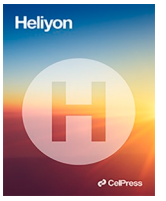
Heliyon 9 (2023) e20413

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon



Multivariate modelling analysis for prediction of glycidyl esters and 3-monochloropropane-1,2-diol (3-MCPD) formation in periodically heated palm oil

Siti Nur Syahirah Nor Mahiran [a], Nurul Huda Abd Kadir [a,*], Maulidiani Maulidiani [a], Tengku Rozaina Tengku Mohamad [b], Nigel J. Gooderham [c], Mahboob Alam [d,**]

[a] Faculty of Science and Marine Environment, Universiti Malaysia Terengganu, Malaysia
[b] Faculty of Fisheries and Food Science, Universiti Malaysia Terengganu, Malaysia
[c] Department of Metabolism, Digestion, Reproduction, Imperial College London, Sir Alexander Fleming Building, London, SW7 2AZ, United Kingdom
[d] Department of Safety Engineering, Dongguk University, 123 Dongdae-ro, Gyeongju-si, Gyeongbuk, 780714, South Korea

ARTICLE INFO

Keywords:
Physicochemical characteristics
Palm oil
Oxidation
Metabolomics
Spectroscopy studies
Glycidyl ester

ABSTRACT

Palm oil is a vegetable oil that is widely used for cooking and deep-frying because of its affordability. However, repeatedly heated palm oil is also prone to oxidation due to its significant content of unsaturated fatty acids and other chemical toxicants such as glycidyl esters and 3-monochloropropane-1,2-diol (3-MCPD). Initially, the physicochemical properties such as colour, viscosity, peroxide, *p*-anisidine and total oxidation (TOTOX) of periodically heated palm oil were investigated. Chemical profiling and fingerprinting of six different brands of palm cooking oil during heating cycles between 90 and 360 min were conducted using Fourier transform infrared (FTIR) and ^{1}H Nuclear Magnetic Resonance (NMR) metabolomics. In addition, the multivariate analysis was employed to evaluate the ^{1}H NMR spectroscopic pattern of repeatedly heated palm oil with the corresponding physicochemical properties. The FTIR metabolomics showed significant different of the chemical fingerprinting subjected to heating duration, which in agreement with the result of ^{1}H NMR metabolomics. Partial least squares (PLS) model revealed that most of the physicochemical properties of periodically heated palm oil are positively correlated (R^2 values of 0.98–0.99) to their spectroscopic pattern. Based on the findings, the color of the oils darkened with increased heating time. The peroxide value (PV), *p*-anisidine value (*p*-AnV), and total oxidation (TOTOX) values increased significantly due to degradation of unsaturated compounds and oxidation products formed. We identified targeted metabolites (probable carcinogens) such as 3-monochloropropane-1,2-diol (3-MCPD) and glycidyl ester (GE), indicating the conversion of 3-MCPD to GE in repeatedly heated oils based on PCA and OPLSDA models. Our correlation analysis of NMR and physicochemical properties has shown that the conversion of 3-MCPD to GE was significantly increased from 180 to 360 min cooking time. The combination spectroscopic techniques with physicochemical properties are a reliable and robust methods to evaluate the characteristics, stability and chemical's structure changes of periodically heated palm oil, which may contribute to probable carcinogens development. This study has proven that combination of NMR and physicochemical analysis may predict the formation of the probable carcinogens of heated cooking oil over time which

* Corresponding author.
** Corresponding author.
E-mail addresses: nurulhuda@umt.edu.my (N.H. Abd Kadir), mahboobchem@gmail.com (M. Alam).

https://doi.org/10.1016/j.heliyon.2023.e20413
Received 27 May 2023; Received in revised form 8 September 2023; Accepted 23 September 2023
Available online 24 September 2023

emphasizing the need to avoid certain heating cycles to mitigate formation of probable carcinogens during cooking process.

1. Introduction

Currently, palm oil is one-third of the rising global demand for vegetable oil as its a resource for everyday necessities and is commonly found in shortening, margarine, chocolates, snacks, packaged food, and fast food [1,2] as well as in food processing industry [3]. In comparison to other vegetable oils, palm oil offers several significant benefits, including low cost, the highest production per hectare, and a wide range of uses [4]. *Elaeis guineensis* is the main source of palm oil native to Africa and the growth has expanded to Southeast Asia, especially Malaysia and Indonesia and become among the biggest world palm oil supply [5]. The demand for palm oil has significantly increased recently, and it is anticipated that this trend will continue in the forthcoming years [6]. However, non-governmental organisations (NGOs) and the media both emphasised the negative impacts of palm oil use on human nutrition at the same time [6].

Palm oil is mainly composed of monounsaturated fatty acid (MUFA) 39%, polyunsaturated fatty acid (PUFA) 10% and saturated fatty acid (SFA) 50% [7]. When these unsaturated compounds are heated, they break down and produce a variety of oxidation products [8]. Oxidation of oil during repeated frying is the main concern as it reacts with atmospheric oxygen and [9] stated that oxidation is more likely to occur in unsaturated fatty acid than a saturated fatty acid. Oil becomes rancid when it is heated repeatedly, causing all of the unsaturated fatty acids to break their double bonds and produce volatile chemicals such as aldehydes, peroxides and ketones [3,8,10]. It reduced the food stability, quality, safety and nutritional values. This occurrence causes the oil to develop unpleasant smells and scents, making it non-ideal for human consumption [11]. It is reported that repeated cooking oil leads to the formation of food contaminants that will cause genotoxic, mutagenic and carcinogenic potential [12,13]. The consumption of unhealthy repeated cooking oil will affected consumer's health such as cardiovascular diseases, increased cholesterol levels in the blood, increased blood pressure, endothelial dysfunction and triggering the formation of cancer [3,14–16]. The production of various harmful substances during the refining of palm oil has also been reported, including the 3- and 2-monochloropropane-1,2-diol (MCPDs), acrylamide, glycidamide, glycidol and its esters (probably carcinogenic substances) when the oils are heated at high temperature and heating time [6,17]. This food contaminant will lead to adverse effects on consumer health. Furthermore, one of the most popular methods for preparing food is deep frying, which is utilized extensively by both customers and the food industry as it enhances sensorial properties [18]. Deep-fried snacks such as deep-fried banana, deep-fried fish fritter, 'keropok goreng' and fried chicken are often available in street vendors served by hawkers in several Southeast Asian countries and pro-long heating process may contribute to MCPDs and glycidol formation. Since toxic compounds may accumulate during cooking, the cooked oil containing food may contaminated with probable carcinogens that has toxicological implications on human health [19]. Nowadays, a major issue with cooking oil is that whether pro-long heating process results in the increase of probable carcinogens in the fritters. This approach may not be prevalent in-home cooking, but it is more prominent practice among hawkers due to cost effective in earning more profit in food business. However, this activity may initiate cancer risk to those who consume the deep fried food in pro-long cooking of the palm oil. Therefore, in order to determine the safety of the periodically heated palm oil, it is important to monitor the quality of the cooking oils by elucidating the changes in their chemical fingerprinting, physicochemical, and nutritional properties. Edible oil safety is a significant concern due to the formation of harmful contaminants during processing and storage. Among these contaminants are glycidyl esters (GE), which are known for their carcinogenic and mutagenic properties. Traditional detection methods for these contaminants are often time-consuming and costly. However, Fourier transform infrared (FTIR) and ^{1}H NMR spectroscopy are gaining interest as rapid and non-destructive alternatives [20,21]. FTIR spectroscopy measures the absorption of infrared radiation, which can uniquely identify samples and detect various food contaminants. Screening the literature indicates that FTIR spectroscopy has been shown to be effective in detecting and quantifying these contaminants in oils. The combination of FTIR spectroscopy and chemometrics, a statistical technique for extracting information from complex data sets, offers a promising approach for accurate and precise detection of GE and MCPDs in oils [22–25]. In spite of numerous research has reported the formation of GE and MCPDs in cooking oil, correlation study on formation of GE and MCPDs with physicochemical changes in periodically heated palm oil is limited. Furthermore, physicochemical characteristics of oils vary depending on how much amount of heating is exposed during cooking and directly it could determine the quality of the oil [8]. Theoretically, repeated heating of any type of cooking oil at different ranges of temperature and heating time will exhibit a change in the characteristics and properties of the oils [26]. These repeated heating affect the oil's appearance, causing it to have a high viscosity, colour darkening, smoke point lowering and oxidative stability also affected, making it more harmful when consumed [27].

In Malaysia, palm-based cooking oil is packaged in two materials which are in a plastic pouch or packet and in a polyethylene terephthalate (PET) bottle [28]. The palm-based cooking oil in plastic packet is a subsidised price of cooking oil which is less expensive than the cooking oil packaged in PET bottles [28]. Continuity of this situation, consumers frequently believe that cooking oil in pouch packaging have lower quality than cooking oil packaged in PET bottles and many consumers assume that the palm-based cooking oil in plastic packet is the adulterated cooking oil. In this study, the palm-based cooking oil in plastic packet samples from different brand (6 brands) were collected from various local grocery stores in Malaysia. The different brands were chosen as to avoid bias of the confounding variables such as manufacturing processes and adulteration of the results obtained. The palm-based cooking oil in plastic packet were selected as the sample in this study due to most vendors utilise this type of cooking oil due to cost effective [29]. As far as this study is concerned, limited research has been conducted on the actual situation of food vendors engaging in repeated deep-fried

cooking using specifically packaged palm oil at various time points. However, there is sufficient literature available on similar research work on various edible oil, which can be used to inform our understanding of the potential health risks of consuming this type of food.

Thus, this study mimics the real scenario during food or fritters cooking process using periodically heated cooking palm oil by fritters vendors. This to evaluate the physicochemical and chemical structural changes during the pro-long heating process which might contribute to probable carcinogens development. Therefore, the objective of this work was to evaluate the physicochemical changes (colour, viscosity, PV, *p*-AnV) that occurred in the repeated cooking oil and to determine the presence of the food contaminants compounds in repeated cooking oils and their changes based on FTIR spectroscopy as a rapid assessment method. Then, the combined NMR and physicochemical techniques was analysed by using chemometric multivariate as further verification of metabolites (GE and MCPDs) present in the repeated palm-based cooking oil as a predictive model.

2. Materials and methods

2.1. Collection of oil samples

Cooking oil samples were collected from one of the fritters vendors in Kuantan, Pahang, Malaysia. Six different brands of packaged palm oil were used for the frying process. The brands were labelled as A, B, C, D, E and F. The samples for frying were bananas, potatoes, fish and shrimp fritters. Nine kilograms of cooking oil were used in the frying process until the last frying cycle without adding fresh oil between the frying cycles. The oil samples (100 mL) were collected and stored in a glass tube for the time point (0 min) before the heating process started. The first frying cycle was started with one of the frying items after the initial heating procedure, followed by the following cycle. Frying of bananas was carried out by deep frying 2 kg of bananas followed by potatoes (2 kg), fish fritters (3 kg) and shrimp fritters (1 kg). At first, oil was heated up to 180 °C and then the bananas were put into it followed by the others. Subsequent frying cycles were performed at an interval of 90 min. The oil samples were collected at five different time points (5 frying cycles) which were at 0, 90, 180, 270 and 360 min. The frying temperature was measured between 180 °C and 220 °C when the samples were collected. After every frying process, 100 mL of oil was collected and cooled at room temperature. Oil samples were collected from minute zero (fresh oil) at the end of every successive cycle. The cooled oil samples were kept in a glass tube and stored at −80 °C until further analysis. The same procedure was repeated for another brand of palm oil the next day.

2.2. Determination of physicochemical properties

2.2.1. Colour analysis

The measurements of colours were measured using a colorimeter (CM-5, Konica Minolta Co., Tokyo, Japan). Before starting with the sample measurements, the colourimeter was calibrated with black and white (Y = 85.5, X = 0.3171, Y = 0.3237) tiles. The oil samples were measured directly by using a colorimeter without any pre-treatment of the samples. Before the next colour measurement, the Petri dish was washed with acetone to remove the residue of the oil sample that may affect the next reading. The colour intensities of each oil sample were measured using the CIELAB (L*a*b*) colour scale. The L* value indicates the lightness of the sample, where white (100) and black (0). The a* value indicates redness (+) to greenness (−) and the b* value indicates yellowness (+) to blueness (−).

