International Food Research Journal 22(4): 1390-1395

Journal homepage: *http://www.ifrj.upm.edu.my*

Physicochemical properties of palm oil and palm kernel oil blend fractions after interesterification

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Article history

Received: 24 July 2014
Received in revised form: 17 December 2014
Accepted: 22 December 2014

Keywords

Fractionation
Chemical interesterification
Enzymatic interesterification
Palm oil
Palm kernel oil

Abstract

The objective of this study was to determine the physicochemical properties of olein and stearin fractions obtained from non-interesterified (NIE), chemically interesterified (CIE) and enzymatically interesterified (EIE) 50:50 palm oil and palm kernel oil blend. The potential applications of both olein and stearin fractions were also identified. Stearin and olein fractions were obtained through a single stage dry fractionation at 25°C. The physicochemical properties analysed include percent yield, fatty acid composition (FAC), iodine value (IV), smoke point, cloud point, slip meting point (SMP) and solid fat content. Results indicated that the percent olein yield was higher from the EIE (85%) and NIE blends (82.2%) than in CIE blend (41.8%). The EIE blend produce liquid fraction with the highest amount of unsaturated fatty acid (~50%). Hence, the olein fraction of EIE blend best met the requirement to be used as frying oil based on the highest smoke point (265.1°C) and lowest cloud point (6.2°C). On the other hand, the stearin fraction of CIE blend might be suitable to be used in margarine formulation as it has SMP close to body temperature.

Introduction

Oil palm *(Elaeis guineensis)* produces two different types of oil which are palm oil and palm kernel oil. The fruit of oil palm yields about 20-22% of its oil from the fibrous mesocarp and 10% of the total yield is from the white kernel flesh (Berger & Noraini, 2005). The application of palm oil and palm kernel oil are very limited in their original form due to their specific chemical composition. To diversify the functions and usage of fats and oils, modification is done especially to improvise the physicochemical characteristics and stability. The frequently used modification methods are fractionation, hydrogenation, blending and interesterification (Khalid *et al.*, 2011). Blending technique is the simplest and cheapest way to modify oils. However, blending does not result in chemical modification of the triacylglycerols composition (Chen *et al.*, 2007).

Interesterification (IE) is a process of rearranging fatty acids within and between triacylglycerols, resulting changes in physicochemical properties of the oils and fats. It has long been used for modification of fat and oil mixtures in industries. The process produces randomly distributed fatty acid residues among the triacylglycerols and usually carried out at high temperature (Zaida and Yusof, 1999; Fauzi *et al.*, 2013). On the other hand, enzymatic interesterification can be regiospecific, react at low temperatures and easy to handle (Ajithkumar, 2011). Palm oil is semisolid at room temperature, while palm kernel oil contains triacylglycerols that melted sharply at about body temperature.

By applying the modification techniques, new product such as oil suitable for edible purposes can be obtained. Hence, the objectives of this study was to determine the physicochemical properties of olein and stearin fractions obtained from the 50:50 non-interesterified, chemically interesterified and enzymatically interesterified palm oil and palm kernel oil blends. The most suitable stearin and olein fractions obtained from this study will be identified for certain food applications.

Materials and Methods

Materials

Refined, bleached and deodoursed (RBD) palm oil (PO) and palm kernel oil (PKO) were obtained from Golden Jomalina Sdn. Bhd., Klang, Malaysia. The chemicals used were either analytical or HPLC grade. Commercial immobilised *Themomyces*

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lanuginosus lipase, Lipozyme TL IM was obtained from Novozyme (Denmark). Palm oil and PKO were melted at 60°C before blending at 50:50 (w/w) ratio.

Chemical and enzymatic interesterification

Chemical and enzymatic interesterification of the oil blends were conducted according to MPOB Test Method (2004) using sodium methoxide and Lipozyme TL IM as catalysts, respectively.

Dry fractionation

Dry fractionation was carried out using a circulatory refrigerated bath (ThermoHaake C25P, Karlrushe, Germany). About 100 g sample was placed in 200 ml borosilicate glass bottle. Sample was heated in the bath at 70˚C for 30 min to destroy the crystal nuclei. The sample was then cooled (using ramping mode) in the same bath to 25˚C in 1 h. While holding at 25˚C for 90 min, the sample was continuously stirred with a helix stirrer (Ika RW11 Labortechnik, Staufen, Germany) at a constant speed of 100 rpm. After 3 h of total heating, cooling and holding time, the sample was immediately subjected to vacuum filtration with Whatman No. 4 filter paper. While filtering, temperature was maintained at 25˚C until filtration process completed.

