages and disadvantages in using either system, but in food application processes, solvent free systems are clearly preferable. For technological purposes, it is important to determine the parameters that affect the productivity of a CBE and find the optimal operation strategy that maximize productivity.

Camel hump and tristearin are interesterified to produce cocoa butter analog. It contains mixtures of fatty acids and most of these are C16:0, C18:0 and C18:1 (Kadim *et al.*, 2002). Shekarchizadeh *et al.* (2009) had studied interesterification of camel hump fat and tristearin using immobilized *Thermomyces lanuginosus* lipase (Lipozyme TL IM) as a biocatalyst in the Supercritical carbon dioxide medium to produce cocoa butter analog. Process conditions (pressure, temperature, tristearin/camel hump fat ratio, water content, and incubation time) were optimized by conducting experiments at five different levels using the response surface method (RSM). The pressure, 10MPa; temperature, 40°C; SSS/CHF ratio, 1:1; water content, 10% (w/w) and incubation time, 3 h were found to be the optimum conditions to achieve the maximum yield of cocoa butter analog.

Refined olive-pomace oil (ROPO) was utilized as a source for the production of a cocoa butter (CB)-like fat. Immobilized *sn*-1,3 specific lipase-catalyzed acidolysis of ROPO with palmitic (PA) and stearic (SA) acids was performed at various substrate mole ratios (ROPO:PA:SA) to produce major triacylglycerols (TAGs) of CB. Products obtained for various substrate mole ratios were compared to a commercial CB in terms of TAG content, melting profile, solid fat content (SFC) and microstructure. The fat produced in a substrate mole ratio of 1:2:6 was the most similar to CB. The product contained 11% POP, 21.8% POS, 15.7% SOS while commercial CB contained 18.9% POP, 33.1% POS and 24.7% SOS. The product had a melting peak of 29.9°C while CB had one of 28.5°C. Polarized light microscope (PLM) images showed that fat crystal network microstructures of this product and CB were very similar (Ciftci *et al.*, 2009).

Substrate oil composition, reaction time, acyl donor, temperature, and pressure affected the triacylglycerol (TG) content of cocoa butter analog during the interesterification reaction catalyzed by lipase in a supercritical carbon dioxide (SC-CO₂) system. Among oil sources used to interact with tristearin, the content of 1(3)-palmitoyl-3(1)-stearoyl-2-monoolein (POS) and 1-palmitoyl-2, 3-dioleoylglycerol (POO) in analog was most similar to the corresponding TG content of cocoa butter when -

Table 3: Properties of subgroups of CBAs

Properties	Cocoa butter equivalent(CBE)	Cocoa butter replacer(CBR)	Cocoa butter substitute(CBS)
Types of fatty acids	non-lauric acid plant fats	non- lauric acid fats	lauric acid containing fat
Physical and chemical properties	Similar in their physical and chemical properties like melting profile and polymorphisms to cocoa butter	The distribution of fatty acid is similar to cocoa butter, but the structure of triglycerides is completely different	Chemically different to cocoa butter, with some physical similarities
Mixing properties	Mixable with it in every amount without altering the properties of cocoa butter	Only in small ratios can mix to cocoa butter.	Suitable only to substitute cocoa butter to 100%.
Main fatty acid	Palmitic (P), stearic (S) oleic acid(O), Linoleic (L), arachidic acid(A)	Elaidic acid (E), stearic acid(S), palmitic (P), linoleic(L)	Lauric acid (L), myristic acid (M)
Main triglycerides	POP, POS, SOS	PEE, SEE	LLL, LLM, LMM
Examples	Palm oil, illipe butter, shea butter, kokum butter, sal fat	Hydrogenated oil, soya oil, rape seed oil, cotton seed oil, ground nut oil, palm olein	Coconut oil, palm kernel oil, MCT

(Brinkmann, 1992; Lipp and Anklam, 1998a)

Table: 4 Physico-chemical properties of different fats commonly used as replacer of CB

