CORRELATION BETWEEN PHYSICOCHEMICAL PROPERTIES OF PALM SUPER/ TOP-OLEINS AND THEIR TRANSPARENT STABILITY

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ABSTRAK

Telah dilakukan proses fraksinasi bertingkat untuk meningkatkan nilai tambah RBD-palm olein. Palm olein difraksinasi menghasilkan super-olein dan super-olein difraksinasi ulang untuk menghasilkan top-olein. Dengan pengulangan proses fraksinasi akan diperoleh fraksi olein dengan derajat ketidak jenuhan yang makin tinggi. Hal ini ditunjukkan dengan makin meningkatnya angka iod dari RBD-palm olein (IV: 57.2) ke top-olein (IV: 71.3). Hasil analisis GC juga menunjukkan terjadinya peningkatan jumlah asam-asam lemak tidak jenuh, yaitu RBD-palm olein (53,88 %), super-olein (59,12 %) dan top-olein (67,51 %).

Penurunan kandungan lemak padat (SFC) teramati secara jelas pada fraksi-fraksi olein dengan derajat ketidak jenuhan yang makin tinggi. Pada suhu 0^{o}C, kandungan lemak padat RBD-palm olein, super-olein dan top-olein adalah 63,4 %, 43,5 % dan 4,3 %. Sedangkan pada suhu 25 ^{o}C, semua sampel minyak berada pada kondisi sepenuhnya cair. Hasil penelitian menunjukkan adanya keterkaitan antara sifat fisiko-kimia minyak fraksi olein dengan kestabilan sifat kejernihannya. Fraksinasi berulang minyak sawit terbukti dapat meningkatkan stabiltas sifat kejernihan. Minyak super-olein akan sesuai digunakan sebagai minyak masak atau minyak goreng sedangkan minyak top-olein mempunyai potensi untuk digunakan sebagai stok minyak untuk pembuatan minyak salad.

Keywords: Palm super-olein, top-olein, SFC, cloud point, transparent stability

INTRODUCTION

Palm oil is a vegetable oil characterized by a high content of Palmitic ($C_{16:0}$; 42.9 %) and Oleic ($C_{18:1}$; 40.8 %) in addition to Linoleic ($C_{18:2}$; 10.2 %) acids at a lesser degree. Refined, Bleached and Deodorized (RBD) palm oil is a semi-solid and forms slurry at ambient temperature within tropical regions with a saturated to unsaturated fatty acids ratio of about 1:1. Therefore, a fat modification process such as fractional crystallization is required to alleviate the problem (Deffense, 1985). Dry fractionation can be applied to modify palm oil properties by dividing the oil into palm olein (liquid fraction) and palm stearin (solid fraction). The process begins by cooling palm oil to get some parts of the oil solidified. A mixture of solid and liquid fractions will then exist in the palm oil after cooling stage. After that, olein fraction is immediately separated from stearin fraction using a filtration process. The quality of olein will be primarily dependent on the crystallization working condition (Hendrix and Kellens, 2007).

One of the most important properties of palm olein is its crystallization behavior. The unwanted crystallization of palm olein during storage may result the formation of cloudiness observed virtually in the bottle or other transparent packages. The presence of cloudiness is often thought as a defect by the consumers although there is no deterioration in the oil quality. It is generally recognized that the consumer demands clear oil without phase separation (Siew, 1998). According to Asadauskas and Erhan (1999), the common problems faced by vegetable oils at low temperatures include cloudiness, precipitation, poor flow ability and solidification. Palm olein that still contains a significant amount of saturated fatty acids (mainly Palmitic) is one of the most affected by that consumer preference. The poor cold stability of palm olein imparts a limitation on its applications especially as cooking oil and salad oil (Ooi *et al.*, 2005).