2.2.2. Viscosity analysis

The measurements of viscosity were measured using a rheometer (TRIOS HR-2 Discovery Hybrid Rheometer, TA Instruments Ltd, New Castle, USA) equipped with a temperature controller unit that was connected to a computer with TRIOS software. A Peltier system at the base of the measuring geometry was used to control the temperature. By using the rheometer software auto-gap function, the superior plate was placed on the sample surface (1 mm). Before the measurement of the samples, the rheometer was set up at a constant temperature (25 °C) and a shear rate of 0.1–100 S^{-1}. A 40 mm Peltier steel cone plate (2°) with a gap of 46 μm was used. A few drops of oil sample were loaded on the rheometer Peltier steel cone plate by using a micropipette for each run of the samples and the measurement was started immediately after the sample was loaded. All data were recorded at 5 s intervals and constant temperature (25 °C) during the shearing. Each measurement was conducted in triplicate (n = 3) for each time point of different oil samples. The data were proceeded for analysis process.

2.2.3. Peroxide value (PV)

Analysis of PV was conducted according to Refs. [30,31] with some modifications. Oil samples (5 ± 0.05 g) were weighed and transferred into a 250 mL Erlenmeyer flask. Then, the solvent acetic acid, glacial (J.T Baker, Fisher Scientific, Loughborough, UK) and chloroform (Merck, Darmstadt, Germany) (30 mL) with a ratio of (3:2 v/v) was added to the flask containing the oil samples. The flask was swirled until the sample was dissolved and saturated potassium iodide (KI) (Merck, Darmstadt, Germany) solution (0.5 mL) was added to the mixture. The flask was shaken for 1 min then distilled water (30 mL) was added. Then, the mixture was slowly titrated with 0.01 N sodium thiosulfate ($Na_2S_2O_3$) (Amresco, US), and adding it with constant and vigorous shaking until the colour changed to light yellow. 10% starch (from wheat) (Merck, Darmstadt, Germany) (1 mL) solution was added to the mixture as an indicator and the mixture changed to blue colour. The mixture was titrated with 0.01 N $Na_2S_2O_3$ until the blue colour disappeared. The same procedure was conducted for the blank sample with no addition of the fat sample. The same procedure as above was done with other oil samples A, B, C, D, E and F with 0, 90, 180, 270 and 360 min. The PV value was calculated by the following equation (1):

$$\text{PV } (mEqperoxide / kgfat) = \frac{(S-B)x\,N\,x\,1000}{Sample\ Weight(g)} \quad (1)$$

where, S = volume of titrant of the oil samples (mL); B = volume of titrant of blank (mL); N = normality of $Na_2S_2O_3$ solution.

2.2.4. p-Anisidine value (p-AnV)

The analysis of *p*-AnV was conducted according to a modified techniques [31,32]. The oil sample (2.0 g) was weighed into a 25 mL volumetric flask. The oil sample was dissolved and diluted with isooctane (25 mL) (Merck, Darmstadt, Germany). The absorbance (A_b) of the solution was measured at 350 nm with a spectrophotometer (UV-1900i Shimadzu UV–Vis spectrophotometer, Shimadzu Corp., Japan). Then, fat solution (5 mL) was pipetted into one test tube and isooctane (blank solution) (5 mL) was into a second test tube. 0.25 g of *p*-Anisidine (Merck, Darmstadt, Germany) was weighed and dissolved in acetic acid, glacial (100 mL) (w/v) (J.T Baker, Fisher Scientific, Loughborough, UK). *p*-Anisidine reagent (1 mL) was added to each test tube and shaken to mix up the reagent and the fat solution. The absorbance (A_s) against isooctane that contains *p*-Anisidine reagent was measured at 350 nm. The same procedure as above was done by using other oil samples. The *p*-AnV value was calculated by using the following equation (2):

$$\frac{p-AnV = 25x(1.2\,As - Ab)}{m} \quad (2)$$

where, A_s = absorbance of the fat solution after reaction with the *p*-anisidine reagent; A_b = absorbance of the fat solution without *p*-anisidine reagent; m = mass of the fat solution, g.

2.2.5. Total oxidation (TOTOX) value

The TOTOX value of the oil samples was calculated based on the formula reported by Ref. [33] as follows equation 3:

$$\text{TOTOX value} = 2\text{PV} + p\text{-AnV} \quad (3)$$

2.3. Fourier transform infrared (FTIR) spectroscopy

All spectra of repeatedly heated oil samples at four different time points (90, 180, 270 and 360 min) were obtained using a Nicolet™ iS20 FTIR spectrometer (Thermo Fischer Scientific Inc., Waltham, MA) equipped with attenuated total reflectance (ATR). The spectrometer was controlled by OMNIC software (Thermo Fischer Scientific Inc., Waltham, MA). In addition, oil samples were measured for FTIR analysis before being subjected to frying (0 min). Measurements were made in transmittance mode on a small amount of each oil sample deposited on the ATR on a multi-bounce crystal plate at a controlled temperature (25 °C). An ATR accessory was used with all spectra measured at a range of 4000 to 650 cm^{-1} and consists of 32 co-addition scans with a strong Happ-genzel apodization at a resolution of 4 cm^{-1}. Scanning of the background spectrum (blank) was measured first before proceeding with the oil samples. Then, the spectra of each sample were subtracted against a fresh background spectrum. Before proceeding with the next sample, the ATR plate was cleaned by using acetone and wiped with soft tissues. The scanning was conducted at room temperature (25 °C) [21].

2.4. ^{1}H Nuclear Magnetic Resonance (NMR) spectroscopy of sample preparation and analysis

Cooking oil sample (100 mg) was weighed and transferred in a 2.0 mL Eppendorf tube. Then, the sample was dissolved in 600 μL deuterated chloroform ($CDCl_3$) with silver foil stabilizer, containing 0.03% TMS. The mixture was vortex and directly transferred into an NMR tube (5 mm × 7 cm, 400 MHz, 5 EA).

^{1}H NMR was measured at an ambient temperature of 25 °C on a 400 MHz NMR spectrometer (Bruker, Karlsruhe, Germany) operating at a frequency of 400.11 MHz. The analysis was performed on all 30 samples. The NMR spectrometer was set accordingly to several parameters for all samples measurement which were at temperature (25 °C), number of scans (128), pulse width (9.36 ms), relaxation delay time (2.0 s) with the total acquisition time of 10 min 53 s and spectrum width of 8012.821 Hz. For chemical shift reference and intensity scaling of all NMR data, TMS was used as an internal standard (reference signal) at δ 0.00. MestReNova 8.1 software (Mestrelab Research S.L, Spain) and Chenomx software (v. 7.6, Alberta, Canada) were used for pre-processing and analysed NMR spectra [21]. The NMRProcFlow (https://nmrprocflow.org/) open-source software was utilized to process and bin all ^{1}H NMR spectral data.

2.5. Multivariate data analysis

Multivariate data analysis (MVDA) is a statistical technique used to examine data sets containing multiple variables. This can help identify patterns and relationships among the variables. In this study, multivariate data analysis of FTIR and ^{1}H NMR data was applied to evaluate the metabolite alteration of repeatedly heated cooking oils. In the generated data matrix, the oil sample names were treated as observations, while the FTIR wavenumbers or NMR chemical shifts were considered as the X-variables. MVDA models such as principal component analysis (PCA) and orthogonal partial least squares discriminant analysis (OPLSDA) were performed using the

SIMCA-P software (v. 14.1, Umetrics, Umeå, Sweden). Thirty samples were used to develop the OPLSDA model from NMR data, while sixty samples were used for FTIR chemometrics. In addition, the correlation between the metabolites determined by ^{1}H NMR analysis and the physicochemical properties was investigated through orthogonal partial least squares (OPLS) analysis. The oil samples before frying (0 min) and after frying (360 min) were used as X-variables, and physicochemical properties including colour, viscosity, PV, p-Av, and TOTOX were used as the Y-variables [21,34].

2.6. Statistical analysis

The data were analysed in triplicate and recorded in mean with standard deviation. The plotted graph was done by using GraphPad Prism Software (San Diego, CA, USA). One-way analysis of variance (ANOVA) was conducted using SPSS (v. 25, SPSS Inc., Chicago, IL)

Table 1
Physicochemical properties of (a) colour (b) viscosity (c) PV (d) *p*-AnV and (e) TOTOX value of periodically cooking period at 0–360 min cooking.

Parameters/Time points (min)	0	90	180	270	360
a) Colour					
L*					
Brand A	29.71 ± 0.01^{a}	29.68 ± 0.01^{a}	29.66 ± 0.03^{a}	29.56 ± 0.04^{b}	28.89 ± 0.05^{c}
Brand B	29.67 ± 0.02^{a}	29.64 ± 0.01^{a}	29.52 ± 0.02^{b}	29.12 ± 0.01^{c}	28.97 ± 0.06^{d}
Brand C	29.61 ± 0.02^{a}	29.57 ± 0.03^{a}	29.35 ± 0.04^{b}	29.24 ± 0.01^{c}	29.15 ± 0.02^{d}
Brand D	29.41 ± 0.03^{a}	29.38 ± 0.01^{a}	29.12 ± 0.02^{b}	29.12 ± 0.02^{b}	29.08 ± 0.01^{b}
Brand E	29.25 ± 0.01^{a}	29.21 ± 0.01^{b}	29.18 ± 0.01^{b}	29.09 ± 0.02^{c}	28.65 ± 0.01^{d}
Brand F	29.23 ± 0.01^{a}	29.15 ± 0.00^{b}	29.02 ± 0.03^{c}	28.82 ± 0.01^{d}	28.64 ± 0.02^{e}
a*					
Brand A	−0.71 ± 0.02^{a}	−0.75 ± 0.01^{a}	−1.16 ± 0.04^{b}	−1.20 ± 0.05^{b}	−1.70 ± 0.08^{c}
Brand B	−0.63 ± 0.05^{a}	−1.06 ± 0.03^{b}	−1.18 ± 0.01^{c}	−1.58 ± 0.01^{d}	−2.22 ± 0.06^{e}
Brand C	−0.74 ± 0.01^{a}	−0.90 ± 0.05^{b}	−1.02 ± 0.03^{c}	−1.39 ± 0.01^{d}	−2.04 ± 0.02^{e}
Brand D	−0.75 ± 0.02^{a}	−0.81 ± 0.03^{a}	−0.99 ± 0.02^{b}	−1.33 ± 0.07^{c}	−1.44 ± 0.04^{d}
Brand E	−0.79 ± 0.02^{a}	−0.88 ± 0.03^{b}	−0.92 ± 0.03^{b}	−1.23 ± 0.04^{c}	−1.33 ± 0.03^{d}
Brand F	−0.63 ± 0.06^{a}	−0.87 ± 0.04^{b}	−1.19 ± 0.04^{c}	−1.30 ± 0.04^{c}	−1.86 ± 0.02^{d}
b*					
Brand A	2.77 ± 0.03^{a}	3.17 ± 0.02^{b}	4.66 ± 0.03^{c}	4.80 ± 0.03^{d}	6.13 ± 0.04^{e}
Brand B	2.32 ± 0.01^{a}	3.86 ± 0.01^{b}	4.57 ± 0.02^{c}	5.74 ± 0.04^{d}	7.19 ± 0.05^{e}
Brand C	2.57 ± 0.03^{a}	3.20 ± 0.04^{b}	3.56 ± 0.02^{c}	4.72 ± 0.02^{d}	6.65 ± 0.02^{e}
Brand D	2.59 ± 0.02^{a}	3.01 ± 0.02^{b}	3.74 ± 0.02^{c}	4.54 ± 0.03^{d}	5.01 ± 0.04^{e}
Brand E	2.61 ± 0.02^{a}	3.07 ± 0.02^{b}	3.37 ± 0.03^{c}	4.38 ± 0.03^{d}	5.70 ± 0.02^{e}
Brand F	2.39 ± 0.01^{a}	3.46 ± 0.01^{b}	4.69 ± 0.06^{c}	5.89 ± 0.03^{d}	6.80 ± 0.02^{e}
b) Viscosity x 10^{-2} (Pa s)					
Brand A	7.44 ± 0.38^{a}	7.70 ± 0.13^{a,b}	8.17 ± 0.86^{a,b}	8.39 ± 0.46^{a,b}	9.03 ± 0.51^{b}
Brand B	6.79 ± 0.50^{a}	8.24 ± 0.63^{b}	9.10 ± 0.08^{b}	9.12 ± 0.21^{b}	9.32 ± 0.64^{b}
Brand C	8.27 ± 0.17^{a}	8.32 ± 0.24^{a}	8.76 ± 0.13^{a,b}	8.74 ± 0.17^{a,b}	9.00 ± 0.30^{b}
Brand D	7.99 ± 0.00^{a}	8.09 ± 0.25^{a}	8.30 ± 0.38^{a}	8.68 ± 0.57^{a}	8.85 ± 0.39^{a}
Brand E	6.66 ± 0.28^{a}	7.35 ± 0.46^{b}	7.42 ± 0.11^{b}	7.60 ± 0.07^{b}	9.70 ± 0.06^{c}
Brand F	6.95 ± 0.09^{a}	7.45 ± 0.13^{b}	7.60 ± 0.09^{b,c}	7.86 ± 0.14^{c}	8.93 ± 0.25^{d}
c) PV (meq O_2/kg)					
Brand A	1.13 ± 0.23^{a}	3.39 ± 0.34^{b}	6.92 ± 0.42^{c}	8.19 ± 0.39^{d}	9.19 ± 0.70^{d}
Brand B	2.65 ± 0.69^{a}	6.23 ± 0.31^{b}	7.88 ± 0.98^{b,c}	9.39 ± 0.71^{c,d}	10.19 ± 0.52^{d}
Brand C	2.32 ± 0.30^{a}	6.36 ± 0.40^{b}	9.72 ± 0.59^{c}	10.84 ± 0.40^{c,d}	11.52 ± 1.12^{d}
Brand D	1.66 ± 0.30^{a}	3.32 ± 0.40^{b}	6.79 ± 0.19^{c}	8.50 ± 0.47^{d}	10.59 ± 1.07^{e}
Brand E	1.26 ± 0.11^{a}	3.53 ± 0.30^{b}	4.86 ± 0.58^{b}	6.73 ± 0.31^{c}	8.91 ± 0.87^{d}
Brand F	1.26 ± 0.42^{a}	2.93 ± 0.81^{b}	4.99 ± 0.20^{c}	8.19 ± 0.61^{d}	10.73 ± 0.51^{e}
d) *p*-AnV (meq/kg)					
Brand A	0.79 ± 0.14^{a}	8.58 ± 0.43^{b}	21.48 ± 0.05^{c}	29.08 ± 0.45^{d}	49.10 ± 0.89^{e}
Brand B	0.55 ± 0.19^{a}	8.73 ± 0.03^{b}	19.20 ± 0.52^{c}	31.23 ± 0.26^{d}	43.89 ± 0.76^{e}
Brand C	0.44 ± 0.14^{a}	7.12 ± 0.22^{b}	20.51 ± 0.86^{c}	26.09 ± 0.26^{d}	46.56 ± 0.53^{e}
Brand D	0.52 ± 0.13^{a}	5.06 ± 0.30^{b}	13.13 ± 0.34^{c}	30.37 ± 0.05^{d}	39.69 ± 0.54^{e}
Brand E	0.93 ± 0.14^{a}	4.82 ± 0.14^{b}	19.63 ± 0.36^{c}	28.60 ± 0.67^{d}	45.35 ± 0.85^{e}
Brand F	0.87 ± 0.16^{a}	5.03 ± 0.36^{b}	15.12 ± 0.42^{c}	29.37 ± 0.26^{d}	44.82 ± 0.66^{e}
e) TOTOX value (meq/kg)					
Brand A	3.05 ± 0.40^{a}	15.35 ± 0.51^{b}	35.31 ± 0.88^{c}	45.46 ± 0.66^{d}	67.48 ± 2.27^{e}
Brand B	5.85 ± 1.32^{a}	21.18 ± 0.66^{b}	34.97 ± 1.53^{c}	50.00 ± 1.51^{d}	64.28 ± 1.59^{e}
Brand C	5.08 ± 0.72^{a}	19.85 ± 0.76^{b}	39.95 ± 1.30^{c}	47.76 ± 0.73^{d}	69.61 ± 2.78^{e}
Brand D	3.84 ± 0.62^{a}	11.71 ± 0.57^{b}	26.70 ± 0.21^{c}	47.38 ± 0.99^{d}	60.86 ± 2.59^{e}
Brand E	3.46 ± 0.19^{a}	11.88 ± 0.46^{b}	29.35 ± 1.05^{c}	42.06 ± 1.23^{d}	63.17 ± 2.48^{e}
Brand F	3.40 ± 0.72^{a}	10.88 ± 1.89^{b}	25.11 ± 0.69^{c}	45.75 ± 1.17^{d}	66.27 ± 1.59^{e}