Fatty acids (%)	Mango seed kernel fat	Shea butter	Sal fat	Illipe butter	Tea seed oil	Kokum kernel fat	CB
Palmitic acid	3-18	3.4-8.0	4.6-8.3	18-21	17.40	-	25.2-33.7
Stearic acid	24-57	37.0-58	34.7-43.2	39-46	4.30	50-60	33.3-40.2
Oleic acid	34-56	33.0-50.0	40.4-42.4	34-37	55.96	36-40	26.3-35.2
Linoleic acid	1-13	3.0-6.65	1.5-2.8	-	21.15	-	1.7-3.6
Arachidic acid	1-4	0.2-2.0	6.1-12.3	-	-	-	-
Triglycerides							
POP	1	3		7	-	Trace	18.9-23.4
SOS	40-59	42	42	45	-	72	27.5-33.0
POS	11-16	6	11	34	-	6	42.8
SOO	23	-	16	26	-	-	-
SOL	-	-	-	5	-	-	-
SLS	-	-	-	5	-	-	-
OOO	5	-	3	6	-	-	-
AOO	-	-	4	-	-	-	-
SOA	4	-	13	-	-	-	-
POO	5	-	-	-	-	-	-
Other physico chemical properties							
Iodine value	39-48	52-56	31-45	29-38	83.73	-	34.74-37.33
Saponification value	-	-	-	-	192.37	-	193.62-196.71
Melting point (C)	34-43	32-45	30-36	37-39	-	-	27-40

(Gunstone, 2011)

analog was prepared with lard. Cocoa butter analog was produced by the interesterification lard and tristearin at a mole ratio of 1.4 as substrates in SC-CO₂ system at 17 MPa, 50 °C, pH 9, for 3 h catalyzed

by an immobilized lipase enzyme (Liu *et al.*, 2007). Cocoa butter replacer was prepared by a combination of dry fractionation, partial hydrogenation and enzymatic inter-esterification from tea seed. The

reaction is catalyzed by sn-1, 3 specific lipase from *Thermomyces lanuginosus*. The developed CBR by enzymatic interesterification of hydrogenated and solid fraction (SF) of tea seed oil at weight percent ratio of 30:70 is used in prepared dark chocolate samples as a replacement for 5%, 10%, 15% and 20% of cocoa butter (CB) and the effect of the replacement on the hardness of the chocolate samples was investigated. Results showed that chocolate samples containing 5% and 10% of the interesterified sample (EIS), had the closer texture to that of CB chocolate than other samples. The solid fat content (SFC) profiles also revealed that blending 10% of EIS with CB in chocolate formulation does not affect the sharp melting point of CB. Based on the results taken from bloom formation, polymorphic structure and sensory evaluation, adding up to 10% of EIS in chocolate formulation reduces the bloom development without adversely affecting the desirable β crystal formation and sensory qualities in the chocolate samples.

A cocoa butter equivalent through enzymatic transesterification of *Pentadesma butyracea* butter with ethyl palmitate in an organic medium using immobilized lipase from *Thermomyces lanuginosa* was produced. The effects of several parameters such as initial ratio of ethyl palmitate–triacylglycerols (TAGs) of *P. butyracea*, the initial water activity of the enzyme preparation, solvent polarity and the enzyme loading were studied. The best result with regard to target TAGs was obtained in nonpolar solvents and low water activity. Thermograms of the products obtained by scanning differential calorimetry were similar to cocoa butter, but with minor differences, due particularly in the presence of trisaturated TAGs (Tchobo, 2009).

Undurraga *et al.* (2001) produced CBEs through enzymatic interesterification of palm oil mid fraction with stearic acid in solvent free system using Novo lipase Lipozyme™ as a catalyst. Zaidul *et al.* (2007c) produced cocoa butter replacer's by blending supercritical carbon dioxide (SC-CO₂) extracted PKO fractions with conventionally extracted palm oil and commercial C18:0 and C18:1 constituents at various ratios. Many other researchers have also reported production of cocoa butter substitutes from the fractionation of palm kernel oil in the literature (Calliauw *et al.*, 2005; Hashimoto *et al.*, 2001). The CBE is produced by enzymatic interesterification of palm oil mid fraction (POMF) with stearic acid in a solvent free system using Novo lipase Lipozyme™ as a catalyst in both in batch and in a continuous packed bed reactor. In this study, stearic acid is used as stearate donor (Undurraga *et al.*, 2001). Lipozyme TLIM catalyze interesterification between RBD palm olein and stearic for the production of cocoa butter equivalent in a batch reactor (Harun *et al.*, 2008). Fatty

