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Cacao Butter and Alternatives Production

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Abstract

Cacao Butter (CB) is a unique vegetable fat product, which is obtained from cocoa beans. CB is solid at room temperatures because of its high proportion of saturated fatty acids such as palmitic and stearic acids. Due to its physicochemical values, CB is used in the production of chocolate, cosmetics, and pharmaceuticals, etc. But the high demand on CB, increases its price and consequently it becomes insufficient for manufacturers or consumers. To overcome this drawback, vegetable fats similar to CB are being utilized to supply this demand. The replacers, substitutes or equivalents of CB are produced from fractioned, hydrogenated or interesterified vegetable oils such as mango butter, shea fat, sal fat, and tallow fat, illipe fat which are mixed with other oils / fats. Analogous fats are called Cacao Butter Replacers (CBR), Cacao Butter Equivalent (CBE) and Cacao Butter Substitutes (CBS) which have different physicochemical characteristics (Melting Point, Solid Fat Content, and Triglyceride). This review gives a brief idea about the cocoa butter production and its composition with alternative fats and fats modification techniques.

Keywords: Cacao butter, Cacao Butter Replacers, Cacao Butter Equivalent, Cacao Butter Substitute.

Kakao Yağı ve Alternatif Üretimi

Özet

Kakao Yağı (CB), kakao çekirdeklerinden elde edilen eşsiz bir bitkisel yağdır. Palmitik ve stearik asitler gibi yüksek oranda doymuş yağ asidi oranı nedeniyle oda sıcaklığında katı hale gelmektedir. Fizikokimyasal değerleri nedeniyle, kakao yağı çikolata, kozmetik, eczacılık ürünlerinin üretiminde kullanılır. Ancak CB'ye olan talebin artmasıyla birlikte, fiyatı artmakta dolayısıyla üreticiler aynı işlevi görecek alternatif yağlara ihtiyaç duymaktadır. Bu sorunları çözmek için CB'ye benzer bitkisel yağ formülasyonları üzerinde araştırmalar yapılmıştır. Mango, shea, tallow, illipe, ve/veya karışım yağları Fraksiyone, hidrojene veya interesterifye edilerek bu kapsamdaki alternatif yağlar üretilmektedir. Bunlar Kakao Yağı Muadiller (CBR), kakao yağı eşdeğerleri (CBE) ve kakao yağı ikame ediciler (CBS) olarak adlandırılmaktadır. Bu alternatif yağlar farklı fizikokimyasal özelliklere (Erime noktası, Katı Yağ Oranı, Triglyserit) sahiptir. Bu makalede, kakao yağı üretimi ve alternatif yağlar ve bileşimleri hakkında bilgiler derlenmeye çalışılmıştır.

Anahtar Kelimeler: Kakao Yağı, Kakao Yağı Muadiller (CBR), Kakao Yağı Eşdeğerleri (CBE) ve Kakao Yağı İkame Ediciler (CBS)

Introduction

The Cacao beans are seeds obtained from the fruit of Cacao tree which is a tropical tree from the Malvacea family (Steinberg et al. 2003). Cacao L. Theobroma was in majority produced in tropical place of Central America, South America and has been spread in West Africa and Europe. After the harvest, Cacao fruit is opened and kept 3 to 5 days or even 7 days for fermentation to ease the separation of pulp and seed (Bujjsse et al., 2006). The pulp is used in distillers and the seeds are used to prepare cocoa powder or chocolate and cocoa butter (CB).

CB is a valuable by-product of the cocoa industry. Cocoa butter (55-56% fat) is obtained

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generally by hydraulic pressing or screw pressing of ripe cocoa beans (Steinberg et al 2003). CB is a light-yellow fat that is characterized by smell and flavor chocolate and is one important compound used in chocolate production which helps the dispersion of the acid composition of CB consists a high proportion of saturated fat mainly consists of palmitic acid and stearic acid (Spangenberg and Dionisi, 2001). CB also contains trace amounts of caffeine and theobromine, which are phenolic compounds. Thus, natural antioxidant contents that recognized to have many therapeutic properties, are important compounds of Cacao Butter. It's also used in the formulation of cosmetics and soap because of its moisturizing and antioxidant properties that give it an anti-aging effect (Carpenter *et al*., 1994; Shukla, 2005). Due to its triglyceride composition, its polymorphic forms can be distinguished in six forms which permit to give many textures (I, II, III, IV, V, VI) (Duck, 1964; Lonchampt, Hartel, 2004). In V form, CB is responsible of chocolate crystallization and this form introduce most high-level melting point. Due to it, chocolate have an excellent quality at ambient temperature (gloss, breakage and texture smoothness) (Wille, Lutton, 1966, Lonchampt, Hartel, 2004). These specific physicochemical properties, chemical composition and unique melting behavior make CB an important ingredient in the confectionery products. European united in 200/36/EC had studied and allowed that in the chocolate production 5% vegetable alternative fat (CBE) can be used mixing with Cacao Butter. Alternative vegetable fats (Figure 1) can be classified as follows:

