Food Oils and Fats: Chemistry and Technology
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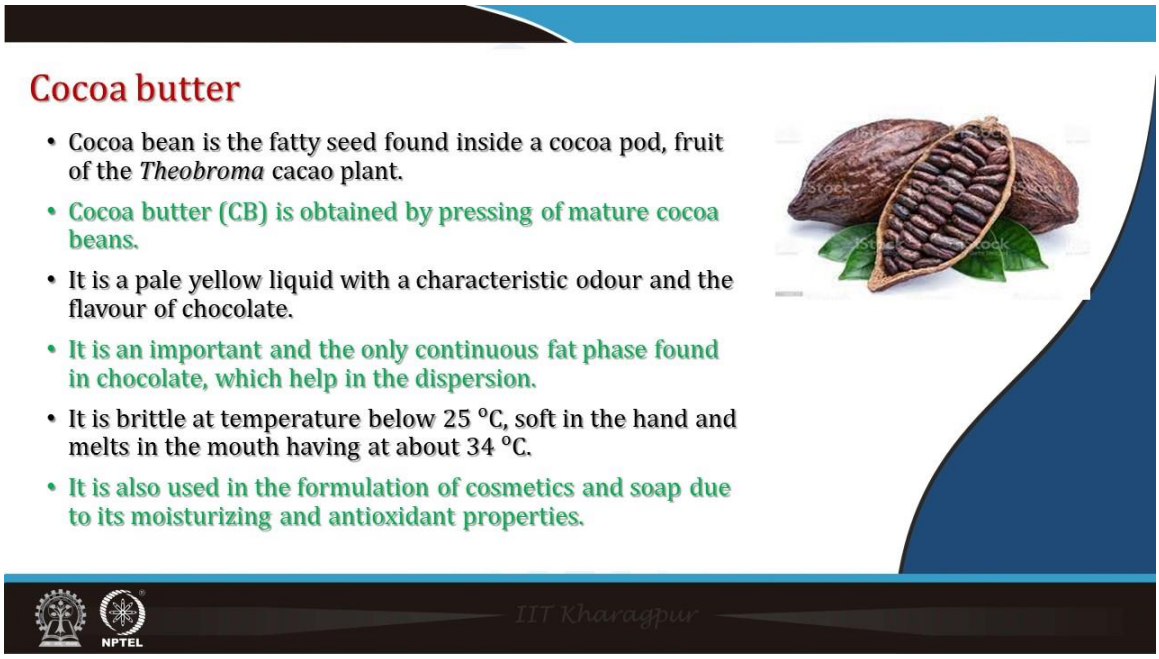
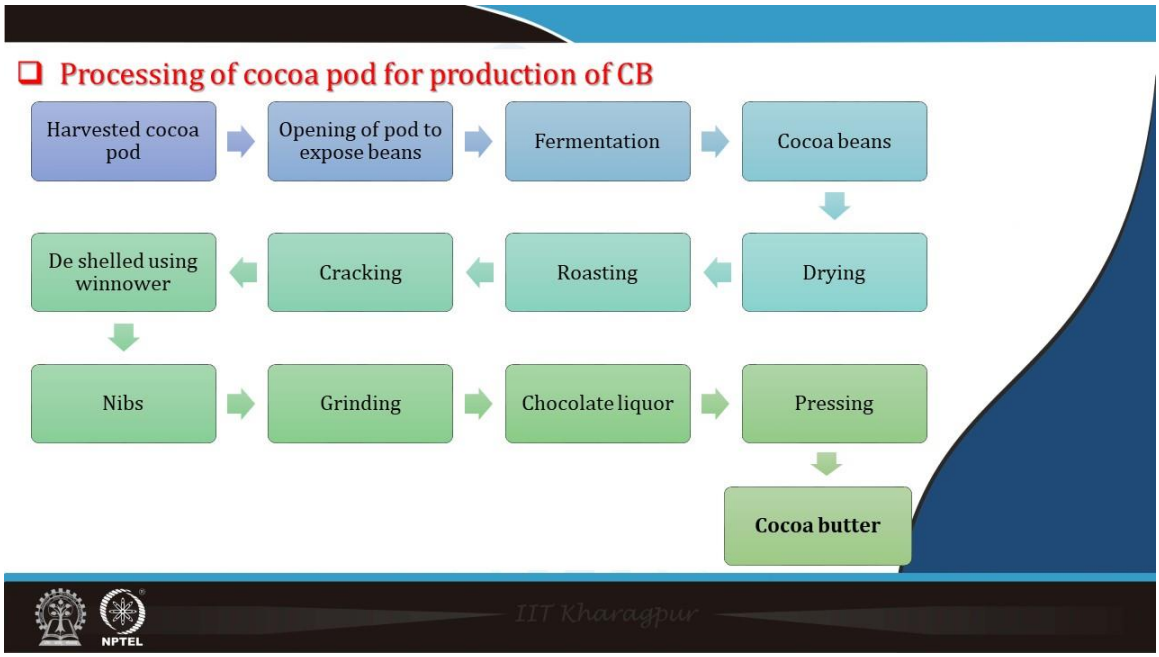
Indian Institute of Technology Kharagpur
Module 10 : Specialty Oils and Fats Products
Lecture 49 : Cocoa/Shea Butter and Structured Triacylglycerols

Hello friends, Namaskar. We are in the 49th lecture of this course. In this lecture, in the next half an hour, we will speak about very important specialty oil and fat products like cocoa and shea butter. The topics that we will discuss in this lecture include physio-chemical properties, nutrition and health benefits, characteristics and manufacturing

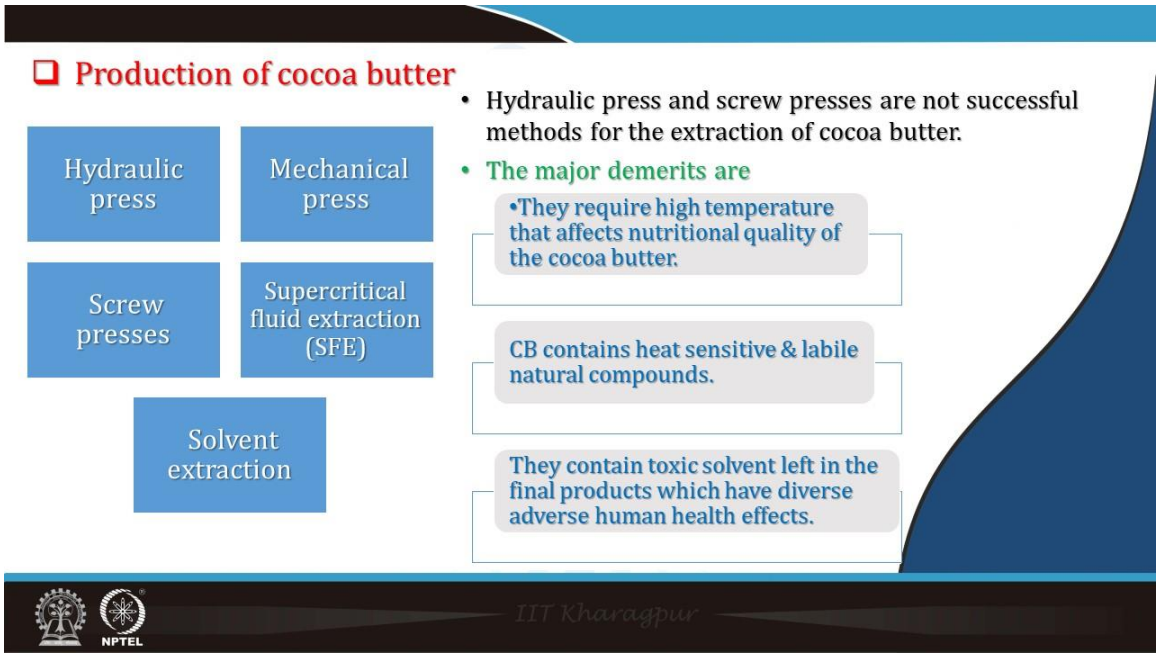
processes, and food usage and other applications of cocoa butter and shea butter. And then finally, before end we will talk about some important aspects of structured triacyle glycerol like low calorie fat and so on.



