Physicochemical Characteristics of Malaysian Crude Palm Kernel Oil[†]

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This study was carried out to determine the physicochemical properties of Malaysian crude palm kernel oil (CPKO). The physicochemical properties showed that the free fatty acid (FFA%) of 3.7±0.1%, acid value of 10.4±0.1 mg/g, iodine value of 20.8±0.6 mg/g, hydroxyl value of 45.06±0.3 mg/g, refractive index at 28°C of g/ml, 1.455, moisture content of 0.5±0.1%, viscosity at 28°C of 40 cP, Lovibond colour (R/Y) at 28°C of 0.5R–20Y. The gas chromatography-flame ionisation detector was used to determine the fatty acid composition in CPKO. The results showed that the dominant fatty acids are lauric acid (44.5±0.7%), oleic acid (18.0±0.5%), myristic acid (16.9±0.1%) and palmitic acid (9.4±0.2%). The major triacylglycerols (TAGs) of CPKO estimated using high-performance liquid chromatography were LaLaLa (32.91%), LaLaM (23.59), LaOLa (9.93%) and CLaLa (9.10%). The differential scanning calorimetry showed that the crystallisation of CPKO displayed two major exothermic regions of CPKO with the saturated TAG at 6.11°C and the unsaturated TAG at -2.10°C. The melting curve of CPKO displayed two endothermic peak regions at 9.13°C and 24.08°C.

Key words: crude palm kernel oil; physicochemical characteristic; triacylglycerol profile; fatty acid composition; thermal behaviour

The oil palm tree (*Elaeis guineensis*) that originated from the western Africa region has quickly spread to other tropical and subtropical regions of the world. In Malaysia, Indonesia, and Africa [1, 2] the oil palm tree has flourished and has quickly developed into a lucrative agricultural crop for the production of palm oil in these countries. The statistics on the cultivation of oil palm revealed that in 1975, Malaysia had around 64,000 hectares of oil palm plantations and since this time, have increased considerably. Sulaiman *et al.* [3] also asserted that in the new millennium, oil palm plantations would cover an area of about 3.37 million hectares of Malaysian soils. In 2015, it was reported that oil palm plantations in Malaysia occupied a land area of a staggering 5.64 million hectares [4].

The fresh fruit bunches (FFB) of the oil palm tree contain two types of oil; crude palm oil (CPO) extracted from the flesh of the fruit (mesocarp), and crude palm kernel oil (CPKO) extracted from the seed or kernel [5]. Crude palm kernel oil (CPKO) is extracted from the kernel or seed of the palm fruit by mechanical screw pressing or via solvent extraction. The kernel oil contains a wide range of fatty acids which are present as the acyl groups in the triacylglycerols of the oil. CPKO is considered a lauric oil because lauric acid is the primary fatty acid in their composition at about 50% [6]. Notably, lauric acid oils are significantly different from other commercial oils and fats. In temperate climates they are solid at ambient temperatures, such as crude palm kernel oil [7]. In the solid state they are hard and brittle but melt sharply and completely below body temperature. Further, they have low unsaturation levels and are therefore, more stable to oxidation compared to other commercial oils. The reason for this distinction is due to their high content of relatively low molecular weight saturated fatty acids, in particular, lauric acid which is present at levels between 40 and 55% [8]. Indeed, the sharpness of their melting curves and low melting point make them particularly useful as fats for synthetic creams, hard butter and similar products. Notwithstanding, the sodium soaps of the low molecular weight acids are hard and stable to oxidation and are also soluble and free lathering [9]. Therefore, this study aims to highlight the physicochemical properties of crude palm kernel oil and to analyse their thermal behaviour. To the best of the researcher's knowledge, no similar study has been carried out in this field.

MATERIALS AND METHODS

Sample Collection

Malaysian crude palm kernel oil (CPKO) was obtained from a local refinery, Sime Darby Company, Kuala Lumpur, Malaysia and stored at 5°C.

Chemicals and Reagent

All chemicals and solvents were used as received. The methanol (99.8%), isopropanol (99.7%), ethanol (95%), pyridine (99%), toluene (99%), hydrochloric acid (36.5%), potassium hydroxide (99%), potassium iodide (99.5%) and sodium sulphate (99%) were purchased from Qrec. The acetonitrile (99.5%) and acetone (99.5%) of HPLC grade were purchased from JT Baker. The Wij's solutions, cyclohexane (99.7%), sodium thiosulphate (99%), n-hexane (99%) and phenolphthalein were purchased from Sigma-Aldrich. The fatty acid methyl ester standard were purchased from BDH and Fluka.

Physicochemical Characteristics

Determination of free fatty acids (FFAs%) and acid value (AV). The American Oil Chemists' Society (AOCS) method estimated the free fatty acids Ca 5a-40 (1990) [10]. Then, 50 ml of isopropanol and 0.5 ml phenolphthalein were poured into a flask and subsequently neutralised by adding sodium hydroxide (NaOH, 0.1 N) until a permanent pink colour was achieved. The neutralised isopropanol was then added to 5 g CPKO placed in an Erlenmeyer flask. The mixture was then heated to 40°C until dissolved after which, the mixture was then titrated with 0.1 N NaOH until forming a light pink colour using 1 ml of phenolphthalein as the indicator. The percentage of free fatty acid was calculated with the underlying Equation 1:

$$\% \text{ FFA as lauric acid} = \frac{20.0 \times N \times V}{W} \qquad (1)$$

where, V is volume of NaOH solution used in (ml); N is normality of NaOH solution in Equivalent per liter (Eq/l); W is the weight of the sample in grams.

$$\text{Acid value} = \% \text{ FFA as lauric acid} \times 2.81 \qquad (2)$$

where, 2.81 is the conversion factor for lauric acid.