Cacao Butter Equivalent (CBE)

CBE is free lauric vegetable fat that can be blended with Cacao butter because its physicochemical properties are analog to those of CB. It can be classified into two groups as a "Cocoa Butter Extenders" (CBEx), which cannot be used at every ratio in formulas, and "Cocoa Butter Improvers" (CBIs) which are similar to CBE, but used for improving soft cocoa butter texture due to its high content of other ingredients of chocolate (Wang et al., 2006). CB is a hard fat below 25 °C, and softens in the hand and melts in the mouth where the temperature is about 34 °C. Triacylglycerols are the major components of Cacao Butter as all vegetable oils/fats. Fatty solid triglycerides (Brinkmann, 1992; Bouscholte, 1994).

Cocoa Butter Replacer (CBR)

It's free lauric vegetable fat with the same fatty acid composition to cacao fat but this fat can be contained trans fatty acid from hydrogenated fat or oil and it is not compatible with cacao fat because their triglycerides compounds are different (Bouscholte, 1994; Reddy, Prabhakar 1990).

Cocoa Butter Substitute (CBS)

CBS is vegetable fat containing lauric acid which has fatty acid composition and triglycerides structure different to cacao fat,only vegetable oil that is suitable for substitution of Cacao Butter up to 100% (Brinkmann, 1992;Bouscholte, 1994). According to functionality of triglycerides, the principal composition of the fats and some examples are summarized in Table 1.

Cocoa Butter

Major Compound

Fatty Acid and Triglycerides

Chocolate liquor is obtained after grinding operation. Chocolate liquor contain generally 50-55% of cacao butter which is produced by mechanical pressing or solvent extraction with hexan, ethanol, petroleum ether (Asep, 2008; Nair, 2010). From chocolate, it is obtained cacao Butter and cacao cake power. Cacao cake is ground and used like food additives during breakfast. Cacao Butter also is the principal element of this party. It's a solid fat at ambient temperature due to the fatty and composition that are palmitic acid (27%), stearic acid (36%), oleic acid (34%) and the position of fatty acid in triglyceride composition. They are in majority symmetric triglycerides with oleic acid at the position 2 that are palmitic-oleic-palmitic, palmitic- oleic-stearic, stearic-oleic-stearic. Its fatty acids and triglycerides compositions confer high melting point, solid fat content and give desirable texture to Cacao Butter when it's used in chocolate manufacturing, confectionery and cosmetic products (Rao, Lokesh, 2003; Simoneau et *a*l., 1999). The fatty acids and triglyceride compositions of cacao butter are shown in table 2 and 3, respectively.

Minor Compound

Sterols and Other Unsaponifiables

The phytosterols are bioactive compounds that are in majority of beta sitosterol, campesterol, stigmasterol, brassicasterol, cholesterol contained in cacao butter. Gegiou and Staphylakis (1985) studied about cacao butter and they detected they phytosterols mentioned in table 4. Another research also revelead that cacao butter is one of phytosterol source and can be influenced by geographical conditions (Kanematsu et al., 1978).

Tocopherol

One of the bioactive compounds is tocopherol. It's an entity of vitamin E recognized like a strong and natural antioxidant detected in the fat of cacao (Erickson et al., 1983). Its tocopherols are distinguished under many forms whose alpha, beta, gamma, delta tocopherols. In general they are classified according to level power ($\delta > \gamma > \beta > \alpha$) but β and γ tocopherols are the dominating.