Cooking and salad oils are used widely in homes, caterers and food manufactures. Cooking and salad oils can be subdivided into salad dressings, household oils and commercial frying oils. Household cooking oils are commonly used for cooking and pan frying. Depending on the type of the oils, the desired physical appearances will be different. Frying oils do not require clarity and transparency as the oils are absorbed in the food. Contrary, cooking oils need to remain clear and transparent at room temperature. Even further, clarity during low temperature storage (< 0°C) is required by that of salad oils (Suk *et al.*, 1987).

The normal arbitrary standard of cloud points for an olein is 10°C or below. The cloud point refers to the temperature at which an olein turns cloudy when the oil is cooled at a rate of 1°C per min. For that reason, most of the commercial palm olein falls into a relatively narrow range of iodine values (56-58). When the purpose is to produce an olein for temperate and cool climates, the required specifications then become more stringent such as a cloud point below 5°C and a minimum iodine value of 60 (Deffense, 1985).

In order to achieve such specifications, fat modification process can be introduced. A multistage dry fractionation is a recommended technique for its simplicity and effectiveness to get oleins with higher iodine value (IV). In the first stage, fractionation produces an olein from the original palm oil. In the second stage, fractionation of palm olein yields a product of higher IV called double-fractionated palm oil or super-olein. In the third stage, fractionation of palm super-olein yields a product of even higher IV called triple-fractionated palm oil or top-olein (Gibon, 2006). In fact, the modification of compositionally heterogeneous palm oil into well-defined fractions with a high added value has always been one of the main challenges of dry fractionation technology (Calliauw *et al.*, 2007).

In this study, attempts were made to characterize the physicochemical properties of RBD-palm olein and its liquid fractions (super-olein and top-olein) obtained by multistage fractional crystallization. Correlation of the physicochemical properties to their transparent stability was then used to evaluate the oil quality and possibility being used for certain types of commercial oils.

MATERIALS AND METHODS

Materials

RBD-palm olein was obtained from a local refinery in the Sumatra plantation. Then, the palm olein was subjected for multistage dry fractionation to obtain palm super-olein and top-olein. A laboratory scale crystallizer equipped with cooling water bath (Julabo, Germany) and pressure filter was used. First RBD-palm olein was melted completely at 70°C for 15 min. The oil was then cooled and kept isothermal at 12°C for 20 hours. And then, the liquid fraction was filtered and collected as palm super-olein. The similar procedure was applied to obtain palm top-olein from the super-olein except the isothermal temperature was set at 6°C.

All chemicals used in this research were either of analytical or high-performance liquid chromatograph (HPLC) grades.

Iodine value (IV)

The IVs of the palm olein, super-olein and top-olein were determined using the AOCS officially recommended method Cd 1b–87.

Mettler Cloud point (MCP)

Cloud points were determined with the FP-90/FP-81HT apparatus supplied by Mettler Toledo. The oleins were filled in capillary tubes to a height of 5 mm and placed in FP-81HT measuring cell. The samples were then cooled at a rate of 1°C/min from a starting temperature at about 10°C above the suspected cloud point. Eventually the result could be read from the FP-90 central processor. Triplicate measurements were done for each sample.

Determination of Fatty Acids (FA) composition

Fatty acid composition of oleins was determined through direct methylation with sodium methoxide and methanol. The obtained fatty acid methyl esters were then diluted with isooctane and were injected into a gas–liquid chromatograph (GLC). The methyl esters were analyzed by GLC (Shimadzu model GC-14B) fitted with a 2 m × 1/8″ stainless steel column packed with GP 3 % SP-2310/2 % SP–2300 on Chromosorb W AW. Injector and detector temperatures were at 230°C. Column oven was operated at a constant temperature of 200 °C. The flow rate of nitrogen carrier gas was 50 mL/min. Individual peaks of fatty acid methyl esters were determined with a Chromatopac Integrator using the retention time of corresponded fatty acid standards. In this research, peaks having an area less than 0.2 % were considered as traces or baseline noises. As the palm olein sample was refined oil and its fatty acid composition was well known, the remaining peaks were then rounded up back to 100 %.