Percent yield

After dry fractionation process, liquid fraction collected from the conical flask was weighed and reported as olein yield (g) while solid fraction on the filter paper was weighed and reported as stearin yield (g). The percentage of yield was calculated as follow:

% Olein = Olein yield (g)/Olein + Stearin (g) x 100%
% Stearin = Stearin yield (g)/ Olein + Stearin yield (g) x 100%
where,

Olein + Stearin yield (g) = 100 g (as the total sample used in this study)

Fatty acid composition

A gas chromatograph (Agilent 6890N) with flame ionisation detector (GC-FID) was used for determination of fatty acid composition. Fatty acid methyl esters (FAME) were prepared by acidic catalysed esterification. Fifty mg of sample was saponified for 30 min using 10 ml of KOH (0.5 mol/l). One ml of concentrated H_2SO_4 then was added. After 30 min, the FAME was extracted with 25 ml of hexane. One µl of the solution was used for injection. The capillary column (EC-WAX, Alltech) 30 m × 0.25 mm ID was used for FAME analyses with temperature of detector at 300°C. Helium with flow rate of 1.5 ml/min was used as carrier gas and oven temperature was set at 220°C. Identification of fatty acid composition was determined by comparing peak retention times with commercial standards.

Iodine value

Iodine value (IV) was determined according to MPOB Test Method (2004). Blank and triplicate determinations were carried out under same conditions. Iodine value was calculated using the following equation:

$$IV = \frac{12.69\ M\ (Vb - Vs)}{W}$$

M = Molarity of sodium thiosulphate solution used
Vb = Volume in mL of sodium thiosulphate solution used for blank test
Vs = Volume in mL of sodium thiosulphate used for sample test
W = Weight in gram of sample

Cloud point

Determination of cloud point was conducted according to MPOB Test Method (2004). The oil sample (60-75 g) was filtered through a Whatman No. 1 filter paper. The filtered oils were heated to 130˚C for 5 min and about 45 ml of the heated oil was poured into a Beatson sample bottle. The bottle and content were cooled in a water-bath that was thermostatically controlled at 5˚C below the expected cloud point. The oils were kept stirred while cooling to prevent super-cooling and solidification of fat crystals on the side or bottom of the bottle. The bottle was removed from the bath and inspected regularly. The cloud point was taken as the temperature at which that portion of the thermometer immersed in the oil is no longer visible when viewed horizontally through the bottle and sample. Samples were run in triplicate and average values were taken.

Slip melting point

Slip melting point (SMP) was determined according to AOCS Method Cc.3.25 (AOCS, 1990). In this method, capillary tubes were filled with fat until 1 cm high column. The temperature at which the fat column rises was reported as SMP. Samples were run in triplicate and mean values were calculated.

Solid fat content

Solid fat content (SFC) was measured using a minispec pulsed Nuclear Magnetic Resonance

Table 1. Percent yield, iodine value, slip melting point, smoke point and cloud point of NIE, CIE and EIE of 50:50 PO:PKO (w/w) blend fractions

Sample	Fractions	Iodine Value	SMP (°C)	% Yield	Smoke Point (°C)	Cloud Point (°C)
NIE	Olein	39.32 ± 0.6^{b}	-	82.82 ± 1.7^{a}	231.67 ± 6.4^{b}	10.97 ± 0.2^{a}
CIE		40.12 ± 1.6^{b}	-	41.75 ± 0.7^{b}	243.30 ± 9.4^{b}	7.93 ± 0.2^{b}
EIE		49.17 ± 1.1^{a}	-	85.04 ± 2.9^{a}	265.13 ± 9.2^{a}	6.27 ± 0.2^{c}
NIE	Stearin	27.42 ± 1.9^{b}	48.33 ± 1.2^{a}	17.18 ± 1.7^{b}	-	-
CIE		33.08 ± 0.3^{a}	36.67 ± 1.2^{c}	58.25 ± 0.7^{a}	-	-
EIE		29.91 ± 2.8^{ab}	44.33 ± 1.2^{b}	14.96 ± 2.9^{b}	-	-

Notes: ^{a,b,c} Means in the same column within the group with different letters are significantly different ($p<0.05$). NIE, Non-interesterified; CIE, Chemically interesterified; EIE, Enzymatically interesterified; SMP, Slip melting point

(pNMR) spectrometer (Bruker, Karlrushe, Germany). The MPOB parallel method was used, in which sample in NMR tube was first melted at 70˚C for 30 min, followed by chilling at 0˚C for 90 min, and then held at each measuring temperature for 30 min prior to measurement (MPOB Test Method, 2004). The process of melting, chilling and holding of samples were carried out in a pre-equilibrated thermostatted water baths. Samples were run in triplicate and the values were averaged.

Smoke point

The temperature at which samples give off a thin, continuous stream of bluish smoke was measured according to AOAC Method (1999).

Statistical analysis

Selected data obtained were subjected to one-way ANOVA to determine significant differences among the samples defined at $p<0.05$. Data analysis was performed using SPSS program version 17.