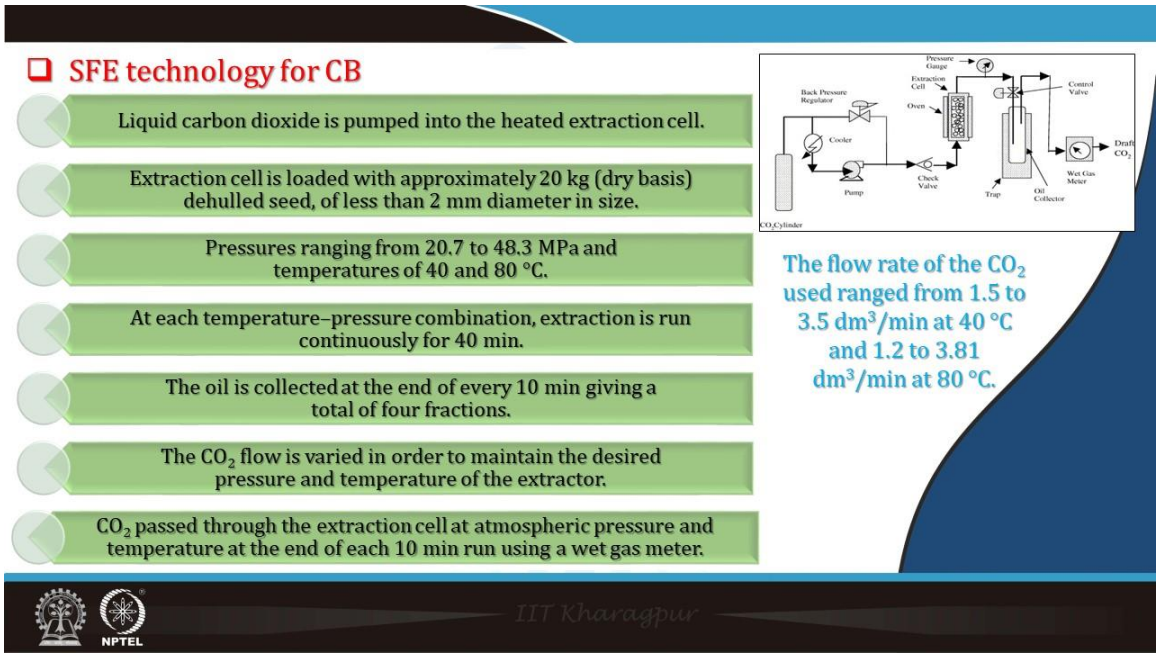
So, let us start with the cocoa butter. Cocoa bean is the fatty seed found inside a cocoa pod, fruit of the Theobroma cacao plant. Cocoa butter (CB) is obtained by pressing of mature cocoa beans. It is a pale yellow liquid with a characteristic odour and the flavour of chocolate. It is an important and the only continuous fat phase found in chocolate, which help in the dispersion. It is brittle at temperature below 25 ^{o}C, soft in the hand and melts in the mouth having at about 34 ^{o}C. It is also used in the formulation of cosmetics and soap due to its moisturizing and antioxidant properties.



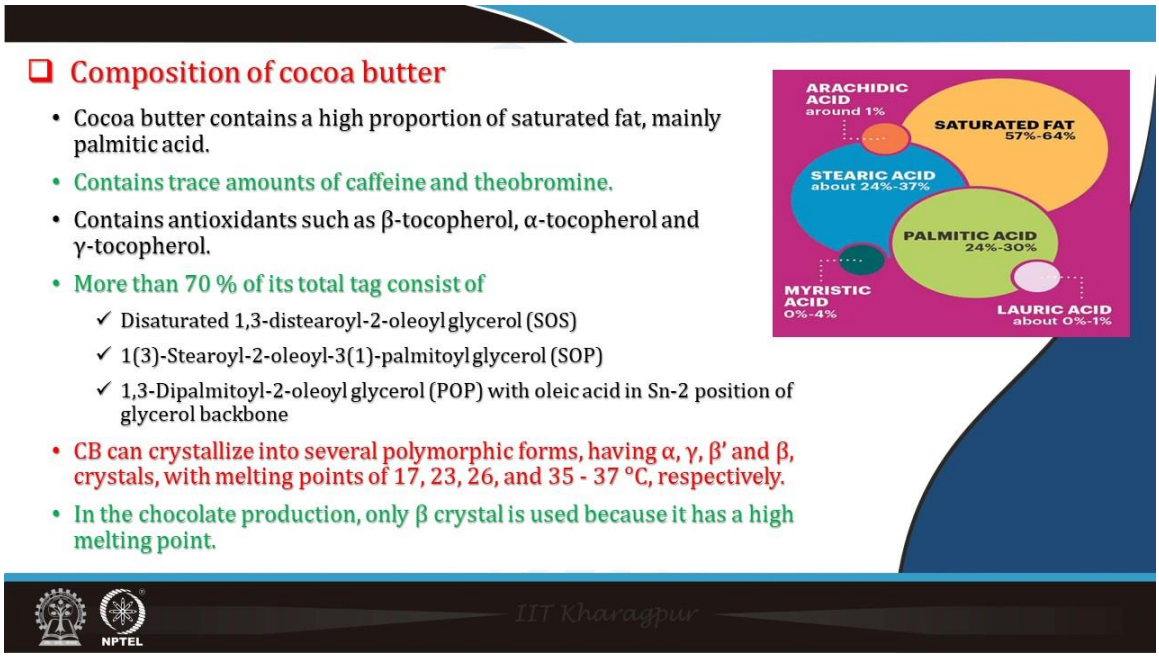
The processing steps of the cocoa include, cocoa harvested from the trees, then the pods are opened and then they are left in an open atmosphere for a few days for the fermentation. Sometimes enzymes are used for assisting the fermentation process. Then these cocoa beans are dried to a suitable moisture content of about 10 to 12 percent and after drying they are roasted. It is during this roasting process the characteristic color and flavor of chocolate develops. Then after roasting, these beans are cracked, which is where the two cortilidens which are normally known as nibs are found. And then these shells or hulls etcetera are blown and these nibs are are the source of the main chocolate or butter and other components. So, these nibs are ground and because of the high fat content when this nib is ground fat gets melted and we get some sort of paste material which is called as chocolate liquor. And this chocolate liquor is further pressed to get the cocoa butter. So, this is in brief the processing steps involved in the cocoa butter production.



Various presses can be used to extract the cocoa butter from the chocolate liquor or cocoa mass or bitter chocolate. They are hydraulic press, mechanical press, screw presses, and supercritical fluid extraction or even sometimes solvent extraction can also be used. However, the hydraulic presses and screw presses are not very successful method for the extraction of cocoa butter. The major demerits of these methods include that they require high temperature and that affects the nutritional quality of the cocoa butter that is after the extraction of the butter the left material which is obtained is a very good source for cocoa beverage manufacturing, and cocoa powder. But its etcetera and other qualities are adversely affected because the hydraulic presses or mechanical presses generate too much pressure as well as temperature. The cocoa butter obviously, contains heat sensitive and heat labile natural compounds. They contain also toxic solvent left in the final products which have diverse adverse human effects, particularly when this solvent extraction is used. So, I think the better technology in this case as well is the supercritical fluid extraction technology.



Liquid carbon dioxide is pumped into the heated extraction cell. Extraction cell is loaded with approximately 20 kg (dry basis) dehulled seed, of less than 2 mm diameter in size. Pressures ranging from 20.7 to 48.3 MPa and temperatures of 40 and 80 °C. At each temperature–pressure combination, extraction is run continuously for 40 min. The oil is collected at the end of every 10 min giving a total of four fractions. The CO2 flow is varied in order to maintain the desired pressure and temperature of the extractor. CO2 passed through the extraction cell at atmospheric pressure and temperature at the end of each 10 min run using a wet gas meter. The flow rate of the CO2 used ranged from 1.5 to 3.5 dm3/min at 40 °C and 1.2 to 3.81 dm3/min at 80 °C.



