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Purification of High Free Fatty Acid Crude Palm Oil Using Molecular Distillation

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The separation of free fatty acid (FFA) from high free fatty acid crude palm oil (HFFACPO) was done by using molecular distillation (MD). The separation parameters was at their boiling points; a feed amount of 2.3 mL/min; an operating pressure of 10 Torr; a condenser temperature of 60 °C; and a rotor speed of 300 rpm. The physico-chemical characteristics of HFFACPO and purified crude palm oil (PCPO) were determined. The results showed that the percentage of free fatty acid decreased from 8.7 ± 0.3 to 0.9 ± 0.1 %; iodine value from 53.1 ± 0.4 to 52.7 ± 0.5 g I_2/100 g; hydroxyl value from 32.5 ± 0.6 to 13.9 ± 1.1 mg KOH/g; unsaponifiable value from 0.31 ± 0.01 and 0.20 ± 0.15 %; moisture content from 0.31 ± 0.01 to 0.24 ± 0.01 % for HFFACPO and PCPO, respectively. Gas chromatography (GC) results showed that the major fatty acids in crude palm oil (CPO) were palmitic acid (44.4 %-45 %) followed by oleic acid (39.6 %-39.8 %). High performance liquid chromatography (HPLC) results showed that the major triacylglycerol (TAG) were POP (30.8-32.4 %) followed by POO (24.9-25.1 %). In general, PCPO showed admirably physico-chemical properties and the quality of purified oil was completely improved.

Keywords: Molecular distillation, High free fatty acid crude palm oil, Hydroxyl value.

INTRODUCTION

Malaysia is one of the major global manufactures in oleochemistry industry. The main source of oleochemicals in Malaysia is palm oil. Malaysian crude palm oil (CPO) consists of free fatty acid (FFA), triacyl-glycerol (TAG), diacylglycerol (DAG) and monoacylglycerol (MAG) which are the major components (95-99 %) and minor components (1-5 %) such as carotenoids, tocopherols, sterols, phosphatides and aliphatic alcohols [1]. Typically, almost 80 % of palm oil is used for human consumption and 20 % as non-edible such as oleochemical [2]. Low free fatty acid crude palm oil showed good physico-chemical properties which included oil yield 37.19 ± 2.04 (%), % FFA 0.65 ± 0.09 (%), moisture content 0.52 ± 0.37 (%) and can be suitable for industrial applications [3]. However, there are not enough studies of analysis and characterization of high free fatty acid crude palm oil (HFFACPO) have not been well reported yet.

Based on the early reports, it was found out that there was an endogenous lipase which also known as triacylglycerol acylhydrolase found in oil palm fruits [3,4]. Microbial lipase is activated in the presence of water during the storage period [5] and upon abscission of the fruit and also when the fruit is bruised during harvest, transportation and storage [6]. The contamination of fungi in palm oil may lead to the split of TAG and FFA formation, thus cause a strong negative impact on crude palm oil quality [7]. Medium chain fatty acids such as lauric acid and myristic acid which apart of liberated fatty acid in crude palm oil can be converted to a series of methyl ketones by certain xerophilic fungi and this phenomenon is known as ketonic rancidity [8]. Length storage of palm fruits especially during period of heavy rainfall thus giving strong negative impact on the quality of crude palm oil.

The currently evolving climate, torrential rainfall, humidity and inadequate storage result in the breakdown of TAG and release of FFA. As a result, the increasing of the level of FFA in CPO more than 5 % will make it unhealthy for human consumption [9]. The quality and price of crude palm oil were influenced by the presence of FFA. The good quality of palm oil should not be contained more than 5 % FFA [10]. Therefore, if the percentage of FFA in CPO is less than 5 % it can be useful for food applications or oleochemicals. On the other hand, if the percentage of FFA in CPO is higher than 5 % it can be beneficial for non-food applications such as bioplastic, biodiesel, biolubricant and surfactants [11,12].

Short-path distillation (SPD), or molecular distillation, is a suitable separation process for the purification and separation of thermally unstable substances as well as for materials with high molecular weight and low vapour pressure, for example, vitamins or FFA by decreasing losses thermal decomposition [13]. Short-path distillation has been used in the middle of the past century to separate glycerols and obtained a high percentage of monoacylglycerols mixtures (97 %) as stated by Kuhrt *et al.* [14]. Free fatty acids have been eliminated from the soybean oil deodorizer distillate and obtained of 81 % tocopherols by removing about 96 % FFA by using short path distillation (SPD) [15]. This technique has also been a useful process to decrease the concentration of unwanted FFA producing from lipase or chemically catalyzed hydrolysis reactions [16]. Recently, technologies have been patented in Malaysia which includes using of SPD for deacidification and deodorization in the pretreatment of red palm oil [17]. However, the separation of FFA from high free fatty acid crude palm oil using molecular distillation has not been well reported yet. Consequently, the quantitative analysis of the oil is important to know if it can be used either in food applications or non-food applications. In this study, free fatty acid separation from HFFACPO by molecular distillation has been carried out. The physico-chemical properties and the composition of HFFACPO and PCPO have also been quantitatively characterized.