Determination of iodine value (IV). The IV of CPKO was calculated in line with the AOCS (1989) method Cd 1-25 and the method proposed by Derawi *et al.* [11]. Approximately 0.5 g of CPKO was placed in a 500 ml flask, followed by the addition of 15 ml of cyclohexane (oil solvent). Next, 25 ml of Wijs solution was added, and the flask was then corked with a stopper. The flask containing the mixture was next shaken gently and placed in the dark for 60 min.

Following one hour of incubation, 20 ml of 10% potassium iodide (KI) solution and 150 ml of distilled water were added to the mixture. The mixture was then titrated with sodium thiosulphate (0.1N $Na_2S_2O_3$) until observing a yellow colour, signifying the iodine had nearly entirely disappeared. Afterward, 1 ml of starch solution (1%) was added, followed by continuous titration until the blue colour vanished after vigorously shaking the flask. The blank was treated with the same condition. The iodine value was determined using Equation 3 as given below:

$$\text{I.V.} = \frac{12.69 \times N(V_b\text{-}V_s)}{W} \qquad (3)$$

where, N is the normality of 0.1 N $Na_2S_2O_3$ solution; Vb is the volume in ml of $Na_2S_2O_3$ solution used for the blank test; VS is the volume in ml of $Na_2S_2O_3$ solution used to determine the sample; W is the weight in grams of the sample test portion.

Determination of hydroxyl value (HV). The hydroxyl value of CPKO was calculated in line with Fernandes *et al.* [12]. Next, 5 g of CPKO was placed in a 250 ml flask containing 5 ml of acetic anhydride-pyridine (1 ml acetic anhydride – 4 ml pyridine) to dissolve the oil. The flask was then immersed in an oil bath maintained at 100°C and shaken vigorously for 1 h. Afterward, the flask was removed from the oil bath and cooled at room temperature in a water bath for at least 10 min. Then, 10 ml of water was pipetted to the solution through the air condenser and shaken vigorously to obtain a homogenous mix. The flask was then returned to the oil bath for 10 min to complete the hydrolysis of the residual acetic anhydride reagent, shaking at regular intervals. The mixture was subsequently cooled in the water bath at room temperature for a minimum of 10 min. Next, 25 ml of neutralised alcohol was added following the cooling process (approximately half, via the air condenser). The condenser was then removed, and the lingering alcohol was washed down the sides of the flask.   A dropper was used to add 1 ml of phenolphthalein, and the mixture was titrated using methanolic potassium hydroxide (0.5 N) to obtain a faint pink colour. The hydroxyl value was calculated using Equation 4:

$$\text{Hydroxyl Value} = \frac{(V_b\text{-}V_s) \times \text{N KOH} \times 56.1}{W} + AV \qquad (4)$$

where, Vb = ml of blank; Vs = ml of titrant; W = weight (g) of the sample; N = normality of the KOH (Eq/l); AV = acid value.

Determination of saponification value. The saponification value of CPKO was measured based on the methods recommended by Salimon *et al.* and Ainie *et al.* [13, 14]. Firstly, 2 g of CPKO was placed in a flask containing 25 ml of ethanolic potassium hydroxide (KOH, 0.5 N) with some boiling stones. The boiling flask was connected to a condenser, and

the mixture was boiled gently for 1 h before the addition of 1 ml of phenolphthalein. The mixture was then titrated with 0.5 N HCl until a pink colour endpoint was obtained. The saponification value was calculated applying Equation 5:

$$S.V. = \frac{56.1 \times N(V_b\text{-}V_s)}{W} \qquad (5)$$

where, Vb = ml of blank; Vs = ml of titrant; W = weight (g) of the sample; N = normality of the KOH (Eq/l).

Determination of Unsaponifiable matter. The determination of the unsaponifiable matter of CPKO in this study was modified from the methods by Abdullah *et al.* [15]. Firstly, 10 g of the sample was placed in a round-bottomed flask containing 30 ml of ethanol and 5 ml of aqueous KOH solution with some boiling stones. The round-bottomed flask was connected to a condenser, and the mixture boiled gradually for 1 h. Afterward, the heating process was stopped, and the reaction mixture was subsequently transferred to a separating funnel. The flask was then rinsed off with 10 ml of ethanol, followed by 20 ml of warm distilled water and then 20 ml of cold distilled water. All washing solutions were also poured into the separating funnel. The contents of the separating funnel were cooled to room temperature before adding 50 ml of hexane. The mixture was then shaken vigorously for 1 min and left for a several minutes to ensure phase separation. The entire soap solution phase was transferred into a second separating funnel, and 50 ml of hexane was subsequently added to the solution. The extraction procedure using 50 ml of hexane was performed five times. Then, 25 ml of 10% (v/v) ethanol was used to wash the combined extracts in the separating funnel three times. The separating funnel was agitated vigorously after each wash to siphon off the ethanol layer. The hexane was completely evaporated under a vacuum using a rotary evaporator. The drying procedure was finalised in a vacuum oven at 75–80°C. The residue was then cooled in a desiccator and weighed (Wr). The residue was subsequently dissolved in 50 ml of 95% ethanol and titrated with 0.02 N NaOH solution using phenolphthalein to indicate the presence of a faint pink colour. Finally, the weight of the free fatty acid residue was determined using Equation 6:

Fatty acids (*g*) (*Wal*) = V NaOH × 0.00056 $\qquad$ (6)

Next, the amount of unsaponifiable matter expressed as a percentage by the weight of the sample was calculated applying Equation (7):

$$\text{Unsaponifiable matter\%} = \frac{(W_r\text{-}W_{al})}{W \text{ of sample}} \times 100 \quad (7)$$

Where, W = weight (*g*) of the sample; Wr = weight in grams of residue; Wal = weight in grams of fatty acids.

Colour

The CPKO colour was determined using a Lovibond tintometer Model F/10508, according to the PORIM test method [14]. The frozen oil samples were melted by placing them in an oven at a temperature of 60°C. The liquefied samples were then placed into an inch cell up to three-quarters full, and the colour was determined at 28°C by achieving the best possible match with the standard colour slides of red and yellow indices.

Refractive Index

The refractive index of CPKO was determined in line with the AOCS Official methods (Cc7-25), as explained by Salimon and Ahmed [16] using a refractometer model (TAGO Co. Ltd. Series No.1211), connected to a Japanese digital thermometer model (DTM-1T) at 26.5°C.

Moisture Content

The moisture content of CPKO was determined using a Moisture Analyser model AND MX-50. Approximately 5 g of the sample was weighed into a moisture dish and dried in the moisture analyser for 30 min at 101°C [10].

Viscosity

The viscosity of CPKO was determined using a Brookfield model RV DV-I+ (U.S.A), with a Spindle (size 5). The viscosity was read in cp (centipoises) directly from the viscometer, which was maintained at 1 min and 100 rpm at room temperature [17].

Density and Specific Gravity

The density of CPKO was measured using a delicate balance. The weight of one millilitre of CPKO placed on a balance was recorded at room temperature. Later, the specific gravity was determined according to The Lund relationship [18].

Gas Chromatography Analysis of Fatty Acid Composition

The fatty acids composition was determined using a Gas Chromatography (Shimadzu GC-17A) equipped with a capillary column BPX 70 (30m × 0.25mm × 0.25 m) and a FID detector. The column temperature was programmed to 120°C, with a 3°C increment per min for 57 min. The injector and detector temperature were set at 260°C and 280°C, respectively. Helium gas as the carrier gas was used with a flow rate of 0.3 ml/min. The parameters of GC were carried out according to Derawi and Salimon [13]. The fatty acid methyl esters (FAME) were prepared using two methods; base catalysed and acid catalysed preparations. FAME was prepared with base-catalysed for transesterification CPKO using the procedural method of Japir *et al.* [19]. Next, 1 ml of

hexane was added to 0.1 ml of CPKO. This was followed by adding 1 ml of sodium methoxide (1.55 g of NaOH in 50 ml of methanol) solution to the oil mixture. The solution was then stirred vigorously for 10 sec using a vortex stirrer and then kept for 10 min for phase separation; the clear FAME solution and the cloudy aqueous layer. The upper FAME layer was carefully decanted. The acid-catalysed for esterification of the fatty acids mixture used the approach proposed by Ichihara *et al.* [20]. Approximately 2 g of the sample was then dissolved in 1 ml of toluene, followed by the addition of 7.5 ml of methanol and 1.5 ml of the reagent solution (9.7 ml HCl 35%, diluted with 41.5 ml methanol and was then stored in a refrigerator). The tube was agitated and subsequently heated at 100°C for a period of 1 h. After cooling, 10 ml of hexane and 10 ml of water were added to the mixture to extract methyl esters contained in the hexane phase. The hexane phase was dried with anhydrous sodium sulphate. The fatty acid content of CKPO was determined using their respective FAME and was injected into gas chromatography for analysis. The identification of the peaks were identified through the retention time, i.e., by means of comparing them with genuine standards analysed under the same condition.

High-performance Liquid Chromatography Method Analysis of Triacylglycerols

High-performance liquid chromatography (HPLC) was performed on the waters model Ultimate 3000 DIONEX with a evaporative light scattering detector and an auto-injection. The separation of TAG, DAG, MAG and FFA of CPKO was carried out with commercially-packed C18 column 5µm × 120Å (4.6 × 250 mm) at room temperature. The mobile phase comprises a mixture of acetone: acetonitrile (63.5%: 36.5%), fixed at a flow rate of 1 ml/min. The sample preparation entailed the dilution of 0.1 ml sample with 1.5 ml acetone to form acetonitrile (63.5: 36.5) mixture. The HPLC was immersed in the mixture and auto-injected with an overall operation time of 35 min. The peaks were identified using the retention times of commercially obtainable TAGs standard. The relative percentages of TAG peaks were evaluated from all peaks that emerged after 10 min [21].