Mean ± SD (n = 3).
^{abcde}Values with different superscripts letter within a row in each oil are significantly different ($p < 0.05$; one-way ANOVA and Tukey's HSD test).
L*:lightness of oil sample (black = 0 and white = 100).
a*:+ve = redness and –ve = greenness.
b*:+ve = yellowness and –ve = blueness.

to analyse the significant differences in the oil samples at different time points. Multiple comparison test by using Tukey's honest significant test (Tukey-HSD) was performed to determine pairwise differences. The obtained results were expressed as a mean of three determinations ±SD with significant level at $p < 0.05$.

3. Results and discussion

3.1. Physicochemical parameters

3.1.1. Colour analysis

In both commercial and household frying experiments, the physical parameter of colour is frequently employed to assess the degree of frying oil deterioration [35]. The oxidation and thermal decomposition of fatty acids, which diffuses into the oil during frying, results in the development of pigments (non-volatile decomposition products and unsaturated carbonyl compounds), which darken the colour of the oil [36]. At time point 0 min, the lightness (L*) of the cooking oil samples in all oil's brands were the highest among the other time points. The colour of the oil at 0 min appears more yellowish than the other time points (Table 1). While, at time point 360 min, L* values decreased with the increasing time of the frying cycles indicate that cooking oils become more darkening in colour. It showed the similar trend of colour changes in all brand of the cooking oils. Meanwhile, the a* and b* colour scale increased with the increase in the number of frying cycles. The a* and b* values increased significantly ($p < 0.05$) until after 5 frying cycles. According to Ref. [37] showed a similar trend of colour changes in repeated cooking oil as the oil were darker, more reddish and yellowish compared to the colour of fresh oil. As in general, during frying, L* values of the oils decreased while a* and b* values increased, as also reported in a previous study [38]. These findings were comparable to the previous study, which found that after 8 h of frying, the L* value of virgin coconut oil declined while the a* and b* values increased [39].

The CIELab colour scales showed that the b* values were increased directly proportional to the increasing of time points. The value of L* were significantly lowest at frying cycle (360 min) with the highest value a* and b* compared to the other frying cycle. Moreover, as the number of frying cycles increased, the oil became darker ($p < 0.05$). The oil's discoloration might be due to unsaturated chemicals forming in the oil, which were thought to be able to absorb energy from the visible electromagnetic spectrum, as well as a rise in the polymer content of the oil that are higher molecular weight products compared to triacylglycerols generated originating from polymerization and oxidation reactions [37]. Additionally, an increase in the polymer content of the oil, resulting from polymerization and oxidation reactions, may lead to the generation of higher molecular weight products compared to triacylglycerols, potentially contributing to the observed discoloration [40]. In actuality, the oil darkened due to the leaching of pigments from the fried food into the frying oil, as well as the Maillard reaction, which resulted in the creation of melanoidin, a brown pigment from fried food into the oils [36,41]. The generation of acrolein has been documented as a result of heating edible vegetable oil. Acrolein vapor has the potential to cause irritation to the eyes, as well as the nasal and respiratory passages, even at low levels of exposure [42]. The increase in the colour values was also due to the polymerization and oxidation of unsaturated fatty acids in the frying medium [43].

3.1.2. Viscosity analysis

Changes in the food that undergoes frying have been attributed to changes in specific physical and physicochemical properties of oils and fats during frying [44]. The higher the oil content in the fried food, the higher the viscosity of the frying oil, as it causes the oil to accumulate more easily on the surface of fried foods and penetrate within during the cooling as a result of thermal polymerization and oxidative deterioration [45,46]. Table 1 indicates that the viscosity of the cooking oils increased as the increasing in the frying cycle. At time point 0 and 360 min, viscosity of the cooking oils was significantly different at ($p < 0.05$) among the samples. The similar trends showed by the different oil brands. For brand D, no significant different showed in the sample at the different time points but others brand showed significant different at certain time points. A previous study by Ref. [38], indicate that the viscosity of oils during frying increased significantly ($P < 0.05$) and affected by repeated frying that has been found to correlate with formation of polymers. The results were in agreement with prior studies [44,47] which found that the observed oil viscosity increased with the number of frying cycles due to the chemical breakdown that occurs during frying. The increasing in viscosity with heating time implies that unsaturated fatty acids are being saturated as double bonds in the fatty acids are converted to single bonds [8]. This phenomenon may also be associated with the polymerization process. While, an increase of viscosity may due to the formation of high molecular weight polymers leading to the higher the degree of deterioration [48]. When the chain length of a triglyceride fatty acid increased during hydrogenation, the viscosity increases and during unsaturation of fatty acids it decreased [36]. As during degradation, hydroperoxide and other degradation products formed, resulting in non-volatile compounds. According to Ref. [8], after the fourth heating, sesame oil viscosity increases by 62%, while mustard oil viscosity increases by 75.8%. During polymerization reaction in the oil within the frying process, the percentage increase as it reflects the formation of oxidized compounds as well as an increase in the formation of monomers, dimers, and trimers [49]. Furthermore, scientific analysis of viscosity has corroborated that Total Polar Compound (TPC) serves as a recognized quality index for evaluating the degradation status of oils utilized in frying processes. When Total Polar Compound (TPC) levels exceed 20–25%, it is an indication that the frying oil should be rejected or replaced, as higher TPC levels are negatively correlated with oil quality, including factors such as viscosity, flavor, and nutritive value of the fried foods [50].

3.1.3. PV analysis

Primary oxidation compound such as hydroperoxides in oil is measured by the peroxide value [51]. Frank et al. (2011) recommended a maximum limit PV for palm oil of 10 meq O_2/kg and 15 meq O_2/kg [52]. Table 1 showed that the PV increased as the heating time increased. Brand B showed that at time point 360 min, PV was 10.19 ± 0.52 exceeded the maximum PV for palm oil. As for brand

C, PV were 2.32 ± 0.30, 6.36 ± 0.40, 9.72 ± 0.59, 10.84 ± 0.40 and 11.52 ± 1.12 meq/kg for 0, 90, 180, 270 and 360 min respectively. At time point 270 and 360 min, showed that PV value for brand C were exceeded the maximum limit for human consumption. While, for brand D and F the PV were 10.59 ± 1.07 meq/kg and 10.73 ± 0.51 meq/kg exceeded maximum limit of the PV at time point 360 min but it showed significant different at ($p < 0.05$) among the oil samples.

The PV is frequently used as an indicator as measurement of oxidative stability and quality of fats and oils [53]. Palm oil also contains a high amount of vitamin E, which may play a role in its resistance to heat oxidative changes [54]. According to Ref. [55], it has been observed that repeated heating destroys up to 99% of vitamin E and eventually leads the fatty acids to oxidation. A study by Ref. [56], after three cycles of deep-frying process, the PV of palm oil increased from 1.9948 to 9.3020 meq O_2/kg oil while for sunflower oil the PV also increased from 10.6359 to 19.3101 meq O_2/kg oil. The increase in PV of oils is related to the formation of unsaturated fatty acid hydroperoxides as a result of the lipid oxidation process consequently, decreasing the nutritional quality [57].

3.1.4. *p*-AnV analysis

The *p*-AnV is a quality indicator used to assess the content of aldehydes in frying oil such as 2-alkenals and 2,4-alkadienals [58]. During repeated frying cycles, *p*-AnV for all brands cooking oil were gradually increased with significant different at $p < 0.05$ (Table 1). At time point 0 min, the *p*-AnV were range in 0.52 ± 0.13 to 0.93 ± 0.14 meq/kg and increased at time point 360 min in the range of 39.69 ± 0.54 to 49.10 ± 0.89 meq/kg for all cooking oils. Conjugated dienes and *p*-anisidine were formed during the thermal and oxidative degradation of oil [59]. The increasing values of the *p*-AnV during repeated frying in cooking oils might be due to the formation of secondary oxidative compounds [41,59]. The *p*-AnV less than 6 indicates good quality of the oil while for fresh frying oil should be less than 4, suggesting an acceptable quality [60,61]. Literature [62,63] suggests that the acceptable limit for *p*-AnB in human consumption is 20 meq/kg. Table 1 showed that at 90 min of deep frying, *p*-AnV of cooking oil of all brands were not exceeded the permitted limit for human consumption. *p*-AnV of brand A and C at time point 180 min were exceeded the permitted limit of 21.48 ± 0.05 and 20.51 ± 0.86 meq/kg but not for the other brands. As the frying cycles increased, the *p*-AnV also increased. It has been demonstrated that the oil would be highly oxidized when the *p*-AnV exceeded the permitted limit [62]. According to Ref. [64], increasing in *p*-AnV occurred when the primary oxidation products breakdown into secondary oxidation products during deep frying process. A studied by Ref. [58], indicated that palm oil, peanut oil and camellia oil showed significant increases in *p*-AnV at 1.70–51.78 meq/kg, 2.25–84.71 meq/kg and 1.36–60.00 meq/kg respectively in 80 frying cycles. The current findings were consistent with previous studies [36,61,65,66], where *p*-AnV correlated with the heating cycles of the oils.