acid composition of mahua (*Madhuca longifolia* or *M. indica*), dhupa (*Vateria indica*) and fat of mango (*Mangifera indica*) seed kernel is interesterified with palmitate and/or stearate for the production of cocoa butter analog (Sridhar *et al.*, 1991). According to mango varieties, the kernels contain about 5.28-15% of fats on dry a basis (Abdalla *et al.*, 2007; Gunstone, 2011; Solis-Fuentes and Duran-de-Bazua, 2004). The major fatty acids contained in mango seed kernel fats are oleic, stearic and palmitic acids. Apart from these fatty acids, it also contains smaller amounts of linoleic, arachidic, behenic, lignoceric and linolenic acids (Solis-Fuentes and Duran-de-Bazua, 2004). Kaphueakngam *et al.* (2009) produced CBE by blending mango seed almond fat (MAF) with palm oil mid-fraction (PMF).

CBE are also produced by the blending of CB with milk fat, lauric fats, MAF or hydrogenated cottonseed oil (Kaphueakngam *et al.*, 2009; Solis-Fuentes and Duran-de-Bazua, 2004). Production of a cocoa butter-like fat from the interesterification of totally hydrogenated cottonseed and olive oils was studied (Chang *et al.*, 1990).

8. Health Effect of Cocoa Butter Alternatives

Generally, Lauric and hydrogenated fats are used to replace CB; these increase the levels of LDH cholesterol and induce arteriosclerosis (Aro *et al.*, 1997; Mensink *et al.*, 2003). Where, CBEs are a blend of stearic acid-rich tropical butter and palm oil mid fractions. CBEs contain high oleic and stearic acids, which do not alter the levels of plasma blood cholesterol. Thus, CBEs represent a healthier and promising alternative. The main sources for CBEs are also fats from tropical species like shea, kokum, illipe or mango kernels, which are rich in stearic acid and SOS and that, are usually blended with palm mid stearins rich in POP (Padley and Timms, 1980). For this it would be of interest to produce SOS-rich fats from a reliable source, such as an oil crop growing in temperate climates like sunflower.

9. Conclusions

CB is a unique and valuable fat. Cocoa trees can be cultivated in a few of the countries make it supply unstable and increasing demand of cocoa butter in confectionery industries increases its price. Due to some technological and chemical problems in CB made it to find cocoa butter alternatives using low cost natural fats having a closer physical property of CB. This helps in introducing fats of some non timber forest products like mango, sal, palm, mahua seed kernel etc. CBA can be produced by either blending of these oils

in different proportion or by their modification using a biocatalyst or chemical catalyst in an optimized condition with different solvent system. However, cocoa butter alternatives have been found unable to overcome the problem is that they couldn't meet the exact demand and unity of cocoa butters. Further

research is needed on the topic to optimize reaction conditions and to discover natural fats combination that can give a substitute to the fatty acid composition of CB and can be precise alternatives of cocoa butter fats that could be able to fulfill the demands of cocoa butter fats.

