

DRY FRACTIONATION OF PALM OIL

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ABSTRACT

The palm oil industry is growing rapidly over the past few decades particularly in Southeast Asia. Palm oil is a unique and versatile oil due to its lipid profile. Various fractions of palm oil can be obtained through fractionation and hence, used for vast applications. Fractionation generally works by cooling the palm oil to form crystals of higher melting fats and separating them from the liquid phase. The main fractions obtained from palm oil are palm olein and palm stearin. This review covers the theory of fractionation, different fractions obtainable by fractionating palm oil, dry fractionation of palm oil, and the advancements achieved in dry fractionation technology. Despite the existing knowledge on palm oil fractionation, the underlying mechanisms involved are not thoroughly understood which warrants future research effort on this aspect.

Keywords: Crystallization, Inter-esterification, Palm oil fraction, Phytonutrients, Stearin.

INTRODUCTION

The palm oil industry has a tremendous contribution to the economy of Malaysia. Palm oil is obtained from the fruit of the oil palm tree, *Elaeis guineensis*. The fruit contains an outer layer of flesh called mesocarp and a seed known as the kernel (Figure 1). Palm oil and palm kernel oil are 2 different oils where the former is obtained through the mechanical pressing of the mesocarp while the latter is derived from the palm kernel [1]. Palm oil is the main ingredient of most domestic and food products such as soap, cooking oil, hair conditioner, and chocolate. Today, it is the vegetable oil with the highest production and utilization. This is mainly due to the high return of investment, less labour intensive [2] along with its unique lipid profile which has an equal ratio of saturated and unsaturated fat [3]. The oil palm is grown in tropical regions, mainly in Indonesia, Malaysia, and Thailand. It originates from the tropical forest of West Africa. The genus *Elaeis* is one of the members of the palm family (Arecaceae) [4]. The palm trees yield fruit bunches after 3 years of planting and have a productive life span of approximately 25 to 30 years [5].

At present, the Southeast Asian countries, especially Indonesia and Malaysia are the main players in the palm oil industry. These 2 countries contributed to 85% of palm oil production around the world in the year of 2017 [6]. At the moment, Malaysia is the second-largest producer of palm oil. The contributing factors to this achievement are

the ideal climate, competent milling and refining technologies, and rigorous research and development [7]. The oil palm plantation covered 5.85 million hectares of land in Malaysia in the year of 2018 [5]. In each oil palm fruit, there is a hard kernel (seed) with a shell lining (endocarp) enclosed by a thick mesocarp. The oil from the mesocarp layer is known as palm oil which composes mainly of palmitic and oleic acid. The palm oil contains nearly 50% saturated fats. On the other hand, palm kernel oil which largely composes lauric acid is obtained from the seed. It contains more than 80% of saturated fats [8].

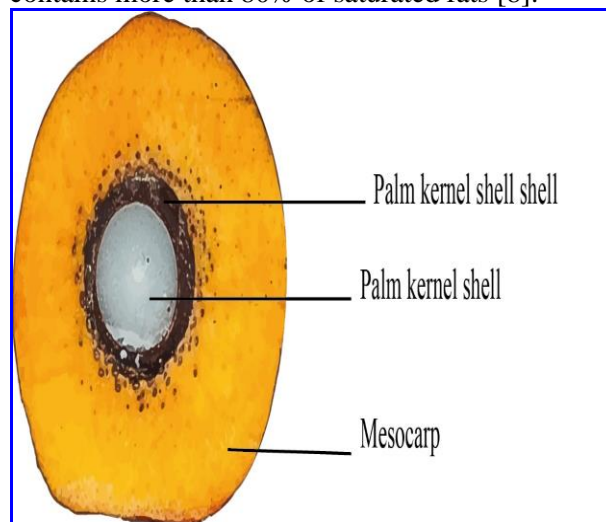


Figure- 1: Cross-section of a palm fruit

As such, palm oil has limited application and hence, fractionation is essential to obtain different fractions of palm oil which can be used in various applications. The palm oil fractionation has an abundance of mono-saturated and di-saturated triacylglycerol (TAG); a semi-solid state of palm oil permit; its separation into a low-melting fraction (olein); and a high-melting fraction

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(stearin) [9]. Fractionation is a method used for the separation of palm oil into individual fractions. It involves the separation of different components or fractions in a mixture based on variations in a property [10]. There are 3 common types of fractionation methods that dry fractionation, detergent fractionation, and solvent fractionation. The next section will be focusing on the details of each fractionation method.

Theory of fractionation

The process of separating the individual components of a mixture is known as fractionation. It is a physical process and is based on certain properties like molecular weight, solubility, volatility, degree of unsaturation, crystallization, and many more [11, 12]. This process is a thermomechanical separation process and it is reversible. The separated components have individual physical and chemical properties, different from each other and the parent mixture [11, 13]. This allows the industry to obtain fractions that melt at distinct temperatures, solid fat content (SFC), degree of saturation for different applications [14]. Fractional crystallization is regularly operated at an industrial scale to isolate and purify a mixture of substances. It works by crystallizing the high melting fatty material into solids followed by separating the liquid portion through filtration [15]. Generally, there are 3 types fractionation: dry fractionation, detergent fractionation, and solvent fractionation [7].