EXPERIMENTAL

High free fatty acid crude palm oil (HFFA-CPO) was obtained from Sime Darby Company, Kuala Lumpur and stored at 4 °C. The chemicals and solvents used in this study such as methanol, pyridine, acetonitrile, ethanol, *n*-hexane and sodium sulphate were aneither analytical grade or high performance liquid chromatography (HPLC).

Separation of free fatty acid: Free fatty acid separation was achieved by using a laboratory short-path distillation VKL 70, from VTA GmbH, Germany. The major parts were a cooling trap for filling with liquid nitrogen (ice), an integral condenser and a vacuum system. The vacuum system was involved a rotary vane pump and diffusion pump. The vacuum was performed of up to 10 Torr, with evaporator surface of 0.04 m^2. The heating of the evaporator was equipped with the jacket circulated and silicon oil. 100 g of HFFACPO was first heated in an oven at 60 °C for 1 h to completely melt. The wiper speed and vacuum pressure of the evaporator were kept constant throughout the experiment at 300 rpm and 10 Torr, respectively. The initial weight of round-bottom flask for distillate and residue were recorded before running the experiment. The melted oil was then introduced into SPD and the evaporator temperature was set at 60 °C to remove the gases from oil. Then the oil was distilled against the boiling point of each palm fatty acid from 173 to 227 °C for single-step separation as shown in Table-1. The weight of the bottle with distillate and residue were recorded [18].

Physico-chemical characteristics

Free fatty acid (% FFA) and acid value (AV): The acidity of oil was carried out according to AOCS Method Ca 5a-40 (1989).

Iodine value (IV): The iodine value was carried out by using Wij's method (British Standard 684: Section 2.13: 1976).

Hydroxyl value (HV): The hydroxyl content was determined according to AOCS. Official Method Cd 13-60.

Saponification value (SV): Saponification value of oil was measured according to British Standards BS 684 2.6.1977.

Unsaponifiable matter (USM): 5 g of crude palm oil was used to determine the unsaponifiable matter according to (A.O.C.S. Ca 6a-40) (1989) [19].

Moisture content: The moisture content of oil was carried out by using air oven method according to AOCS Ca 2c-25[20].

Viscosity: The viscosity of oil was determined by using Brookfield model DV-I (U.S.A) equipped with a spindle no. 5 and stirred for 1 min and 100 rpm at ambient temperature [21].

Refractive index: The refractive index of oil was done according to American Oil Chemists' Society (AOCS) Official methods Cc 7-25 using refractometer (TAGO Co. Ltd. Series No. 11506, Japan) [20].

Specific gravity: It was determined by using digital balance; we placed 1 mL of the sample on the digital balance and recorded its weight at ambient temperature [22].

Colour: The colour of oil was estimated according to AOCS Official methods Cc 13b – 45 (97) using a Lovibond Tintometer 181059 Model F (U.K).

Fatty acid composition (FAC) of crude palm oil: The fatty acid methyl esters (FAMEs) were prepared using two methods: acid catalyzed and base catalyzed preparations. In acid catalyzed preparation, a reagent mixture of 5 mL methanol and 1.25 mL concentrated hydrochloric acid (36.5 %) was used. 1 g of the oil sample was placed in a small (50 mL) two-neck round-bottom flask, equipped with a standard taper joint (19/38) and short condenser. Afterwards, 3.75 mL methanol was added to 0.75 mL of the previous reagent followed by 0.75 mL of toluene. The mixture was then heated at 65 °C for 1.5 h. The heated mixture was subsequently transferred into a separatory funnel. 7.5 mL of hexane and 5 mL distilled water were added to the mixture. Afterwards, the mixture was left to stand until two distinct layers emerged. The upper layer was decanted and dried using anhydrous sodium sulphate Na_2SO_4 overnight. 1.0 µL of the FAMEs was then injected into a gas chromatograph.