References

- Abdalla AEM, Darwish SM, Ayad EHE and El-Hamahy RM (2007). Egyptian mango by-product 1. Compositional quality of mango seed kernel. *Food Chemistry*, 103: 1134-1140.
- Ali MA, Gafur MA, Rahman MS and Ahmed GM (1985). Variations in fat content and lipid class composition in ten different mango varieties. *Journal of the American Oil Chemists' Society*, 62 (3): 520-523.
- Aro A, Jauhiainen M, Partanen R, Salminen I and Mutanen M (1997). Effects on serum and lipoprotein lipids, apolipoproteins, lipoprotein (a), and lipid transfer proteins in healthy subjects. *American Journal of Clinical Nutrition*, 65: 1419-1426.
- Asep EK, Jinap S, Tan TJ, Russly AR, Harcharan S and Nazimah SAH (2008). The effects of particle size, fermentation and roasting of cocoa nibs on supercritical fluid extraction of cocoa butter. *Journal of Food Engineering*, 85: 450-458.
- Bloomer S, Adlercreutz P and Mattiasson B (1990). Triglyceride interesterification by lipases. Cocoa butter equivalents from a fraction of palm oil. *Journal of the American Oil Chemists' Society*, 67(8): 519-525.
- Bouscholte M (1994). Verwachte EU-goedkeuring plantaar- dige vetten geeft chocolade nieuwe marktkansen. *Food Management*, 23: 12-15.
- Brinkmann B (1992). Kakaobutteraustauschfette. *Zucker and Stisswarenwirtschaft*, 8: 268-270.
- Bouscholte, M. (1994) Verwachte EU-goedkeuring plantaar- dige vetten geeft chocolade nieuwe marktkansen. *Food Management*, 23: 12-15.
- Calliauw G, Foubert I, De Grevt W, Dijckmans P, Kellens M and Dewettinck K (2005). Production of cocoa butter substitutes via two-stage fractionation of palm kernel oil. *Journal of the American Oil Chemists' Society*, 82: 783-789.
- Chang MK, Abraham G and John VT (1990). Production of cocoa butter-like fat from interesterification of vegetable oils. *Journal of the American Oil Chemists' Society*, 67(11): 832-834.
- Chong CN, Hoh YM and Wang CW (1992). Fractionation procedures for obtaining cocoa butter-like fat from enzymatically interesterified palm olein. *Journal of the American Oil Chemists' Society*, 69(2): 137-140.
- Ciftci ON, Fadilog'lu S and Gogus F (2009). Utilization of Olive-Pomace Oil for Enzymatic Production of Cocoa Butter-like Fat. *Journal of American Oil Chemists' Society*, 86: 119-125.
- Erickson JA, Weissberger W and Keeney PG (1983). Tocopherols in the unsaponifiable fraction of cocoa lipids. *Journal of Food Science*, 38: 1158-1162.
- Gunstone FD (2011). *Vegetable Oils in Food Technology Composition, Properties and Uses*, Willy-Blackwell, CRC Press, 291-343.
- Harun A, Kamaruddin and Shaharin FAM (2008). Lipozyme TLIM catalyzed interesterification for the production of cocoa butter equivalent in a batch reactor. *Journal of Biotechnology*, S356-S401; doi:10.1016/j.jbiotec.2008.07.818.
- Hashimoto S, Nezu T, Arakawa, H, Ito T and Maruzeni S (2001). Preparation of sharpmelting hard palm midfraction and its use as hard butter in chocolate. *Journal of the American Oil Chemists' Society*, 78 (5): 455-460.
- Hassan M, Philippe JB, Alain P and Gerard G (1995). Production of cocoa butter equivalents from prickly-pear juice fermentation by an unsaturated fatty acid auxotroph of *Cryptococcus curvatus* grown in batch culture. *Process Biochemistry*, 30(7): 629-634.
- Jimenez-Bermudez M, Silva-Hernandez ER, Solis-Fuentes JA and Duran-de-Bazua MC (1995). La grasa de semilla de mango comoposible sustituto de la Manteca de cacao. In: *Congreso Iberoamericano de Ingenier_ia de los Alimentos, November 4-7. S.P. Brazil*.
- Joaquin JS, Miguel AB, Enrique M-F and Rafael GID (2011). Production of stearate-rich butters by solvent fractionation of high stearic-high oleic sunflower oil. *Food Chemistry*, 124: 450-458.
- Kadim IT, Mahgoub O, Al-Maqbaly RS, Annamalai K and Al-Ajmi DS (2002). Effects of age on fatty acid composition of the hump and abdomen depot fats of the Arabian camel (*Camelus dromedarius*). *Meat Science*, 62: 245-251.
- Kaphueakngam P, Flood A and Sonwai S (2009). Production of cocoa butter equivalent from mango seed almond fat and palm oil mid-fraction. *Asian Journal of Food and Agro-Industry*, 2 (04): 441-447.
- Kheiri MSA (1982). Formulation, Evaluation and Marketing of Cocoa Butter Replacer's Fat. *Palm Oil Research Institute of Malaysia (PORIM), Kuala Lumpur*.
- Knapp AW (2007). Cocoa and chocolate: their history from plantation to consumer. *Whitefish, MT.: Kessinger Publishing LLC*.
- Lakshminarayana G, Chandrasekhara-Rao T and Ramalingaswamy PA (1983). Varietal variations in