Then let us talk about composition of the cocoa butter. It contains a high proportion of saturated fat mainly the palmitic acid you can say saturated fats are around 57 to 64 percent, Palmitic acid is 24 to 30 percent, even the stearic acid the content is around 24 to 37 percent. It also contain about 0 to 1 percent lauric acid, 0 to 4 percent myristic acid and arachidic acid may be around 1 percent. Cocoa butter contains a high proportion of saturated fat, mainly palmitic acid. Contains trace amounts of caffeine and theobromine. Contains antioxidants such as β-tocopherol, α-tocopherol and γ-tocopherol. 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), 1,3-Dipalmitoyl-2-oleoyl glycerol (POP) with oleic acid in Sn-2 position of glycerol backbone CB can crystallize into several polymorphic forms, having α, γ, β' and β, crystals, with melting points of 17, 23, 26, and 35 - 37 ^{o}C, respectively. In the chocolate production, only β crystal is used because it has a high melting point. The cocoa butter contains trace amount of caffeine and theobromine. It contains antioxidants such as beta tocopherol, alpha tocopherol and gamma tocopherol.

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.
- The nature of the crystalline lattice also affects the hardness of the cocoa butter.

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 (°C)	29 - 40

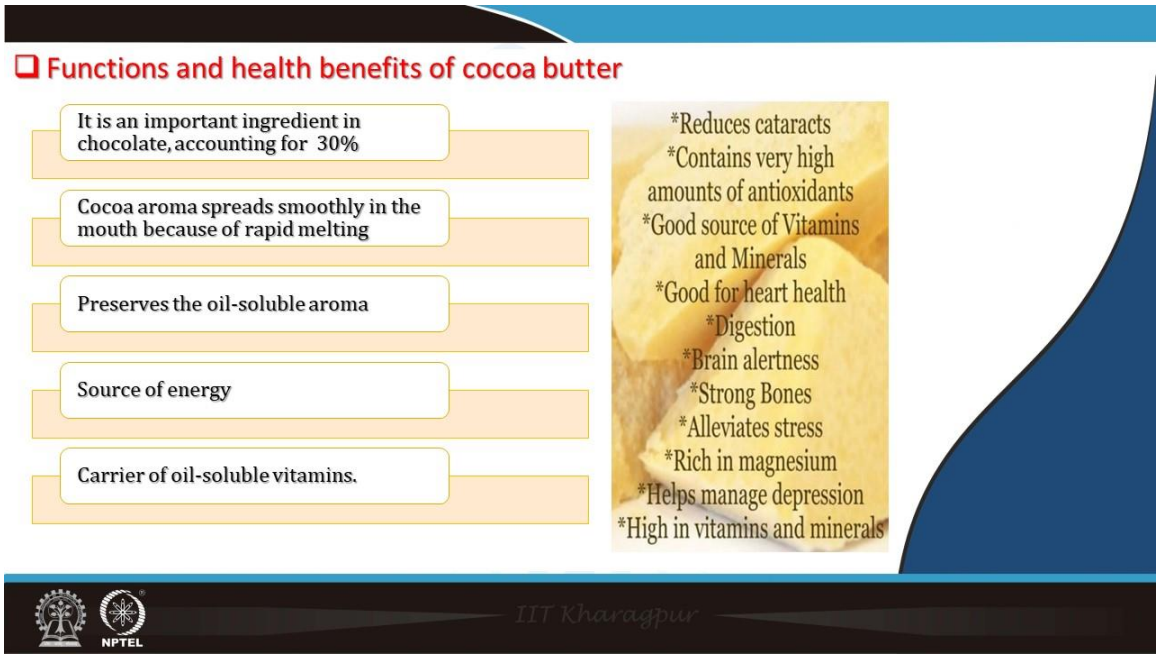
Properties of cocoa butter are mainly dependent to its triglyceride composition. Cocoa butter has a sharp melting point ranges from 27 to 35°C. At room temperature, it is hard and brittle. The nature of the crystalline lattice also affects the hardness of the cocoa butter.Its iodine value is 32 to 35 gram iodine per 100 gram, Saponification value 192-199 mg KOH/g, acid value 1.04-1.68 mg NaOH/g, peroxide value 1-1.10 meq O2/kg, and melting point is 29 to 40 degree Celsius.

The characteristic diffraction peaks and melting temperature of the cocoa butter polymorphs

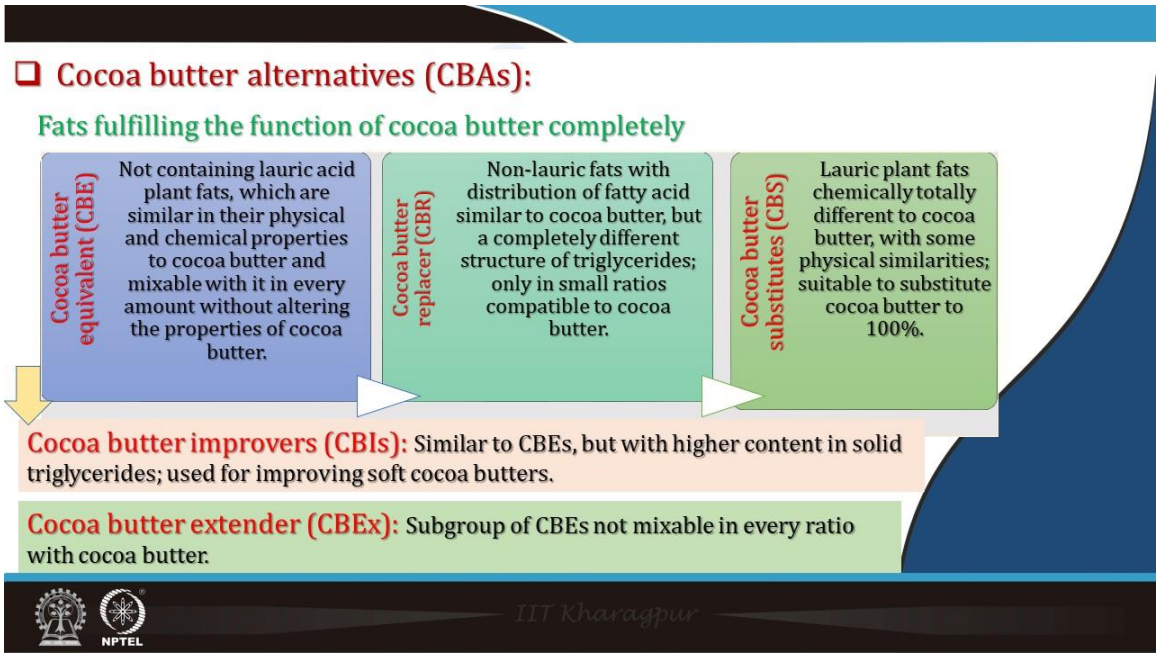
Form I (γ) is the most unstable polymorph with a melting temperature 14°C
Form II (α) has a melting temperature around 20°C
Form III (β′) with a melting temperature around 22°C
Form IV (β′) has a melting temperature around 24°C
Form V (β′) melts at around 30°C
Form VI (β) has a melting temperature around 32°C

- ✓ Form V is considered the optimal polymorph by the confectionery industry.
- ✓ Provides appropriate melting temperature to allow storage at room temperature.
- ✓ Provides a smooth melting of chocolate in the mouth.
- ✓ Provides chocolate products with the ability to break apart easily; good demolding properties.
- ✓ Polymorph V is not readily obtained by simple cooling, but rather by using a tempering protocol.

Now, this the cocoa butter by proper tempering in the process different polymorphs of the cocoa butter can be found and all these polymorphs play a very significant role in various bakery and confectionary products. And the different polymorphs formed are like form I gamma, which is the most unstable polymorph with a melting temperature of around 14 degree Celsius. Another form is the form II that is called alpha form it has a melting temperature around 20 degree Celsius. Form III polymer that is beta prime form, it has a melting temperature of around 22 degree Celsius. Form IV that is again beta prime form which has a melting temperature of around 24 degree Celsius. Form VI beta, it has a melting temperature of around 32 degree Celsius. Form V is considered the optimal polymorph by the confectionery industry. Provides appropriate melting temperature to allow storage at room temperature. Provides a smooth melting of chocolate in the mouth. Provides chocolate products with the ability to break apart easily; good demolding properties. Polymorph V is not readily obtained by simple cooling, but rather by using a tempering protocol.



The functions and health benefits of cocoa butter include it is an important ingredient in chocolate accounting for 30 to 35 percent. Cocoa aroma spreads smoothly in the mouth because of its rapid melting. It preserves the well soluble aroma, it is a source of energy, it is a carrier of oil soluble vitamins. The cocoa butter is known to reduce cataracts, it contains very high amounts of antioxidants, it is a good source of vitamins and minerals, it is good for heart health, digestion, brain alertness, it makes our bones strong, it alleviates stress, it is rich in magnesium, helps manage depression and it is high in vitamins and minerals.