Physico-Chemical Properties

Cocoa butter is a multi-dimensional and multifunctional butter because of its high amounts of glycerol-linked saturated fatty acids forming triglycerides whose oleic acid is attached in position 2. The triglyceride (TAG) of CB gives it a melting point between 18-37 °C; this is due to the fact that it is the only oil appropriating 6 crystalline forms according to the polymorphic property namely I (18 °C), II (22 °C), III (24-26 °C), IV(28-32 °C) ,V(33-34 °C),VI (35-37 °C) (Lonchampt, Hartel, 2004;Wille, Lutton, 1966; Talbot, 1999). According to some researchers, it is solid at room temperature (25 °C) and begins to melt from body temperature (33-34 °C). The physico-chemical properties are presented in table 5 (Jahurul et al., 2013). The indexes of saponification, iodine, peroxide and acid influence cacao butter chemical properties. Low iodine value indicate that it contains small unsaturation proportion compared to other oils such as sunflower oil, cotton oil, soybean oil (Spangenberg and Dionisi, 2001; Lipp et al, 2001; Afoakwa et al., 2008; Bootello et al., 2012). The number of double bonds of fatty acid is called iodine value and saponification value is potassium hydroxide quantity necessary to saponify one gram of oil. It also gives an idea of the molecular weight and the length of the chain contained in the oil. When the saponification number is high, the molecular weight is small or the carbon chains is short. Similarly, the molecular weight is large or the carbon chain is long if the saponification index is low.

Cocoa Butter Alternatives (CBA)

High demand and low production of cacao butter increased its selling and buying prices. This became a handicap for many companies involved in the processing of cacao into chocolate. To overcome this handicap, researchers invented and made available to all, a replacement fat in place of cacao butter named Cocoa Butter Alternatives (CBA). CBA are produced from vegetable oils recognized and standardized by Directive 2000/36 / EC of the European Union. CBA are constituted into three subgroups listed below:

Cocoa Butter Equivalents (CBE)

The first group of CBA is CBEs which is a fat that does not contain lauric acid. Therefore it is called non-lauric CBE (Bootello et al., 2012). CBE consists of symmetrical triglycerides, monounsaturated

Table 1. Physicochemical composition of Cacao Butter Alternatives (Brinkmann, 1992)

CBA	Fat	Functionality	Fatty acids	Triglycerides
Cocoa Butter Replacer(CBR)	Soybean oil, cotton oil, sunflower oil palm olein	Free lauric fat is Partially compatible and different triglycerides	Elaidic and/or oleic stearic palmitic acids	PEE SEE
Cocoa Butter Substitute(CBS)	Coconut oil, Palm kernel oil	Lauric fats, suitable for 100% substitution only	Lauric, myristic	LLL LLM LMM
Cocoa Butter Equivalent(CBE)	Palm olein and stearin Mango fat Palm mid fraction tallow	Free lauric fat is compatible with Cacao Butter and physicochemical characteristics analog to CB	Palmitic, stearic oleic acids	SOS POP POS

P: Palmitic acid , O: Oleic acid , S: stearic acid , L: Lauric acid , E: Elaidic acid , M: Myristic acid

Table 2. Cacao butter fatty acids composition according to some countries (Lipp, Anklam, 1998)

Origin	Brazil	Ghana	Ivory Coast	Malaysia
Lauric	0-1	0-1	0-1	0-1
Palmitic	25.1	25.3	25.8	24.9
Stearik	33.3	37.6	36.9	37.4
Oleic	36.5	32.7	32.9	33.5
Linoleic	3.5	2.8	2.8	2.6
Linolenic	0.2	0.2	0.2	0.2
Arachidic	1.2	1.2	1.2	1.2
Behenic	0.2	0.2	0.2	0.2

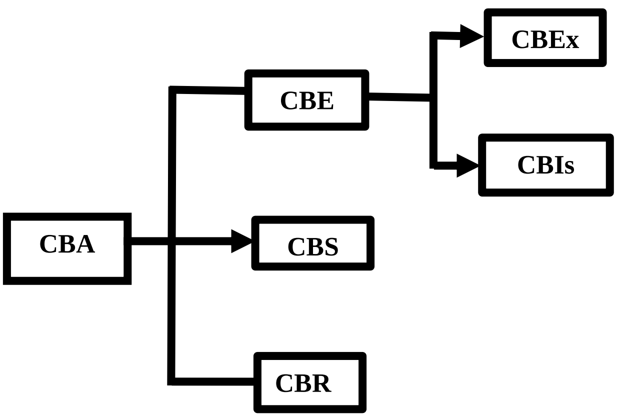

Figure 1. Cacao Butter Alternatives diagram

Table 3. According to some countries, Cacao butter triglycerides composition (Podlaha et al, 1984)

