DRY FRACTIONATION OF RBD (REFINED BLEACHED AND DEODORIZED) PALM OIL

Fraksinasi kering minyak sawit murni

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ABSTRACT

It has been done an investigation about dry fractionation of RBD-palm oil to obtain stearin and olein fractions. Dry fractionation was conducted using a pilot plant crystallizer equipped with a high pressure filtration. Initial palm oil comprised of two major TAG, namely POP (27.88 %) and POO (24.51 %). After dry fractionation, there were accumulations of more saturated TAG in stearin fraction (POP: 31.93 %, PPP: 21.89 %). Meanwhile, more unsaturated TAG was accumulated in olein fraction (POO: 30.76%, OOO: 6.84 %). At a yield of 65 %, it was produced the olein fraction with IV: 59.7 and CP: 3.9°C. It was also found that stearin fraction had a lower iodine value (IV: 35.8) than the original palm oil (IV: 51.4) because of the accumulation of more saturated TAG. Olein fraction also showed the similar result but at the other way around. These variations of chemical composition on the palm oil and its fractions influenced their thermal behavior. The thermogram of palm oil as measured by DSC showed two melting peaks. After dry fractionation, the higher melting peak still remained in the stearin fraction ($T_{p\text{-}stearin}$: 47.49°C) and the lower melting peak stayed on the olein fraction ($T_{p\text{-}olein}$: 6.01°C).

***Keywords**: dry fractionation, palm oil, olein, stearin, DSC*

ABSTRAK

Telah dilakukan penelitian tentang pengolahan minyak sawit murni menjadi fraksi padat (stearin) dan fraksi cair (olein) dengan proses fraksinasi kering. Fraksinansi dilakukan menggunakan alat skala laboratorium yang terdiri dari tabung kristalisasi yang dihubungkan dengan penyaringan bertekanan. Hasil penelitian menunjukkan bahwa di dalam minyak sawit murni terkandung dua komponen utama triacylglycerol (TAG), yaitu POP (27.88%) dan POO (24.51%). Setelah dilakukan proses fraksinasi, kandungan TAG dengan derajat kejenuhan tinggi terakumulasi pada fraksi stearin (POP: 31.93%, PPP: 21.89%). Sementara itu, pada fraksi olein terakumulasi TAG dengan derajat ketidakjenuhan tinggi (POO: 30.76%, OOO: 6,84%). Pada tingkatan hasil 65%, fraksi olein yang diperoleh mempunyai nilai IV ('iodine value'): 59.7 dan CP ('cloud point'): 3.9°C. Angka iod dari fraksi stearin (IV: 35.8) akan lebih rendah dari minyak sawit (IV: 51.4) karena terkonsentrasinya TAG dengan derjat kejenuhan tinggi. Hal yang berkebalikan terjadi pada fraksi olein. Fakta ini memperkuat grafik dari analisa DSC, dimana dua puncak leleh pada sampel minyak sawit akhirnya terpisah menjadi masing-masing satu puncak leleh utama pada fraksi stearin dan fraksi olein. Puncak leleh pada suhu yang lebih tinggi akan merujuk pada fraksi stearin ($T_{p\text{-}stearin}$: 47.49°C) sedangkan puncak leleh pada suhu yang lebih rendah akan merujuk pada fraksi olein ($T_{p\text{-}olein}$: 6.01°C).

***Kata kunci**: fraksinasi kering, minyak kelapa sawit, olein, stearin, DSC*

INTRODUCTION

Dry fractionation of fats and oils is the simplest and the cheapest among fractional crystallization processes. It is also well known as 'natural' or 'green' technology since the process does not dispose any effluent or chemical (Gibon, 2006). In contrast to detergent or solvent fractionation, dry fractionation does not require additional substances. The results of dry fractionation are stearin/hard-fraction and olein/liquid-fraction (De Greyt *et al*., 2003).