Cocoa butter alternatives that is CBA's are fats fulfilling the functions of cocoa butter completely, normally there are various like in the earlier classes we discussed about mango kernel oil, kokum butter, etcetera. They may be of three types like cocoa butter equivalent (CBE), Cocoa butter replacer (CBR), and Cocoa butter substitutes (CBS). Cocoa butter equivalent (CBE) are not-lauric acid plant fats, which are similar in their physical and chemical properties to cocoa butter and mixable with it in every amount without altering the properties of cocoa butter. Cocoa butter replacer (CBR) are non-lauric fats with distribution of fatty acid similar to cocoa butter, but a completely different structure of triglycerides; only in small ratios compatible to cocoa butter. Cocoa butter substitutes (CBS) are lauric plant fats chemically totally different to cocoa butter, with some physical similarities; suitable to substitute cocoa butter to 100%. Cocoa butter improvers (CBIs) are similar to CBEs, but with higher content in solid triglycerides; used for improving soft cocoa butters. Cocoa butter extender (CBEx): Subgroup of CBEs not mixable in every ratio with cocoa butter.

Storage and packaging of CB

- Because cocoa butter melts easily, it should be stored away from light and heat in a cool, dry spot.
- It can also be kept in the refrigerator. Cocoa butter will last several years if stored properly.
- Cocoa butter can be stored in several different containers, from a zip lock plastic bag to a plastic container with a lid, to a glass jar or container.

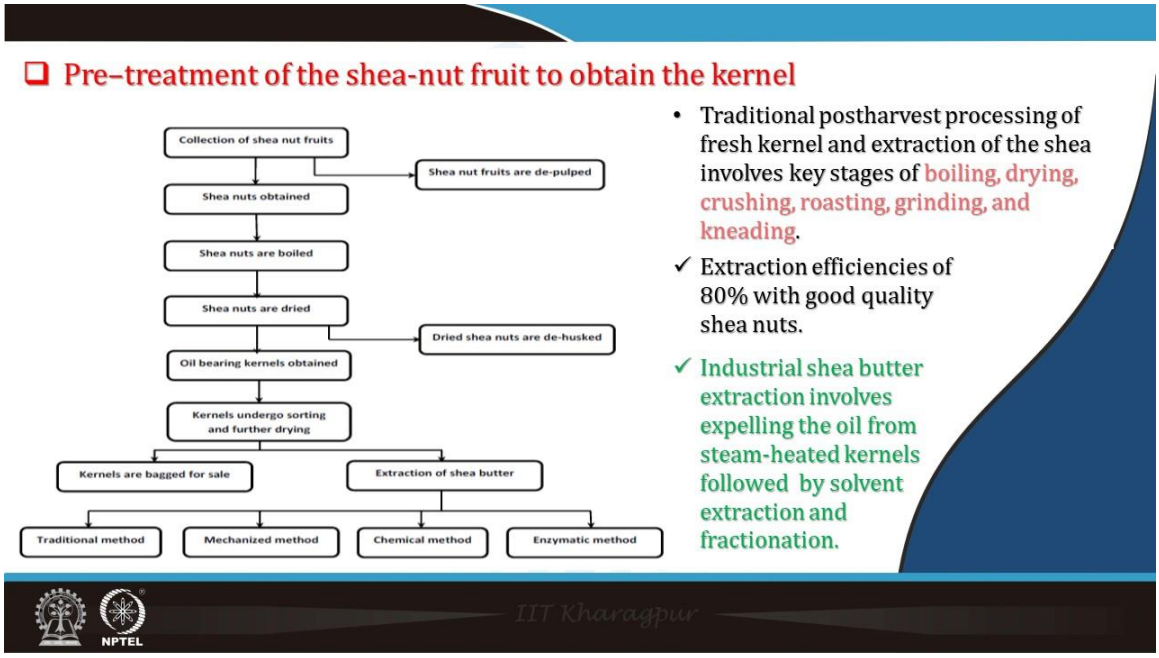
As far as the storage and packaging of the cocoa butter is concerned, as it melts easily it should be stored away from light and heat in a cool dry place. It can also be kept in the refrigerator. Cocoa butter will last several years if stored properly. Cocoa butter can be stored in several different containers, from a zip lock plastic bag to a plastic container with a lid, to a glass jar or container.

Shea butter

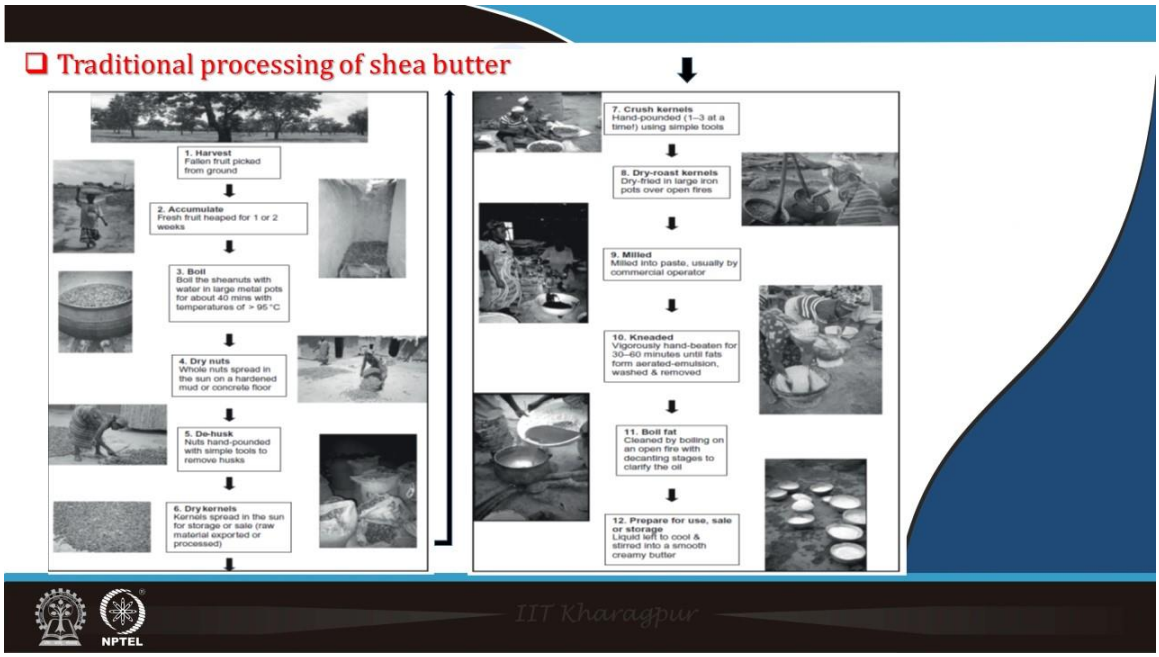
- Shea butter as a yellowish–grey solid material or yellowish white in colour with a strong smell extracted as fat from the kernels of the shea-nut tree *Vitellaria paradoxa*.
- Shea butter is used extensively in the food, pharmaceutical, and cosmetic industries.
- It is often used as cocoa butter substitute by chocolate manufacturers and for margarine and baking purposes.
- Shea butter is as good as table oil because of its high nutritive value and low cholesterol levels.
- It can be consumed raw without any further physical or chemical treatments or refinement.