Origin	Ivory Coast	Malaysia	Ghana	Nigeria
OOO	0.8	0.8	0.4	0.5
POO	4.4	2.7	2.6	3.2
PPO	15.9	13.8	15.2	14.8
SOO/PPP	6.0	3.8	4.5	5.1
PSO	36.6	36.6	37.3	37.4
OOA	1.0	1.6	1.4	1.2
PPS	0.4	0.6	-	0.7
SSO	23.8	28.4	26.8	26.4

Table 4. Phytosterol composition of Cacao Butter (Staphylakis, Gegiou; 1985)

Phytosterols Free sterol (mg/l00 g fat)	
Brassicasterol	0,9
Campesterol	18,7
Stigmasterol	60,1
B-Sitosterol	123,3
Cholestanyl	1,1
5-Avenasterol	5,6
Cholesterol	1,9
Cycloeucalenol	0.96

Table 5. Physico-chemical properties of Cacao Butter (Jahurul et al., 2013)

Characteristics	%
Iodine index (g I_2/100g)	31-36
Saponification index (mg KOH/g)	191-199
Acid index (mg NaOH/g)	1.04-1.68
Peroxide index (meq O_2/kg)	1.00-1.10
Melting point	33-34^{o}C

Table 6. Comparison of process for the preparation of CBE from selected raw materials (Stewart, Timms, 2002)

Fat raw material	Origin	Processing	İngredient	Main triglyceride
İllipe butter	*Shorea stenoptera*	-	Fat	POS, SOS
Palm oil	*Elaeis Guineenis*	2 fractionation	Mid fraction	POP
Sal fat	*Shorea robusta*	1 fractionation	Stearin fraction	SOS, SOA
Shea butter	*Viellaria paradosa*	1 fractionation	Stearin fraction	SOS
Kokum butter	*Garcinia indica*	-	fat	SOS
Mango seed fat	*Mangifera india*	1 fractionation	Stearin fraction	SOS, POS

P: Palmitic acid , O: Oleic acid , S: stearic acid , A: Arachidic acid

acids such as oleic acid, which is most often in position 2 or beta. Due to its physicochemical characteristics, CBE is compatible at 5% blending with cacao butter in chocolate production without influence the physical characteristics of the finished product (Shukla, 2005; Bohacenko et al., 2005). The CBE are also constituted into 2 groups: Cocoa Butter Improves (CBIs) and Cocoa Butter Extenders (CBEx). These fats can be used partially with

CB except CBEx which is incompatible with CB. According to the publication of Spangenberg and Dionisi (2001); Ganesh and Rekha (2013), CBEs are obtained during a process of refining and/or fractionation excluding possibility of enzymatic modification of triglycerides structure and hydrogenation because of its non-containment trans fatty acid. Thus, it operates the refining to remove contaminants from the oil entering process, and / or fractionation to bring back the input oil to a desired state (solid). The refined and fractionated oil is subjected to chemical or enzymatic interesterification to obtain the desired level of CBEs (Salas *et al.*, 2011). In general, the fat used in the production of CBEs are standardized and presented as suitable for its production (Table 6). These oils presented are mixed with stearic acid (Salas *et al*., 2011). CBEs are obtained by assembling of the structured crystals which increase over time and develop the melting point thereof. At this level, the functionality of CBEs is identical to that of CB (EU Directive 2000/36 / EC). CBIs are one of vegetable fats that are characterized by high melting point and are high solid fat content.

Cocoa Butter Replacers (CBR)

CBRs are one of the fats used to replace CB. They are recognized as the second fat that does not contain lauric acid called non-lauric fat (McGinley, 1991). These physical characteristics are fundamentally similar to those of CB but of different chemical characteristics (palmitic acid, elaidic acid) and different triglycerides (1-Palmityl 2, 3-dielaidoylglycerol, 1-Palmityl 2-Elaidyl 3-Stearylglycerol) (nStewart, Timms, 2002). Due to the difference between the chemical characteristics, CBR can be mixed in a very limited amount with CB so that the finished product is not influenced. According to many researchers, fats intended for the production of CBR must undergo refining and then hydrogenation and fractionation (Table 7). In this way the oils are brought back to the solid and liquid state (stearin, olein). Since hydrogenation is a modification technique that can induce trans fatty acid, the input oil may contain this acid, which is known to be harmful to health. With regard to its high solid content, CBRs can be used in chocolate manufacturing, coating, stuffed and nuggats.