Dry fractionation

Dry fractionation is the most commonly employed technique to separate palm oil into its components because it is simple in execution, environment friendly, and is associated with the lowest cost in contrast to other methods [11, 14]. In this method, the oil is cooled to the desired temperature and the TAG is crystallized to form solid under controlled programmed cooling. Then, the formed crystals are separated by filtration [11, 13]. Since dry fractionation does not take in any other chemicals in the process, no effluent is generated at the end of the process. This gives an advantage of no cost is needed to treat the effluent or further purify the components. Besides, this is also associated with the minimum loss of products [12]. Dry fractionation is usually employed due to its cost-effectiveness and good yield. The nutrition, oxidative stability, cold stability as well as the organoleptic properties are improved in fractions obtained with dry fractionation [14].

There are 3 steps involved in dry fractionation. The initial step is supercooling. The next step is crystallization where solid crystals

(stearin) are formed in the bulk liquid. The third step is the separation of solids from the olein, the liquid phase. The selectivity control of both the second and third steps is the controlling factor of the crystals form and their composition. It is affected by the extent of compatibility of different TAG present within the solid crystals. Besides, the heat transfer properties of crystallizer and the efficiency of separation will also affect the quality of separated fractions [14]. Usually, the oil is melted completely before crystallization to remove the thermal memory. This is essential because the presence of crystal memory will have a negative impact on both the repeatability of the process and the product yield. Then, the oil is cooled in a controlled manner and is maintained under a super-cooling state for crystallization to take place [9].

In the context of crystallization, nucleation and crystals growth occur. Nucleation takes place when the melt is supercooled. Supercooling is a phenomenon where the melting fraction is at a significantly lower temperature than the temperature at thermodynamic equilibrium [16]. Furthermore, three types of nucleation are categorized as homogenous nucleation, heterogeneous nucleation, and secondary nucleation. Both homogenous and heterogeneous nucleation falls under primary nucleation. Homogenous nucleation takes place when nuclei are formed spontaneously in the bulk mixture without any foreign substances, whereas heterogeneous nucleation takes place when nuclei formation occurs on the surface of extraneous substances present within the crystallizer such as the wall or the agitator. On the other hand, secondary nucleation occurs due to the removal of tiny crystals from the part of presenting crystals and they act as the new nuclei in the crystallizer [12, 13].

After the establishment of nuclei, crystal growth follows where the TAG molecules present in the bulk mixture are incorporated onto the formed nuclei [13]. During this period, the heat of crystallization must be optimally liberated and the viscosity of the slurry must be seamlessly controlled to ensure uniform crystal growth [11]. The rate of crystal growth has a directly proportional relationship with supercooling but it is inversely proportionate with the viscosity of the oil. The viscosity increases as cooling proceeds. The viscosity is related by the quantity of solid present, crystal size distribution, and interaction between crystals. There is a tendency for crystals to attract each other resulting in agglomeration held by weak bonds. This leads to the entrapment of liquid within the crystal structures and hence

resulting in poor separation [9]. Therefore, adequate, non-destructive agitation is vital to ensure the process of crystallization is continuous and uniform [12].

After the crystallization is optimum, the slurry will be subjected to separation. TAG can be found as crystals, as a liquid in the bulk phase or liquid entrapped on the crystals. Various separation equipment can be used to separate both solid and liquid phases, like vacuum filters, which include rotary drum filter or belt filter, press filters, and centrifuges [13]. Today, automatic membrane press filter is preferred because high pressure can be applied during filtration, removing the liquid trapped in the solid phase which results in more yield of liquid (olein). Furthermore, after the filtration is over, the stearin cake can be squeezed further to remove any liquid entrapped in the cake [12]. Unlike other equipment, filtration with a membrane press filter is less sensitive to any structural changes of the crystals due to higher pressure differences that can be applied [13].

Detergent fractionation

Detergent fractionation was established to enhance the separation of crystals from the liquid phase [13]. As indicated by the terms, detergents, together with an electrolyte are used in this process during the cooling of palm oil. Commonly, sodium lauryl sulfate, the detergent, is used together with sodium or magnesium sulfate. The detergent is adsorbed onto the surface of crystals to displace the liquid oil entrapped in the crystals and prevent the large agglomeration of crystals. Magnesium sulfate plays a role in ensuring the detergent to attach to the crystals rather than to emulsify the liquid oil with water. The hydrophilic head interacts with ions present in the mixture. Ironically, the hydrophobic tail of the detergent is attracted to the crystals. This in turn forms a charged layer which wet the crystals into aqueous phase [17]. The mixture is now consisting of a water phase (stearin) and a liquid oil phase (olein). The individual phases can be split employing centrifugation. Then, the olein is washed with water and dried to get rid of the excess detergent present while the stearin is melted and is again subjected to centrifugation to separate the detergent. After separation, the stearin is washed and dried [11]. The advantage of detergent fractionation is the less entrainment of liquid oil in fractions that can be obtained from palm oil.

the crystals [17]. Detergent fractionation is less commonly used today because of the cost issue and risk of contamination of fractions by the detergent [11, 13].

