PHYSICOCHEMICAL PROPERTIES OF PALM STEARIN AND PALM MID FRACTION OBTAINED BY DRY FRACTIONATION

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ABSTRACT

Palm stearin was obtained from the 1st dry fractionation at a yield of 27.6 % with IV: 37.6 and SMP: 51.8 °C while palm mid fraction (PMF) was obtained from the 2nd dry fractionation at a yield of 24.1 % with IV: 45.8 and SMP: 42.7 °C. Palm stearin consisted mainly of POP (31.06 %), PPP (20.61%) and POO (15.81 %) while palm mid fraction had disaturated TAG (such as POP: 61.05 % and POSt: 11.76 %) as the major constituents. From melting properties, palm stearin had a higher melting temperature (T_M: 46.7 °C) than that of PMF (T_M: 38.5 °C). It was also shown that, in general, palm stearin had higher solid fat content at any temperature compared to PMF. Palm stearin will likely be suitable as hard stock for shortenings and PMF has potency in margarine formulations.

Keywords: *Palm stearin, PMF, dry fractionation, DSC, SFC*

INTRODUCTION

Palm oil is being used increasingly in foods such as for frying oil, margarines, shortenings or confectionery products. The versatility to different food applications is the result of a unique chemical composition of palm oil (Edem, 2002). Palm oil differs from many of the common vegetable oils in its high level of palmitic acid reaching up to 44%. In contrast, soybean oil and canola oil only contain 11 % and 5 % of palmitic acid, respectively. Then, it was revealed that addition of palm oil to other fats destined for shortening and margarine production has a beneficial effect on their textural quality due to the polymorphic stability (Ghosh and Bhattacharyya, 1997; Yap et al., 1989).

Palm stearin is produced commercially from palm oil by fractional crystallization. One of the most established techniques of fractional crystallizations is dry fractionation. Dry fractionation of palm oil will result in two fractions, namely palm olein and palm stearin. Palm stearin is the solid fraction obtained from dry fractionation. As the hard fraction, palm stearin accumulates the high melting triacylglycerols of the initial palm oil. The physical characteristics of palm stearin found to be different from those of palm oil and palm olein (Hendrix and Kellens, 2007).

Gibon (2006) noticed that the liquid fraction obtained from dry fractionation of palm oil, palm olein, recently has become a relatively cheap primary commodity because it is formed in high proportions in a single stage fractionation. For this reason, attention has been focused on multistage dry fractionation to produce olein with higher iodine value. The second stage of dry fractionation produces super olein (as the liquid fraction) and palm mid fraction/PMF (as the solid fraction).

Palm stearin and palm mid fraction are the high melting fractions obtained from dry fractionation. Due to their high melting point, they have limited uses in the manufacture of edible food products. However, since both oils are considered as by products and posses cheaper prices, palm stearin and palm mid fraction have a striking potency to be used as a fat stock (Undurraga et al., 2001; Lai et al., 2000). A fundamental understanding of their chemical composition with respect to the physical states and the factors which control the physical state (such as thermal treatment and tempering) is of importance for the control of product quality and for the possible extension of the range of products (Arima et al., 2007; Busfield and Proschogo, 1990).

As both palm stearin and palm mid fraction are obtained almost at the same level of dry fractionation process (present as the solid fractions), then the purpose of this research is to reveal the differences on their physicochemical properties. The resulted data could serve as measures in considering them for appropriate uses in a food system and controls of product quality.

MATERIALS AND METHODS

Materials

RBD (Refined, Bleached and Deodorized)-palm oil was obtained from local refinery. Then, the palm oil was subjected for dry fractionation to obtain the stearin (POs) and the olein fraction. At the first stage, the palm oil was crystallized using a cycle temperature program at 18 °C for 12 hours. The olein fraction was further fractionated to obtain super olein and palm mid fraction (PMF). A cycle temperature program at 12 °C for 20 hours was applied for the crystallization process. All chemicals were either of analytical or high-performance liquid chromatograph (HPLC) grades.