For base catalyzed preparation, the FAMEs were prepared by blending 0.1 mL of sample with 1 mL of hexane. 1 mL of sodium methoxide (CH_3ONa) (1.55 g NaOH and 50 mL of methanol) was subsequently added to the sample, followed by vigorous shaking until a cloudy mixture was obtained. Afterwards, 1 mL of distilled water was added to the mixture.

TABLE-1
BOILING POINTS OF PALM FATTY ACID

	Palm saturated fatty acids				Palm unsaturated fatty acids	
Fatty acid	Lauric acid	Myristic acid	Palmitic acid	Stearic acid	Oleic acid	Linoleic acid
Boling point [Ref. 25] (°C/10 Torr)	173	193	212	227	223	224

The mixture was kept at room temperature until two distinct layers appeared. The FAMEs layer was gradually decanted and dried over anhydrous sodium sulphate [23]. 1 µL of the FAMEs was then injected into a gas chromatograph.

Gas chromatography-flame ionization detector analyses of crude palm oil: Gas chromatography analyses were performed using gas chromatograph (Model 5890 SERIES II GC, HEWLETT PACKARD, USA) software equipped with flame ionization detector (FID) and a BPX-70 fused silica capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness). The injector temperature was maintained at 280 °C. Operating conditions were as follows: helium as the carrier gas was at a flow rate of 1 mL/min, injection volume 1 µL and a split ratio of 60:1. The oven temperature was maintained at 120 °C and increased to 245 °C and hold for 15 min at a rate of 3 °C per min for 56.6 min of analysis. The FAME peaks were classified and quantified by comparison their peaks area and retention times with that pure standard FAMEs.

Triacylglycerol profile of crude palm oil

Samples preparation: 10 mL of oil sample was diluted with 30 mL hexane and dehydrated using 10 g of anhydrous sodium sulphate overnight. Then the samples were filtrated through filter paper and the hexane was evaporated under reduce pressure. Next, a 100 µL of oil sample was dissolved in a mixture (1 mL) of acetone and acetonitrile (63.5:36.5) and mixed vigorously using a vortex mixture until it became completely dissolved. The mixture was filtrated twice using a 0.45 µL disposable LC filter disk. About 5 µL of the sample was injected into HPLC, a total running time of 40 min.

High-performance liquid chromatography (HPLC) analysis: Triacylglycerol composition has been investigated on HPLC system consisting of Waters 1525 Binary HPLC Pump, equipped with Waters 2707 Auto-sampler and Waters 2424 Evaporative Light Scattering Detector ELSD Bridge TM, Waters, BEH Technology, USA. The isocratic separation of TAGs was evaluated by reverse phase HPLC on C18 column (C18 column, 4.6 × 250 mm, 5 µm).

Fourier transforms infrared spectroscopy (FTIR): Fourier transforms infrared spectroscopy (FTIR) has been determined according to Salimon *et al.* [24].

RESULTS AND DISCUSSION

Separation of free fatty acid: The separation of free fatty acid from HFFACPO was achieved for each fatty acid according to at their boiling point [25], 10 Torr and 300 rpm as shown in Table-1. The oil was heated at 60 °C to remove the gases. Then the oil was injected again and the temperature was increased to 173 °C to separate lauric acid. Then the distillate (lauric acid) was collected and the residue was injected into the tank and distillated at 193 °C to separate myristic acid. This procedure was repeated with increasing the temperature for single-step separation to separate another free fatty acid as shown in Table-1.

The HFFACPO to become acceptable for human consumption should be purified. Essentially, minimal free fatty acid, a bland taste, a light colour and a good oxidative stability are required. Consequently, the oil was purified using molecular distillation. The objective of the distillation is to remove the undesirable minor constituents in the oil such as FFA with the slightest possible damage to the acylglycerols and minimum loss of the desirable constituents.

It can be seen in Table-2 the acidity and iodine value for high free fatty acid crude palm oil (HFFACPO), purified crude palm oil (PCPO) and distillate free fatty acid (DFFA). It can be noted that the acidity of oil decrease after molecular distillation due to removing FFA. The iodine value for HFFACPO is slightly close to iodine value for DFFA. It can be concluded that the action of microbial lipase works on the hydrolysis of each TAG and this means that the action of the enzyme is random and not specific to a particular type of TAG.