Thermal Behaviour

The thermal properties of CPKO were investigated using a differential scanning calorimeter (DSC 822e Mettler Toledo calibration) to obtain the melting and crystallisation curves. DSC analysis was carried out according to [22]. The weight of the samples in the 49 ml sealed aluminium pan ranged between 5 mg and 8 mg. Next, the samples were placed in an oven for 30 min, in the freezer for 90 min and then left at room temperature for 48 h. Then, each sample was exposed at 5°C and was used directly to run at -60°C to 60°C to -60°C with a heating rate of 10°C.

Fourier Transform Infrared Spectroscopy Analysis of CPKO

Fourier Transforms Infrared Spectroscopy (FTIR) was carried out according to Sherazi *et al.* [23]. FTIR spectra of the CPKO were recorded (Perkin Elmer Spectrum GX spectrophotometer) in the range of 400 4000 cm^{-1}. FTIR was used to measure functional groups of the CPKO. A very thin film of sample was covered on NaCl cells (25 mm ID × 4 mm thickness) and was used for the analysis.

NMR Analysis of CPKO

The nuclear magnetic resonance analysis (NMR) for proton ^{1}H and ^{13}C (NMR) was carried out according to Gunstone *et al.* [24]. The spectra were recorded on a Bruker AV400111 (USA) 400 MHz at 30°C. Tetramethylsilane (Me4Si) was used as an internal chemical shift reference. About 25 mg of sample was dissolved in 1 ml of deuterated chloroform (CDCl$_3$) in all experiments.

RESULTS AND DISCUSSION

Physicochemical Characteristics of CPKO

The similarity and difference between the physicochemical properties of CPKO and CPKOMS can be seen in Table 1, which is a comparison of the sections of the Malaysian Palm Oil Board Standards dealing with identity and quality characteristics. The percentage of FFAs in oil is an indication of their level of degeneration and quality. Also, the duration and storage conditions of the seeds are factors that may affect the value of free fatty acid [25]. Accordingly, the result shows that the average value of free fatty acid% for CPKO is 3.7% in the range compared with the Malaysian standard. Notably, FFA is one of the most important quality parameters in the palm kernel oil industry as it indicates the level of deterioration of the oil [26]. The FFA limit in Malaysian palm kernel oil mills is 5%. The acid value was determined to be 10.4±0.1 mg NaOH/g oil for CPKO. The hydroxyl value for CPKO was 45.06±0.3 mg KOH/g. This value means the existence of free fatty acid, MAG and DAG in CPKO was due to the hydrolysis of triacylglycerides resulting from the humidity and temperature results. The iodine values of the CPKO measured in this study was 20.8±0.6 gI2/100 g, as shown in Table 1. The disparity in these values can be attributed to the fatty acid composition, where the percentage of unsaturated fatty acid in CPKO is compatible compared to the unsaturated fatty acid content of standard CPKO [27]. Similarly, the saponification value of CPKO was 244.04±0.1 mg KOH/g and was also compatible with the range of typical crude palm kernel oil. Olanrewaju *et al.* and Agatemor [28, 29] reported that a high saponification value contains a high proportion of lower fatty acids. This quality in the oil quantifies its use in soap production. The

colour of the CPKO varies from a light yellow to a brownish yellow. The Malaysian Palm Oil Board Standards state that the maximum red and yellow colour of crude palm kernel oil is 8R and 60Y [30]. In this study the colour of CPKO was 0.5 red /20 yellow in a Lovibond colour. Further, the data for viscosity at 28°C showed that CPKO exhibited the highest resistance to flow with viscosity of 40 cP. Accordingly, the high refractive index of CPKO is attributable to the high number of carbon atoms in their fatty acid composition [31]. The Density of the sample also showed a slight difference and was in the range of 0.9 g/ml for CPKO and the specific gravity of CPKO was 0.9 g/ml. The moisture content for CPKO is close to the moisture content of the crude palm kernel oil standards.

Notably, it is one of the most important characteristics to identify the quality of the oil.

FTIR Analysis of CPKO

FTIR spectroscopy can be used to infer the molecular structures of substances from absorption bands characteristic of specific functional groups, which are presented as spectra of peaks [32]. FTIR spectrum of CPKO is frequently dominated with the bands representing TAGs. The characteristic peaks of the main functional groups in CPKO is shown in Table 2. Figure 1 shows a representative set of infrared spectrum of CPKO in the range of 600 to 4000 cm^{-1}. The strong absorption band of CPKO at 1739.4 cm^{-1} is probably due to the esterified carbonyl function, which is also accountable for the band at 1165 cm^{-1}. The band at 3006 cm^{-1} indicates =C-H stretch for Sp2 (aliphatic), while the bands at 2921cm^{-1} and 2853 cm^{-1} indicate C-H stretching vibration for Sp3 (aliphatic) in CPKO.

Table 1. Physicochemical properties of CPKO.