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The dry fractionation process mainly consists of two steps. The first step is the crystallization in which solid crystals are produced in a liquid matrix by a cooling process. The second step is a filtration process where the liquid phase is separated from the crystals (Hendrix and Kellens, 2007). In the crystallization stage, the oil is melted in order to destroy the memory effect before it is cooled in crystallizer chamber. The presence of crystal memory (seeds or lamellar structures within the melted state) can negatively affect the yield and process repeatability (Maalssen *et al.*, 1996).

According to Calliauw *et al.* (2005), the quantity of olein that is physically trapped on the crystals could significantly be decreased if the crystallization is conducted carefully. The round and spherical shaped crystals may help to reduce the olein from being trapped between crystals during filtration. For good separation, the crystal formed must be firm, sandy and uniformly spherical in size. The crystal shape and size distribution are determined by the way the melted oil is cooled and agitated (Zaliha *et al.,* 2004).

Recently, filter press is considered more economical by many users of fractionation plants. The advantage lies mainly for the higher olein yield by applying a pressure to the cake during filtration. High pressure can expel the liquid fraction that physically trapped on the crystal. The olein quality is normally not affected by the filtration pressure unless stearin passes through the filter cloth (squeeze through). This could eventually arise if the size and the thickness of the crystals are not adequate (Gibon, 2006).

The oil palm (*Elaeis guineensis*) originated from South Africa is the most efficient oil-producing plant with about 4.5 ton of oil per hectare per year. There are two distinct products of oil palm: the palm oil, which is derived from the fruits flesh, and the palm kernel oil, which is derived from the fruits kernel (Siew, 2002). A significant change in the oil palm industry has taken place during the past season, as Indonesia surpassed Malaysia in production of palm oil and is now the world leader. This designation will continue and Indonesia's production rate will outpace Malaysia for the foreseeable future. In 2006/07, Indonesia and Malaysia account for about 87 percent of world production where Indonesia and Malaysia contributed 15.900 and 15.881 million tons of palm oil, respectively. Indonesia is forecast to produce 18.3 million metric tons of palm oil in 2007/08 (Cruthfield, 2007).

Palm oil is by far the most important fractionated oil. Today, industrial installations exist that fractionate up to 2000 tons of palm oil per-day. Both crude and refined palm oil are fractionated, the latter being the predominant (De Greyt *et al*., 2003). It is the purpose of the research to characterize the chemical and melting behaviour of refined palm oil and its fractions by which the dry fractionation is applied as the separation technique.

MATERIALS AND METHODS

Materials

RBD (Refined, Bleached, and Deodorized) palm oil was obtained from Sumatra plantation. Then, the palm oil was subjected for dry fractionation to obtain the stearin and the olein fraction. The dry fractionation process was done in a pilot plant crystallizer equipped with high pressure filtration. All chemicals were either of analytical or high-performance liquid chromatography (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. The HPLC system consisted of Waters 515 HPLC pump, Waters 2414 refractive index detector, Waters 717 HPLC with auto sampler unit and Waters silica column.

Iodine Value (IV)

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

Slip Melting Point (SMP)

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

Mettler Cloud Point (CP)

Cloud points were determined with the FP-90/FP-81HT apparatus, supplied by Mettler Toledo. The procedure recommended by Mettler for edible oils and fats (cooling rate: -1^{o}C/min, starting at approximately 10 ^{o}C above the suspected cloud point) was used.

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 fast cooled to -80^{o}C at cooling rate -25^{o}C /min and kept for 1 min in order to ensure complete solidification.

Melting profiles were recorded from –80 to 70 °C at a heating rate of 25°C /min.

RESULTS AND DISCUSSION

RBD-palm oil was fractionated into stearin fraction (the cake, as solid phase) and olein fraction (the filtrate, as liquid phase). Physical appearances in room temperature (25-30°C), the stearin was solid while the olein was liquid compared to the initial palm oil that was semi-solid. The physical changes of the fractions compared to the initial RBD-palm oil were influenced mainly by shifted in the chemical compositions. As consequences, thermal behaviour of the oils was found to be different among each other.

Iodine Value (IV), Slip Melting Point (SMP) and Cloud Point (CP) Attributes

RBD-palm oil initially had an IV value 51.4 and cloud point 24.8°C. After dry fractionation process, stearin was produced with an IV value 35.8 and slip melting point 52.7°C and olein with an IV value 35.8 and cloud point 3.9°C. The dry fractionation of RBD-palm oil was depicted at Figure 1.