TABLE-2
EFFECT OF MOLECULAR DISTILLATION ON THE QUALITY OF HIGH FREE FATTY ACID CRUDE PALM OIL

Parameter	HFFACPO	PCPO	DFFA
Weight (g)	100	90	10
Free fatty acid (%)	8.7 ± 0.3	0.97 ± 0.1	97.3 ± 0.5
Acid value (mg NaOH/g)	19.1 ± 0.6	2.1 ± 0.2	213 ± 1.1
Iodine value (g I_2/100 g)	53.1 ± 0.4	52.7 ± 0.5	53.1 ± 0.8

Notes: HFFACPO = High free fatty acid crude palm oil; PCPO = Purified crude palm oil; DFFA = Distillate free fatty acid.

Physico-chemical characteristics of crude palm oil: Free fatty acid content (%FFA) of oil samples was 8.7 ± 0.3 % and 0.9 ± 0.1 % for HFFACPO and PCPO, respectively. It can be seen that, there is a significant difference due to the removing of free fatty acid by using molecular distillation. Free fatty acid value for HFFACPO was close to 8.5 % as reported in the literature [26]. The high value of FFA in HFFACPO may be due to several factors such as weather (raining and draught), harvesting (ripe, young and over ripe) and fruit management (handling and processing). Fermentation prefers the actions of lipolytic enzymes which are responsible for hydrolyzing triacylglycerol in the seeds and liberating free fatty acid. The acid values recorded in the analysis are 19.1 ± 0.6 and 2.1 ± 0.2 mg NaOH/g oil for HFFACPO and PCPO, respectively. The acidity is essential in deciding the application of oil either for industrial applications or human consumptions. The quality of the crude palm oil influenced by the content of FFA, wherein the good quality of crude palm oil should not contain more than 5 % FFA [10].

Hydroxyl value was 32.5 ± 0.6 and 13.9 ± 1.1 mg KOH/g for HFFACPO and PCPO, respectively. This variation due to changing on the level of FFA, as a result, an increase in % FFA caused also an increase in the level of DAG and MAG in oil. It can be seen in Table-3 the acidity of HFFACPO is higher than acidity of PCPO. The oil that contains high % FFA due to the splitting of TAG by the action of microbial lipase and increasing the level of DAG and MAG which leads to increasing of hydroxyl value.

The iodine value shows the level of unsaturation in oil and is one of the chemical significant characteristics of the oil. The iodine value of the oils ranged from 53.1 ± 0.4 (HFFACPO) to 52.7 ± 0.5 g/100 g (PCPO) as shown in Table-3. The variation between these values refers to the fatty acid composition of oil as shown in Table-3. This may refer to that unsaturated fatty acid was oxidized during distillation.

TABLE-3
PHYSICO-CHEMICAL CHARACTERISTICS OF CRUDE PALM OIL

Parameters	Unit	HFFACPO[b]	PCPO	MCPOs[a]
FFA (as palmitic acid)	%	8.7 ± 0.3	0.9 ± 0.1	≤ 5
Acid value	mg NaOH/g	19.1 ± 0.6	2.1 ± 0.2	≤ 10.95
Hydroxyl value	mg KOH/g	32.5 ± 0.6	13.9 ± 1.1	–
Iodine value (Wijs)	g I_2/100 g	53.1 ± 0.4	52.7 ± 0.5	50.4 to 53.7
Saponification value	mg KOH/g	200.6 ± 0.8	197.8 ± 1.4	194 to 205
Unsaponifiable matter	%	0.31 ± 0.01	0.20 ± 0.15	0.19 to 0.44
Moisture content	%	0.31 ± 0.01	0.24 ± 0.01	0.25
Refractive index at 28 °C	–	1.4669 ± 0.0003	1.4670 ± 0.0002	1.4521-1.4541[c]
Specific gravity at 28 °C	g/mL	0.869 ± 0.009	0.858 ± 0.006	0.8889 to 0.8896[c]
Viscosity at 28 °C	cP	69 ± 0.6	72 ± 1.5	–
Colour at 28 °C	–	50 R[d] – 50 Y[e]	50 R-50 Y	–

[a]Source: MS814:2007 [Ref. 32]; [b]HFFACPO = High free fatty acid-crude palm oil; PCPO = Purified crude palm oil; MCPOs = Malaysian crude palm oil standard; [c]Estimated at 50 °C; [d](Red); [e](Yellow)

Saponification value evaluates of oxidation through storage period and also indicates decomposition of the oils [27]. Saponification value for HFFACPO and PCPO were of 200.6 ± 0.8 and 197.8 ± 1.4 mg KOH/g, respectively. Saponification value has a significance in the industrial applications of oil specially for soap production and it is also a feasible means for characterizing oil [28]. The oil with the low value of saponification value can be used for producing the candle, soap and raw materials for lubricants [29].