Transparent stability

Cold test was determined according to AOCS Official Method Cc 11-53. Oleins were heated to 130 °C to remove moisture and crystals that may have been present. The oils were then filtered and filled in 200 mL bottles completely. Next, the bottles were equilibrated at 25 °C in a water bath followed by an ice-water bath for 5.5 h. Oils that remained visually clear after 5.5 h passed the cold test.

Subsequently, the modification of cold test was done by storing the samples at cool temperature (20 °C and 10 °C). The observation for cloudiness was conducted every day for a maximum period of 90 days.

Solid fat content (SFC)

Solid fat content 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 for 15 min to erase the crystal memory and chilled at 0°C for 90 min. Then, the oils were held at each measuring temperature (0 °C, 5 °C, 10 °C, 15 °C, 20 °C and 25 °C) for 30 min prior to measurements. The average result of triplicate measurements was reported.

RESULTS AND DISCUSSION

Palm olein may further be fractionated to obtain fractions which will suit for certain functions, such as for cooking oil or salad oil. The versatility of those fractions is affected by the degree of fractionation. The resulted physicochemical properties of olein fractions (super-olein and top-olein) will mostly determine their quality and usage in commercial products. Therefore, the oleins have a strong potency in providing various types of edible oil among other vegetable oils.

Iodine value (IV) and Mettler cloud point (MCP) of oleins

RBD-palm olein initially had an IV value 57.2 and cloud point 6.6 °C. After the second stage fractionation, super-olein with an IV value 62.8 and cloud point 2.7 °C was produced. In the third stage, super-olein was further fractionated resulting top-olein with an IV value 71.3 and cloud point -3.7 °C. Iodine value (IV) and cloud point (MCP) of RBD-palm olein, super-olein and top-olein were given in Table 1.

Table 1. Iodine value (IV) and cloud point (MCP) of RBD-palm olein, super-olein and top-olei

Parameters	Samples*		
	RBD-palm olein	Super-olein	Top-olein
Iodine value	57.2±0.45	62.8±0.31	71.3±0.39
Cloud point (°C)	6.6±0.13	2.7±0.11	-3.7±0.26

* The average and standard deviation of triplicate measurements were given.

As shown in Table 1, a multiple stage dry fractionation yielded oleins toward increasing iodine values. During dry fractionation, higher melting triacylglycerols were crystallized out first while lower melting triacylglycerols remained in the liquid fraction. Nevertheless, the liquid fraction still possessed some degree of saturation. In a multistage dry fractionation, therefore, the later stage required a lower crystallization temperature. Mamat *et al*. (2005) confirmed that lower fractionation temperature resulted in the olein having more unsaturated fatty acids compared to those at higher fractionation temperatures. As iodine value measures the amount of double bonds, oils holding more unsaturated fatty acids will have higher iodine value. It means that top-olein has the highest degree of unsaturation compared to the other two oleins.

Cloud point of oleins had a negative correlation to its iodine value as indicated in Table 1. It is known that unsaturated fatty acids have lower melting points compared to saturated fatty acids. As consequence, oils with higher unsaturation give lower crystallization temperatures. Cloudiness can be used as a simple visual tool for the indication of oil solidification. The major components of clouding material in palm olein commonly are saturated triacylglycerols in addition to several minor components such as free fatty acids and diacylglycerols. Sulaiman *et al.* (1997) showed that trisaturated triacylglycerol (such as PPP, MPP and PPS) strongly induced clouding of palm olein. For certain types of palm olein with very high iodine value, saturated diacylglycerol (especially 1,3-dipalmitin) started to play a role on clouding since the amount of trisaturated triacylglycerol depleted.