3.1.5. TOTOX value

TOTOX value measurement has been used widely to evaluate oxidative degradation of dietary lipids [36]. This value indicates the quality of the oil or fat, as well as its oxidation condition and the presence of degradation products resulting from prior oil oxidation. TOTOX value of all cooking oil samples were significantly increased ($p < 0.05$) as the frying cycles increased. The result from Tables 1 and 2 showed that at time point 0 min (before cooking), TOTOX value for brand A, B, C, D, E and F were 3.05 ± 0.40, 7.85 ± 1.32, 5.08 ± 0.72, 3.84 ± 0.62, 3.46 ± 0.19 and 3.40 ± 0.72 meq/kg respectively. It was drastically increased with the increasing heating cycles until at time point 360 min, the TOTOX values were 67.48 ± 2.27, 64.28 ± 1.59, 69.61 ± 2.78, 60.86 ± 2.59, 63.17 ± 2.48 and 66.27 ± 1.59 meq/kg for brands A, B, C, D, E and F. It showed greater differences in TOTOX value in each time point.

TOTOX value represents the total oxidation condition of an oil as it reflected from the PV and *p*-AnV of the oil [36,67]. This result is in agreement with [68], who reported similar pattern of result in which TOTOX value increased as the frying cycles increased for palm oil and corn oil. The lower the TOTOX value, the higher the oil quality since it is more resistant to oxidative rancidity [69]. Good

Table 2
Physicochemical properties of colour, viscosity, PV, *p*-AnV and TOTOX value before cooking (0 min).

Brands/ Parameters	Colours			Viscosity x 10^{-2} (Pa s)	PV (meq O_2/ kg)	*p*-AnV (meq/ kg)	TOTOX value (meq/ kg)
	L*	a*	b*				
Brand A	29.71 ± 0.01[a]	−0.71 ± 0.02[a]	2.77 ± 0.03[a]	7.44 ± 0.38[a]	1.13 ± 0.23[a]	0.79 ± 0.14[a]	3.05 ± 0.40[a]
Brand B	29.67 ± 0.02[a]	−0.63 ± 0.05[a]	2.32 ± 0.01[a]	6.79 ± 0.50[a]	2.65 ± 0.69[a]	0.55 ± 0.19[a]	5.85 ± 1.32[a]
Brand C	29.61 ± 0.02[a]	−0.74 ± 0.01[a]	2.57 ± 0.03[a]	8.27 ± 0.17[a]	2.32 ± 0.30[a]	0.44 ± 0.14[a]	5.08 ± 0.72[a]
Brand D	29.41 ± 0.03[a]	−0.75 ± 0.02[a]	2.59 ± 0.02[a]	7.99 ± 0.00[a]	1.66 ± 0.30[a]	0.52 ± 0.13[a]	3.84 ± 0.62[a]
Brand E	29.25 ± 0.01[a]	−0.79 ± 0.02[a]	2.61 ± 0.02[a]	6.66 ± 0.28[a]	1.26 ± 0.11[a]	0.93 ± 0.14[a]	3.46 ± 0.19[a]
Brand F	29.23 ± 0.01[a]	−0.63 ± 0.06[a]	2.39 ± 0.01[a]	6.95 ± 0.09[a]	1.26 ± 0.42[a]	0.87 ± 0.16[a]	3.40 ± 0.72[a]

Mean ± SD (n = 3).
Statistical analysis was carried out by using mutivariate analysis and Tukey's HSD test.
[abcde]Values with different superscripts letter within a row in each oil are significantly different ($p < 0.05$; one-way ANOVA and Tukey's HSD test).
L*: lightness of oil sample (black = 0 and white = 100).
a*: +ve = redness and –ve = greenness.
b*: +ve = yellowness and –ve = blueness.

quality of oil indicated TOTOX value in range between 2 and 9 [70,71] and the German Society for Fat Sciences recommended a TOTOX value of less than 20 for refined and virgin vegetable oils [72]. Oils with a TOTOX value of more than 32 meq/kg should be discarded, while those with a value of 10–30 meq/kg are still suitable for human consumption [71]. As result in Table 1, at time point 180 min for brand A, B and C showed TOTOX value exceeded the limit value for human intake. At time point 270 and 360 min, all brands of the cooking oil indicated TOTOX value exceeded the permitted limit. Therefore, the quality of the oil deteriorated as the heating cycles increased.

3.2. FTIR spectroscopy

3.2.1. FTIR spectrum analysis of repeated cooking oil

The FTIR analysis has been used to determine the composition of cooking oils subjected to repeated heating. A typical FTIR spectrum of repeated cooking oil for all brands with different time points were shown in Fig. 1 in the range of 650–4000 cm^{-1}. Fig. 1 shows the variables that were proven (but not limited) to lie between some of the identified functional bands of an oil FTIR spectrum. The spectrum patterns for all of the frying oil systems appear to be similar, with just minor changes. Therefore, multivariate analysis was conducted to analyse the differences between heating cycles of the cooking oils.

The hydrolysis of oil during frying and the generation of free fatty acids, mono, and diglycerides may be due to the decreased in absorbance since almost all of the peaks' percentage transmittance rose [73]. With repeated use, these chemicals accumulated in the frying oil as the hydroperoxides likewise decreased, which may be caused by the hydroperoxides' breakdown and secondary oxidation initiation [73]. The details of the bands were shown in Tables 3 and 4 that can be attributed to the specific mode of vibrations [21,29,74,75]. At bands 2853, 2922 and 2956 cm^{-1} showed the strong band absorptions resulting from C–H symmetrical stretching vibration of CH_2, C–H asymmetrical stretching vibration of CH_2 and C–H asymmetrical stretching vibration of CH_3 respectively. Besides, the strong single peak was observed at 1745 cm^{-1} of the C═O stretching vibration of esters whether carboxylic acid or triglycerides.

The bands in the region 1379 and 1466 cm^{-1} were mainly attributed to C–H symmetrical and scissoring bending vibrations of CH_2 (methylene) and CH_3 (methyl) aliphatic group, respectively. Furthermore, C–O stretching vibrations (CH_2 wag) were observed at 1160 and 1239 cm^{-1}. Band in the 1100 cm^{-1} region was due to stretching vibration of C–O ester groups. The band at 720 cm^{-1} attributed to the out-of-plane vibration (CH wag) and overlapping of $(CH_2)_n$ rocking vibration. Aromatic compounds' in-plane C–H bending vibrations are also known to occur in this region, however it exists as a complex band [21]. The intensities of the vibrational frequency at bands 720 cm^{-1} were the lowest than the others wavelength. Different brands of cooking oils indicate almost similar pattern in the position of the FTIR peaks as it contains similar triglyceride composition in the oils.

3.2.2. Discrimination of repeatedly heated cooking oils by PCA model from FTIR spectroscopy

Utilizing the statistical approach known as Principal Component Analysis (PCA) facilitates the reduction of dimensionality inherent in datasets, all the while retaining the utmost inherent variance. This methodology was concomitantly employed with Fourier transform infrared (FTIR) spectroscopy to evaluate the formation of oxidation byproducts in employed culinary oil [79]. PCA stands as a valuable tool for deciphering intricate patterns and trends within intricate datasets, showcasing pronounced utility particularly within realms such as chemistry and materials science. In this study, PCA was employed to determine the association between the frying oils of different heating cycles. PCA is an unsupervised clustering approach that offers a basic knowledge of the relationship between the samples [78]. According to Fig. 2, the PCA score plot shows the separation into different clusters of the repeated cooking oil. The autofit of SIMCA treatment shown this PCA was a good model as fitness value, R^2X (0.962) and predictive value, Q^2 (0.939) was obtained from the analysis. A PCA model can be concluded as a good model when the R^2X and Q^2 value were more than 0.5 [80]. This demonstrates that the model is well fitted and has a high level of predictability. Fig. 2 showed that the different cooking oils with

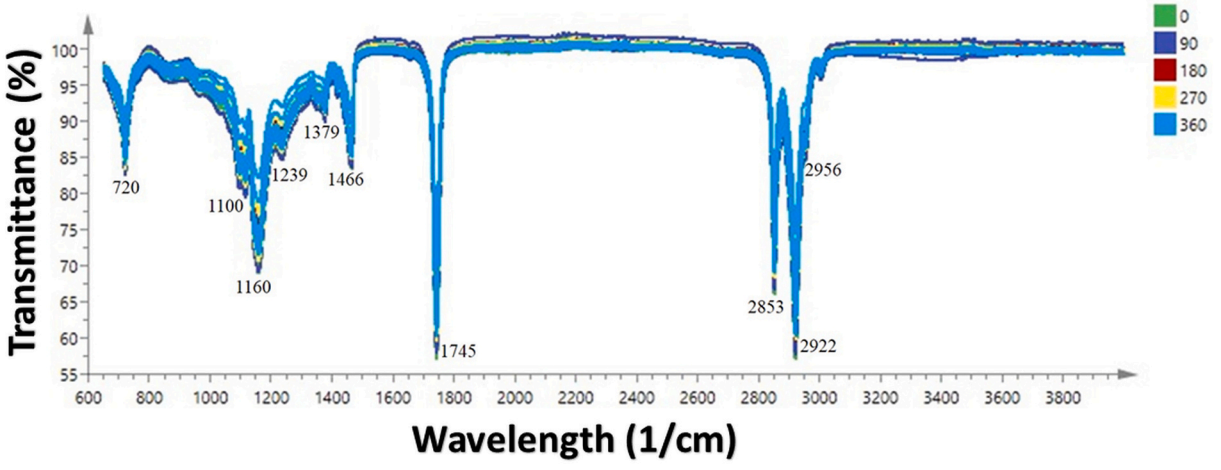


Fig. 1. FTIR spectra of repeated cooking oil of six brands cooking oil, scanned at 4000-650 cm^{-1}.

Table 3
Cooking oil samples at specific wavenumbers of bands on FTIR spectra in mid-infrared region, along with assigned functional group and modes of vibration.

Wavenumbers (cm^{-1})	Functional groups	Peak assignment
720	$-(CH_2)_n-$	Bending (rocking)
1100	−C−O	Stretching
1160	$-C-O-CH_2-$	Stretching (bending)
1239	$-C-O-CH_2-$	Stretching (bending)
1379	$-C-H\ (-CH_3)$	Bending (symmetrical)
1466	$-C-H\ (-CH_2, CH_3)$	Bending (scissoring)
1745	−C═O (ester group)	Stretching
2853	$-C-H\ (CH_2)$	Stretching (symmetrical)
2922	$-C-H\ (CH_2)$	Stretching (asymmetrical)
2956	$-C-H\ (CH_3)$	Stretching (asymmetrical)

Table 4
Wavenumbers of bands on FTIR spectra in mid-infrared region of food contaminants (3-MCPD and glycidyl ester (GE)).

Compound	Description	In-text citation
3-MCPD	– 700-800 cm^{-1} corresponds to the C–Cl stretch bond in aliphatic chloro compounds.	[29]
	- At region of 1300–1150 $cm^{-}1$, CH2 wagging.	[29,74]
	– 1500-650 cm^{-1}, the deformation and bending of C–H and the stretching vibrations of C–O.	[20]
	- Stretching of the C═O double bond causes the biggest peak to appear at about 1745–1740 cm^{-1}.	[75]
	- The peaks of stretching vibration of the C–O ester groups were detected in the region of 1238-1163 cm^{-1}.	[76]
	- The peak in the regions of 2852 and 2922 cm^{-1} indicate the methylene (-CH2-) and methyl (-CH3-) groups stretching vibrations.	[29]
	- In the range of 3000-2800 cm^{-1}, there were noticeable strong band absorptions caused by the associated C–H stretching vibration.	[29,72,75] [77]
	- A chloride ion was substituted for one of the OH groups of the glycerol backbone at either the 2- or 3-position, MCPD's chemical structure was quite simple when it exists in the free form.	
GE	- These regions (900–675 cm^{-1}) correlated to aromatic C–H out-of-plane bending.	[21]
	- Numerous organic compounds are known to have various band structures between 1150 and 950 cm^{-1}.	[21]
	- In-plane C–H bending vibrations of aromatic compounds were also known to exist in this region, but it exists as a complex band.	[28]
	- Furthermore, the peaks at region 1724-1755 cm^{-1} were determined, which corresponded to esters and carboxylic acid.	[78]

repeated heating cycles were separated into three clusters without outliers. The principal component 1 (t1) of the PCA were contributed 58.7% of the variance while, the principal component 2 (t2) were contributed 34.0% of the variance. Thus, the sum of the total variance for the two components contributed 92.7% with the hotelling's T^2 at 95%.