The unsaponifiable matter of HFFACPO and PCPO shows of 0.31 ± 0.01 % and 0.20 ± 0.15 %, respectively, it can be seen that the unsaponifiable matter for PCPO decreased may due to the effect of high temperature during distillation. The unsaponifiable matter of oil depends on the liquidity and presence of water[30].

The physical properties of the CPO are reported in Table-3. The high refractive index of these oils is attributable to the high number of carbon atoms in their fatty acid composition [31]. The moisture content for PCPO is close to a moisture content of crude palm oil standard. It is one of the most important characteristics to identify the quality of the oil.

Fatty acid composition of crude palm oil: The free fatty acid (FFA) composition of HFFCPO and PCPO subjected to acid catalyzed preparation comprises palmitic acid (44.4-45.9 %), oleic acid (39.2-37.2 %) and linoleic acid (10.7-11 %) as shown in Table-4, were the major composition of free fatty acid, whereas the minor fatty acids were stearic acid (4.2-4.1 %), myristic acid (1.1-1.3 %) and lauric acid (0.4-0.5 %), respectively.

The composition of fatty acid in oil was showed that palmitic acid (44.4-45 %), oleic acid (39.8-39.6 %), followed by linoleic acid (10.0-9.6 %) as shown in Table-4, were the major composition of fatty acid, whereas the minor fatty acids were stearic acid (4.4-4.6 %), myristic acid (1.1-1.0 %) and lauric acid (0.3-0.2 %) for HFFACPO and PCPO, respectively.

The GC-FID results show a slight difference between free fatty acid and fatty acid compositions in HFFACPO and PCPO prepared with acid and base catalysts. The results suggest that TAG, DAG and MAG were possibly completely hydrolyzed by the base catalyzed preparation. It is evident in Table-4 that the compositions of acid and base catalysts based HFFA-CPO and LFFA-CPO are slightly similar. The distinctiveness of the GC peaks is dependent on the number of carbon and boiling point of each fatty acid. The higher the retention times for the peaks detected, the greater the carbon number. The results suggest that retention time and boiling point increased with increasing intermolecular forces due to the double bond in the FFA backbone for the same carbon chain length such as oleic and stearic acid.

Triacylglycerol profile of crude palm oil: The content of triacylglycerol (TAG) for HFFACPO and PCOP is a principal determinant of oil quality due to its industrial potential. In the present work, HFFACPO showed that MAG of 2.2 %. However, MAG level was lower in PCPO of 0.9 % due to the variation in FFA contain as shown in Table-5. Diacylglycerol level and TAG level for HFFACPO and PCPO showed (8.2 %, 78.9 %) and (7.7 %, 91.3 %), respectively.

TABLE- 4
FREE FATTY ACID AND OIL COMPOSITION FOR HFFACPO AND PCPO

FAC (%)	Acid catalyst		Base catalyst		DFFA	MPOBs[a]
	HFFACPO	PCPO	HFFA CPO	PCPO		
Lauric acid	0.4	0.5	0.3	0.2	0.1	0-0.5
Myristic acid	1.1	1.3	1.1	1.0	1.0	0.9-1.5
Palmitic acid	44.4	45.9	44.4	45.0	47.9	39.2-45.8
Stearic acid	4.2	4.1	4.4	4.6	4.6	3.7-5.4
ΣSFA	50.1	51.8	50.2	50.8	53.6	45.3-55.4
Oleic acid	39.2	37.2	39.8	39.6	37.2	37.4-44.1
Linoleic acid	10.7	11.0	10.0	9.6	9.2	8.7-12.5
ΣUSFA	49.9	48.2	49.8	49.2	46.4	44.8-57.3

Notes: [a]Source: MS814:2007 [Ref. 32]; MPOBs = Malaysian Palm Oil Board specification; FAC = Fatty Acid Composition; HFFACPO = High free fatty acid-crude palm oil; PCPO = Purified crude palm oil; ΣSFA= Total of saturated fatty acid; ΣUSFA= Total of unsaturated fatty acid; DFFA = Distillate free fatty acid.

The levels of FFA, MAG and DAG leads to affected the level of TAG in the oil. It has been reported that there is an endogenous lipase (triacylglycerol acylhydrolase) in oil palm fruits [9] and it is the first enzyme to be implicated in the degradation of TAG[6]. Microbial lipase becomes more active in the present of water and could react with oil and therefore due to breakdown TAG and liberated DAG, MAG and FFA [3]. The change in TAG profile due to poor quality and the oil become not suitable for human consumption. It can be seen in Table-5 the percentage of TAG for PCPO is 91.3 % and this value was close to the standard crude palm oil. However, before molecular distillation, the percentage of TAG for HFFACPO showed 78.9 % and was closed with crude red palm oil 80.14 % as reported by Kumar and Krishna [30]. The results showed that molecular disti-llation has significantly affected on the composition of oil due to improvement the quality of oil by removing FFA and increasing the percentage of TAG 91.3 % as shown in Table-5.