Solvent fractionation

Insolvent fractionation, the oil to be fractionated is dissolved in a suitable organic solvent before cooling and the start of crystallization. The crystals formed are separated through filtration and individual fractions are recovered through the evaporation of the solvent. The most used solvents are acetone or hexane. Other solvents include methanol, isopropyl alcohol, and 2-nitropropane. The selection of solvent is according to its polarity, toxicology, risk of explosion, and energy needed for its recovery [18]. Since the solvent is used, the fractionation process occurs under the diluted condition and so the viscosity of the oil is low. This aids in molecular diffusion and increases the rate of crystallization. Hence, only a short period is needed for crystallization and the mixture can be filtered with ease [19]. High separation efficiency can be achieved through solvent fractionation, giving more yield and higher purity of each fraction. In a dilute condition, only a little amount of liquid oil will be entrapped in the solid phase after the removal of the solvent. Besides, with lower viscosity of the oil, it is much easier to filter the crystal slurry. Hence, the separation efficiency of more than 90% is achievable with solvent fractionation [20].

Nevertheless, solvent fractionation is associated with fire hazards as well as high capital investment and production costs. The solvents used are volatile and explosive. Hence, a closed system together with a nitrogen blanket is necessary to prevent an explosion. In terms of solvent recovery, more heat is needed for solvents with the high heat of evaporation. Furthermore, the solvent ought to be removed up to certain standards of limit prior to discharge. Steam stripping as well is required for the recovery of certain solvents [17]. These considerations make the solvent fractionation less applicable. It is still being used in the manufacturing of specialty fats like cocoa butter (CB) replacement fats [11, 19]. The table below tabulates the advantages and disadvantages of different fractionation methods [21]. After understanding the various types of fractionation, the next section will be discussing the various

Table 1: The advantages and disadvantages of different fractionation methods.

SI. No.	Fractionation methods	Advantages	Disadvantages
1.	Dry fractionation	<ol style="list-style-type: none"> 1. Uncomplicated process 2. Inexpensive 3. Chemicals are not added 4. Zero effluent produced 5. No loss of oil 6. The feed can be fractionated multiple times 	<ol style="list-style-type: none"> 1. High viscosity impairs crystallization 2. The restricted extent of crystallization
2.	Detergent fractionation	<ol style="list-style-type: none"> 1. The tendency for crystals to remain in the aqueous phase 2. Reduce the amount of liquid oil trapped in the crystals 	<ol style="list-style-type: none"> 1. Costly 2. Product is likely to be contaminated 3. Additional accessories are required
3.	Solvent fractionation	<ol style="list-style-type: none"> 1. Reduced viscosity 2. Shorter process time 3. High separation efficiency 4. Higher yield 5. Higher products purity 	<ol style="list-style-type: none"> 1. High capital investment 2. High production costs 3. Fire and explosive hazards 4. Hazardous chemicals and effluent

Fractions of palm oil

Palm oil can be processed into different fractions with fractionation. This is important because different fractions with specific physicochemical properties can be used in certain applications [16]. The figure below shows the fractions that can be obtained by fractionating palm oil.

Palm oil

Palm oil refers to the oil obtained from the mesocarp. 94 - 98% of palm oil and its components are composed of TAG whereas the remaining is composed of monoacylglycerols,

diacylglycerols (5 - 8%), and other phytonutrients [22]. Palm oil contains a nearly equal ratio of saturated and unsaturated fatty acids with 5 - 9% trisaturated TAG (SSS), 43 - 49% disaturated TAG (SUS), 38 - 44% monosaturated TAG (SUU), and 6 - 8% triunsaturated TAG (UUU) [13, 23]. Palmitic and oleic acid account for 44-45% and 39-40% of total fatty acids respectively. The rest of the fatty acids are linoleic acid (10 - 11%). Table 2 shows the TAG composition of palm oil [16, 21].