As shown in the PCA score plot in Fig. 2, the repeated frying oil for 0 and 90 min cannot be separated into two different clusters but both time point was located on the t1 positive side of the plot. At the earlier heating cycles, both time point was mixed up as it indicates that there are no significant changes have occurred during the heating process. As the time points increased, the plots were moved to the t1 negative side of the plot. The plot for 180, 270 and 360 min were well separated with the plot at 0 and 90 min. It is clearly shown that the oxidation has occurred as the heating time increased that leads to the formation of peroxide [16]. The physical and chemical properties of the oils changed as frying of the food samples occurred at different frying cycles. This outcome was consistent with the

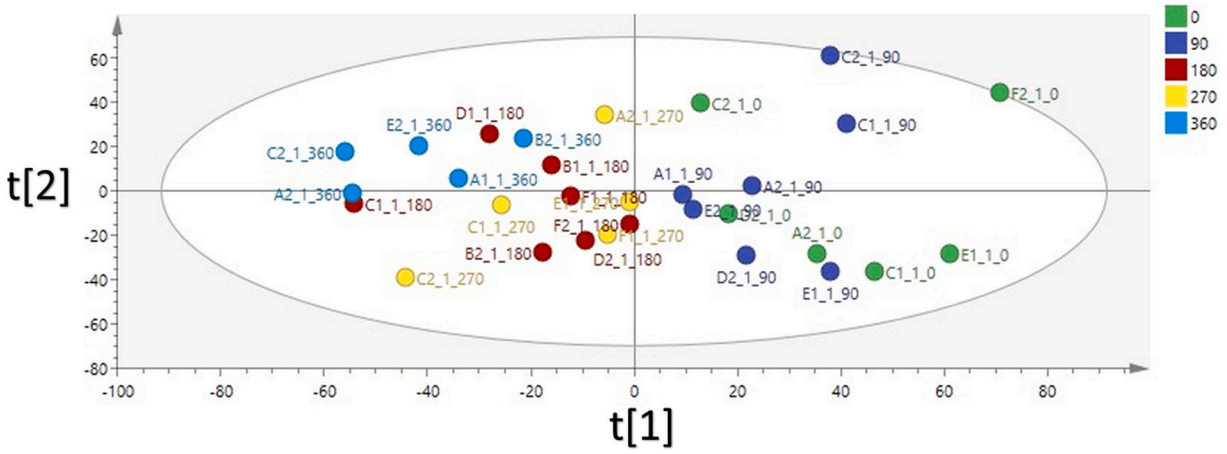
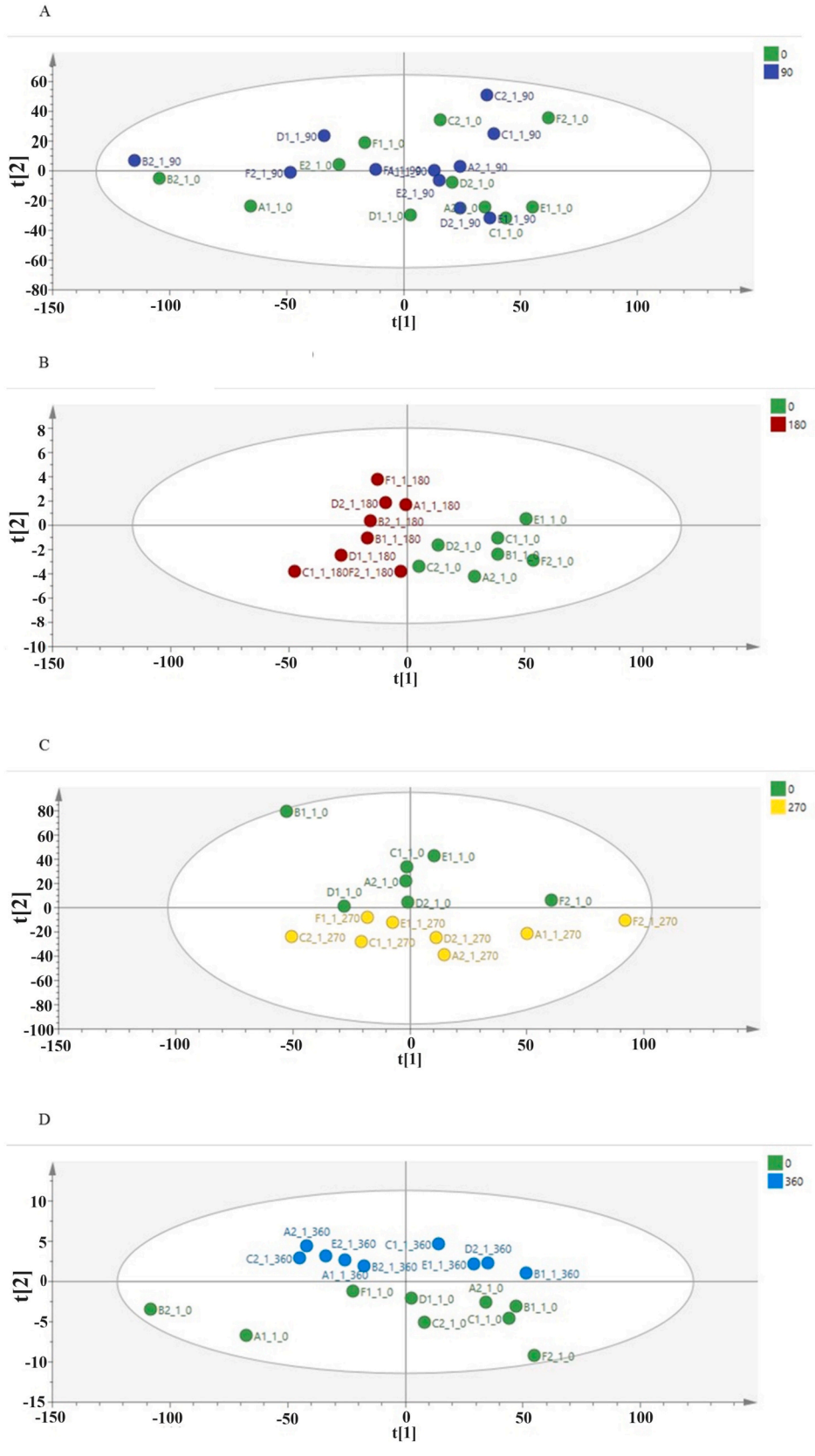


Fig. 2. FTIR spectra representing all of the frying cooking oils according to PCA score plots (t1 vs. t2).



(caption on next page)

Fig. 3. PCA score plots indicates comparison between two different cooking time clusters of A) 0 vs 90 min B) 0 vs 180 min C) 0 vs. 270 min and D) 0 vs 360 min.

earlier findings at section 3.1.1 (Table 1). At the time point 180 and 270 min, the plot was mixed up together but not at 360 min. At the time point 360 min, the plot was located at the upper t1 negative side of the plot. It was well separated from the others time points. Overall trend showed that the plots for all time points were located from positive to the negative side t1 of the plot as the heating time increased.

The PCA score plots in Fig. 3 showed that the comparison between time points in each brand of the cooking oils. According to Fig. 3 (A), the PCA score plot for time point 0 vs. 90 min could not separate into different clusters but the autofit of SIMCA showed the high values. The autofit of SIMCA treatment shown this PCA was an acceptable model with fitness value, R^2X (0.982) and predictive value, Q^2 (0.966) was obtained from the analysis. The principal component 1 (t1) of the PCA contributed 75.6% of the variance while, the principal component 2 (t2) contributed 18.4% of the variance. Hence, the sum of the total variance for the two components contributed 94% with the hotelling's T^2 at 95%.

Fig. 3 (B) PCA score plot indicate that the time point 0 and 180 min were separated into two different cluster without outliers. The autofit of SIMCA treatment shown this PCA was a good model as R^2X (0.983) and Q^2 (0.959) was obtained from the analysis. This demonstrates that the model is well fitted and has a high level of predictability. The principal component 1 (t1) and principal component 5 (t5) were contributed 64.5% and 0.3% of the variance, respectively. The sum of the total variance for the two components was 64.8%. The plot at time point 0 min were located at t1 positive side of the plot while, plot at time point 180 min were located at t1 negative side of the plot.

Fig. 3 (C) showed that the plot at time point 0 and 270 min were well-separated into two different cluster without outliers at the second component (t2). The autofit of SIMCA treatment shown this PCA was a good model as R^2X (0.977) and Q^2 (0.955) was obtained from the analysis. This demonstrates that the model is well fitted and has a high level of predictability. The principal component 1 (t1) and principal component 2 (t2) were contributed 50.1% and 42.9% of the variance, respectively. The sum of the total variance for the two components was 93% with the hotelling's T^2 at 95%. The plot at time point 0 min were located at t2 positive side of the plot while, plot at time point 270 min were located at t2 negative side of the plot.

As shown in Fig. 3 (D), the PCA score plot shows the separation of plot in 0 and 360 min into two different clusters at the second component (t4). The autofit of SIMCA treatment shown this PCA was a good model as fitness value, R^2X (0.982) and predictive value, Q^2 (0.96) was obtained from the analysis. This demonstrates that the model is well fitted and has a high level of predictability. The principal component 1 (t1) of the PCA were contributed 67% of the variance while, the principal component 4 (t4) were contributed 0.6% of the variance. Thus, the sum of the total variance for the two components contributed 67.6% with the hotelling's T^2 at 95%. The plot at time point 0 min were located at t4 negative side of the plot while, at time point 360 min were located at t2 positive side of the plot.

The results prove that PCA model based on FTIR spectra can be used to identify the correlation between heating cycles. The developed model can be regarded as a first indication of the usefulness of FTIR analysis combined with chemometrics for determining the correlation in different time points [78]. In brief, FTIR spectroscopy proves valuable in scrutinizing the chemical constitution of cooking oils, with PCA offering a means to unearth patterns and trends within the FTIR data [80].

3.3. Cooking oils analysed by ^1H NMR spectroscopy

3.3.1. Discrimination of repeatedly heated cooking oils by OPLS-DA model from ^1H NMR spectroscopy

Although there were clear visual differences between different frying cycles in the six different brands cooking oil in PCA of FTIR

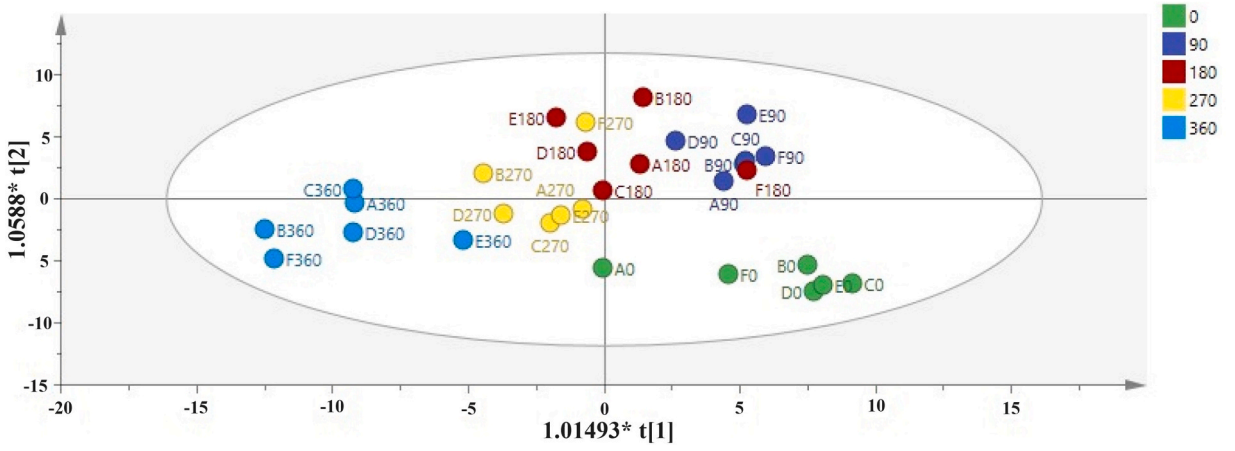


Fig. 4. OPLSDA score scatter plot model from ^1H NMR spectra representing all of the repeated frying cooking oils.

spectra (Fig. 2). However, FTIR chemometrics had several limitations due to its ability to only detect functional groups of metabolites. Therefore, in order to accurately differentiate the oil samples based on their frying cycles and to identify the structure of metabolites, ^{1}H NMR analysis was conducted as shown in Fig. 4. The samples were further analysed using OPLS-DA to obtain a more clearly visual differences in the repeated cooking oils. OPLS-DA was introduced as supervised model to classified into two or more group (classes) by using multivariate data [81]. OPLS-DA are powerful statistical modelling tools that give insights into experimental group separations based on NMR high-dimensional spectrum observations [82]. As a result, when PCA fails to reveal group separation, OPLS-DA is frequently used as an alternative approach [82]. Fig. 4 showed that the plot in OPLS-DA were separated into five different clusters according to its time points. OPLS-DA model was validated using goodness of fit, prediction of Y and permutation test. Autofit of OPLS-DA in the SIMCA resulted in two components with the goodness-of-fit ($R^2 = 0.895$) and goodness-of-prediction ($Q^2 = 0.314$). It indicates that the OPLS-DA model is well reasonable. A value > 0.5 was chosen as a criterion for identifying acceptable models in terms of R^2Y [83].