TABLE-5
COMPOSITION OF MALAYSIAN HIGH FREE FATTY ACID CRUDE PALM OIL AND PURIFIED CRUDE PALM OIL

CPO (%)	HFFACPO	PCPO
ΣFFA	10.7	0.1
ΣMAG	2.2	0.9
ΣDAG	8.2	7.7
ΣTAG	78.9	91.3

Notes: CPO = Crude palm oil; HFFACPO = High free fatty acid-crude palm oil; PCPO = Purified crude palm oil; FFA = free fatty acid; MAG = Monoacylglycerol; DAG = Diacylglycerol; TAG = Triacylglycerol.

The TAG composition of HFFACPO and PCPO were analyzed. Results from profile phase HPLC showed that the both oil samples contain at less fourteen significant TAGs as shown in Figs. 1 & 2 and Table-6. The TAGs composition was identified according to the equivalent carbon number (ECN) [30]. The major TAGs of HFFACPO and PCPO were POP (24.9 % and 25.1 %), POO (30.8 % and 32.4 %), PLO (10.1 % and 8.9 %), PLP (8.9 % and 8.2 %) and PPP (5.3 % and 6.7 %), respectively. However, the minor TAGs were OOO (4.5 % and 4.4 %), PLL (2.9 and 1.7), SOO (2.7 % and 2.5 %), OLO (1.8 % and 1.5 %), PSS (1.3 % and 1.9 %) and the other TAGs were in proportion of ≤ 0.6 % (Table-6). It can be seen that TAGs profile of HFFACPO and PCPO were slightly different due to removing only FFA by molecular distillation.

FTIR spectrum of crude palm oil: The FTIR spectra of HFFACPO and PCPO are shown in Fig. 3. The major peaks and their assignment to functional groups are shown in Table-7. The FTIR spectroscopy analysis of HFFACPO showed the appearance of the absorption band at 1712 cm^{-1} which referred to the carbonyl (C=O) carboxylic acid, whereas disappearance in PCPO due to removing FFA by molecular distillation which appeared with increasing the percentage of FFA in crude palm oil. FTIR showed characteristics of strong sharp absorption bands of HFFACPO and PCPO at 1746 and 1747 cm^{-1} due to the functional groups of esterified carbonyl C=O, respectively. FTIR peaks at 2923 to 2855 cm^{-1} showed the CH_2 and CH_3 scissoring of HFFACPO and PCPO. FTIR peaks of HFFACPO and PCPO showed the appearing of the peak at 3005 cm^{-1} which referred to (stretching aliphatic) of the double bond C=C while at a wavelength of 3473 cm^{-1} signify -OH stretching of HFFACPO and PCPO, respectively.