Results and Discussion

Percent yield

The percent olein and stearin yields are given in Table 1. The enzymatic interesterified (EIE) and non-interesterified (NIE) 50:50 PO:PKO blend significantly ($p<0.05$) produced higher olein fraction (85.0% and 82.8%, respectively) than chemically interesterified blend (41.8%). While for stearin fraction, CIE 50:50 PO:PKO blend produced significantly higher ($p<0.05$) yield (58.2%) than NIE and EIE (17.2% and 14.9%, respectively). In dry fractionation, high and low melting triacylglycerols are separated by partial crystallisation based on differences in melting points of triacylglycerols and followed by filtration (Sellami *et al*., 2012). Triacylglycerols are redistributed into two phases during dry fractionation process. The more saturated triacylglycerols are gradually concentrated into solid phase (stearin) as the fractionation process proceeds while the more unsaturated one is left in the liquid phase (olein).

Iodine value

Iodine value (IV) is a measure of degree of unsaturation and is used to characterise fats and oils. The iodine values for both fractions of NIE, CIE and EIE 50:50 PO: PKO are shown in Table 1. The EIE olein fraction had significantly ($p<0.05$) higher IV than CIE and NIE olein fractions. For stearin fraction, the CIE had significantly higher ($p<0.05$) iodine value than NIE but was not significantly different ($p>0.05$) from the EIE. The olein fractions had high IV than their respective stearin fractions indicating olein fractions were more unsaturated than their stearin fractions. Iodine value of olein is related to smoke point and cloud point of the blend fractions. The higher the iodine value, the higher the smoke point and the lower the cloud point.

Most of the low melting triacylglycerols (TAG) had been separated during the single dry fractionation process. Result shows that EIE olein has the best properties as frying oil as it has significantly the highest ($p<0.05$) smoke point and the lowest cloud point. The iodine value of stearin fractions are related to slip melting point of fats. The higher the degree of unsaturation, the lower the slip melting point will be. In this study, the CIE stearin fraction has the highest IV and the lowest slip melting point as shown in Table 1.

Slip melting point

The slip melting points of NIE, EIE and CIE stearin fraction is given in Table 1. The slip melting point of NIE stearin (48.3°C) was significantly highest ($p<0.05$) among the EIE (44.3°C) and CIE (36.7°C). The stearin fraction of NIE blend melted at highest temperature indicating it is more saturated than CIE and EIE stearins. The slip melting point of the NIE, EIE and CIE oil blends before dry fractionation were 27.7°C, 27°C and 29.5°C, respectively. Changes in melting characteristics of stearin are generally due to redistribution of the fatty acid chains within the triacylglycerol molecules (Sellami *et al*. 2012).

Table 2. Fatty acid composition (%) of NIE, EIE and CIE 50:50 PO:PKO blend fractions

Fatty acid	Fractions	NIE 50:50 PO:PKO	EIE 50:50 PO:PKO	CIE 50:50 PO:PKO
C12:0	Olein	23.45	31.27	23.71
C14:0		8.46	4.89	8.50
C16:0		26.49	10.15	25.16
C18:0		3.27	4.23	2.89
C18:1		31.45	40.58	32.37
C18:2		6.87	8.88	7.37
C12:0	Stearin	23.79	23.25	24.46
C14:0		10.13	9.91	9.06
C16:0		34.51	32.70	29.52
C18:0		3.75	3.68	3.72
C18:1		22.84	25.07	27.06
C18:2		4.97	5.39	6.18

Notes: C12:0, Lauric; C14:0, Myristic; C16:0, Palmitic; C18:0, Stearic; C18:1, Oleic; C18:2, Linoleic; EIE, Enzymatically interesterified; CIE, Chemically interesterified; NIE, Non-interesterified, PO, Palm oil; PKO, Palm kernel oil

The low and high melting triacylglycerols has been separated by partial crystallisation and fitration in dry fractionation process.

Sakina (2000) revealed that interesterified fat made with blends of palm oil had the slip melting point decreased as quantity of palm kernel oil in the mixture increased due to presence of short or medium chain fatty acids in palm kernel oil. Melting properties of stearin become very important characteristic in making food products especially margarine. According to deMan *et al*. (1989), margarine that has fairly low solids at low temperatures allow it to be spreadable directly from refrigerator. In addition, fat blends should be completely melted below 37°C for good oral melt down. Hence this study shows that CIE stearin is suitable to be used as table margarine as it has melting point close to 37°C.