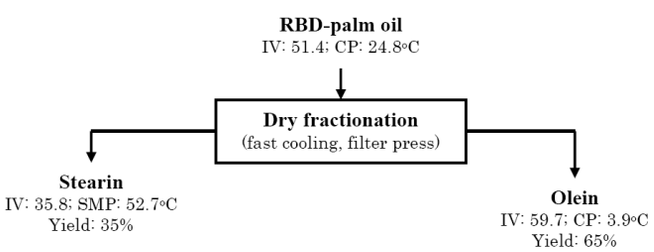

Figure 1. The dry fractionation of RBD-palm oil

Figure 1 showed that stearin had lower IV than RBD-palm oil. The decrease of IV value corresponded with the shifted form of semi-solid RBD-palm oil (IV: 51.4) into solid stearin (IV: 35.8). Iodine value is generally used as a measure of saturation / unsaturation of fats and oils. The higher saturation will impart the harder oil. It was demonstrated that stearin comprised more saturated triacylglycerols. Since IV measures the presence of the double bonds of the fats and oils, higher saturated triacylglycerols will result in the lower IV value. Contrariwise, higher unsaturated triacylglycerols that contain more double bonds will result in the higher IV value.

Saturated triacylglycerols obviously had higher melting properties compared to unsaturated triacylglycerols. As dry fractionation proceeds, the cooling stage had induced higher melting triacylglycerols to crystallize first. The different melting properties of various triacylglycerols will determine whether they were solid or remained liquid during the crystallization process. Olein which contained lower melting triacylglycerols had a lower cloud point (3.9°C) compared to RBD-palm oil and stearin.

Olein receives higher economical interest because its price is significantly higher than stearin. In industrial processes, the yield of olein was optimized to grab the economical advantage without sacrificing its quality parameters. In this investigation, dry fractionation with filter press could produce an olein with IV: 59.7 and CP: 3.9°C at a yield level of 65%. The olein fraction was clear at room temperature and suitable as frying oils.

Triacylglycerols Distribution of Palm Oil and Its Fractions

Since fractionation affects at first the triacylglycerol composition rather than the fatty acids composition of palm oil, HPLC can be used to monitor the fractions. HPLC is indeed an efficient and rapid method which separates the triacylglycerols by chain length and degree of unsaturation (Zainal and Yusoff, 1999). Triacylglycerols distribution of RBD-palm oil and its fractions was given in Table 1. With respect to the higher and lower melting fraction, the triacylglycerols have also been grouped in terms of saturated (S) and unsaturated fatty acids (U).

TABLE 1. TRIACYLGLYCEROLS DISTRIBUTION OF RBD PALM OIL AND ITS FRACTIONS

TAG-species	TAG distribution (%)		
	RBD-palm oil	Stearin	Olein
LLO	0.56	0.21	0.59
PLL	2.38	1.02	1.98
MLP	0.15	0.16	0.11
OOL	2.12	0.55	2.80
POL	11.13	5.69	12.87
PLP	8.90	8.52	9.62
MPP	0.48	1.66	-
OOO	4.21	1.80	6.24
POO	24.51	13.11	30.75
POP	27.88	31.93	26.62
PPP	5.74	21.89	0.25
StOO	3.22	1.01	3.24
POSt	6.28	5.61	4.45
PPSt	1.54	5.20	-
StOSt	0.64	0.86	0.48
PStSt	0.26	0.78	-
SSS **(Grouped TAG)***	8.02	29.53	0.25
SUS	43.85	47.08	41.28
SUU	41.24	20.83	48.84
UUU	6.89	2.56	9.63

* Where: S (saturated fatty acids) and U (unsaturated fatty acids); M (Myristic), P (Palmitic), St (Stearic), O (oleic) and L (Linoleic).