- content characteristics and composition of mango seed and fat. *Journal of the American Oil Chemists' Society*, 60(1): 88-89.
- Lipp M and Anklam E (1998b). Review on cocoa butter and alternatives for use in chocolate. Part B: Method of analysis. *Journal of Food Chemistry*, 62(1): 73-97.
- Lipp M and Anklam E (1998a). Review on cocoa butter and alternatives for use in chocolate. Part A: Compositional data. *Journal of Food Chemistry*, 62(1): 73-97.
- Liu KJ and Shaw JF (1997). Synthesis of cocoa butter equivalent by lipase-catalyzed interesterification in supercritical carbon dioxide. *Journal of the American Oil Chemists' Society*, 74: 1477-1482.
- Liu KJ, Chang H-M and Liu K-M (2007). Enzymatic synthesis of cocoa butter analog through interesterification of lard and tristearin in supercritical carbon dioxide by lipase. *Food Chemistry*, 100: 1303-1311.
- Jahurul MHA, Zaidul ISM, Norulaini NAN, Sahena F, Jinap S, Azmir J, Sharif KM and Mohd Omar AK (2013). Cocoa butter fats and possibilities of substitution in food products concerning cocoa varieties, alternative sources, extraction methods, composition, and characteristics. *Journal of Food Engineering*, 117: 467-476.
- Maheshwari B and Yella Reddy S (2005). Application of kokum (*Garcinia indica*) fat as cocoa butter improver in chocolate. *Journal of the Science of Food and Agriculture*, 85: 135-140.
- McGinley L (1991). Analysis and quality control for processing and processed fats. In Analysis of oilseeds, fats and fatty foods (JB Rossel and JL Pritchard Eds). *Elsevier Applied Science, London*, 441-498.
- Mensink RP, Zock PL, Kester AD and Katan MB (2003). Effects of dietary fatty acids and carbohydrates on the ratio of serum total to HDL cholesterol and on serum lipids and apolipoproteins: A meta-analysis of 60 controlled trials. *American Journal of Clinical Nutrition*, 77: 1146-1155.
- Mojovic L, Siler-Marinkovic S, Kukic G and Vunjak-Novakovic G (1993). *Rhizopus arrhizus* lipase-catalyzed interesterification of the midfraction of palm oil to a cocoa butter equivalent fat. *Enzyme and Microbial Technology*, 15: 438-443.
- Moreton RS (1988). Physiology of lipid accumulating yeast. In: Single cell oil (RS Moreton Eds.). *London: Longman Scientific and Technical*, 1-32.
- Nair PKP (2010). 5-Cocoa (*Theobroma cacao* L.). The Agronomy and Economy of Important Tree Crops of the Developing World. *Elsevier, London*, 131-180.
- Nesaretnam K and Ali AR (1992). Engkabang (Illipe)-an excellent component for cocoa butter equivalent fat. *Journal of the Science of Food and Agriculture*, 60, 15-20.
- Olajide JO, Ade-Omowaye BIO and Otunola ET (2000). Some physical properties of shea kernel. *Journal of Agricultural Engineering Research*, 76: 419-421.
- Padley FB and Timms RE (1980). The determination of cocoa butter equivalents in chocolate. *Journal of the American Oil Chemists' Society*, 57: 286-293.
- Pease JJ (1985). Confectionery fats from palm oil and lauric oil. *Journal of the American Oil Chemists' Society*, 62(2): 426-430.
- Raju VK and Reni M (2001). Kokam and Cambodge. In: Handbook of Herbs and Spices (KV Peter Eds.). *Woodhead Publishing Limited, Cambridge*, 207-215.
- Rao R and Lokesh BR (2003). TG containing stearic acid, synthesized from coconut oil, exhibit lipidemic effects in rats similar to those of cocoa butter. *Lipids*, 38: 913-918.
- Reddy SY and Prabhakar JV (1989). Confectionery fats from sal (*Shorea robusta*) fat and Phulwara (*Madhuca butyracea*) butter. *Food Chemistry*, 34: 131-139.
- Reddy SY and Prabhakar JV (1990). Cocoa butter substitutes from sal (*Shorea robusta*) fat. *International Journal of Food Science and Technology*, 25: 711-717.
- Reddy SY and Prabhakar JV (1994). Cocoa butter extenders from kokum (*Garcinia indica*) and phulwara (*Madhuca butyracea*) butter. *Journal of the American Oil Chemists' Society*, 71: 217-219.
- Shekarchizadeh H, Kadivar M, Ghaziaskar HS and Rezayat M (2009). Optimization of enzymatic synthesis of cocoa butter analog from camel hump fat in supercritical carbon dioxide by response surface method (RSM). *Journal of Supercritical Fluids*, 49: 209-215.
- Shukla VKL (1995). Cocoa butter properties and quality. *Lipid Technology*, 7: 54-57.
- Simoneau C, Hannaert P and Anklam E (1999). Detection and quantification of cocoa butter equivalents in chocolate model system: analysis of triacylglyceride profiles by high resolution GC. *Food Chemistry*, 65: 111-116.
- Smith KW (2001). Cocoa butter and cocoa butter equivalents. In: *Structured and Modified Lipids (F D Gunstone Eds.)*, Marcel Dekker Inc., New York, 401-422.
- Solis-Fuentes JA and Duran-de-Bazua MC (2004). Mango seed uses: thermal behaviour of mango seed almond fat and its mixtures with cocoa butter. *Bioresource Technology*, 92: 71-78.
- Solis-Fuentes JA (1998). El aprovechamiento de residuos solidos y liquidos de la agroindustria alimentaria, cinco ejemplos. M.S. Thesis. *Facultad de Quimica, UNAM. Mexico*.
- Sridhar R, Lakshiminarayana G and Kaimal TNB (1991). Modification of selected Indian vegetable fats into cocoa butter substitutes by lipase-catalyzed esters interchange. *Journal of the American Oil Chemists' Society*, 68: 726-730.