Smoke point

The smoke point of NIE, EIE and CIE 50:50 PO: PKO olein fraction is as indicated in Table 1. The EIE olein fraction had significantly higher ($p<0.05$) smoke point (265.1°C) than olein obtained from NIE (231.7°C) and CIE (243.3°C) blends. According to Berger (2005), the recommended smoke point for palm oil must be above 215°C (preferably above 220°C) and smoke point of oil is dependent on the content of some minor component especially the free fatty acids. Based on the result, the olein blend fractions analysed were suitable to be used as frying oil. The higher the smoke point, the better the frying oil will be. The EIE blend fraction has the best quality as frying oil as it has the highest smoke point.

Cloud point

Cloud point is an important analysis to determine the temperature at which oil turned to be cloudy due to the first stage of crystallisation. The cloud points of olein obtained from all blends ranged between 6.3 to 11°C as shown in Table 1. The NIE olein had significantly ($p<0.05$) the highest cloud point (10.9°C) followed by CIE (7.9°C) and EIE (6.3°C). The olein of NIE blend appeared to be cloudy at high temperature compared to CIE and EIE olein. The lowest cloud point of olein from EIE blend was due to higher unsaturated fatty acids (as indicated in Table 2) compared to olein from the NIE and CIE blends. The cloud point is closely related to degree of unsaturation where the more unsaturated a sample is, the lower the cloud point will be (Khalid *et al*., 2011). Lai *et al.* (2005) reported that cloud point value for palm oil is +11.5°C. This shows that chemical and enzymatic modification of palm oil and palm kernel oil blend render the cloud points of olein to be lower than normal palm oil.

Solid fat content

The suitability of oils and fats for a particular application is greatly influenced by their solid fat content (SFC). This characteristic is important to determine the spreadability, general appearance and organoleptic properties of fat and oil especially margarine (Jirasubkunakorn *et al.*, 2007). The solid fat content of stearin fraction is related to fatty acid content and triacylglycerol in that particular component. The SFC of stearin is given in Figure 1.

The SFC profiles of all the stearin fractions were similar. Generally, the NIE stearin had high SFC value compared to EIE and CIE stearin. The NIE stearin totally melted at 50°C, while EIE stearin and CIE stearin melted at 45°C and 40°C, respectively. There were no significant difference ($p>0.05$) in SFC between the EIE and CIE stearin fractions at all measured temperatures. High amount of saturated fatty acids contributed to high SFC.

Fatty acid composition

The fatty acid composition of olein and stearin fractions are shown in Table 2. The major fatty acid

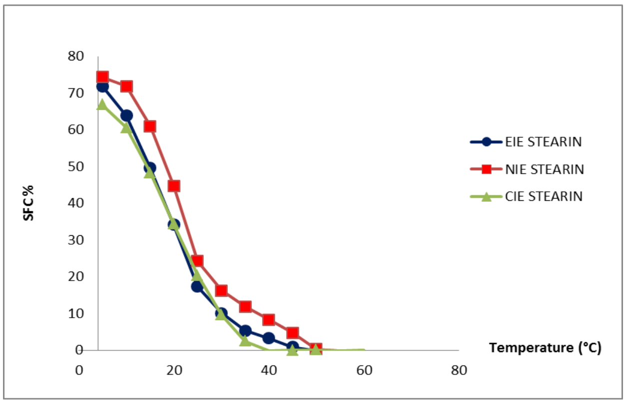

Figure 1. Percent of solid fat content of NIE, CIE and EIE of 50:50 PO:PKO stearin fractions as a function of temperature

in olein fraction was oleic acid with 40.58% in EIE, followed by 32.37% in CIE and 31.45% in NIE. For stearin fraction, palmitic acid present in large amount with 34.51%, 32.70% and 29.52% in NIE, EIE and CIE blends, respectively. The different amounts of fatty acids presence in the fractions even though from the same blend ratio was due to the rearrangement of fatty acids the glycerol backbone during interesterification. Other fatty acids that present in appreciable amounts in both the olein and stearin fractions were lauric and myristic acids. The fatty acid composition influenced the physical properties of the fractions.

Conclusion

Single fractionation of the NIE, CIE, and EIE 50:50 PO:PKO blends at 25°C produced stearin and olein with different physicochemical properties. The olein fraction from EIE PO:PKO blend has the highest IV (49.2) and smoke point (265.1°C) with the lowest cloud point (6.3°C) due to presence of high amount of unsatutared fatty acids (~50%) compared to NIE and CIE olein fractions. Hence, EIE olein fraction has the most suitable properties for frying purpose. On the other hand, CIE PO:PKO blend produced the highest amount stearin fraction with the highest IV (33.08) and had SMP close to body temperature (36.7°C). Thus, this stearin fraction has the most suitable properties to be used for table margarine formulation.

Acknowledgements

The financial support for this project was provided by Fundamental Research Grants Scheme (FRGS), Ministry of Higher Education, Malaysia, while the equipment and facilities was supported by Universiti Teknologi MARA and Malaysian Palm Oil Board.

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