OPLS-DA model was constructed using all the cooking oil samples in the study to observe any groupings in the data set. The best separation was obtained in two principal components t1 and t2 with 15.1% and 8.1% of variation, respectively. OPLS-DA scores plot of the NMR data revealed a significantly separation between each time points of the samples. From the scores plot, four clear separated clusters were identified by OPLS-DA without any notable outliers (Fig. 4). The samples of 90 min and 180 min were in the same cluster, indicating that they have a similar chemical profile. At time point 0 min, the plots were located at t1 positive side of the plot. Then, at time point 90 min, the plots were positioned at upper t1 positive side of the plot while, at time point 180 min, the plots were located at the middle t1 positive and negative side of the plot. As the cooking oils were heated at 270 min, the plots were located at t1 negative side of the plot near the middle line (0) of the t1. At the time point 360 min, the plots were located at t1 negative side of the plot. It shows that all samples were clustered according to the time points. The plots in the OPLS-DA model showed a clear S shape pattern parallel with the time points (as shown in Fig. 5 (A, B, C, D and E)).

Model validation techniques such as permutation testing were used to ensure that the model produced was accurate and predictive [84]. In the validation of the model, R^2 indicates the model fitness significant, while Q^2 determines the predictive quality of the model [85]. According to Ref. [86], stated that if the regression line (Q^2) had a negative intercept and all the permuted R^2 values on the left were lower than the original point on the right, the model was considered as excellent and reliable with the R^2 value was not more than 0.5 and Q^2 was < -0.05. The R^2 parameter was used to measure model quality, while the Q^2 value was used to assess model predictability and the value of Q^2 is always lower than R^2 [86,87].

A permutation test (20 permutation cycles) was performed to assess the acceptability of the model (Fig. 5). In this study, all R^2 values ranged between 0.505 and 0.559 while, Q^2 values ranged between -0.189 and -0.237 for all time points. At time points 0 min, the values of R^2 and Q^2 were 0.559 and -0.217, respectively (Fig. 5A). Besides, the permutation test values for 90 min were 0.505 (R^2) and -0.203 (Q^2) while, for 180 min were 0.547 (R^2) and -0.237 (Q^2) (Fig. 5B and C). Fig. 5D showed that R^2 and Q^2 values were 0.536 and -0.208 at the time point 270 min. At the last heating cycles which was at 360 min, the permutation value for R^2 and Q^2 were 0.527

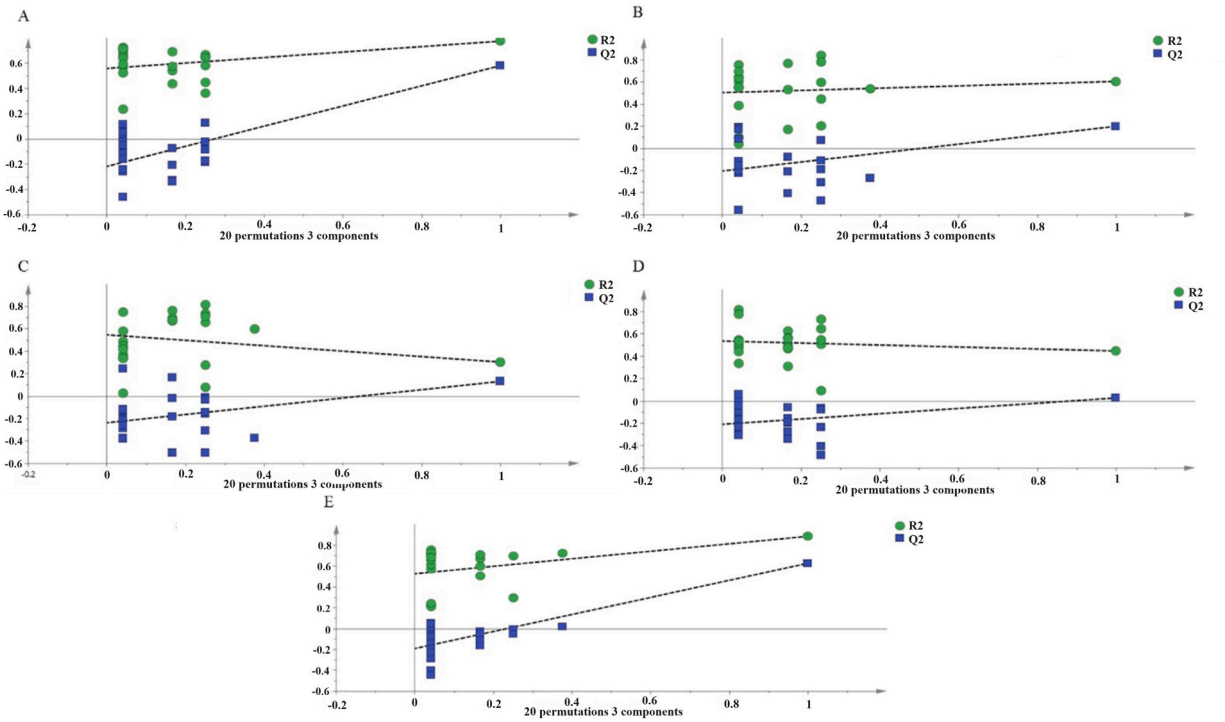


Fig. 5. Permutation test of OPLS-DA model at different frying cycles of 0, 90,180, 270 and 360 min (A, B, C, D and E).

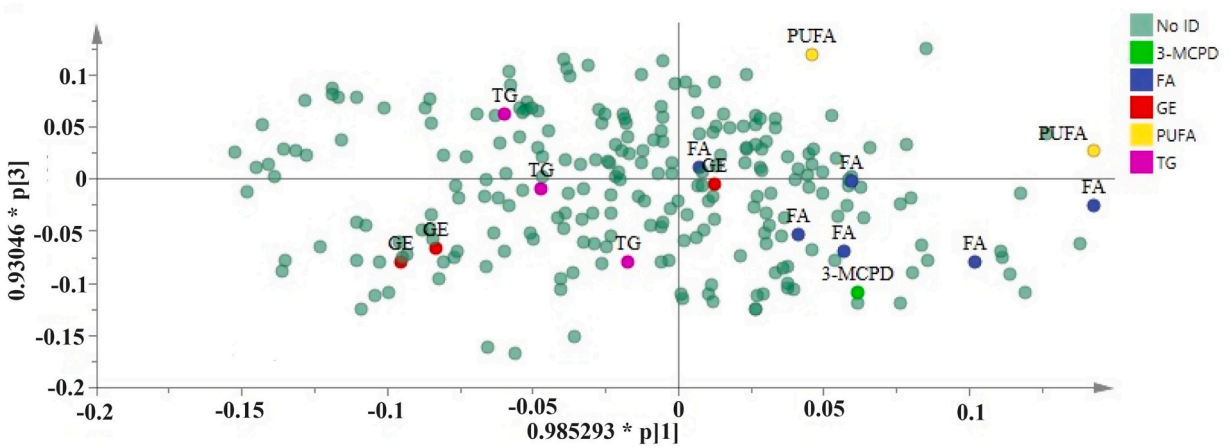


Fig. 6. The variables in dotted represent the metabolites responsible for differentiation in OPLSDA loading score plots.

and −0.189, respectively. Hence, all model was acceptable as it had showed the criteria of a good fitness and predictive qualities.

3.3.2. Identification of metabolites of repeatedly heated cooking oils based on OPLS-DA model

The OPLS-DA loading score plot of ^{1}H NMR was constructed to investigate the metabolites responsible for the separation of cooking oils subjected to different cycles of repeated heating (refer to Fig. 4). Identification of oil metabolites was conducted by comparing the ^{1}H NMR characteristic signals of metabolites including PUFA, FA, TG, 3-MCPD, and GE as shown in Fig. 6 with the signals of standard compounds available in the databases and published literature [21,29,88]. The complete structure elucidation of these metabolites is presented in Table 5.

The loading score plot suggests that the distribution of the metabolites directly related to the heating cycles of the oils. Five metabolites including FA, 3-MCPD, PUFA, TG and GE were identified in the plots. According to this, PUFA, FA and 3-MCPD, located on the right side of the p(1) plot, were found to be higher in the samples of 0, 90, and 180 min compared to the others. Meanwhile, GE and TG, positioned on the left side of the p(1) plot, were identified as characteristic metabolites of the extended frying periods at 270 and 360 min. Thus, the classification of the identified metabolites in the plot can be related to the heating cycles of the cooking oils. 3-MCPD were found to form during early heating cycle (90 min) and then after several heating cycles it leads to the formation of GE at the end heating cycle which at 360 min. The formation of 3-MCPD occurs early in the heating process and requires only minimal heating while GE will continue increased during the heating period [89–91]. A study by Refs. [88,91] showed that the concentration of 3-MCPD were reduced when the heating cycle was prolonged. [92], stated that GE and MCPD are convertible. The breakdown and oxidation of 3-MCPD during extended deep-frying is commonly regarded as the source of the reduction in 3-MCPD in frying oil as the

Table 5
Chemical shift assignments of characteristics signals in ^{1}H NMR spectroscopy of some metabolites in the repeated cooking oils.

No.	Functional group	Compound	Chemical shift (δ_H)/splitting pattern
FA			
1.	Acyl group-omega 6	CH_3	0.89 (t, J = 6.8 Hz)
2.	Acyl group	CH_2(n)	1.27 (m)
3.	Acyl group	-OCO–CH_2–CH_2-	1.61 (m)
4.	Acyl group-omega 9	-CH_2–CH═CH–	1.99 (m)
5.	Unsaturated fatty acids	-CH_2CH═CH	2.03 (m) 2.07 (m)
6.	Acyl group	–OCO–CH_2–CH_2–	2.33 (m)
PUFA			
7.	Acyl group – linoleic, linolenic acid	= $CHCH_2CH$ =	2.77 (t, J = 6.4 Hz)
8.	Acyl group – linoleic, linolenic acid	-CH═CH-	5.36 (m)
TG			
9.	TG	CH_2-α (–CH_2–OCO–)	4.15 (q, J = 5.6 Hz)
10.	TG	CH_2-α′ (1′a,b-CH_2–OCO–)	4.31 (dd, J = 4.4, 12.0 Hz)
11.	TG	CH-β (2′-CHOCO–)	5.28 (m)
12.	GE		4.47 (dd, J = 4.0, 11.6 Hz), 3.98 (dd, J = 5.6, 12.0 Hz), 2.91 (t, J = 6.0 Hz), 2.70 (m), 2.36 (m)
13.	3-MCPD		3.72 (d, J = 4.8 Hz), 2.36 (m)

δ_H in ppm. Splitting pattern: doublet (d), triplet (t), multiplet (m), doublet of doublets (dd), quartet (q).