Cocoa Butter Substitutes (CBS)

CBS are third type of fats recognized belonging to Cocoa Butter Alternatives CBA. Its contain lauric acid and short chains of acid located in triglycerides (trisatures). CBS is recognized to have high lauric and myristic acids amounts. This confer it physical form like Cacao Butter but to chemical composition differents (Shukla, 2005; Young, 1983; Bohacenko et al. 2005). The use of CBS in certains food products such as chocolate don’t need the tempering process due to the saturated fatty acid content. Its compatibility depends to the mixture vegetable fat and Cacao Butter. Shukla (2005), and Wainwright (2000) revealed that CBS is produced essentially to palm kernel or coconut oil because they contain high lauric and myristic acids. Those fats are subjected to hydrogenation or fractionation or interesterification processing in order to an acceptable solid content or to have hard fat and are blended with others fats for CBS formulation. This CBS can be used to good stability of the final product, an easy production processing of certains products (Lonchampt, Hartel, 2004). Because of this, the hydrogenated fractions of the different oils are crystallized to obtain the beta prime form; in this form, the hydrogenated fractions may be exempted from the tempering performance process. The physico-chemical characteristic of CB and CBS is the cause of their very low mixability. When mixing of the two fats (CB and CBS), CBS is very demanding in terms of barrier and less demanding in humidity. In the nutritional field, hydrogenated CBS has non-beneficial properties because it contains trans fatty acid which is known to accumulate LDL-bad cholesterol and to remove HDL-good cholesterol (Shukla, 2005; Young, 1983; Bohacenko et al., 2005). Hydrogenated CBS has physical properties (consistency, melting point) similar to CB allowing it to be used in the production of chocolate, chocolate stocking, and coatings (Shukla, 2005).

Origin of vegetable fats used for the production of CBA

According to Directive 2000/36/EC, European Union has defined the vegetable fats that must be used in the production of CBA fats. Those do not must be in no case derived from animal oils. They are mentioned below.

Borneo tallow fat (*Shorea stenoptera*)

The *shorea stenoptera* is a tropical tree of Dipterocarpaceae family generally grown in Malaysia, Philipines. Called also illipe butter, Borneo Tallow fat is obtained from the nuts of this tree (Jahurul et al, 2013; Lipp et al, 2001). According to some published results, borneo tallow nuts or grains consist of 60% fats that are pale green. The fatty acid compositions (palmitic acid 18-21%, oleic acid 34-37%, stearic acid 39-46%) are similar to those of CB. These high proportions of acid (palmitic, oleic, stearic acids) can be directly used for CBE without modification (hydrogenation, fractionation, interesterification). Illipe butter is influenced by POP (8-9%), POS (23-33%), and SOS (43-46%). They are close to those of CB. It’s also characterized by a melting point located between 37-38°C which allows it to be very stable at oxidation (Firestone, 1999; Gunstone, 2011)

Shea Fat (*Vitellaria paradoxa*)

Shea fat is produced from the seeds of shea tree which is usually planted in West and Sub-Saharan Africa. These nuts are also called Vitellaria paradoxa nuts or the butyrospermum parkii L. tree. It is composed of 4-8% palmitic, 41-58% stearic, 33-50% oleic, 4-8% linoleic and 40-42% SOS, 26% SOO, 5-6% POS, 5% SOL, 5% SLS, 6% OOO (Gunstone, 2011). Due to high saturated fatty acid amounts, shea nuts melting point is elevated (32-45°C) and it’s semi-solid at ambient temperature. Like majority of vegetable fats, shea butter is a fat containing important amounts of unsaponifiable value. Those main unsaponifiable contents are hydrocarbon, sterols and triterpene alcohols (Peers, 1977; Jocobsberg, 1974).

Sal fat (*Shorea robusta*)

Sal fat is obtained from the nuts of the tenkgawang tree, mainly grown in India, Malaysia, Borneo, Java and philipines. Sal nuts contain 16-20% fat and dispose of 52% saturated and 40% unsaturated fatty acids (Table 8). It also has minor components such as unsaponifiable materials (0.6-1.3%), sterols (600-4300 mg / kg) and natural antioxidants such as tocopherol (100 mg / kg). Sal fat is subjected to the fractionation process to obtain a stearin phase and an olein phase. The stearin phase is generally used for the production of CBE by mixing it with other oils (Gunstone, 2011; Reddy, Prabhakar, 1989).