Now let us talk about shea butter. Shea butter are yellowish–grey solid material or yellowish white in colour with a strong smell extracted as fat from the kernels of the shea-nut tree *Vitellaria paradoxa* . Shea butter is used extensively in the food,

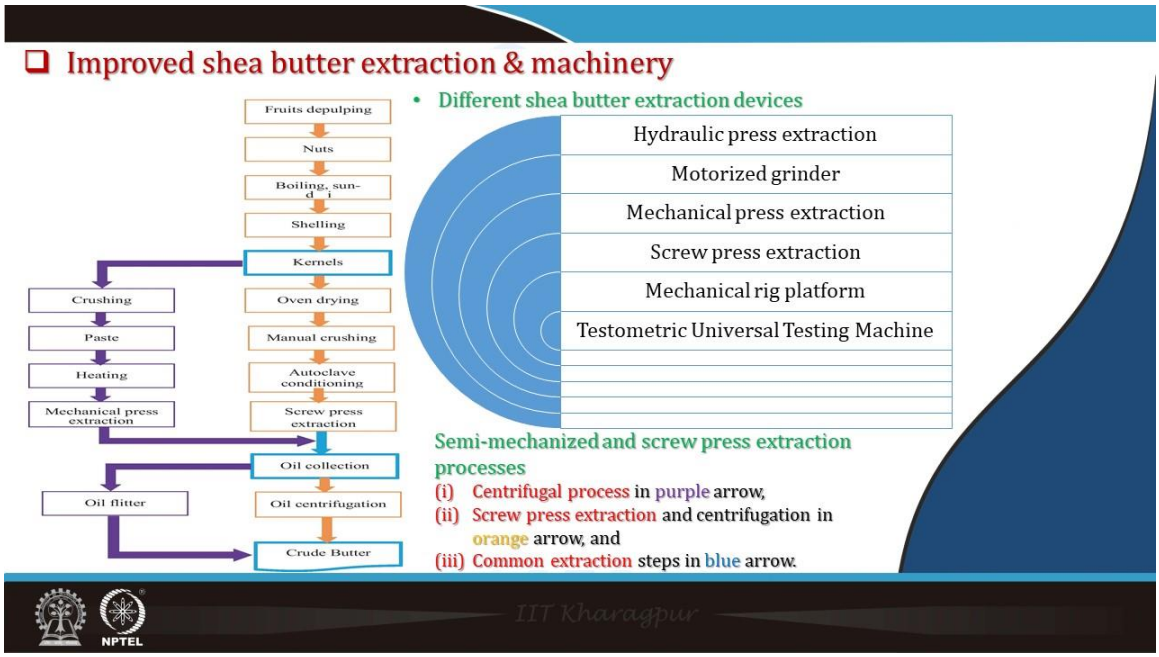
pharmaceutical, and cosmetic industries. It is often used as cocoa butter substitute by chocolate manufacturers and for margarine and baking purposes. Shea butter is as good as table oil because of its high nutritive value and low cholesterol levels. It can be consumed raw without any further physical or chemical treatments or refinement. And you can see in the figure, the shea nuts and the pulp. So, fruit pulp is removed and the shea nut is obtained and this nut is then processed for getting the butter.



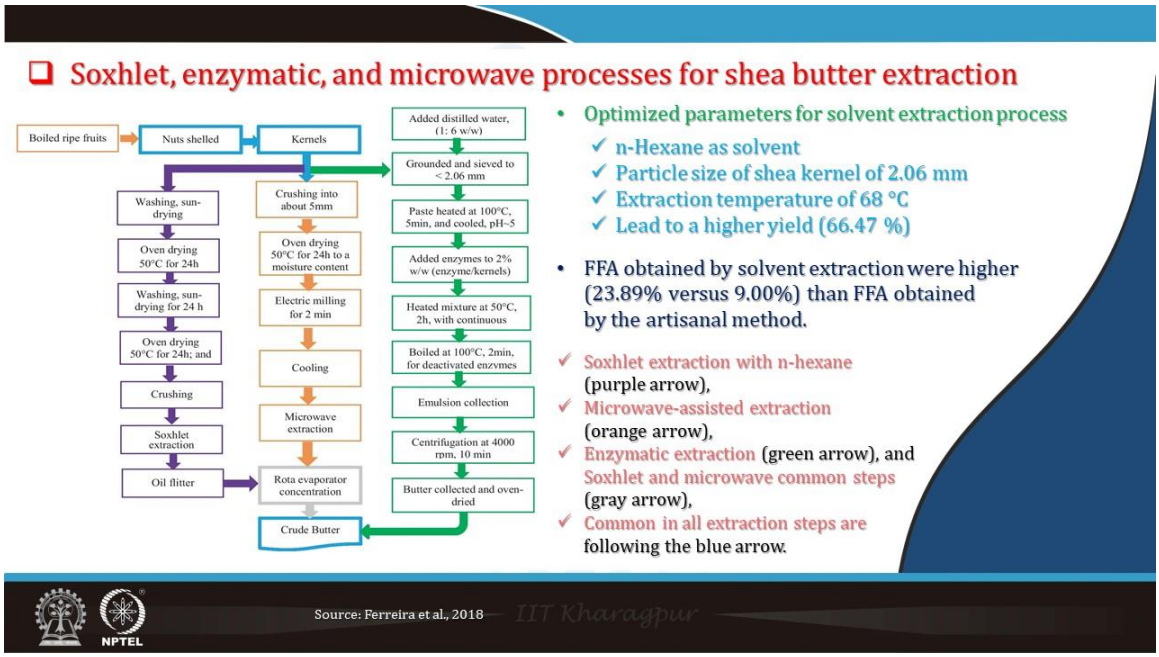
The pretreatment of the shea-nut fruit is done to obtain the kernel. Traditional postharvest processing of fresh kernel and extraction of the shea involves key stages of boiling, drying, crushing, roasting, grinding, and kneading. Extraction efficiencies of 80% with good quality shea nuts. Industrial shea butter extraction involves expelling the oil from steam-heated kernels followed by solvent extraction and fractionation.



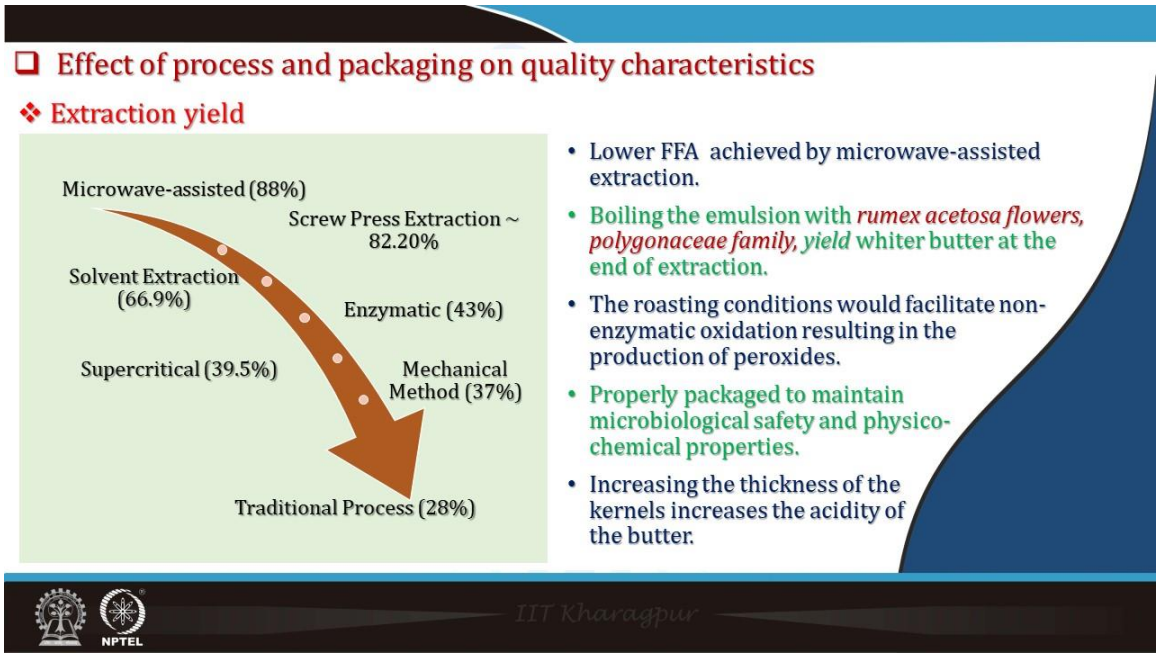
This slide shows the traditional processing of shea butter that is first fruits are harvested from the tree or the fallen fruit are picked from the ground. The fresh fruits are heaped for about 1 to 2 weeks and then they are boiled with water in a large metal pot for about 40 minutes at a temperature more than 90 degree Celsius. The whole nuts are spread in the sun on a hardened mud or concrete floor and nuts are hand-pounded with simple tools to remove the husks, because when it is dried the dehulling becomes easier. The kernels obtained after dehulling or the hull removal are spread in the sun for storage or for sale, the raw material is either exported or processed. The kernels are hand pounded which is 1 to 3 at a time using small simple tools and then dry fried in a large iron pot over the open fires. Finally, they are milled into paste usually by commercial operators then vigorously hand blended for about 30 to 60 minutes until the fat for aerated emulsion, is washed and removed. The fat obtained is cleaned by boiling on an open fire with decanting stages to clarify the oil. In the last step, the liquid left is cooled and then stirred into a smooth creamy butter.