After dry fractionation, the chemical property of stearin and olein was found different to the initial chemical property of RBD-palm oil. RBD-palm oil mainly comprised POP, POO and POL with their distribution in the oil 27.88%, 24.51% and 11.13%, respectively. The distribution shifted to more saturated triacylglycerols for stearin with an increase in POP (31.93%) and a decrease in POO (13.11%) and POL (5.69%). It was observed also a remarkable increase in trisaturated content, such as PPP (from only 5.74% in RBD-palm oil to 21.89% in stearin).

The liquid fraction, olein, showed an increase of unsaturated triacylglycerols from the initial RBD-palm oil. The distribution of POO and POL increased to 30.75% and 12.87%, respectively. As a filtration process only included the liquid part for olein, the trisaturated triacylglycerols (PPP, PPSt, MPP and PStSt) were hardly seen present in the oil. The complete removal of very high melting triacylglycerols (such as trisaturated TAG) will assure the stability of olein toward cloudiness during storage.

The grouped-TAG demonstrated that the increase of monosaturated triacylglycerols (SUU) content in olein imparted higher iodine value. Compared to RBD-palm oil, the olein was enriched in monosaturated triacylglycerols. In contrast, the disaturated triacylglycerols (SSU) remained fairly close to that of RBD-palm oil. According to Deffense (1985), of the disaturated triacylglycerols (SSU and SUS), the asymmetrical isomer crystallized in the stearin while the symmetrical isomer occurred more in the olein due to the intersolubility effect. The last class, the triunsaturated triacylglycerols (UUU) was hardly different from that of palm oil except in the hard stearin.

Melting Behavior as Measured by Differential Scanning Calorimetry (DSC)

The DSC melting curve of RBD-palm oil was presented at Figure 2. In spite of the compositional complexity of RBD-palm oil, only two major peaks were displayed. The presence of two main groups of peaks in the thermogram was evidence for illustrating the easy separation of olein and stearin during the dry fractionation process. The melting peak at low temperature observed with the peak-maximum at 9.57°C could be associated to the contribution for the olein fraction. Meanwhile, the melting peak at high temperature observed with the peak-maximum at 43.72°C could be associated to the contribution for the stearin fraction.

The two major peaks displayed on DSC melting thermograms were due to the high diversity in the triacylglycerols composition of RBD-palm oil. Intersolubility and polymorphism were supposed to play a considerable role in the formation of the two major peaks. The position of low melting peak on RBD-palm oil thermogram seemed to correlate with SUU, symmetrical isomer of SUS and UUU content while the position of high melting peak seemed to correlate with SSS and asymmetrical isomer of SSU.

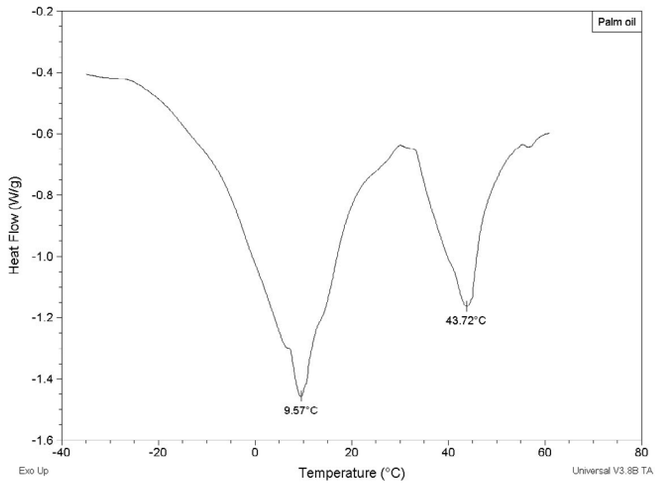

Figure 2. Melting behavior of RBD-palm oil as measured by DSC

As shown at Figure 3, the DSC melting curve of stearin fraction consisted of a major single peak in addition to a small peak with a shoulder at lower temperature. The major peak had a peak-maximum at 47.49°C which almost coincided with the melting peak at higher temperature on the melting thermogram of RBD-palm oil. It seemed that the high melting triacylglycerols of RBD-palm oil were retained in stearin fraction during fractionation process. HPLC analysis showed that the high melting triacylglycerols (such as PPP, PPSt and POP) were markedly increase compared to the initial distribution in RBD-palm oil.