Palm and kernel oil (*Elaeis guinensis*)

Palm tree is a tree that ground generally in tropical region. Called *Elaeis Guinensis*, it is one the tree whose fruit gives two different oil that are palm oil and palm kernel oil. The fat amounts of those depend to geographic place. They round in tropical countries such as Malaysia, Indonesia and İvory coast. Palm fruit contains approximately 43-50% of crude palm oil and palm kernel also contain approximately 25% of palm kernel oil. The main fatty acids and triglycerides of palm oil are respectively palmitic, oleic acids and POP, POS, SOS and those of palm kernel oil are myristic and lauric acids and PLL, PMM (Gee, 2007). Nutritionally palm oil is recognized being an oil containing high polyphenol, antioxidant, carotenoids chlorophyll amounts that play an important role in food preservation, nutrition and health. It also contains a high toco amounts whose tocopherol (500-1000 mg/kg) and tocotrienol making of it one of the oil having a high oxidative stability and introduce some phytosterols (320-650 mg/kg) such as β-sitosterol, campesterol, stigmasterol (Gee, 2007). Palm and kernel oil can be fractioned and crystallized to obtain solid phase (stearin) and liquid phase (olein), others are palm mid fraction, super olein and stearin, hard palm mid fraction. stearin, palm mid fraction and hard palm mid fraction can be used in chocolate, confectionery, Cacao Butter Equivalent, Cacao Butter Replacer or cosmetic manufacturing because they are high melting points and solid fat content than palm oil and palm olein (Bloomer et al., 1990; Lipp et al., 2001)

Kokum kernel Fat (*Garcinia indica*)

Kokum kernel fat is a pale-yellow fat from the nuts of a green kokum tree. Kokum fat is a solid fat at ambient temperature and has a high solid phase yield. The nuts of the kokum tree or *Garcinia indica* contain 40-50% fat, mainly grown in India (Vidhate, Singhal, 2013). This fat has very important physicochemical characteristics. In particular its point of fusion is between 38-42°C. Its fatty acid composition such as 50-60% stearic acid and 36-40% oleic acid confer significant solid phase. It has 72% of SOS including oleic acid in the beta or 2 position (symmetrical triglyceride). Kokum kernel fat is suitable for use in CBE production (Gunstone, 2011).

Mango butter (*Mangifera indica Linn*.)

The kernel of Mango (*Mangifera Indica L*) is a main source to production of mango butter. This tree is cultivated generally in West Africa, Indonesia and Brazil. Containing about 7-15% of fat, mango seed represents 6% proteins, 77% carbonhydrate, 2% dietary fiber and 2% ash (Ca, Na, P, N, Mg) (Abdalla et al., 2007). After the removal of the mango pulp, the kernels are broken to extract the nuts to dry and crush them. From the powders of the nuts, the fats are extracted by soxhlet extraction in the laboratory. Mango butter is essentially 44-48% of saturated fatty acid including stearic acid (37.76%) and 52-56% unsaturated in major oleic acid (46.22%), refractive index 1.443 to 40 °C, melting point 30 °C, unsaponification matter 2.9%, free fatty acid 1.5% and saponification number 195, phospholipids 2.7-3.3% and glycolipids 1.1-1.4% (Fahimdanesh, Bahrami, 2013). The major triglycerides contained in this fat are 10-16% of POS, 25-59% of SOS, 1-9% of POP, 23% of SOO, 5% of POO, 4% of SOA and 5% of OOO (Pantzaris, Ahmad, 2001).

Oil modification techniques for fat alternatives formulation

For the formulation of alternative fats CBAs, the vegetable oils entering the process must be brought to a certain number of degree of solidity. To do this, they are subject to modification techniques to change their state at room temperature. The modification techniques involved in the production of these fats are fractionation-crystallization, hydrogenation, interesterification and the blending of oils (Segall et al., 2005; Raju, Reni, 2001).

Fractionation

One of the most widely used and most non-trans fatty acid modification techniques is fractionation. The fractionation consists in separating the oil at the liquid origin in two phases. One of the phases is a liquid composed essentially of olein called olein phase. The other is solid consisting essentially of stearin called phase stearin. The mechanism is to recool slowly after heating the oil to facilitate the formation of the cristals that make up the polymorphism. Fractionation is divided into 3 parts: bloc (dry), solvent and Surfactant (detergent) fractionations (Gümüşkesen, Yemişçioğlu, 2010).