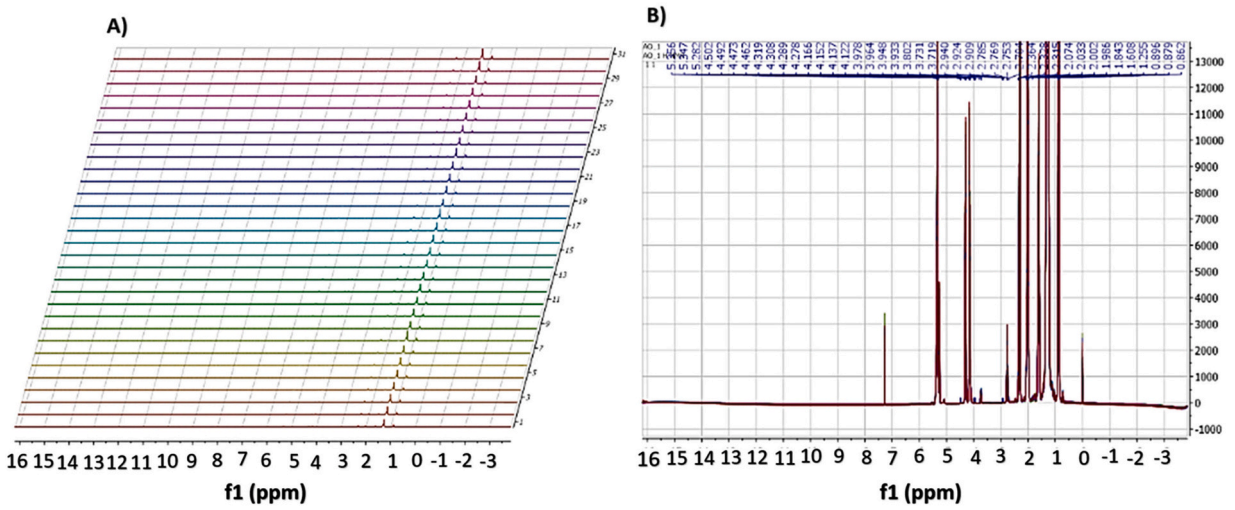


Fig. 7. A) shows a stack spectrum of the 400 MHz ^{1}H NMR spectra of the used cooking oil in $CDCl_3$ from δ 0.00 to 16.00. B) shows a superimposed spectra of the same data.

frying cycle increased [92]. Literature [93] has stated that direct intramolecular rearrangement or deacidification of 3-MCPD could lead to the GE formation following different pathway, depending on the reaction time and temperature or vice versa. Thus, the result indicates that the GE formed from the breakdown of 3-MCPD as the heating cycles increased.

3.3.3. ^{1}H NMR spectra of the cooking oils and metabolites identification

The ^{1}H NMR spectra of all cooking oil samples with different heating cycles are shown in Fig. 7 (A, B). A stack spectrum in NMR involves stacking individual scans to enhance the signal-to-noise ratio. This improves peak visibility and highlights the strength of the signal relative to the noise in the spectrum. The 400 MHz ^{1}H NMR spectrum of used cooking oil is complex, containing multiple peaks presented in Fig. 7. All of the spectra showed signals at ranged δ 0.0 to 16.0. Assignments of some signals of the metabolites were tabulated in Table 4. According [21], stated that cooking oil specifically palm oil contains of mixed glycerides and a high level of unsaturated fatty acids as the main composition of the palm oil.

In this study, the identification and quantification of the metabolites in the cooking oils were successfully conducted using ^{1}H NMR spectroscopy. Based on ^{1}H NMR spectroscopy analysis, several predominant signals were detected such as fatty acids (FA), polyunsaturated fatty acids (PUFA) and triglycerides (TG). FA was identified based on the characteristic signals of omega 6 (CH_3) positioned next to acyl group with the triplet signals at δ_H 0.89 ppm ($J = 6.8$ Hz). Besides, FA of CH_2(n), -OCO–CH_2–CH_2-, –OCO–CH_2–CH_2– positioned next to acyl group were identified with multiple signals at δ_H 1.27, 1.61 and 2.33 ppm. The signals at δ_H 1.99 ppm were matched with the characteristic signals of omega 9 (-CH_2–CH═CH–) [94]. Unsaturated fatty acids (-CH_2CH═CH) also was successfully identified based on the multiple signals observed at δ_H 2.03 and 2.07 ppm. –OCO–CH_2–CH_2– positioned next to acyl group was identified with multiple signals at δ_H 2.33 ppm. Additionally, certain PUFA in the form of linoleic and linolenic acids were recognized using the signal appearance of triplet signals at δ_H 2.77 ppm ($J = 6.4$ Hz) which were the characteristics of methylene that positioned next to the double bonds of the acyl group and multiple signals at δ_H 5.36 ppm (-CH═CH-). TG were also identified on quartet and doublet of doublet signals at δ_H 4.15 ppm ($J = 5.6$ Hz) and δ_H 4.31 ppm ($J = 4.4$, 12.0 Hz), respectively along with the multiple signals at δ_H 5.28 ppm (-CH═CH-). The presence of GE and 3-MCPD in repeated palm cooking oil was also indicated by the ^{1}H NMR spectra,

Table 6
Identification of compounds in palm-based cooking oil using ^{1}H NMR spectroscopy.

Compound		Chemical shift (δ_H)/splitting pattern	In-text citation
FA	Palmitic acid Stearic acid Oleic acid	0.89–0.91 (t), 1.27–1.29 (m), 1.61 (m), 2.33 (m)	[21,94,96]
	Oleic acid	1.99 (m)	[21,94,96]
	Oleic Acid Linoleic Acid α-Linolenic Acid	2.03–2.07 (m)	[21,94,96]
PUFA	Linoleic Acid α-Linolenic Acid	2.75–2.79 (t), 5.36 (m)	[21,94,96]
TG		4.13–1.15 (q), 4.31–4.33 (dd), 5.28 (m)	[21,96,97]
GE		4.46–4.78 (dd), 3.97–3.98 (dd), 2.91 (t), 2.70 (m), 2.36–2.38 (m)	[21,95,97]
3-MCPD		3.71–3.74 (d), 2.36 (m)	[21]

δ_H in ppm. Splitting pattern: doublet (d), triplet (t), multiplet (m), doublet of doublets (dd), quartet (q).

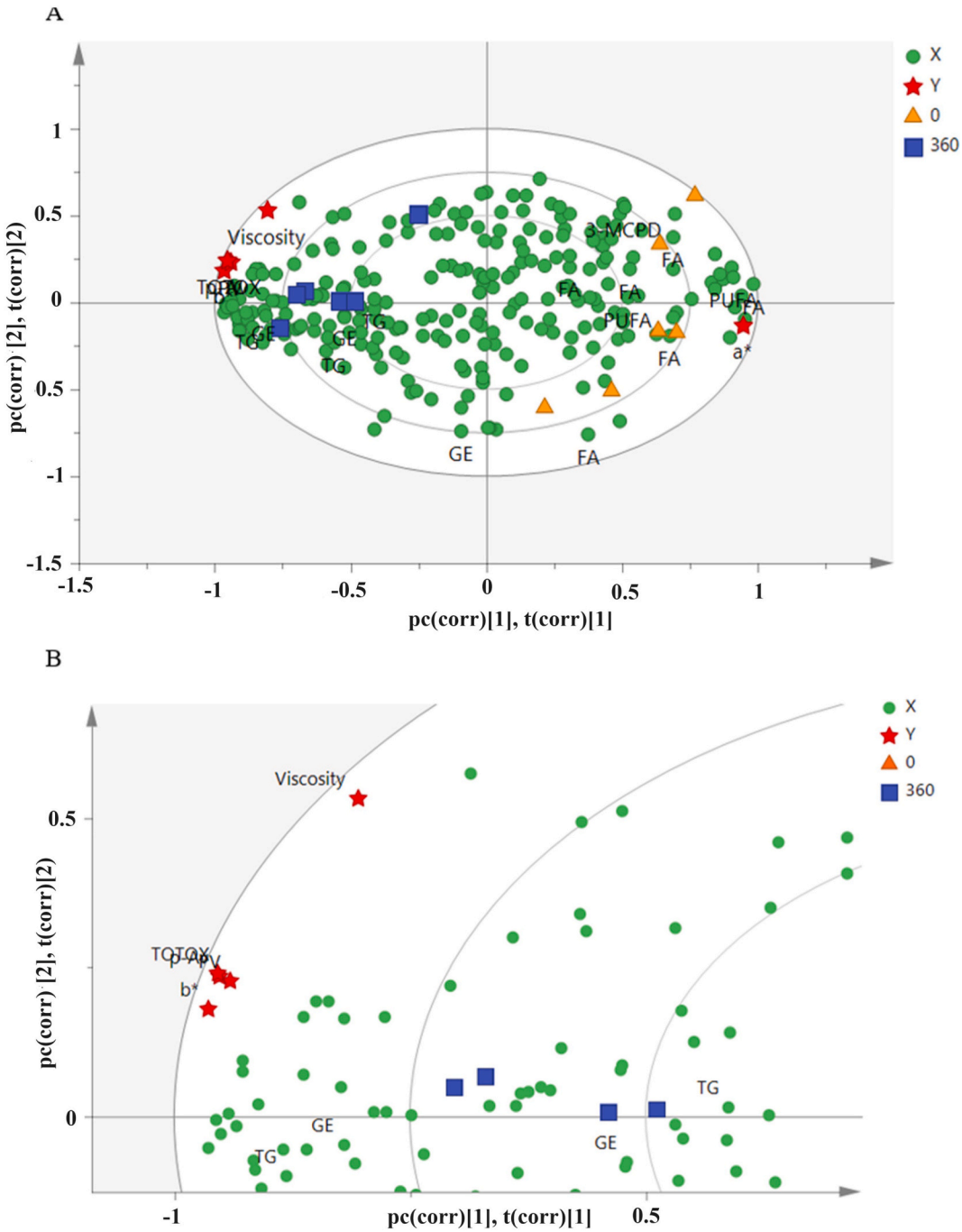


Fig. 8. The biplots obtained from partial least-square (PLS), indicating the relationship of the metabolites variations from ^{1}H NMR spectra with the physicochemical properties (a*, b*, TOTOX, *p*-Av, PV) and the frying cycles at 0 and 360 min. (A) Overall PLS biplot; (B) Expanded PLS biplot.

despite of its minor concentrations. The 3-MCPD was identified based on the characteristics signals of doublets and multiplet signals at δ_H 3.72 (J = 4.8 Hz) and 2.36 ppm assigned to methylene protons [21]. However, due to overlap with fatty acid signals, several 3-MCPD signals were unable to be identified. Most of the signals of the GE were managed to be determined in ^{1}H NMR spectrum although the detection in low concentration. The characteristics of triplet and multiplet signals at δ_H 2.91 (J = 6.0 Hz) and 2.70 ppm were identified based on the epoxy methylene of GE. Besides, the characteristic signals of methylene that connected to the acyl group were observed at doublet of doublets signals of δ_H 4.47 (J = 4.0, 11.6 Hz) and 3.98 ppm (J = 5.6, 12.0 Hz). The assignment of compounds was supported by comparison with the literature data [21,95]. The compounds that were successfully identified in ^{1}H NMR spectrum were listed in Table 5 and compared with previous findings as shown in Table 6.

3.4. Correlation of identified metabolites with physicochemical properties of repeatedly heated cooking oil samples by PLS model

A supervised partial least-squares analysis (PLS) was subsequently applied to identify the correlation of identified metabolites including PUFA, FA, TG, 3-MCPD, and GE with physicochemical properties oil samples at two different time points (0 and 360 min). The PLS biplot of the repeated cooking oils and physicochemical properties were separated into two clusters without any remarkable outliers as shown in Fig. 8 (A, B). The model has shown high class discriminant R^2Y and Q^2 values of 0.986 and 0.824, respectively, indicating that the physicochemical properties were significantly affected by the frying cycles and the formation of the metabolites. The physicochemical properties of colour (b*), PV, *p*-Av and TOTOX were clustered on the negative side of the biplot in the same side with the frying cycle at 360 min and metabolites (GE, TG). This finding has shown positive correlation as the physicochemical properties increased and the formation of metabolites GE and TG with the increasing frying cycles. However, the physicochemical properties of colour (a*) was clustered on the positive side of the biplot in the same side with the frying cycle at 0 min and metabolite (3-MCPD, FA, PUFA). A clear separation of the colour (a*) and (b*) as this showed that the frying had darkened the colour of the oil, making it denser and more viscous, as well as increased its peroxide value and *p*-anisidine value [37]. Thus, the above findings from this study have supported by this multivariate analysis and could be a precision method of prediction for food toxicants formation in the future. In brief, cooking oil can also be investigated using PLS to identify other metabolites that correlate with physicochemical properties [98]. This information can be used to improve methods for assessing the quality of cooking oil, in order to prevent the formation of harmful compounds during cooking.