Determination of Triacylglycerol (TAG) Distribution

The distribution of the triacylglycerols was determined by HPLC, according to AOCS Official Method Ce 5b–89, with a differential refractometer as detector. Minor practical adjustments to the flow rate and mobile phase composition were made in order to improve TAG separation. All equipments (pump, column, auto sampler and detector) were supplied by Waters®. Analysis was done in duplicate.

Iodine Value (IV)

The IV of the palm oil and fractionated products was determined using the AOCS officially recommended method Cd 1b–87.

Slip Melting Point (SMP)

SMP was determined according to AOCS (method Cc. 3.25). Capillary tubes filled with fat (1 cm high) were chilled at 10±1°C for 16 h before being immersed in a beaker of cold distilled water. The water bath was stirred and heated. The temperature was recorded when the column of fat in the capillary tubes rose in the tube.

Determination of Melting Behaviour by DSC

DSC analyses were carried out using a Q1000 DSC (TA Instruments, New Castle, USA) with a refrigerated cooling system (TA Instruments) using aluminum SFI pans. Calibration was made with indium and *n*-dodecane standards. Nitrogen was used as purge gas in order to prevent condensation in the cells. An empty aluminum SFI pan was used as reference. The samples were quickly cooled to -80°C at cooling rate -5°C /min and kept for 5 min in order to ensure complete solidification. Melting profiles were recorded from –80 to 70 °C at a heating rate of 5°C /min.

Solid fat Content (SFC)

SFC of oleins was determined with a Bruker wide-line pulse nuclear magnetic resonance (pNMR) spectrometer (Karlsruhe, Germany) using a direct measurement method. The equipment was calibrated with three supplied standards (0%, 29.8%, and 70.8%). Samples were melted at 70°C and then chilled at 0°C for 90 min. Next, the samples were held at each measuring temperature for 30 min prior to measurements. The average of triplicate analysis was reported.

RESULTS AND DISCUSSION

Palm Stearin (PS) and Palm Mid Fraction (PMF) Obtained by Dry Fractionation

Palm stearin and palm mid fraction are obtained by dry fractionation and present as byproduct in which both are the hard fractions (the solid phase after a filter press separation). Palm stearin is the solid phase of RBD-palm oil fractionation while palm mid fraction is the solid phase of palm olein fractionation. Even though both palm stearin and palm mid fraction are the solid phases of the dry fractionation process, it seems that they have different physicochemical properties. The main reason is RBD-palm oil and palm olein which served as raw materials for dry fractionation have different levels of unsaturation. Iodine value (IV), slip melting point (SMP) and the yield of oil fractions from a multistage dry fractionation of RBD-palm oil are depicted on Figure 1.

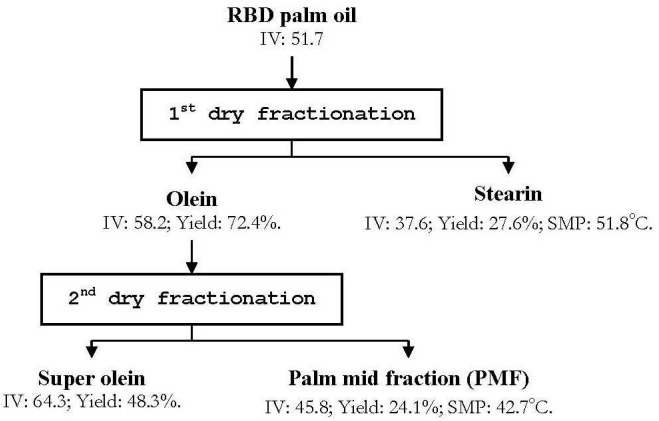

Figure 1. A multistage dry fractionation of RBD-palm oil

From the 1st dry fractionation, stearin was obtained at a yield of 27.6 % with IV: 37.6 and SMP: 51.8 °C. Stearin had a lower IV compared to RBD palm oil with an initial IV: 51.7. According to Knothe (2002), iodine value was used as a general measure of the unsaturation of the oil. IV shows the amount of double bonds present in the fatty acids. As the oil is more liquid (less saturated), it will impart a higher iodine value. This then showed that the stearin composed mainly of the more saturated fraction of triacylglycerols of RBD palm oil. The examples of high saturated triacylglycerols occurred

in the palm oil are trisaturated TAG (such as MPP, PPP and PPSt) and disaturated TAG (such as POP, POSt and MOP).