Parameter	CPKO	CPKO$_{MS}$ [a]
FFA (as lauric acid) (%)	3.7 ±0.1	5 max
Acid value (mg NaOH/g)	10.4±0.1	-
Iodine value (Wijs) (gI$_2$/100 g)	20.8±0.6	17.0-20.0
Saponification value (mg KOH/g)	244.04±0.1	243-249
Unsaponifiable matter (%)	0.7±0.1	0.1-0.8
Average molecular weight (g/mol)	689.6±0.15	-
Hydroxyl value (mg KOH/g)	45.06±0.3	-
Moisture content at 28°C (%)	0.5±0.1	0.5 max
Refractive index at 28	1.455	1.4500 – 1.4518
Viscosity at 28°C (cp)	40	-
Density (g/ml)	0.9	0.9040 -0.9050
Specific gravity (g/ml)	0.976	-
Lovibond colour (R/Y) at 28°C	0.5R –20Y	8 Red max and 60 Yellow max.

[a] [24, 30] CPKO: crude palm kernel oil; CPKO$_{MS}$: Malaysian crude palm kernel oil standards.

Table 2. The functional groups of CPKO regarding the main wavenumber in the FTIR.

Functional Group	Wavenumber (cm^{-1})
OH stretching (FA)	-
C = C bending vibration (aliphatic)	3006
C-H stretching vibration (aliphatic)	2921,2853
C = O stretching vibration (ester)	1739.4
C = O stretching vibration (carboxylic acid)	-
C-H scissoring and bending for methylene	1465
=C–H (*cis*) Unsaturated	1417
-CH3 sym deformation	1377
-C-O-Stretching vibration(ester)	1238 1165
C-H group vibration (aliphatic)	722

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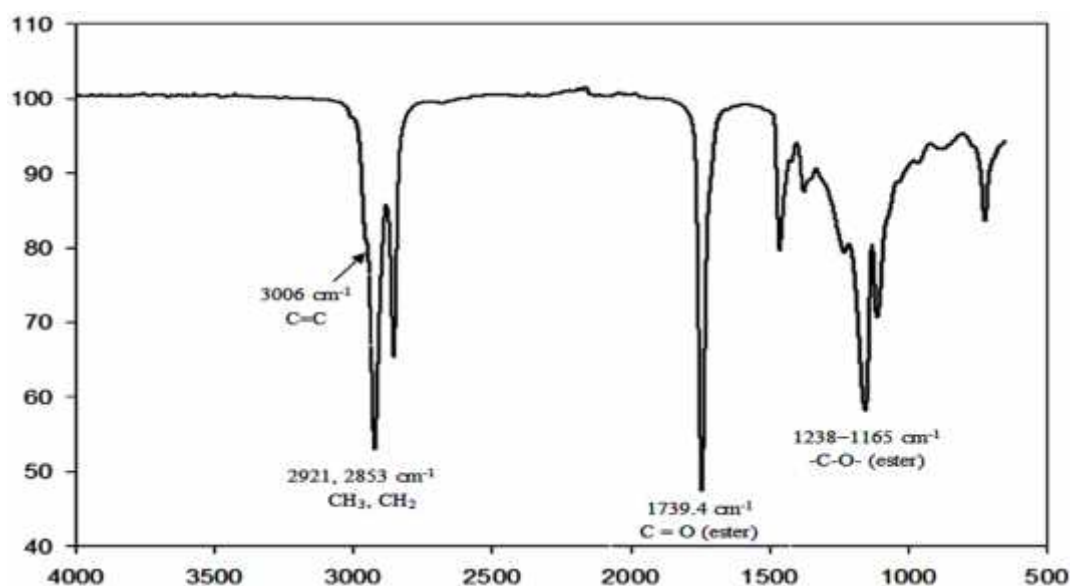Crude Palm Kernel Oil

Figure 1. FTIR spectra of CPKO.

NMR Spectrum of CPKO

Nuclear magnetic resonance (NMR) spectroscopy was used to identify the signal intensity of the functional atoms in CPKO. The analysis of CPKO was carried out using ^{1}H NMR and ^{13}C NMR. The results are discussed in detail in the following subsections: The major signal assignments in the ^{1}H NMR spectrum of the CPKO is shown in Table 3 and shown in Figure 2. The signals at 0.88-0.87 ppm are assigned to - CH3 (terminal methyl in alkyl chain). The terminal methyl - CH2 is denoted by 1.25-1.29 ppm of CPKO. The acyl methylene (-CH2-COOR) is indicated in CPKO by the peaks at 2.28-2.32 ppm. Other identified bonds are methylene groups of glyceryl- CH2-O-CO-R (– esterified glycerol) denoted by peaks at 4.11-4.16 ppm for CPKO. Peaks indicate the - esterified glycerol (-CH–OCOR) at 4.27 - 4.31 ppm for CPKO.

The major signal assignments in the ^{13}C NMR spectrum of the CPKO is shown in Table 4 and shown in Figure 3. The peak at 14.07 ppm indicates carbon atoms of the methyl groups affixed to the end of the acyl chains, while the peaks at 22.67-34.18 ppm denote the methylene carbon atoms in fatty acid moieties of CPKO. The glycerol carbons of triacylglycerols resonate in the spectral region of 60 to 70 ppm. The values for glycerol carbons ( ) at 68.87 ppm and those for glycerol carbons ( ) and ( ) were 62.06 ppm. The olefinic carbons of unsaturated fatty acids of CPKO triacylglycerols which are appear between (127.86- 130.14 ppm). The signals at 172.79 ppm and 173.21 ppm refer to the carbon atom of the carbonyl group.