A small peak with a shoulder on the heating thermogram of stearin fraction showed that the fractionation process still left some high unsaturated triacylglycerols in the hard

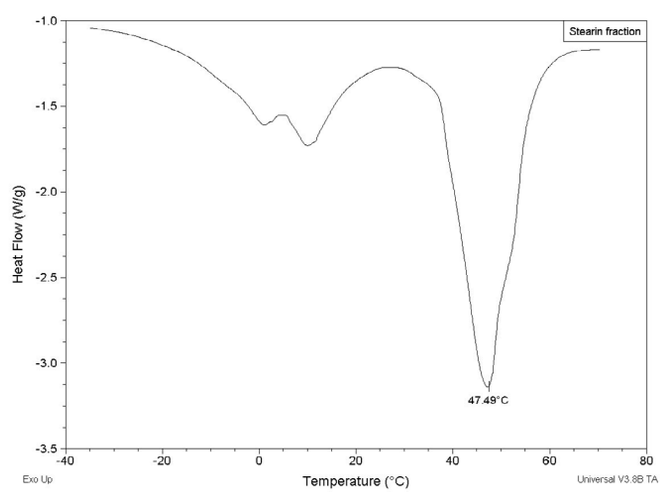

Figure 3. Melting behavior of stearin as measured by DSC

fraction (*e.g.* UUU: 2.56%). It will be impossible to remove all unsaturated triacylglycerols from the hard fraction since intersolubility and entrapment are always present on physical processes, such as dry fractionation. The small peak in the lower temperature of the melting thermogram most probably corresponded to UUU and SUU.

The DSC melting curve of olein fraction was presented at Figure 4. It was observed that the melting thermogram consisted of one major peak at the lower temperature in addition to a small peak with a long shoulder at the higher temperature. By comparing the peak-maximum of major peak on olein fraction (6.01°C) to the peak-maximum of the melting peak at lower temperature on RBD-palm oil (9.57°C), it was shown that the major peak of olein fraction could come from the melting peak at lower temperature on RBD-palm oil. The major peak of olein fraction most probably consisted of SUU and UUU.

A small peak with long shoulder at higher temperature of olein melting thermogram showed that high melting triacylglycerols were present in small quantity. The peak most probably correlated to SSS and some part of SUS. According to Plees (2006), small quantity of PPP or diacylglycerols could induce the crystallization at higher temperature. And it is naturally found that diacylglycerols will present in palm olein up to 5%.

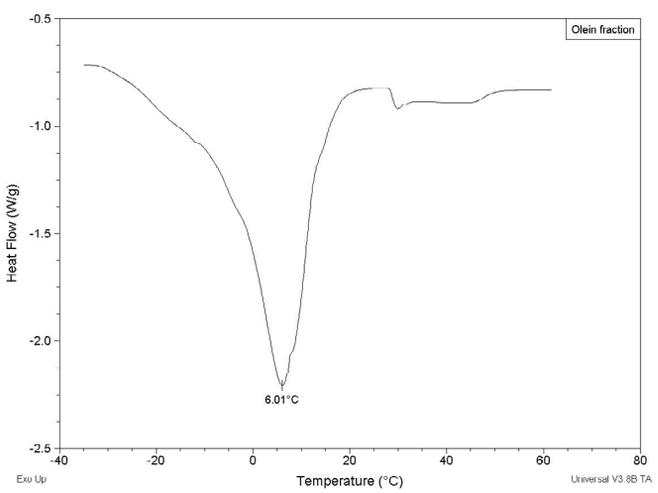

Figure 4. Melting behavior of olein as measured by DSC

CONCLUSIONS

The two endothermic peaks displayed on the thermogram of RBD-palm oil were separated into an individual peak of stearin and olein fraction after dry fractionation process. The melting peak at high temperature which comprised more saturated TAG was in the stearin fraction while the melting peak at lower temperature which comprised more unsaturated TAG was in the olein fraction. The dry fractionation process could produce an olein with IV: 59.7 and CP: 3.9 °C at a yield of 65%.

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