Palm mid fraction, at the other hand, was the hard fraction obtained from the 2nd stage of dry fractionation. The iodine value of palm mid fraction (IV: 45.8) was lower than that of RBD palm oil (IV: 51.7) and palm olein (IV: 58.2). It means the saturation degree of triacylglycerols present in the PMF was higher than that in RBD palm oil. However, it was shown that the saturation degree of triacylglycerols present in the PMF was still lower compared to palm stearin which had an IV: 37.6.

The crystallization temperature for the 2nd dry fractionation was also found significantly lower than the 1st dry fractionation. Since the iodine value of palm olein (IV: 58.2) was higher than the iodine value of RBD palm oil (IV: 51.7), palm olein had high-melting triglycerides with lower saturation degree compared to those of RBD palm oil. The lower saturation degree of triacylglycerols will impart the lower melting and crystallization temperature of those triacylglycerols. As the result, palm olein required a lower crystallization temperature to obtain sufficient amount of the solid fraction during the 2nd dry fractionation.

Triacylglycerols (TAG) Distribution of Palm Stearin and Palm Mid Fraction

According to Neff *et al*. (2001), triacylglycerol composition (i.e., kinds and quantities of individual TAG) and triacylglycerol structure (i.e., kinds and quantities of individual fatty acids (FA) located at the glycerol moiety carbons) affect the food formulation product functional properties, such as: melting point range, solid fat index, and crystal structure. These physical properties then affect food properties from texture to taste. Also, the fat oxidative stability is, partially, dependent on the TAG distribution and structure. The TAG content of the palm stearin and palm mid fraction was given in Table 1.

As shown at Table 1, palm stearin consisted mainly of POP (31.06 %), PPP (20.61 %) and POO (15.81 %) while palm mid fraction had POP (61.05 %) as the main constituent. These results were in accordance with the investigation done by Arima (2007). Although both palm stearin and palm mid fraction were hard fractions of dry fractionation, their TAG distribution were likely different. Palm stearin had trisaturated TAG (such as PPP and PPSt) and monounsaturated TAG (such as POP and POSt) as the main constituents. Meanwhile, palm mid fraction was composed mainly of monounsaturated TAG (such as POP, and POSt).

During the 1st dry fractionation, the high-melting glycerides of RBD-palm oil accumulated in the stearin fraction (as palm stearin). Palm stearin almost acquired all trisaturated TAG which is present in the RBD palm oil. It was shown that

Table 1. Triacylglycerols distribution of Palm Stearin and Palm Mid Fraction

TAG-species*	TAG distribution (%)	
	Palm Stearin	Palm Mid Fraction
LLO	0.26	tr**
PLL	0.89	0.88
OOL	0.84	0.92
POL	5.53	4.51
PLP	8.74	6.18
OOO	1.92	0.83
POO	15.81	5.63
POP	31.06	61.05
PPP	20.61	2.85
StOO	1.62	1.02
POSt	5.6	11.76
PPSt	5.65	3.13
StOSt	0.79	1.24
PStSt	0.68	tr

* Where: P (Palmitic), St (Stearic), O (oleic) and L (Linoleic). **tr: trace.

trisaturated TAG increased considerably in palm stearin while POP as the major TAG in RBD palm oil decreased. Trisaturated TAG in palm stearin increased up to 20.61 % and 5.65 % for PPP and PPSt, respectively.