Fatty acids composition of oleins

The composition of fatty acids in the samples was measured by gas chromatography (GC) after a conversion of the fatty acids to their equivalent methyl esters to increase volatility in the carrier gas. Consequently, fatty acid compositions were calculated as fatty acid methyl esters (FAME). Compositions of saturated and unsaturated FAME in the samples were given in Table 2.

Table 2. Fatty acids composition of RBD-palm olein, super-olein and top-olein

TAG-species	FAME composition (%)		
	RBD-palm olein	Super-olein	Top-olein
M (Myristic)	1.14	0.99	0.67
P (Palmitic)	40.76	34.91	26.17
S (Stearic)	4.32	4.98	5.65
Total: (Saturated fatty acids)	**46.22**	**40.88**	**32.49**
O (Oleic)	43.29	47.23	53.63
L (Linoleic)	10.59	11.89	13.88
Total: (Unsaturated fatty acids)	**53.88**	**59.12**	**67.51**

RBD-palm olein contained both saturated and unsaturated fatty acids. As shown in Table 2, palmitic acid (C16:0) was the main component in the saturated fraction of RBD-palm olein followed by stearic acid (C18:0) and myristic acid (C14:0). The amount of saturated fatty acids in RBD-palm olein was 40.76 %, 4.32 % and 1.14 % for palmitic, stearic and myristic acid, respectively. The total amount of saturated fatty acids was decrease as RBD-palm olein continued to be refractionated, from 46.22 % in RBD-palm olein to 32.49 % in top-olein. According to Neff *et al*. (2001), types and quantities of individual fatty acids (FA) in triacylglycerols (TAG) affected the functional properties of oil such as: melting point range, solid fat index, and crystal structure. These physical properties eventually determined the end food product attributes especially texture and hardness. Also, the fat oxidative stability was dependent on the degree of fatty acid unsaturation. Triacylglycerols with high degree unsaturation oxidized faster resulting in shorter shelf life.

As shown in Table 2, unsaturated fatty acids in the samples were mainly oleic acid (C18:1) and at a lesser degree of linoleic acid (C18:2). The amount of unsaturated fatty acids in RBD-palm olein was 43.29 % and 10.59 % for oleic acid and linoleic acid, respectively. Other unsaturated fatty acids namely palmitoleic acid (C16:1) and linolenic acid (C18:3) were too low to be detected. However, both fatty acids alongside with lauric acid (C12:0) might be found as traces in palm olein (Edem, 2002). No *trans*-fatty acids were found in any of the samples. The total amount of unsaturated fatty acids was increase as the oleins further refractionated, from 53.88 % in RBD-palm olein to 67.51 % in top-olein. Liu *et al.* (2002) demonstrated that oleic acid (C18:1) possessed the beneficial property of lowering LDL-cholesterol (thus reducing the risk of cardiovascular disease) while maintaining the oxidative stability. Thus, oleins had a combination of physical and nutritional advantageous over either saturated vegetable oils or hydrogenated oils.