Table 3. The main signals present in ^{1}H NMR spectrum of CPKO.

Assignment	CPKO (ppm)
–**CH**$_3$ (terminal methyl)	0.88 – 0.87
–(**CH**$_2$)n–(saturated alkyl chain)	1.25-1.29
–**CH**$_2$–CH=CH–**CH**$_2$-	1.99-2.03
–**CH**=**CH**–	5.32
-**CH**$_2$-COOR , acyl methylene	2.28-2.32
-**CH**$_2$-O-CO-R (– esterified glycerol)	4.11-4.16
CH–OCOR (- esterified glycerol)	4.27-4.31

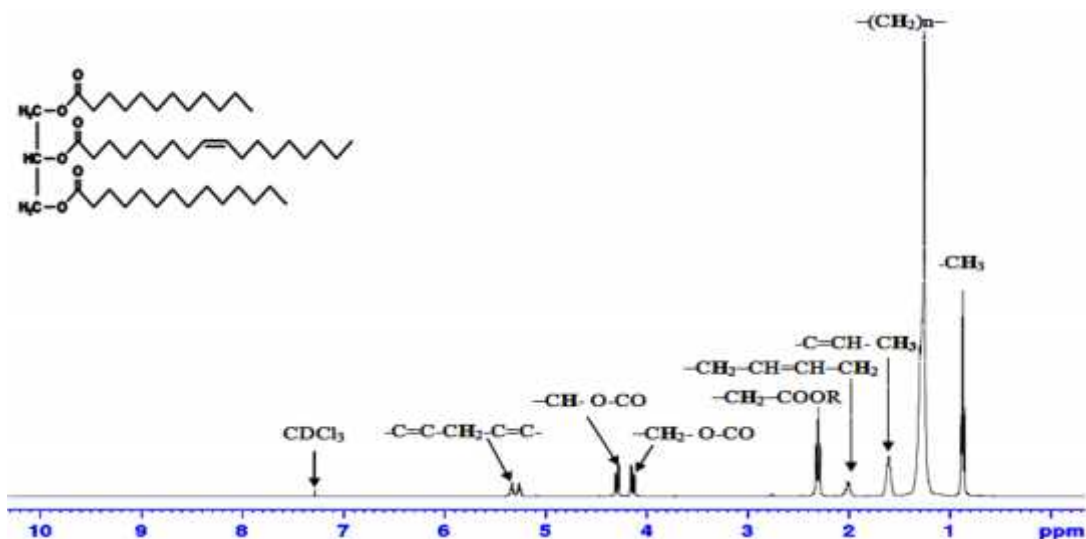**Figure 2.** ^{1}H NMR spectrum of CPKO.

Table 4. The main signals present in ^{13}C NMR spectrum of CPKO.

Assignment	CPKO (ppm)
–CH$_3$	14.07
-(CH$_2$)n-	22.67-34.18
-CH$_2$-O-CO-R glycerol carbons ( ) & ( )	62.06
CH–OCOR glycerol carbons ( )	68.87
-HC=CH- (Olefinic Carbone)	127.86- 130.4
CH$_2$–OCOR (carboxylic ester)	172.79-173.21

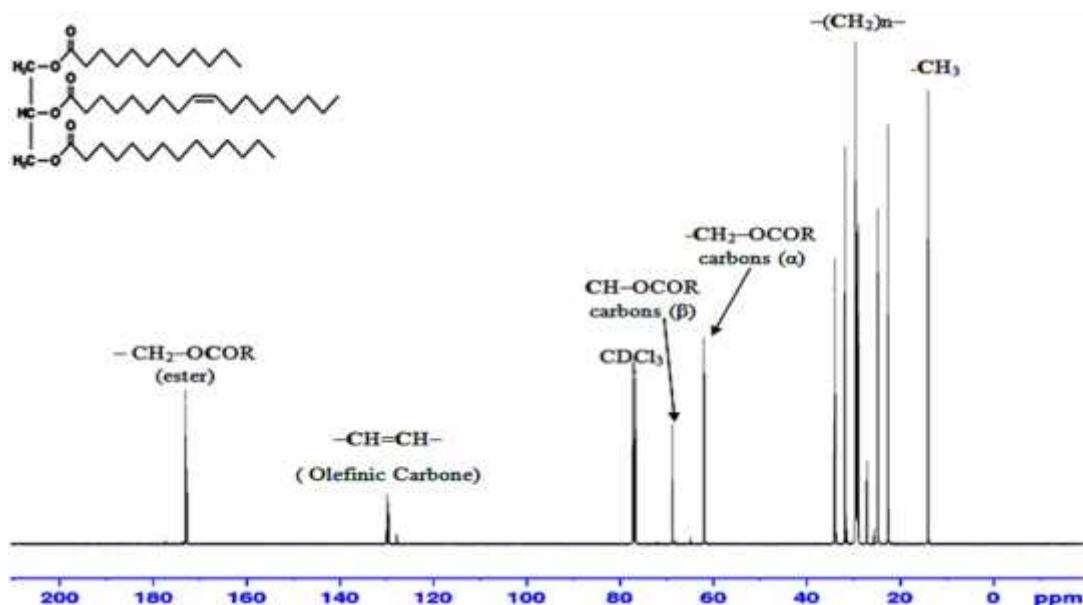**Figure 3.** ^{13}C NMR spectum of CPKO.