On the 2nd dry fractionation, palm olein was used as the raw material. As the high-melting glycerides of RBD-palm oil accumulated in palm stearin, palm olein contained only small amount of trisaturated TAG. The high-melting glycerides of palm olein then shifted to the monounsaturated glycerides, especially POP whose melting temperature was just next to the trisaturated TAG. During the 2nd dry fractionation, monounsaturated TAG as the high-melting glycerides of palm olein accumulated in the solid fraction (as PMF). Palm mid fraction then was composed mainly of monounsaturated TAG (POP: 61.05 % and POSt: 11.76 %) in addition to a small amount of leftover trisaturated TAG (PPP: 2.85 % and PPSt: 3.13 %).

Melting Behavior of Palm Stearin and Palm Mid Fraction

From the melting thermogram obtained by DSC measurements, three parameters can be extracted namely melting temperature (T_M), offset temperature (T_O) and melting heat (ΔH_M). The melting temperature demonstrated the temperature at which the melting curve reaches their maximum, or so, the temperature at which the phase transition occurred the fastest. The offset temperature was determined by the intersection of the baseline at higher temperature with the absolute highest tangent of the curve. Meanwhile, the area

of the peak accounted for the total released melting heat. The non-isothermal DSC melting profiles were given in Table 2.

Table 2. Melting behavior of palm stearin and palm mid fraction as measured by DSC

Sample	Non-isothermal DSC melting profiles*		
	T_M (°C)	T_O (°C)	ΔH_M (J/g)
Palm Mid Fraction	38.5 ± 0.9	40.7 ± 1.3	116.7 ± 3.9**
Palm Stearin	46.7 ± 1.8	49.8 ± 1.6	128.4 ± 5.2

* T_M, T_O and ΔH_M were melting temperature, offset temperature and melting heat, respectively.

** Mean ± SD were reported.

According to Tan and Che Man (2002), accurate comparisons of the calorimetric experiments in the edible oils can only be done when DSC experiments were carried out at the same scanning rate. The use of slow scan rates was advisable in that it minimized instrumental lag in output response and, at a given temperature, the reaction being examined was closer to chemical equilibrium. In this research, the scanning rate of 5 °C was applied. However, several difficulties might be encountered in melting heat determination. Two of special significances were: (1) the baseline for the melting curve might not be horizontal, and (2) the peak was not generally symmetrical. The baseline of DSC curves was often different before and after a peak, due to changes in the physical properties of the sample during the reaction which produced the peak, and thus it was difficult to determine the baseline to be used for melting heat determination. Therefore, interpretation of melting heat must be done with caution.

As shown in Table 2, PMF had a lower melting temperature (T_M: 38.5 °C) than that of palm stearin (T_M: 46.7 °C). The lower melting temperature of PMF was caused by the higher unsaturation degree of TAG which was indicated by the higher value of IV compared to palm stearin. The higher unsaturation degree of TAG, the lower melting temperature will be. PMF will completely solidify at 40.7 °C while palm stearin will completely melt at 49.8 °C.

According to Nor Aini and Miskandar (2007), shortenings were referred to naturally occurring fats that were solid at room temperature and used to 'shorten' mainly baked products. Palm stearin will likely be suited as a base stock for shortenings. Palm stearin had the higher melting temperature and was composed mainly of trisaturated and monounsaturated triacylglycerols. Tripalmitin (PPP) is β crystal tending and can provide strength and structure to the products. In the Middle East, South, and Southeast Asian countries (particularly India), a shortening-like product called "*vanaspati*" was made by the hydrogenation of blended oils. In the Indian context, *vanaspati* was widely used as an inexpensive substitute for ghee (dehydrated butter oil), which has a grainy structure that was similar to *vanaspati*. Of the polymorphic forms, β crystals were the most desirable because of their bigger sizes, higher density and greater stability (Mayamol *et al.*, 2004).

PMF was softer than palm stearin. PMF will be more appropriate to be used as the raw material for margarine. Margarine is a water-in-oil emulsion in which water droplets are kept separately by the fat crystals. Due to its softness, PMF can provide and enhance the plasticity of the product at low temperature ranges. The quality of margarines is to some extent dependent on the formulation and processing. The melting point of the oil formulation can be adjusted by incorporating more liquid oil into the blend (Lai *et al.*, 2000).