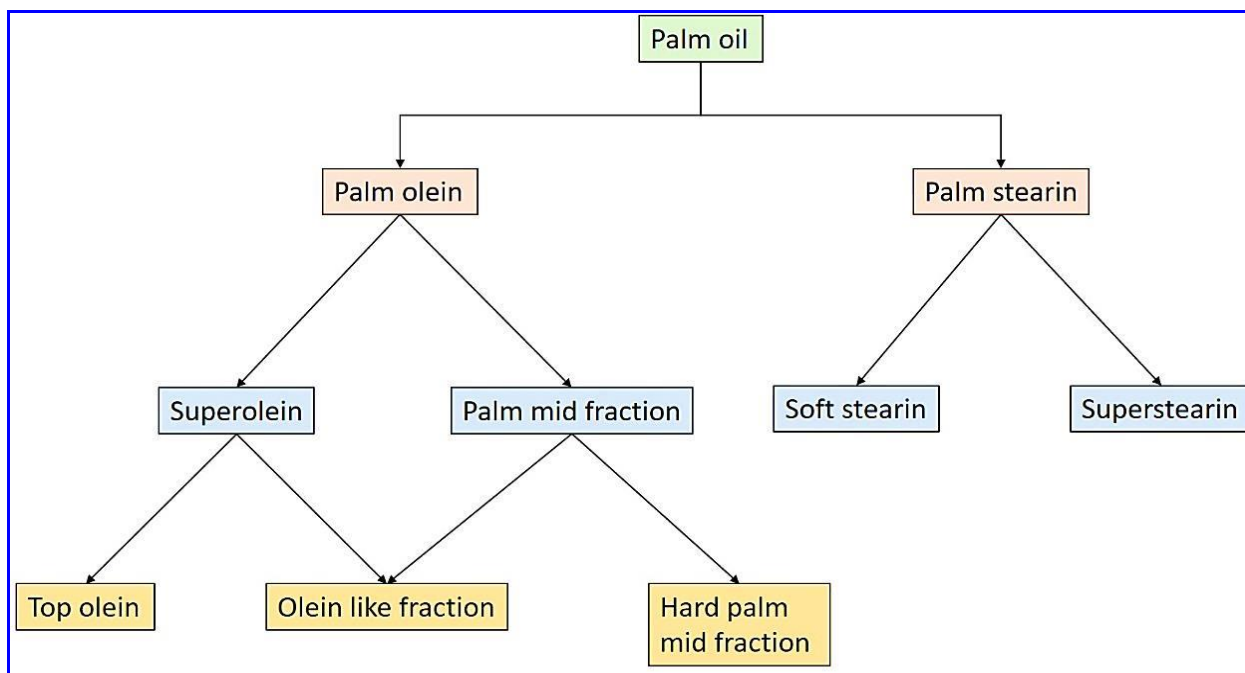


Figure 1: Fractions obtained upon the fractionation of palm oil.

Table 2: Triacylglycerol compositions of palm oil.

SI. No.	Triacylglycerol	Composition (%)
1.	Trisaturated	0.8 - 9
1a.	MPP	0.7
1b.	PPP	5.1
1c.	PPS	0.8
2.	Disaturated	38.5 - 50.3
2a.	MLP	0.9
2b.	PLP	8.9
2c.	POP	27.7
2d.	POS	4.6
2e.	SOS	0.3
3.	Monosaturated	31.8 - 44.4
3a.	PLL	1.9
3b.	PLO	10.8
3c.	POO	24.3
3d.	SOO	2.1
4.	Triunsaturated	4.8 - 9.8
4a.	OLL	0.6
4b.	OLO	2.0
4c.	OOO	3.9

(Abbreviation: M: myristic acid; P: palmitic acid; S: stearic acid; O: oleic acid; and L: linoleic acid)

Palm oil can be straightforwardly fractionated into olein and stearin. With further fractionation of olein and stearin, different fractions with distinct physicochemical properties can be obtained for various applications. Table 3 depicts the characteristics of Malaysian crude palm oil and its fractions [24].

Table 1: Characters of Malaysian crude palm oil and its fractions.

SI. No.	Characteristic	Observed value (min. to max.)		
		Crude palm oil	Palm olein	Palm stearin
1.	Apparent density at 50°C (g/ml)	0.8896 - 0.8896	0.8969 - 0.8977	0.8813 - 0.8844
2.	Refractive index, n_D , 50°C	1.4521 - 1.4541	1.4589 - 1.4592	1.4482 - 1.4501
3.	Saponification value (mg KOH/g oil)	194 - 205	194 - 202	193 - 205
4.	Unsaponifiable matter (%)	0.19 - 0.44	0.3 - 1.30	0.30 - 0.90
5.	Fatty acid composition, weight percentage as methyl esters (%)	-----	-----	-----
5a.	Lauric acid (C12:0)	0.0 - 0.5	0.2 - 0.4	0.1 - 0.3
5b.	Myristic acid (C14:0)	0.9 - 1.5	0.9 - 1.2	1.1 - 1.7
5c.	Palmitic acid (C16:0)	39.2 - 45.8	38.2 - 42.9	49.8 - 68.1
5d.	Palmitoleic acid (C16:1)	0 - 0.4	0.1 - 0.3	<0.05 - 0.1
5e.	Stearic acid (C18:0)	3.7 - 5.1	3.7 - 4.8	3.9 - 5.6
5f.	Oleic acid (C18:1)	37.4 - 44.1	39.8 - 43.9	20.4 - 34.4
5g.	Linoleic acid (C18:2)	8.7 - 12.5	10.4 - 12.7	5.0 - 8.9
5h.	Linolenic acid (C18:3)	0.0 - 0.6	0.1 - 0.6	0.1 - 0.5
5i.	Arachidic acid (C20:0)	0.0 - 0.5	0.2 - 0.6	0.3 - 0.6
6.	Iodine value	50.4 - 53.7	56.0 - 59.1	27.8 - 45.1
7.	Slip melting point (°C)	33.8 - 39.2	19.2 - 23.6	46.6 - 53.8
8.	Total carotenoids, as β -carotene (mg/kg)	474 - 689	500 - 1200	300 - 600

Palm olein

Upon fractionation of palm oil, the liquid fraction obtained is palm olein. Even though palmitic acid preferentially migrates towards palm stearin, it

retains the TAG profile of palm oil [22]. Palm olein is mainly composed of oleic acid (43%) and palmitic acid (41%). A relatively lower level of linoleic acid (11%) was also observed [25]. At

ambient temperature (warm climate), palm olein exists in liquid form. It could be blended with other vegetable oils to get liquid oil that can withstand even lower temperatures. For instance, the oil mixture of palm olein with more than 70% of soft oil (soybean oil, canola oil, or corn oil) is able to stay clear at 0°C for a minimum duration of 5 hours. The resistance against oxidation of soft oil is also improved by palm olein. Generally, there are 2 grades of palm olein, namely standard olein with IV of 56 - 59 and cloud point (CP) of 10°C and super olein with IV of >60 and CP of 2 - 5°C. The abundance of tocotrienols can be found in olein due to preferential partitioning during fractionation [7]. This made palm olein as suitable oil used for frying. The characteristics of Malaysian palm olein are shown in Table 3.