Bloc fractionation

Bloc fractionation is one of modification technique don't introduce trans fatty acid during process. It permits to obtain a cheaper oil/fat occurring two types of fat from liquid oil. One is liquid oil called olein which contain such as main fatty acid (oleic) and other is stearin that is solid at ambient temperature containing high stearic acid, its melting point is high and iodine value is low (Gibson, 2006; De Greyt et al, 2003). The process of dry fractionation of oil is mentioned in figure 2. The main mechanism of this technique is to: crystallize oil by cooling to produce the solid cristals and separe the solid

Table 7. Comparison of process for the preparation of CBR from selected raw materials (Cooper, 1993)

Oil raw materiel	Origin	Processing	İngredient	Main Triglycerides
Soybean oil	*Laguminosae*	Hydrogenation 1 fractionation	Stearin fraction	SEE
Rapseed oil	*Cruciferae*	Hydrogenation 1 fractionation	Stearin fraction	PEE
Cotton seed oil	*Gossypium hirsutm*	Hydrogenation 1 fractionation	Stearin fraction	PEE
Olive oil	*Olea europa*	Hydrogenation 1 fractionation	Stearin fraction	SEE
Palm kernel oil	*Elaeis guineensis*	Hydrogenation 2 fractionation	Mid fraction	PEE

P: Palmitic acid, E: Elaidic acid, S: Stearic acid

Table 8. Fatty acid and triglycerides composition of Sal fat (Kolhe,1981)

Main fatty acid	%
Palmitic	5
Stearic	44
Oleic	40
Linoleic	2
Arachidic	4
Triglycerides	%
SOS	42
POS	11
SOO	16
SOA	13
OOO	3
AOO	4

cristals (stearin) and liquid matrix (olein) by filtration called fractionation (Fahimdanesh, Bahram, 2013; Maalssen et al., 1996). The crystallization process depends to temperature, mixing speed. Cooling oil if mixing speed is slow, the cristal formation will be good, arranged and the olein phase will be reduced significantly. Thus, the cristal forms and size distribution will be carefully determined (Zaliha et al, 2004).

Solvent Fractionation

This technique introduces the steps of oil dissolving in a volumetric solvent in a certain volume ratio, fractionating at the determined temperature and time, and distilling off the solvent phase in the crystals separated by filtration. Apolar (hexane) or polar (acetone, 2-nitropropane, iso-propyl alcohol) solvents are used as solvents. The viscosity of the oil is reduced by the use of the solvent, so that difficulties are encountered in separating the solid and liquid phases after the crystallization process (Kayahan, 2002). For example, palm oil is mixed with hexane in fractionation crystallization by this method. İn the first stage, the sample is subjected to approximately 45°C and reduced to 32°C and in second step cooled about 10°C. The resulting gives stearin phase separated from the olein phase by continuous rotary drum filter and hexane is removed by distillation process. The olein phase is recrystallized in the first tank by cooling to 7 °C and in the second tank by cooling to 4 °C. The resulting, stearin is separated from the olein phase by filtration and hexane removed by distillation. The stearin phase obtained in the second stage is used in the production of CBE (Gümüşkesen, Yemişçioğlu, 2010).

Surfactant fractionation

Surfactant fractionation is a modification technique using detergent such as sodium lauryl sulphate to form a solid complex between solid phase and surfactant. Complex formation results from liquid fraction separation to solid fraction. This process can be realized in batch or continuous system. The mechanism of this process is to separe stearin phase (solid complex phase) to olein phase (liquid phase) using detergent and plate separator. The plate separator forms a complex phase with stearin. Thus, it's heated to permit liberation of stearin from surfactant. To eliminate detergent residue, stearin phase is washed with distilled water and separed surfactant can be used another fractionation processing (Kayahan, 2002; Rezekyah et al., 2018)