Table 2 indicated that the melting heat of palm stearin (ΔH_M: 128.4 J/g) was higher than that of palm mid fraction (ΔH_M: 116.7 J/g). According to Tan and Che Man (2002), the oil sample with a higher degree of saturation requires more energy during the melting process. When the oil becomes more saturated, it will need higher energy for processing. In the industrial fractionation of vegetable oils, it is an important procedure to control the heat by varying the rate of heat removal and agitation.

Solid Fat Content of Palm Stearin and Palm Mid Fraction

The percentage solid fat content (% SFC) of palm stearin and palm mid fraction was measured as a function of temperature. In general, palm stearin had higher SFC at any temperature. As palm stearin was more saturated than palm mid fraction, palm stearin contained more high-melting glycerides. High melting glycerides melted later and imparted higher SFC at a given temperature. Palm stearin and palm mid fraction were almost completely melted at the temperature 35 °C and 60 °C.

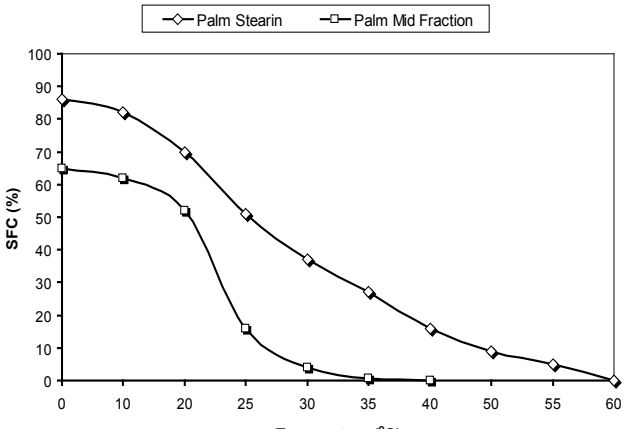

Figure 2. Solid fat content (%) of palm stearin and palm mid fraction

As shown at Figure 2, the SFC of palm stearin was gradually decreased form 86 % at 0 °C to almost completely

liquid at 60 °C. The trend of decreasing SFC on palm stearin might be affected by its wide-ranging TAG content which was mainly POP, PPP and POO. Nevertheless, the trend of decreasing SFC on palm mid fraction was found to be different. The SFC of palm mid fraction was slightly decreased from 0°C to 20°C and then suddenly dropped at 30°C. It was recognized that the TAG content of palm mid fraction which had only diunsaturated (POP and POSt) as the majority could give such effects.

According to Jirasubkunakorn *et al.* (2007), the crystallization behavior, crystal properties and melting profile of vegetable oils were important for their application in food products. Shortenings were required to display a plastic behavior across a range of temperatures. The solid fat content of the fat blend was a major factor that determined the texture of the fat. However, the fat crystal polymorph and the microstructure of the network of crystalline particles also determined the mechanical properties of the fat. As palm stearin had broader SFC, it would be more suitable for shortenings.

The physical properties of margarine were also dictated by the SFC, particularly of the high melting glycerides, because these TAG were thought to set the trend in the polymorphic crystal behavior (Lai *et al.*, 2000). The softer palm mid fraction could be utilized in the margarine formulation to give the best possible consistency requirements for composition, packing and handling.

CONCLUSION

Palm stearin and palm mid fraction had different physicochemical properties although both of them were the solid phases obtained from dry fractionation process. Palm stearin consisted mainly of POP (31.06 %), PPP (20.61 %) and POO (15.81 %) while palm mid fraction had POP (61.05 %) as the main constituent. From melting properties, palm stearin had a higher melting temperature (T_M: 46.7 °C) than that of PMF (T_M: 38.5 °C). It was also shown that, in general, palm stearin had higher solid fat content at any temperature compared to PMF.

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