Fatty Acid Composition

The fatty acid composition of CPKO is summarised in Table 5. By comparison, it was proven from this work that the fatty acid compositions are within the standard permitted by the Malaysian palm oil standard. The composition of CPKO prepared with base catalyst comprises: Lauric acid (44.5±0.7%),

Oleic acid (18.0±0.5%), Myristic acid (16.9±0.1%), Palmitic acid (9.4±0.2%), Linoleic acid (2.9±0.1%), Stearic acid (2.6±0.1%), Caprylic acid (2.9±0.1%) and Capric acid (2.8±0.1%) as shown in Table 5. The free fatty acids (FFAs) composition of CPKO subjected to acid catalysed preparation comprises: Lauric acid (52.1±0.8%), Oleic acid (11.8±0.5%), Myristic acid (16.4±0.1%), Palmitic acid (7.3±0.1%), Linoleic acid (1.9±0.1%), Stearic acid (1.8±0.1%), Caprylic acid (4.6±0.2%) and Capric acid (4.1±0.05%) as shown in Table 5.

According to the GC results, there was a slight difference between free fatty acid and fatty acids compositions in CPKO using acid and base catalysts respectively to determine the composition of free fatty acids and base catalysed to determine the oil composition as shown in Table 5. The results indicated that all TAG, DAG, and MAG were hydrolysed by base catalysed. Also, the separation of gas chromatography peaks relied on the number of carbon atoms and the boiling point of fatty acid. The higher the retention times for the detected peak, the greater the carbon number. The retention time and boiling point increased with increased intermolecular force due to the double bond in the backbone of fatty acid for the same carbon chain length such as stearic acid and oleic acid.

High-Performance Liquid Chromatography Method Analysis of Triacylglycerols

The results obtained from the reversed phase HPLC indicate that the CPKO is composed of at least nineteen relevant TAGs (Figure 4) in which the mechanism of separating the TAGs involves the chain length and degree of unsaturation of the fatty acids [33]. Table 6 shows the TAG composition of CPKO. The main TAG of crude palm kernel oil (CPKO) contained a wide range of medium-chain TAG species such as LaLaLa, LaLaM, LaLaP, CaLaLa, CLaLa and LaOLa where La is lauric acid, M is myristic acid, Ca is caprylic acid, C is capric acid and O is oleic acid. The major TAG composition of CPKO was trisaturated (79.5%), followed by disaturated (15.83%), monosaturated (4.03%) and tri-unsaturated (0.64%) as shown in Table 6.

Table 5. FA composition in CPKO with base-catalysed transesterification (%) and FFA composition of CPKO with the acid-catalysed esterification.

Fatty acid composition	Relative composition (%)		
	Base catalyst	Acid catalyst	Range
	CPKO	CPKO	
Caprylic acid $C_{8:0}$	2.9±0.1	4.6±0.2	3.2–4.7
Capric acid $C_{10:0}$	2.8±0.1	4.1±0.05	2.9–3.5
Lauric acid $C_{12:0}$	44.5±0.7	52.1±0.8	45.4–49.8
Myristic acid $C_{14:0}$	16.9±0.1	16.4±0.1	15.4–17.2
Palmitic acid $C_{16:0}$	9.4±0.2	7.3±0.1	7.9–9.3
Stearic acid $C_{18:0}$	2.6±0.1	1.8±0.1	1.9–2.3
Oleic acid $C_{18:1}$	18.0±0.5	11.8±0.5	13.7–17.0
Linoleic acid $C_{18:2}$	2.9±0.1	1.9±0.1	2.1–2.9
Saturated Fatty acid	79.1	86.3	
Unsaturated Fatty Acid	20.9	13.7	
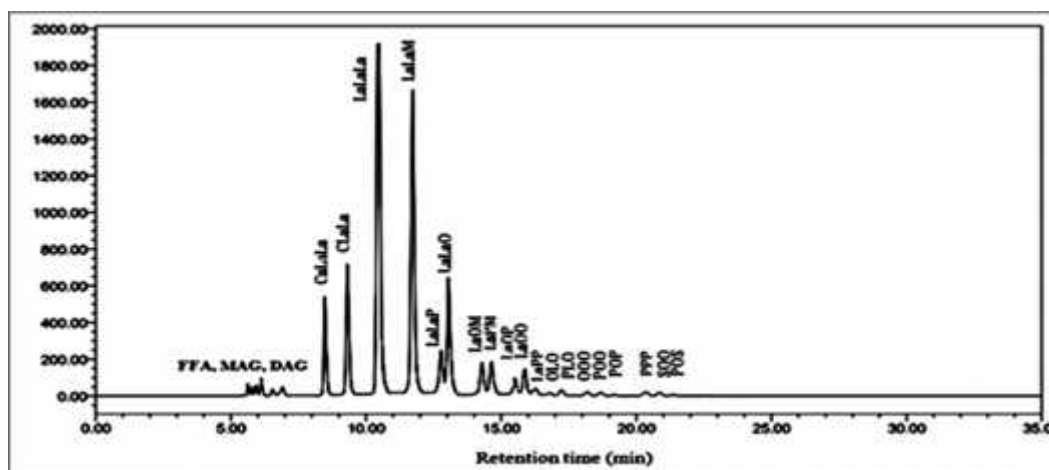
Figure 4. HPLC chromatogram of crude palm kernel oil.