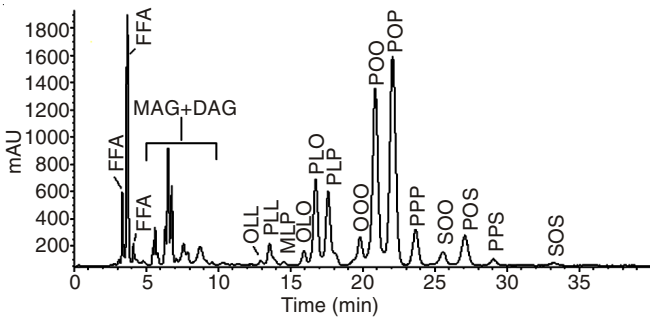

Fig. 1. Triacylglycerol profile of HFFACPO

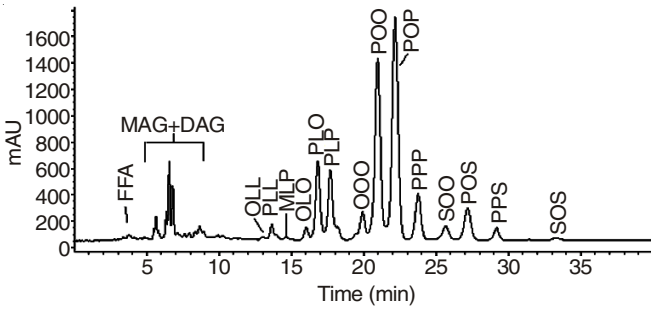

Fig. 2. Triacylglycerol profile of PCPO

TABLE-6
TAG COMPOSITION OF MALAYSIAN HIGH FREE FATTY ACID CRUDE PALM OIL AND PURIFIED CRUDE PALM OIL

TAG type	ECN	Composition (%)		
		HFFACPO	PCPO	MCPOs[a]
OLL	44	0.6	0.2	0.2-0.9
PLL	44	2.9	1.7	1.3-3.4
MLP	44	0.5	0.5	0.2-1.0
OLO	46	1.8	1.5	1.3-2.3
PLO	46	10.1	8.9	9.0-11.2
PLP	46	8.9	8.2	6.5-11.0
OOO	48	4.5	4.4	3.3-6.6
POO	48	24.9	25.1	20.5-26.2
POP	48	30.8	32.4	27.1-31.0
PPP	48	5.3	6.7	0.7-7.2
SOO	50	2.7	2.5	1.0-3.6
POS	50	5.3	5.6	4.6-5.9
PPS	50	1.3	1.9	0.1-1.8
SOS	52	0.4	0.4	0.1-1.4

[a]Malaysian crude palm oil standard [Ref. 33]; [b]P = palmitic acid; O = Oleic acid; L = Linoleic acid; M = Myristic acid; ECN = Equivalent carbon number [CN-(2×ND)]; HFFACPO = High free fatty acid-crude palm oil; PCPO = purified crude palm oil.

Conclusion

Molecular distillation showed improving the quality of oil by removing the free fatty acid at their suitable separating conditions. The results indicate that HFFACPO showed high free fatty acid above the minimal content that cannot be used as food applications. The disappearance of carboxylic acid (C=O) group peak has been noted by FTIR for PCPO. The PCPO has shown admirably physico-chemical properties and could be suitable for industrial and food applications. In view of the current study, HFFACPO requires pre-treatment refinery stages such as distillation process to produce edible oil.

TABLE-7
FTIR FUNCTIONAL GROUPS OF HFFACPO AND PCPO AND THEIR WAVELENGTHS

Wavelength of HFFACPO	Wavelength of PCPO	Functional group
3473	3473	OH stretching
3004	3005	C=C bending vibration (aliphatic)
2923, 2855	2927, 2855	C-H stretching vibration (aliphatic)
1476	1747	C=O stretching vibration (ester)
1712	–	C=O stretching vibration (carboxylic acid)
1459	1465	C-H scissoring and bending vibration (aliphatic)
1235, 1165, 1118	1235, 1165, 1117	C-O-C stretching vibration (ester)
722	722	C-H group vibration (aliphatic)

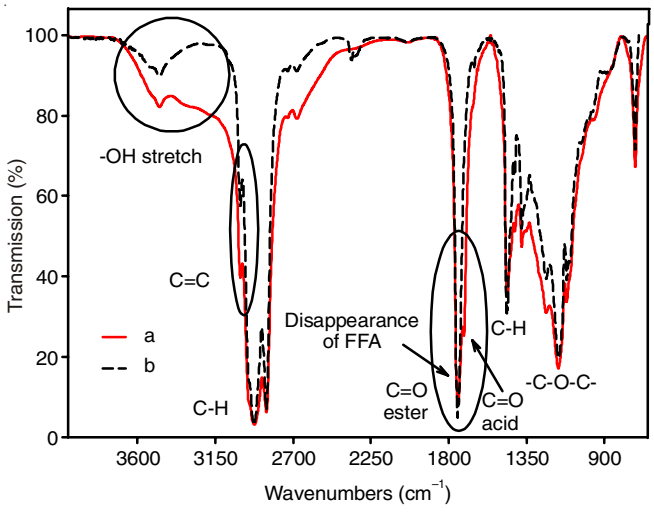

Fig. 3. FTIR spectrum of HFFACPO (a); PCPO (b)