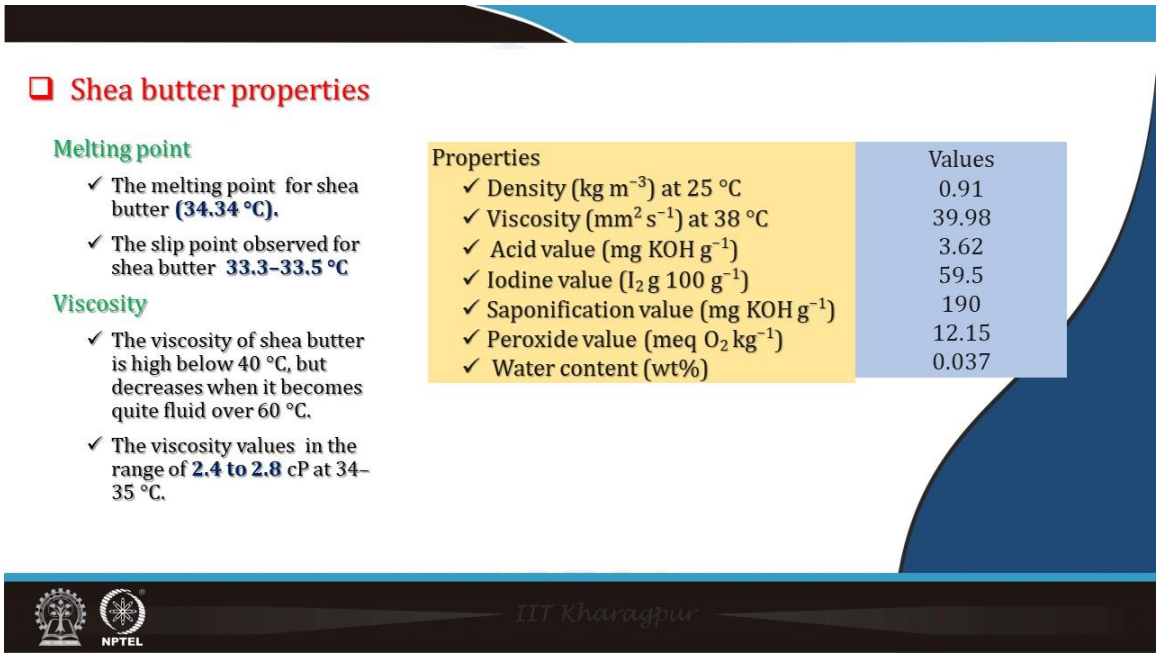
The improved shea butter extraction process and machinery includes different extraction techniques such as hydraulic press extraction, motorized grinder, mechanical press extraction, screw press extraction, mechanical rig platform and testometric universal testing machine. Some of the Semi-mechanized and screw press extraction processes are shown in the figure, a centrifugal process in the purple arrow, screw press extraction, and centrifugation in the orange arrow, and common extraction steps in blue arrow. So, these are some of the processes like centrifugal presses or screw press extraction is used. The kernels obtained are crushed the paste is heated and then they are put into mechanical extraction. The oil is obtained is filtered and crude butter is obtained.



Improved process such as solvent extraction, enzymatic and microwave processes of the shea butters are also applied. The kernels after washing and sun drying, oven dried at 50 degree Celsius for 24 hours, washing, sun drying for 24 hours, again oven drying, then crushing, soxhlet extraction and oil filter and rota-evaporator used for concentration and crude butter is obtained. In the microwave assisted extraction the kernels are crushed into about 5 mm, they are oven dried at 50 degree Celsius for 24 hours, then electric milling for 2 minutes, cooled and subjected to microwave extraction. In the enzymatic extraction, like in soxhlet and microwave the kernels are grounded, added with the water and made to paste, heated to 100 degree Celsius for 5 minutes, added enzyme to 2 percent, then the mixture is heated at 50 degree Celsius for 2 hours, then boiled at 100 degree Celsius for 2 minutes for deactivating the enzyme and then emulsion is collected, centrifuged at 4000 rpm for 10 minutes and butter is collected and oven dried. Optimized parameters for solvent extraction process, n-Hexane as solvent, particle size of shea kernel of 2.06 mm, extraction temperature of 68 °C, lead to a higher yield (66.47 %). The FFA obtained by solvent extraction were higher (23.89% versus 9.00%) than FFA obtained by the artisanal method.



So, if we let us see the effect of various process parameter or packaging on the quality characteristics, particularly the extraction yield if you say the microwave assisted it gives maximum extraction of about 88 percent of shea butter whereas, the traditional process gives least 28 percent extraction. Mechanical methods yield around 37 percent extraction, super critical gives about 40 percent extraction. Enzymatic extraction gives 43 percent, solvent extraction gives around 70 percent and screw press extraction gives 82 percent yield. Lower FFA achieved by microwave-assisted extraction. Boiling the emulsion with rumex acetosa flowers, polygonaceae family, and yield whiter butter at the end of extraction. The roasting conditions would facilitate non-enzymatic oxidation resulting in the production of peroxides. Properly packaged to maintain microbiological safety and physico-chemical properties. Increasing the thickness of the kernels increases the acidity of the butter.



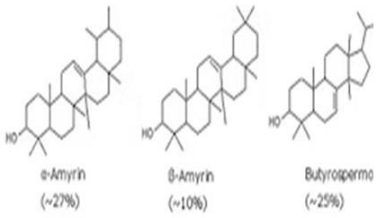
The properties of the shea butter are melting point is in the range of about 34-35 degree Celsius. The slip point observed are at around 33.3 to 33.5 degree Celsius. The viscosity of the sea butter is high below 40 degree Celsius, but it decreases when it becomes quite fluid over 60 degree Celsius. The viscosity values in the range of 2.4 to 2.8 cP at 34 to 35 degree Celsius. The other properties of the shea butter are density at 25 degree Celsius is 0.91 kg per cubic meter, viscosity at 38 degree Celsius is around 39.98 mm square per second. This acid value is 3.62 milligram KOH per gram, iodine value is 59.5 iodine gram per 100 gram, saponification value is 190 milligram KOH per gram, peroxide value may be 12.15 meq oxygen per kg, and water content is 0.037 weight percent and these properties will be influenced by the storage conditions, extraction methods, variety, and etcetera.

Composition of shea butter

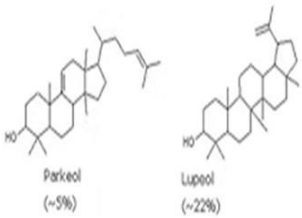
- Saponifiable fraction
  - ✓ The average fat content in shea kernels varies between 45 – 53 %.
  - ✓ Palmitic, stearic, oleic, linoleic, and arachidonic with percentage of 4, 41.5, 46.4, 6.6, and 1.3 %, respectively.
  - ✓ The fatty acid composition is dominated by stearic and oleic acids 85 – 90 % of the total fatty acids.
  - ✓ The major triglycerides are SOO (33 %), OOO (19 %), and SOS (20 %)
  - ✓ The levels of the triglycerides Palmitic-Oleic-Stearic (POS) were relatively low (3.6 –7.6 %).
  - ✓ The high stearic acid content gives the shea butter its solid consistency, while higher percentage of oleic acid determines softness.

So, as far as the composition of sea butter is concerned saponifiable fractions, the average fat content in shea kernels varies between 45 – 53 %. Palmitic, stearic, oleic, linoleic, and arachidonic with percentage of 4, 41.5, 46.4, 6.6, and 1.3 %, respectively. The fatty acid composition is dominated by stearic and oleic acids 85 – 90 % of the total fatty acids. The major triglycerides are SOO (33 %), OOO (19 %), and SOS (20 %). The levels of the triglycerides Palmitic-Oleic-Stearic (POS) were relatively low (3.6 –7.6 %). The high stearic acid content gives the shea butter its solid consistency, while higher percentage of oleic acid determines softness.