Solid fat content (%SFC) and transparent stability of oleins

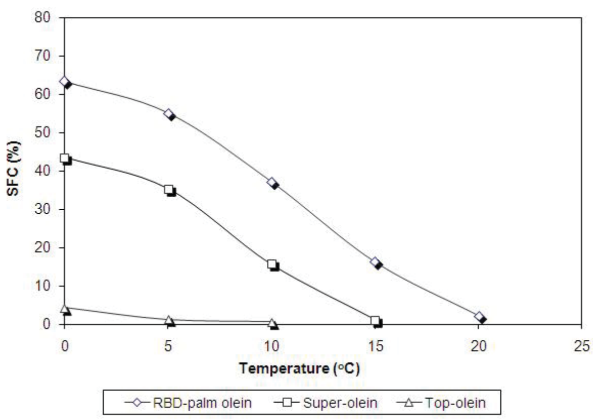

Figure 1. Solid fat content (%) of RBD-palm olein, super-olein and top-olein

The solid fat content (SFC) of each olein was measured as a function of temperature. As shown in Figure 1, the SFC of RBD-palm olein had higher values than the SFC of super-olein and top-olein. At temperatures above 25^{o}C, all oleins were completely melted. In general, it was also found that the evolution of SFC curves was dependent on the measuring temperatures where those of lower temperatures had higher rates. For example, top-olein was completely liquid at 15^{o}C while super-olein and palm-olein contained a solid fat of 1.1% and 16.3 % respectively. When it was measured at 0 ^{o}C, the SFC value of top-olein increased slightly to 4.3 % while those of super-olein and palm-olein increased significantly to 43.5 % and 63.4 % respectively. As a multistage dry fractionation proceeded, it was produced oleins with more unsaturated fatty acids content. It also meant that larger portion of high melting point TAGs was removed from the oleins with the advancements of dry fractionation.

Palm olein is preferred for deep frying medium in the snack foods industry. The oil is often regarded as a heavy duty frying oil where reusing of the oil is considered to be normal. It can be done as palm olein consists mainly of saturated fatty acid (palmitic) and monounsaturated fatty acid (oleic) which are oxidatively stable (Haizam *et al.*, 2008). Nevertheless, Nor Aini *et al.* (1992) stated that retail markets require the clear, bright, and attractive oil. The reason is that they sell the oil in transparent plastic containers or glass bottles. This fact suggests that there is a demand of oils with low solid fat content at lower temperature such as super-olein and top-olein.

Transparent stability of RBD-palm olein, super-olein and top-olein was measured by cold test and its modifications. The modification tests included observations of the oleins for cloudiness by storing them at cool temperature (20 ^{o}C and 10 ^{o}C). Table 3 showed that top-olein had satisfactory transparent stability while super-olein remained clear for 39 days in the storage at 20 ^{o}C. Since consumer demands clear cooking oil, super-olein is appropriate for both tropical and temperate regions while top-olein possess even a higher quality. On the other hand, RBD-palm olein can cater a limited market, suitable mainly in tropical region.

Table 3. Transparent stability of RBD-palm olein, super-olein and top-olein

Transparent stability	Samples		
	RBD-palm olein	Super-olein	Top-olein
Storage at 20^{o}C*	7 d	39 d	> 90 d
Storage at 10^{o}C	< 1 d	1 d	12 d
Cold test	Fail	fail	fail

* The modification test was conducted utmost for 90 d (days) in a cool room. Oil that begun to cloud indicated fail on the cold test.

Oils destined for the manufacture of salad dressings must remain clear at refrigerated temperatures because crystallization will destabilize emulsions. A good quality salad oil should pass cold test which states that the oil must remain clear for 5.5 h at 0 °C (Nor Aini *et al.*, 1992). Unfortunately, all three samples failed the cold test as shown in Table 3. However, top-olein only contained a trace amount of crystals at 0 °C and remained clear for 12 days at 10 °C. Vereecken *et al.* (2009) showed that melting point of saturated triacylglycerols can be depressed by blending it with liquid oil. In an ideal system, the decrease on melting point can be estimated by Hildebrand equation. Therefore, top-olein can possibly be used as salad oil after having minor modification such as blending the oil with other higher unsaturated liquid oils.

CONCLUSION

Utilizing a multistage dry fractionation, RBD-palm olein can be further fractionated to obtain super-olein and top-olein. The latter fraction possesses the highest iodine value but lowest cloud point as it contains more unsaturated fatty acids than that of others. Cloud point of oleins has a negative correlation to its iodine value and oleins with lower cloud point have better transparent stability during storage at low temperature. Based on the cold stability test and solid fat content, RBD-palm olein will be suitable as cooking oil in tropical countries while super-olein will fit as cooking oil in more temperate regions. For future work, top-olein will be mixed with those of higher unsaturated liquid oils to get oil blends which have appropriate properties as salad oil.

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