Superolein is nothing but an olein with a higher IV (>60). Triacylglycerol(TAG) is absent while monosaturated TAG content is high in the superolein. The main fatty acids in super oleinare oleic acid (47%) and palmitic acid(35%) [25]. As compared to the standard olein, it is clearer and has a lower CP due to a much lower SFC. Like the standard olein, superolein can be utilized for cooking and frying as well as mix with other unsaturated oils for different applications.

Palm stearin

Palm stearin is the solid fraction attained after the fractionation of palm oil. It is enriched with palmitic acid and the oleic acid content is about half of the palmitic acid. Hence, this resulting in

lower IV value and higher slip melting point [25]. Stearin is composed of 29 - 35% SSS, 43 - 49% SUS, 19 - 21% SUU and 3 - 4% UUU [23]. Various applications of palm stearin include as a natural hardstock to produce trans-free fat, production of food products, production of soap, and oleochemicals [26]. The characteristics of Malaysian palm stearin are summarized in Table 1.

Palm mid fraction

Fractionation of either palm olein or palm stearin produces palm mid fraction (PMF). The major component of PMF is disaturated TAG (75%) while the minor component is monosaturated TAG (<30%). The 2 major fatty acids in PMF are palmitic acid (58%) and oleic acid (32%) [25]. The PMF obtained from palm olein has softened properties, reflected by its slip melting point and SFC. The PMF obtained by fractionating stearin is also known as a hard fat [27]. PMF has a sharp melting profile and a slip melting point of 35 - 36°C due to high POP content. This property made PMF suitable for usage in confectionery fats.

Palm phytonutrients

Phytonutrients are present in palm oil and they comprise approximately 1% of the weight of palm oil. The phytonutrients are carotenoids, vitamin E (tocopherols and tocotrienols), coenzyme Q10, phytosterols, squalene, phospholipids, and palm phenolics. The content and possible physiological action of each phytonutrient are tabulated below [21, 25]. The next section will be discussing the dry fractionation of palm oil.

Table 2:List of phytonutrientcontent and possible physiological actions.

SI No.	Palm phytonutrients	Contents (ppm)	Possible physiological actions
1.	Vitamin E	600 - 1000	- Neuroprotection - Anti-cancer - Anti-angiogenesis - Anti-atherosclerotic - Impediment of cholesterol synthesis - Cardioprotection - Bone protection - Antioxidant - Skin protection - Anti-inflammatory
2.	Carotenoids	500 - 700	- The precursor of vitamin A - Prevention of xerophthalmia (night blindness) - Anti-cancer
3.	Palm phenolics	40 - 70	- Anti-oxidative - Anti-microbial - Anti-atherogenic - Anti-cancer - Anti-diabetic - Anti-hypertensive

			<ul style="list-style-type: none"> - Anti-inflammatory - Cardio-protective - Prevent age-related muscular degeneration - Cognitive enhancement
4.	Phytosterols	300 - 620	- Hypocholesterolemic
5.	Squalene	250 - 540	<ul style="list-style-type: none"> - The metabolic precursor of steroidal compounds including cholesterol - Anti-oxidative - Strengthen the immune system
6.	Phospholipids	20 - 100	- Synergistic effects with tocopherols in antioxidant properties
7.	Co-enzyme Q10	10 - 80	<ul style="list-style-type: none"> - Anti-oxidative - Cardioprotective - Anti-cancer

Dry fractionation of palm oil

Palm oil is multipurpose oil in which fractions with distinct physicochemical characteristics can be obtained through multistage dry fractionation [14]. Before discussing the details of palm oil dry fractionation, it is essential to know that there are 4 classes of TAG, namely trisaturated (SSS), disaturated (SSU-SUS), monosaturated (SUU-USU) and fully unsaturated (UUU) TAG. They have distinct physicochemical properties and are meant for different applications [22]. The rationale of palm oil fractionation is the selective crystallization of various TAGs by their distinct melting points [9]. Dry fractionation first separates the trisaturated fraction, followed by disaturated and monosaturated fraction [13]. The unsaturated fatty acids tend to partition towards palm olein while saturated fatty acids tend to partition towards palm stearin. For minor components, diacylglycerol (DAG), squalene, vitamin E, carotenoids are more likely to distribute in palm

olein while monoacylglycerols, sterols, and lipids tend to migrate towards in palm stearin [28].

The fact that palm oil can be easily fractionated into stearin, the solid fraction, and olein, the liquid fraction is supported by the melting behaviour of each measured by differential scanning calorimetry (DSC). The DSC melting curve of palm oil shows 2 peaks, at 9.57°C and 43.72°C, which can be associated with the contribution of olein and stearin fraction respectively. Besides, the individual DSC melting curve of olein and stearin portray peak maximum at 6.01°C and 47.49°C respectively. These match with the 2 peaks that are detected in the DSC melting curve of palm oil [29]. A slight peak in the higher temperature region of the olein DSC melting curve indicates the presence of a little high melting TAG that remains in the olein. On the other hand, short peaks in the lower temperature region implies that there is a small amount of olein trapped in the stearin crystals during the separation stage [22].