Table 6. Triacylglycerol composition of CPKO.

Triacylglycerol species	ECNs	Composition (%)
Trisaturated		
CaLaLa	32	6.03
CLaLa	34	9.10
LaLaLa	36	31.91
LaLaM	38	23.59
LaLaP	40	4.75
LaPM	42	2.96
LaPP	44	0.95
PPP	48	0.21
Total		**79.5**
Disaturated		
LaLaO	42	9.93
LaOM	44	3.51
LaOP	46	1.79
POS	52	0.5
POP	50	0.10
Total		**15.83**
Monosaturated		
LaOO	48	2.61
POO	52	0.44
PLO	52	0.68
SOO	54	0.3
Total		4.03
Tri-unsaturated		
OLO	44	0.15
OOO	48	0.49
Total		**0.64**

ECNs = equivalent carbon number. Ca: caprylic acid, C: capric acid, La: lauric acid, M: myristic, P: palmitic, S: stearic, O: oleic, L: linoleic acid.

Thermal Behaviour

DSC determined the effect of cooling rates on the crystallisation curve and heating rates on the melting curves of CPKO as shown in Figure 5. The endotherms in each melting curve have been labelled in the order of increasing temperatures, while the exotherms in each crystallisation curve were marked in the order of decreasing temperatures [34]. The melting curve for CPKO displayed two endothermic peak regions (Figure 5) due to the presence of high melting of saturated fatty acids and low melting of unsaturated fatty acids. In CPKO, a fully saturated TAG showed a peak at a higher temperature range at 9.13°C. The crystallisation curve displayed two exothermic regions of CPKO (Figure 5). In CPKO, the first region showed one peak in the high-melting group. The temperature of this region began at 6.11°C, of which was the area where the liquid started to solidify and therefore indicated the more saturated crystallised TAG. Also, the second region showed one peak in the low-melting group. In this area, the crystalline started from a more unsaturated TAG fraction at -2.10°C, as shown in Figure 5.

CONCLUSION

This study showed that the physicochemical properties of Malaysian crude palm kernel oil were similar compared to the Malaysian crude palm kernel oil standards. The dominant fatty acids found in crude palm kernel oil were lauric acid, myristic acid and oleic acid. The triacylglycerol of crude palm kernel oil contained a high saturated TAG and a low unsaturated TAG. The analyses performed by FTIR for crude palm kernel oil were positive. The FTIR analyses also showed strong absorption of the ester carbonyl peak at 1739.4 cm^{-1} and 1238 cm^{-1}. On the basis of the results of this study, DSC could provide information about the nature of TAG interaction in CPKO. Recognition of the pattern of interactions in TAG could also be helpful in many industries.
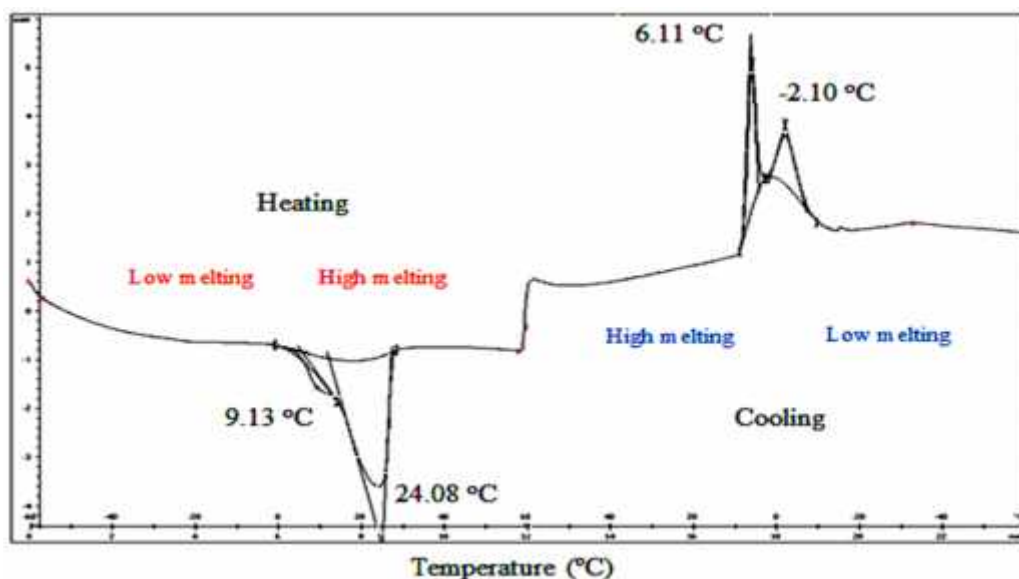
Figure 5. Heating and cooling profiles of CPKO.

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