- Talbot G (1999). Chocolate temper. In: Industrial Chocolate Manufacture and Use (ST Beckett Eds.). Blackwell Science, Oxford, pp. 218-230.
- Tchobo FP, Piombo G, Pina M, Soumanou MM, Villeneuve P and Dominique CK Sohounhloue (2009). Enzymatic synthesis of cocoa butter equivalent through transesterification of pentadecanoyl butyrate. *Journal of Food Lipids*, 16, 605-617.
- Undurraga D, Markovits A and Erazo S (2001). Cocoa butter equivalent through enzymic interesterification of palm oil midfraction. *Process Biochemistry*, 36: 933-939.
- Vidhate GS and Singhal RS (2013). Extraction of cocoa butter alternative from Kokum (*Garcinia indica*) kernel by three phase partitioning. *Journal of Food Engineering*, 117: 464-466.
- Wang HX, Wu H, Ho CT and Weng XC (2006). Cocoa butter equivalent from enzymatic interesterification of tea seed oil and fatty acid methyl esters. *Food Chemistry*, 97: 661-665.
- Zaidul ISM, Nik Norulaini NA, Mohd Omar AK and Smith Jr. RL (2006). Supercritical carbon dioxide (SC-CO₂) extraction and fractionation of palm kernel oil from palm kernel as cocoa butter replacers blend. *Journal of Food Engineering*, 73: 210-216.
- Zaidul ISM, Norulaini NAN, Omar AKM and Smith Jr. RL (2007c). Blending of supercritical carbon dioxide (SC-CO₂) extracted palm kernel oil fractions and palm oil to obtain cocoa butter replacers. *Journal of Food Engineering*, 78: 1397-1409.
- Zarringhalami S, Sahari MA, Barzegar M and Hamidi-Esfahan Zi (2010). Enzymatically modified tea seed oil as cocoa butter replacer in dark chocolate. *International Journal of Food Science and Technology*, 45: 540-545.