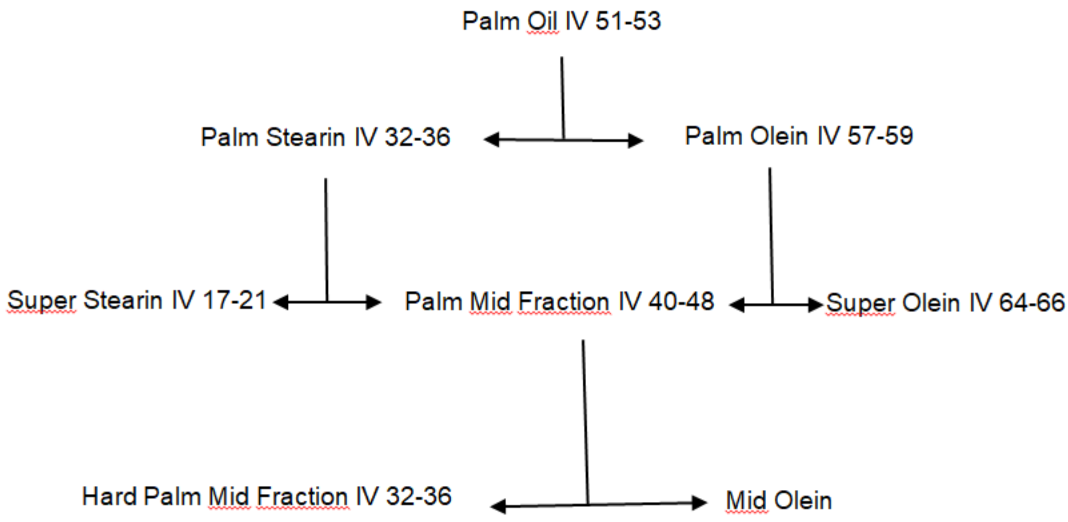

Figure 2. Dry Fractionation of palm oil for palm oil fraction (Gümüşkesen, Yemişçioğlu, 2010)

Hydrogenation

Hydrogenation processing has been invented to obtain solid phase from a vegetable oil containing high unsaturated fatty acids (mono, polyunsaturated fatty acids) such as soybean oil, sunflower oil, etc. To obtain this solid phase, unsaturated vegetable oil is treated with hydrogen and catalyst (Nickel) presence called hydrogenation reaction. In this reaction, hydrogen fixation on double bonds of vegetable hydrogenated oil can be used in alternative fats production blending with other vegetable oil (e.g. full hydrogenated oil and palm stearin or palm olein). Partial hydrogenation is recognized oil make according to the condition of temperature, pressure, mixing, catalyst rate and type. There are two hydrogenation types that are full hydrogenation and partial hydrogenation (Kayahan, 2002). Full hydrogenation is total fixation reaction of hydrogen on double bond of unsaturated fatty acids with a good condition of temperature, pressure and mixing rate. There is not trans fatty acid presence in full hydrogenation according to researcher Kayahan, 2002. Full as reaction that produced trans fatty acid because of the selectivity of reaction. Selective acid will give it:

Trien → Dien → Monoen → Saturated carbon of double bond according to the number and position of double bond (Kayahan, 2002; reaction is fixation speed of hydrogen on the Albert, 2006). Example selectivity in linolenic.

This reaction depends to temperature, pressure, mixing speed, catalyst (nickel) activity and type. Partial hydrogenated fat can be used in margarine, shortening manufacturing (Albert, 2006)

Interesterification

Contrarily to hydrogenation processing, interesterification is one of modification technique that make by rearrangement of fatty acids of triglycerides. Fatty acids transfer in the same triglyceride called intraesterification and the fatty acid transfer between two triglycerides or more are called interesterification. Technique purpose is to modify the physicochemical characteristics of oil/fat, free trans fatty acid and thus to evite the disease caused from it (Nor, Noor, 2005). Interesterification or intraesterification make by two process namely chemical and enzymatic processing (Kayahan, 2002). Each processing introduce advantages and disadvantages but enzymatic or continuous interesterification is recently invented to evite the randomization using specific immobilized lipase (1, 3 regiospecific lipase in CBE production). Chemical or random interesterification is batch processing that is the most applied interesterification because it's simpler, cheaper than continuous interesterification (Sreen, 1976; Yassin, 2003).

Conclusion

CB is a valuable and technological fat which is produced to beans obtained from in majority in African countries. Its price is expensive due to its low productions in some countries like European countries. To overcome that, alternatives fats similar to CB are invented. However, they introduce any differences in chemical compositions that are trans fatty acid in CBR and lauric acid in CBS. Trans and lauric acids are recognized as bad to the health. In addition, CBA can contain LDL due to mixing of vegetable fats. Cocoa Butter Equivalents physical characteristics are completely similar to cocoa butter that permit to use 5% with CB. CBA can be produced and sold cheaper in food industries.

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