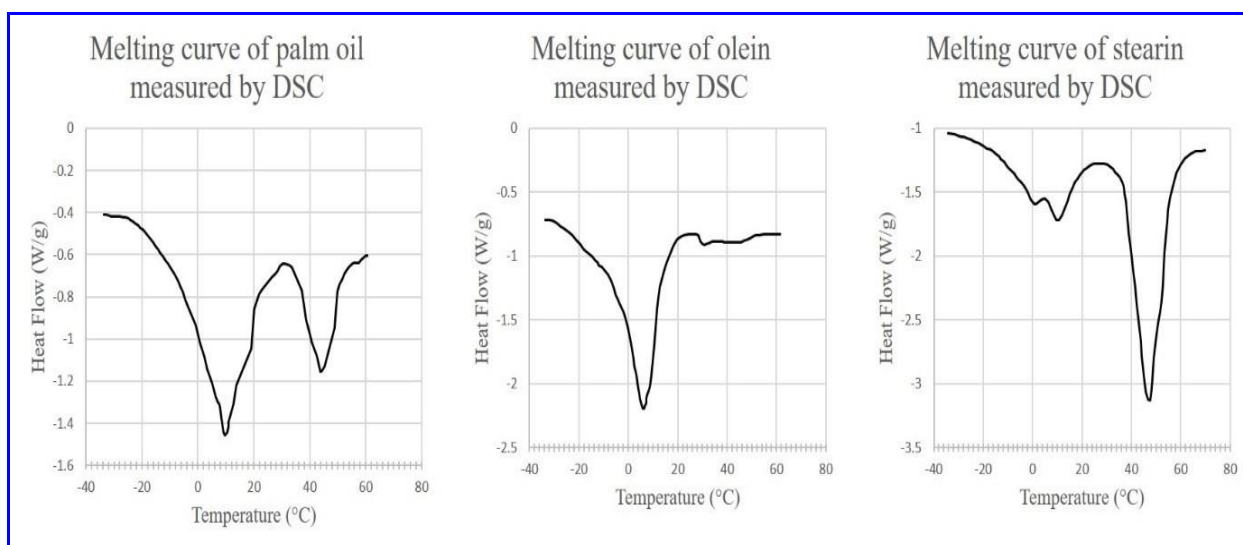


Figure 2: DSC melting curve of palm oil, olein and stearin.

Commodity fats

Following single step fractionation, palm oil can be separated into stearin (solid phase) and olein (liquid phase). The palmitic acid inclines to partition towards the stearin. Nevertheless, the fatty acid composition of triglycerides for palm oil and olein remains to be similar [22]. The purpose of the first fractionation is to remove most of the trisaturated TAG to improve the stability of olein under cold temperatures. The yield for palm olein is high in a single step of fractionation, making it a cheap primary commodity [11].

In a study by Nusantoroin 2007, it was reported that the refined, bleached, and deodorized (RBD) palm oil has an IV of 51.4 and CP of 24.8°C. The RBD palm oil consists of POP (27.88%), POO (24.51%), and palmitoyl-oleoyl-linoleoyl glycerol (POL) (11.13%). Upon fractionation, the stearin showed an increase in tri-palmitoyl glycerol (PPP) and POP level and a decrease in POO and (POL) level, with an IV of 35.8, slip the melting point of 52.7°C while the olein showed an increase in unsaturated triacylglycerols with an IV of 59.7 and CP of 3.9°C. Olein is enriched with monosaturated TAG while trisaturated TAG was hardly observed to be present in the olein [29]. Among the disaturated TAG, asymmetrical isomer concentrates in stearin while the symmetrical isomer concentrates in olein due to inter-solubility [13]. The IV is a measure of the extent of unsaturation, hence, the reduced IV value of stearin as compare to palm oil is relevant to the fact that the higher melting (saturated) TAG is enriched in stearin. This is associated with an increase in the melting point of stearin as

compared to that of palm oil. The higher IV and lower CP of olein can be justified by the concentration of lower melting TAG [22].

However, it is unavoidable that some other classes of TAG will be present in the trisaturated fraction owing to intersolubility. The first step of dry fractionation will remove the SSS level in the olein fraction with SSU-SUS content remains unchanged. In the second step, after which SSS was completely removed, the disaturated TAG content is being removed which produces super olein with a higher IV and a lower CP [13]. The monosaturated TAG, particularly POO improves the CP but trisaturated TAG will negatively impact the CP by initiating post crystallization at low temperatures [7]. Palm super olein and PMF can be obtained through further steps of fractionation of palm olein. Palm super olein has the IV in the range of 64 - 72 whereas PMF has the IV in the range of 32 - 48. Palm super olein is used in colder climates due to its lower CP while PMF is used in producing cocoa butter equivalent (CBE) and in confectionery fats. Similar wise, super stearin and PMF can be obtained by fractionating palm stearin. The super stearin is very hard with IV of below 10. It is used in infant formulations [28].

Value-added products

Higher value-added products can also be obtained from the multistep fractionation of palm oil. These products include top olein, super stearin, and hard palm mid fraction. It can be classified into 3 routes, the solid route, the hard PMF route, and the liquid route [11].