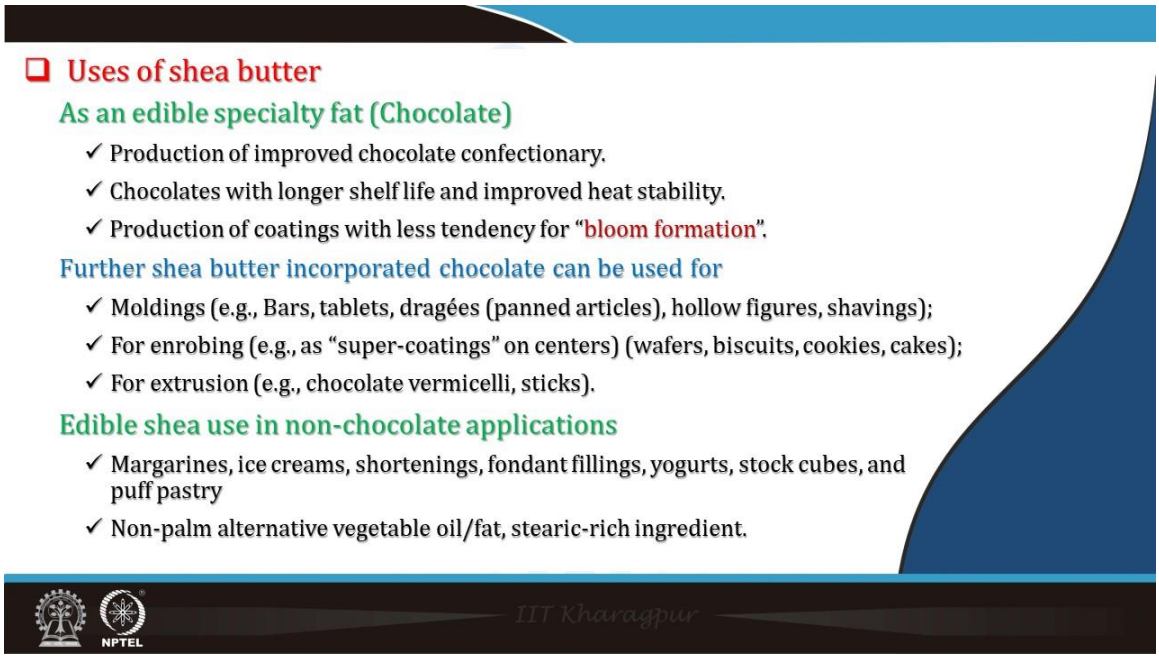
- Unsaponifiable fraction
  - ✓ Shea butter has high level (5 –15 %) of non-saponifiable lipid (NSL).
  - ✓ Two-thirds of the vitamin E found in shea butter occurs in the form of α-tocopherol followed by δ (15%), γ (14%), and β (7%) tocopherols.
  - ✓ Shea butter NSL also contain high levels (upto 6 %) of phytosterols.
  - ✓ The phenolic profile of shea butter is composed of catechin family compounds similar to green tea.
  - ✓ The most prominent component in shea kernels is gallic acid (27%).



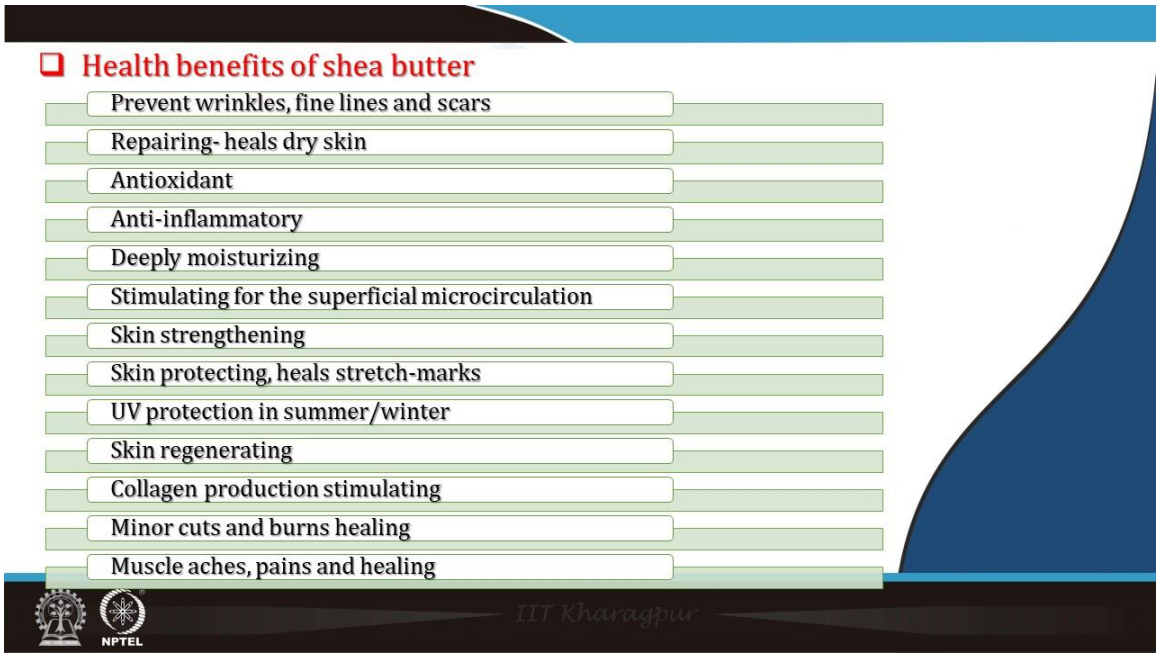
Gallocatechin	(23%)
Epigallocatechin	(16%)
epigallocatechingallate	(13%)
gallocatechingallate	(7%)
Catechin	(3%)
Epicatechin	(3%)
epicatechingallate	(3%)



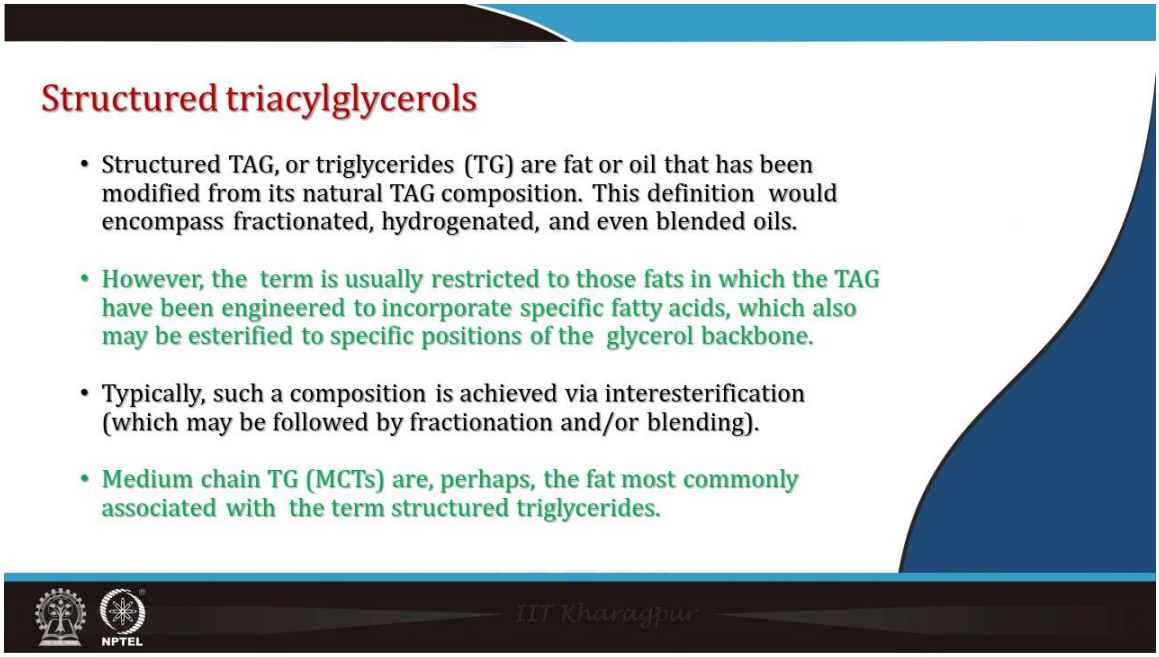
For the presence of unsaponifiable fraction, shea butter has high level (5 –15 %) of non-saponifiable lipid (NSL). Two-thirds of the vitamin E found in shea butter occurs in the form of α-tocopherol followed by δ (15%), γ (14%), and β (7%) tocopherols. Shea butter NSL also contain high levels (upto 6 %) of phytosterols. The phenolic profile of shea butter is composed of catechin family compounds similar to green tea. The most prominent component in shea kernels is gallic acid (27%).