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REFERENCES

1. S. Goh, Y. Choo and S. Ong, *J. Am. Oil Chem. Soc.*, **62**, 237 (1985).
2. Y. Basiron and C.K. Weng, *J. Oil Palm Res.*, **16**, 1 (2004).
3. C.-H. Tan, H.M. Ghazali, A. Kuntom, C.-P. Tan and A.A. Ariffin, *Food Chem.*, **113**, 645 (2009).
4. G.F. Ngando Ebongue, R. Dhouib, F. Carrière, P.-H. Amvam Zollo and V. Arondel, *Plant Physiol. Biochem.*, **44**, 611 (2006).
5. Y.B. Che Man, M.H. Moh and F.R. van de Voort, *J. Am. Oil Chem. Soc.*, **76**, 485 (1999).
6. R. Sambanthamurthi, K. Sundram and Y.-A. Tan, *Prog. Lipid Res.*, **39**, 507 (2000).
7. C. Mohankumar, C. Arumughan and R. Kaleysa Raj, *J. Am. Oil Chem. Soc.*, **67**, 665 (1990).
8. J.L. Kinderlerer, *Int. Biodeter. Biodegrad.*, **33**, 345 (1994).
9. G.F.N. Ebongue, P. Koona, B. Nouy, S. Zok, F. Carrière, P.-H.A. Zollo and V. Arondel, *Eur. J. Lipid Sci. Technol.*, **110**, 505 (2008).
10. S. Adjei-Nsiah, A. Zu and F. Nimoh, *J. Agric. Sci.*, **4**, 111 (2012).
11. N.S. Harun, N.N.M. Talip, L.K. Hong, M.S.M. Jamil and R.M. Yusop, *Malaysian. J. Anal. Sci.*, **17**, 139 (2013).
12. L.K. Hong, N.S. Harun, M.S.M. Jamil and R.M. Yusop, *Malaysian. J. Anal. Sci.*, **17**, 101 (2013).
13. J. Cvengros, M. Mrázek and G. Kmetty, *Chem. Pap.*, **53**, 102 (1999).
14. N.H. Kuhrt, E.A. Welch and F.J. Kovarik, *J. Am. Oil Chem. Soc.*, **27**, 310 (1950).
15. P. Martins, V. Ito, C. Batistella and M.W. Maciel, *Sep. Purif. Technol.*, **48**, 78 (2006).
16. G. Arzate-Martínez, A. Jiménez-Gutiérrez and H.S. García, *Ind. Eng. Chem. Res.*, **50**, 11237 (2011).
17. B. Nagendran, U. Unnithan, Y. Choo and K. Sundram, *Food Nutr. Bull.*, **21**, 189 (2000).
18. C.M. Yeoh, E.T. Phuah, T.K. Tang, W.L. Siew, L.C. Abdullah and T.S.Y. Choong, *Eur. J. Lipid Sci. Technol.*, **116**, 1654 (2014).
19. J. Salimon, B.M. Abdullah and N. Salih, *Int. J. Chem. Eng.*, **Article ID 574780** (2012).
20. J. Salimon and W.A. Ahmed, *Sains Malaysiana*, **41**, 313 (2012).
21. A.I. Bamgboye and O.I. Adejumo, *Nutr. Food Sci.*, **40**, 186 (2010).
22. F. Gunstone, Vegetable Oils in Food Technology: Composition, Properties and Uses, John Wiley & Sons (2011).
23. K.A. Alabi, L. Lajide and B.J. Owolabi, *Fount. J. Nat. Appl. Sci.*, **2**, 32 (2013).
24. J. Salimon, B.M. Abdullah and N. Salih, *Chem. Cent. J.*, **5**, 67 (2011).
25. S.C. Cermak, J.A. Kenar and R.L. Evangelista, Distillation of Natural Fatty Acids and Their Chemical Derivatives, INTECH Open Access Publisher (2012).
26. C.L. Chong, Z. Kamarudin, P. Lesieur, A. Marangoni, C. Bourgaux and M. Ollivon, *Eur. J. Lipid Sci. Technol.*, **109**, 410 (2007).
27. A.-A. Neagu, I. Niþa, E. Botez and S. Geaca, *Analele Universitatii "Ovidius" Constanta-Seria Chimie*, **24**, 121 (2013).
28. A.S. Olanrewaju and O.E. Moriyike, *Am. J. Food Nutr.*, **1**, 34 (2013).
29. C. Agatemor, *Pak. J. Nut.*, **5**, 306 (2006).
30. P.P. Kumar and A.G. Krishna, *Grasas Aceites*, **65**, e018 (2014).
31. O.S. Falade, A.S. Adekunle, M.A. Aderogba, S.O. Atanda, C. Harwood and S.R. Adewusi, *J. Sci. Food Agric.*, **88**, 263 (2008).
32. T.T. Sue and T. Pantzaris, Malaysian Palm Oil Board, Kuala Lumpur, Malaysia (2009).
33. Y. Tan, K. Ainie, W. Siew, Y. Mohtar and C. Chong, Report on Project CT 351/97, Viva Report, 7 (1997).