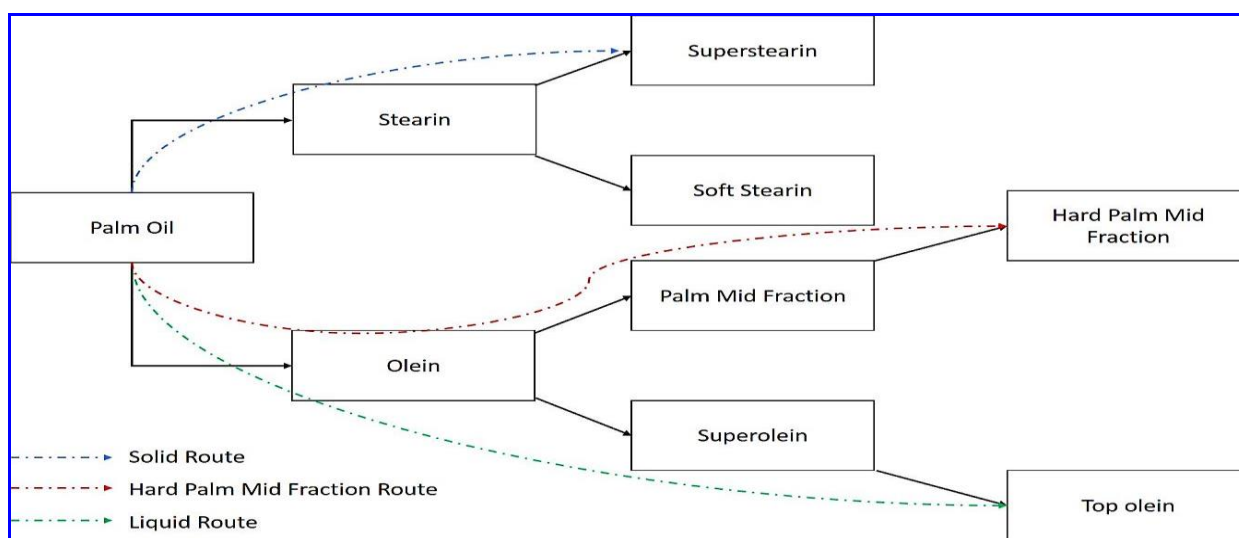


Figure 4: Dry fractionation of palm oil via the solid route, the liquid route, and the hard palm mid fraction route.

The solid route leads to the production of super stearin in 2 steps, from palm oil to palm stearin and from palm stearin to super stearin. The super stearin comprises about 90% of saturated fatty acids, mostly PPP (constitutes >65%), which results in a very low IV of 12-14. Hence, super stearin is very hard below 40-45°C and melts at 65-70°C. Super stearin serves as a substitute for hydrogenated fats and in the production of margarine and shortenings have a low content of trans-fat. On the other hand, soft stearin can also serve as a material for margarine and shortening fats [20].

The next route is the hard PMF route. There are 2 routes to produce PMF, the olein route, and the stearin route. Olein route is the better way to obtain CBE because the disaturated TAG selectively concentrates more in soft PMF after the second fractionation step, upon fractionation, produces hard PMF with upto 85-90% of disaturated TAG. Besides, the DAG content can be kept at an adequately low level to avoid adverse effects on the crystallization of the fraction [13]. Usually, hard PMF is obtained through a chain of fractionation steps. Firstly, the palm oil is fractionated to obtain olein, which in turn is further fractionated to obtain super olein (IV 64-66) and soft PMF (IV 44-45). The soft PMF may have some excess of PPP. The topped soft PMF with an IV of 46-47 can be used as a suitable material for fabrication of hard PMF with good quality which contains at least 65% of POP. This confers hard PMF a steep melting profile just like that of CB. Hence, hard PMF plays an important role in the production of CBE [11, 30].

On the other hand, superolein (IV 64-66) is obtained via the liquid route. Top olein (IV 70-72) can then be obtained by fractionating the superolein. The parameter that appraises the cold resistance of oil is CP. It is the temperature in which solidification and clouding of oil occur when cooled at a particular rate. With the removal of trisaturated TAG followed by disaturated TAG, the IV becomes higher while the CP of successive liquid fractions from palm oil becomes lower. Like olein and superolein, top olein is used as cooking oil but it can withstand lower temperatures without clouding [11, 31].

Advancement and improvement in dry fractionation

Technology advancements have been achieved in several aspects like cooling, agitation, crystallization which results in improvement of the productivity of dry fractionation and the product yield. These include modification of crystallizer

design, continuous fractionation, modification of cooling program, the addition of crystallization additives, and enzymatic interesterification.

Modification of crystallizer design

A usual crystallizer contains a cooling coil and an agitator. The design of the crystallizer can drastically influence the mass and heat transfer between the cooling substance and the oil. Modifications are made on the crystallizer design to save costs, obtain fractions with higher purity, and to increase the product yield. For instance, cooling coils with double layers are able to transfer the heat more efficiently and maintain a uniform temperature throughout the oil. Subsequently, these help in minimizing the disturbance on the degree of crystal growth. Apart from that, the usage of hybrid cooling coils allows shorter cooling times and provides a higher yield. The crystallizers are tall and slim, which contain agitators with programmable speed to ensure efficient heat and mass transfer. Besides, the agitators have lower dish end and radial paddle to avoid settling down of crystallizing slurry at the bottom of the crystallizer [12].