The uses of shea butter are as an edible specialty fat (Chocolate), production of improved chocolate confectionary, chocolates with longer shelf life and improved heat stability. Production of coatings with less tendency for "bloom formation". Further shea butter incorporated chocolate can be used for moldings (e.g., Bars, tablets, dragées (panned articles), hollow figures, shavings); For enrobing (e.g., as "super-coatings" on centers) (wafers, biscuits, cookies, cakes); For extrusion (e.g., chocolate vermicelli, sticks). Edible shea use in non-chocolate applications are margarines, ice creams, shortenings, fondant fillings, yogurts, stock cubes, and puff pastry. Non-palm alternative vegetable oil/fat, stearic-rich ingredient.

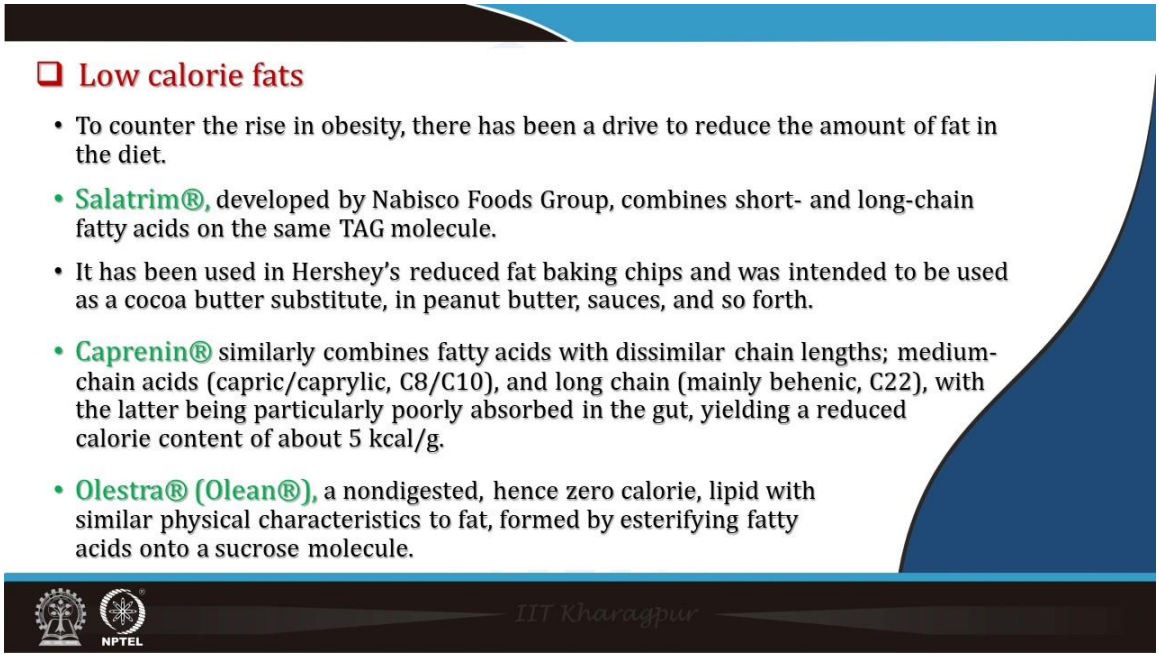


The health benefits of shea butter numerous like they prevent wrinkles, fine lines and scars, repair, heals, dry skin, anti-oxidant, anti-inflammatory, deep moisturizing, stimulating for the superficial microcirculation, skin strengthening, skin protecting, skin regenerating, minor cuts and burns are healed, muscle aches, pains are healed.

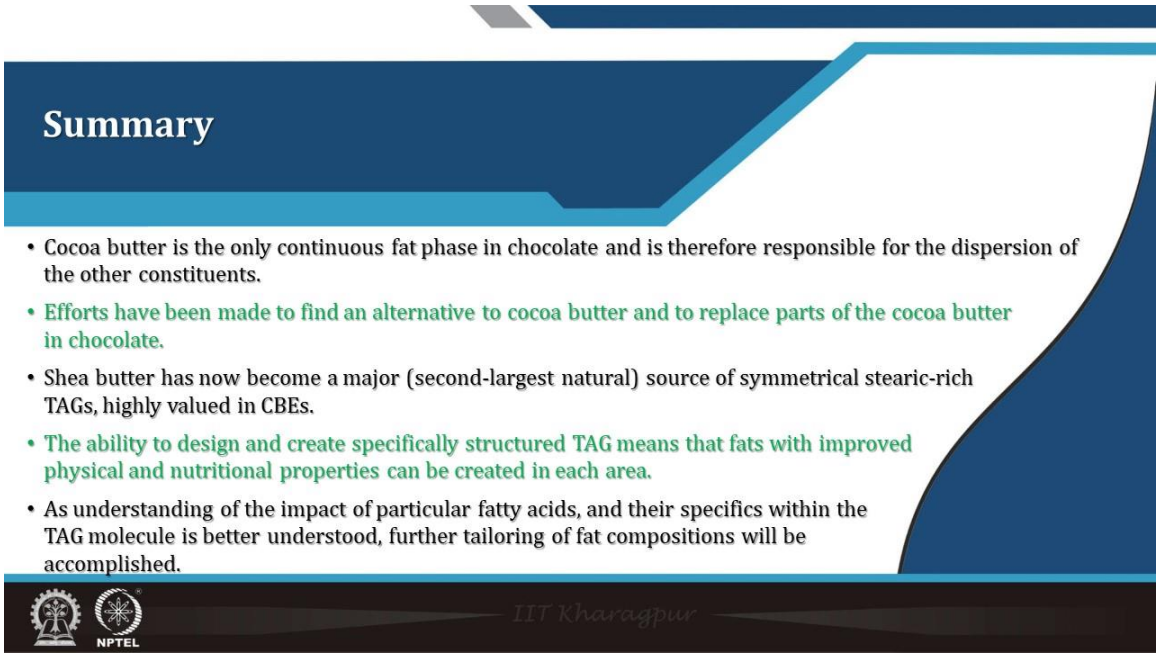


So, now let us talk about little bit structured triglycerols. Structured TAG, or triglycerides (TG) are fat or oil that has been modified from its natural TAG composition. This definition would encompass fractionated, hydrogenated, and even blended oils. However, the term is usually restricted to those fats in which the TAG have been

engineered to incorporate specific fatty acids, which also may be esterified to specific positions of the glycerol backbone. Typically, such a composition is achieved via interesterification (which may be followed by fractionation and/or blending). Medium chain TG (MCTs) are, perhaps, the fat most commonly associated with the term structured triglycerides.



The structured triglyceroles are used in various modifications to produce low calorie fats. To counter the rise in obesity, there has been a drive to reduce the amount of fat in the diet. Salatrim®, developed by Nabisco Foods Group, combines short- and long-chain fatty acids on the same TAG molecule. It has been used in Hershey's reduced fat baking chips and was intended to be used as a cocoa butter substitute, in peanut butter, sauces, and so forth. Caprenin® similarly combines fatty acids with dissimilar chain lengths; medium- chain acids (capric/caprylic, C8/C10), and long chain (mainly behenic, C22), with the latter being particularly poorly absorbed in the gut, yielding a reduced calorie content of about 5 kcal/g. Olestra® (Olean®), a nondigested, hence zero calorie, lipid with similar physical characteristics to fat, formed by esterifying fatty acids onto a sucrose molecule.



So, with this I will like to summarize this lecture by saying Cocoa butter is the only continuous fat phase in chocolate and is therefore responsible for the dispersion of the other constituents. Efforts have been made to find an alternative to cocoa butter and to replace parts of the cocoa butter in chocolate. Shea butter has now become a major (second-largest natural) source of symmetrical stearic-rich TAGs, highly valued in CBEs. The ability to design and create specifically structured TAG means that fats with improved physical and nutritional properties can be created in each area. As understanding of the impact of particular fatty acids, and their specifics within the TAG molecule is better understood, further tailoring of fat compositions will be accomplished.

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These are the references used in the preparation of this lecture. With this thank you very much for your patience hearing. Thank you.