Continuous fractionation

Continuous fractionation is possible through the modifications made on crystallization and the process flow, whereby one or more crystallizers in series are used. The oil is gradually cooled to initiate crystallization. The crystallizing slurry is then continuously withdrawn from the previous crystallizer and filtered while molten fat is continuously fed the series of crystallizers [12]. The Desmet Ballestra group reconceptualized and reengineered the mobilizer to produce IConFrac, a continuous crystallizer. It can work all day long and plug flow is achieved. IConFrac is fully automated and has a transparent process control. Hence, it offers advantages like less labour demanding, increased capacity, improved filtration, energy-saving, and minimize the product variation between batches. Apart from that, IConFrac gives more olein yield with better cold stability [32].

Modification of cooling programme

The process of fractionation can be made better through modification of the cooling programme. The crystals produced by the Malaysian Palm Oil Board (MPOB) modified fractionation programme are smaller and have a uniform distribution of size. This leads to easier and better filtration of palm oil fractions by reducing the amount of olein trapped in the stearin cake and hence, increasing the yield of olein [12].

Addition of crystallization additives

Crystallization additives may influence the nucleation, crystal growth, morphology, size distribution, polymorphic stability of crystals [33]. PGE mix-8 is a polyglycerol ester made up of a mixture of palmitic, oleic, and stearic acids. The olein yield increases as the dosage of PGE mix-8 used increased. Besides, the fatty acid composition of olein from palm oil treated with PGE mix-8 is similar to that of olein from untreated palm oil. This indicated the PGE mix-8 improves the olein yield and does not affect the fatty acid profile of olein. However, the fatty acid composition of stearin was changed by the addition of PGE mix-8. It was observed that the total saturated fatty acids level increase, the desaturated fatty acids level decrease while the polyunsaturated fatty acid level remains unchanged. This indicates that purer stearin is formed upon the addition of PGE mix-8 [12].

Similar results were obtained from the study by Jun Hao, 2019, and Saw et al., 2020. Apart from those results mentioned above, they also reported that the average crystal size reduced as the dosage of PGE mix-8 used increases. This is associated with a decreasing number of larger crystals formed [33, 34]. This is due to the occurrence of heterogeneous nucleation where the PGE mix-8 molecules act as a foreign material for nucleation. They also hamper crystal growth by blocking the molecule packing, the adsorption of lipid molecules at the kink sites of growing crystals. As a result, more number of nuclei with smaller and more uniform size are formed [33]. The addition of PGE augmented the nucleation of crystals. The yield of olein also increases by means of PGE mix-8 due to less entrainment of olein in stearin cake [34]. Based on all the results reported, we can then infer that the use of PGE mix-8 improves the efficiency of filtration due to a more uniform crystal size distribution.

Enzymatic inter-esterification

Inter-esterification is a reaction that involves the interchange of fatty acids of TAGs that occurs within and between the TAG molecules. This leads to modification of the physical properties of the TAGs like crystallization and melting behaviour, SFC, and polymorphic behaviour but not the fatty acid profile [26, 35]. Interesterification can be conducted chemically or enzymatically. Chemical interesterification involves the use of catalysts and conducted in a harsh condition (100–120°C), leading to the generation of by-products that need to be eliminated by bleaching and washing [36]. On the other hand, enzymatic interesterification is

performed at a lower pressure (55-70°C) and temperature [26]. Enzymatic interesterification is gaining more interest as an alternative for partial hydrogenation in producing fats having low trans-fat content to be used in pastry or confectionery [29]. The advantages of enzymatic interesterification include simpler process, low investment cost, no production of trans-fat, do not involve the use of chemicals or solvents, and thus post modification treatment is not required [36]. Final products with better quality and more resistance against oxidation can be produced with enzymatic interesterification. It can be specific or non-specific [30]. Enzymatic interesterification can be either non-specific or specific.

Fractionation, particularly dry fractionation is the cornerstone of obtaining various fractions of palm oil, and thus adds values to the end products derived from palm oil and its fractions. Ultimately, this helps to harness the maximum benefit and value of the palm oil industry. Even though the technology involved in dry fractionation is not complex, the underlying mechanism that governs the entire process, including nucleation and crystal growth is rather complicated. Many factors are affecting both nucleation and crystal growth such as polymorphism, TAG composition, and crystallization kinetics, just to name a few [16]. Studies have reported various findings and outcomes associated with different factors but there is no consensus or clear mechanism on how each factor affects fractionation. Future research work on this aspect is warranted. It is undeniable that the palm oil industry has a massive contribution to the economy of major palm oil-producing countries like Indonesia and Malaysia. Although palm oil is mainly produced in Southeast Asia, the practical yield does not reach the maximum possible yield. This is mainly due to improper establishment of oil palm plantation, inappropriate supplementation of nutrients, and poor management of plantation [37]. These issues will affect the actual yield of palm oil through factors like light radiation, pollination, soil irrigation, usage of fertilizer, pests, and disease control [38]. Therefore, it is essential not only to focus on the fractionation of palm oil into its fractions but also on the above-mentioned factors to maximize the yield and profit of the industry.

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