4. Conclusion

As the conclusion, the results of the present study showed that repeatedly heated cooking oil between 180 °C and 220 °C at different frying cycles (270–360 min) has a significant effect on the oxidative stability of the oil. The oxidative stability of the oil decreased with increasing frying temperature and frying cycle. The physicochemical properties between the different frying cycles of the cooking oil have been studied. The study illustrates that the viscosity of the oils increases with the increasing frying time due to the breakdown of double bond in fatty acids. As palm-based cooking oils contain high percentage of PUFA, lipid oxidation also occurred as the PV and *p*-AnV increased thus lead to the formation of primary and secondary oxidation compounds. This may be due to the prolonged frying time during the deep-fried. The formation of GE could be observed in the cooking oils at the last frying cycle through the OPLSDA modelling. This indicates that the 3-MCPD was converted to the GE during the repeated cycles of the frying. The formation of these food contaminants can lead to the harmful effect to consumer's health. This finding helps hawkers of the fritters vendors, food service or any food stalls to set a safety limit in using cooking oil and directly it will reduce the rate of major health problems such as cancer, cardiovascular disease, diabetes and others. The quality of the oil can be measured through the correlation between the parameters and also in real-time measurement. The conclusive results of combining of FTIR and ^{1}H NMR spectroscopy techniques suggest both techniques are robust and reliable for the detection of GE and 3-MCPD in palm-based cooking oil. FTIR spectroscopy can be used a preliminary analytical tool to detect the functional groups of metabolites of interest, while NMR spectroscopy is employed to verify the presence and provide structural information of GE and 3-MCPD. In addition, the chemometrics approach using FTIR and ^{1}H NMR techniques are useful tool for identifying the metabolite alteration in repeatedly heated cooking oils. This method also could assess the quality and safety of the various type of pro-long heated cooking oils in the future.

Author contribution statement

Siti Nur Syahirah Nor Mahiran: Performed the experiments; Analysed and interpreted the data; Wrote the paper. Nurul Huda Abd Kadir: Conceived and designed the experiments; Analysed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper. Maulidiani Maulidiani: Analysed and interpreted the data; Contributed reagents, materials, analysis tools or data. Tengku Rozaina Tengku Mohamad: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data. Nigel J. Gooderham: Contributed reagents; materials, analysis tools; Wrote the paper. Mahboob Alam: Conceived and designed the experiments; Analysed and interpreted the data; Wrote the paper.

Data availability statement

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We are gratefully to Ministry of Higher Education Malaysia for the funding (FRGS/1/2018/WAB11/UMT/02/1) and Universiti Malaysia Terengganu (59539).

References

[1] Y. Shigetomi, Y. Ishimura, Y. Yamamoto, Trends in global dependency on the Indonesian palm oil and resultant environmental impacts, Sci. Rep. 10 (1) (2020) 1–11, https://doi.org/10.1038/s41598-020-77458-4.

[2] J.F.D. Tapia, S.S. Doliente, S. Samsatli, How much land is available for sustainable palm oil? Land Use Pol. 10 (2021), 105187 https://doi.org/10.1016/j.landusepol.2020.105187.

[3] K. Ganesan, K. Sukalingam, B. Xu, Impact of consumption and cooking manners of vegetable oils on cardiovascular diseases-A critical review, Trends Food Sci. Technol. 71 (2018) 132–154, https://doi.org/10.1016/j.tifs.2017.11.003.

[4] C. Hinkes, I. Christoph-Schulz, Consumer attitudes toward palm oil: insights from focus group discussions, J. Food Prod. Market. 25 (9) (2019) 875–895, https://doi.org/10.1080/10454446.2019.1693468.

[5] P.Y. Gan, Z.D. Li, Econometric study on Malaysia's palm oil position in the world market to 2035, Renew. Sustain. Energy Rev. 39 (2014) 740–747, https://doi.org/10.1016/j.rser.2014.07.059.

[6] G.A. Guadalupe, M.J. Lerma-García, A. Fuentes, J.M. Barat, M.D.C. Bas, I. Fernández-Segovia, I, Presence of palm oil in foodstuffs: consumers' perception, Br. Food J. 121 (9) (2019) 2148–2162, https://doi.org/10.1108/BFJ-09-2018-0608.

[7] S.H. Zulkiply, V. Balasubramaniam, N.A.A. Bakar, A.A. Rashed, S.R. Ismail, R. S, Effects of palm oil consumption on biomarkers of glucose metabolism: a systematic review, PLoS One 14 (8) (2019), e0220877, https://doi.org/10.1371/journal.pone.0220877.

[8] S.R. Valantina, V.M. Kumar, T. Devasena, T, Selected rheological characteristics and physicochemical properties of vegetable oil affected by heating, Int. J. Food Prop. 19 (8) (2016) 1852–1862, https://doi.org/10.1080/10942912.2015.1024849.

[9] H. Schulz, Fatty acid oxidation, in: Encyclopedia of Biological Chemistry, second ed., 2013, pp. 281–284, https://doi.org/10.1016/B978-0-12-378630-2.00071-2.

[10] J. Lozano-Castellón, J.F. Rinaldi de Alvarenga, A. Vallverdú-Queralt, R.M. Lamuela-Raventós, Cooking with extra-virgin olive oil: a mixture of food components to prevent oxidation and degradation, Trends Food Sci. Technol. 123 (2022) 28–36, https://doi.org/10.1016/j.tifs.2022.02.022.

[11] E.N. Frankel, Antioxidants in lipid foods and their impact on food quality, Food Chem. 57 (1) (1996) 51–55, https://doi.org/10.1016/0308-8146(96)00067-2.

[12] S. Srivastava, M. Singh, J. George, K. Bhui, A.S. Murari, Y. Shukla, Genotoxic and carcinogenic risks associated with the dietary consumption of repeatedly heated coconut oil, Br. J. Nutr. 104 (9) (2010) 1343–1352, https://doi.org/10.1017/S0007114510002229.

[13] G. Ambreen, A. Siddiq, K. Hussain, Association of long-term consumption of repeatedly heated mix vegetable oils in different doses and hepatic toxicity through fat accumulation, Lipids Health Dis. 19 (1) (2020) 69, https://doi.org/10.1186/s12944-020-01256-0.

[14] N.E.G. Frank, M.M.E. Albert, D.E.E. Laverdure, K. Paul, Assessment of the quality of crude palm oil from smallholders in Cameroon, J. Stored Prod. Postharvest Res. 2 (3) (2011) 52–58, https://doi.org/10.5897/JSPPR.9000006.

[15] C.Y. Ng, X.F. Leong, N. Masbah, S.K. Adam, Y. Kamisah, K. Jaarin, Heated vegetable oils and cardiovascular disease risk factors, Vasc. Pharmacol. 61 (1) (2014) 1–9, https://doi.org/10.1016/j.vph.2014.02.004.

[16] R.P. Venkata, R. Subramanyam, Evaluation of the deleterious health effects of consumption of repeatedly heated vegetable oil, Toxicol Rep 3 (2016) 636–643, https://doi.org/10.1016/j.toxrep.2016.08.003.

[17] EFSA Panel on Contaminants in the Food Chain (CONTAM), Risks for human health related to the presence of 3- and 2-monochloropropanediol (MCPD), and their fatty acid esters, and glycidyl fatty acid esters in food, EFSA J. 14 (5) (2016), e04426, https://doi.org/10.2903/j.efsa.2016.4426.

[18] G. Márquez-Ruíz, M.V. Ruiz-Méndez, J. Velasco, C. Dobarganes, Preventing oxidation during frying of foods, in: Oxidation in Foods and Beverages and Antioxidant Applications, 2010, pp. 239–273, https://doi.org/10.1533/9780857090331.2.239.

[19] B.M. Siddique, I.I. Muhamad, A. Ahmad, A. Ayob, M.H. Ibrahim, M.O. Ak, Effect of frying on the rheological and chemical properties of palm oil and its blend, J. Food Sci. Technol. 52 (3) (2015) 1444–1452, https://doi.org/10.1007/s13197-013-1124-6.

[20] Y.H. Wong, K.M. Goh, F. Abas, M. Maulidiani, K.L. Nyam, I.A. Nehdi, H.M. Sbihi, M.M. Gewik, C.P. Tan, Rapid quantification of 3-monochloropropane-1,2-diol in deep-fat frying using palm olein: using ATR-FTIR and chemometrics, Lwt 100 (2019) 404–408, https://doi.org/10.1016/j.lwt.2018.10.088.

[21] K.M. Goh, M. Maulidiani, R. Rudiyanto, F. Abas, O.M. Lai, K.L. Nyam, F.A. Alharthi, I.A. Nehdi, C.P. Tan, The detection of glycidyl ester in edible palm-based cooking oil using FTIR-chemometrics and ^{1}H NMR analysis, Food Control 125 (2021), 108018, https://doi.org/10.1016/j.foodcont.2021.10801.

[22] R. Jamwal, S. Kumari, S. Kelly, A. Cannavan, D.K. Singh, Rapid detection of pure coconut oil adulteration with fried coconut oil using ATR-FTIR spectroscopy coupled with multivariate regression modelling, Lwt 125 (2020), 109250, https://doi.org/10.1016/j.lwt.2020.109250.

[23] I.B. Hammouda, A. Zribi, A.B. Mansour, B. Matthäus, M. Bouaziz, Effect of deep-frying on 3-MCPD esters and glycidyl esters contents and quality control of refined olive pomace oil blended with refined palm oil, Eur. Food Res. Technol. 243 (2017) 1219–1227, https://doi.org/10.1007/s00217-016-2836-4.

[24] O. Özdikicierler, N. Yüksek, F. Yemişçioğlu, Occurrence of 3-MCPD and glycidyl esters during potato chip production: effect of oil type, frying count and chlorine based textural enhancer usage, Riv. Ital. Sostanze Grasse 97 (4) (2020) 7–13.

[25] Y. Yuan, C. Cui, H. Liu, X. Li, Y. Cao, Y. Zhang, H. Yan, Effects of oxidation and hydrolysis of frying oil on MCPD esters formation in Chinese fried dough sticks, LWT 154 (2022), 112576, https://doi.org/10.1016/j.lwt.2021.112576.

[26] G. Bansal, W. Zhou, P.J. Barlow, H.L. Lo, F.L. Neo, Performance of palm olein in repeated deep frying and controlled heating processes, Food Chem. 121 (2) (2010) 338–347, https://doi.org/10.1016/j.foodchem.2009.12.034, 2010.

[27] K. Ganesan, K. Sukalingam, B. Xu, Impact of consumption of repeatedly heated cooking oils on the incidence of various cancers- A critical review, Crit. Rev. Food Sci. Nutr. 59 (3) (2019) 488–505. https://www.tandfonline.com/doi/abs/10.1080/10408398.2017.1379470.

[28] N.A. Mohd Hassim, N.H. Ismail, S. Kanagaratnam, W.R. Awg Isa, N.L. Habi Mat Dian, Quality of commercial palm-based cooking oil packed in plastic pouch and polyethylene terephthalate (PET) bottle, Journal of Oil Palm Research 33 (3) (2021) 493–513, https://doi.org/10.21894/jopr.2020.0089.

[29] K.M. Goh, M. Maulidiani, R. Rudiyanto, Y.H. Wong, M.Y. Ang, W.M. Yew, F. Abas, O.M. Lai, Y. Wang, C.P. Tan, Rapid assessment of total MCPD esters in palm-based cooking oil using ATR-FTIR application and chemometric analysis, Talanta 198 (2019) 215–223, https://doi.org/10.1016/j.talanta.2019.01.111.

[30] AOCS, Official Methods and Recommended Practices of the American Oil Chemists' Society, 2005.

[31] M.H. Yoong, T.M. Tengku Rozaina, Effects of mangrove apple (Sonneratia caseolaris) fruit extract on oxidative stability of palm olein under accelerated storage, Food Res. 5 (1) (2021) 461–470, https://doi.org/10.26656/fr.2017.5(1).445.

[32] AOCS, P. Anisidine Value, AOCS Official Methods Cd 18-90, AOCS Press, Champaign, USA, 1997.

[33] F. Shahidi, U.N. Wanasundara, Methods for measuring oxidative rancidity in fats and oils, 2, Food Lipids: Chemistry, Nutrition, and Biotechnology (2002) 465–487, https://www.cabdirect.org/cabdirect/abstract/20053045474.

[34] N.H. Shuib, K. Shaari, A. Khatib, Maulidiani, R. Kneer, S. Zareen, S.M. Raof, N.H. Lajis, V. Neto, Discrimination of young and mature leaves of Melicope ptelefolia using 1H NMR and multivariate data analysis, Food Chem. 126 (2) (2011) 640–645, https://doi.org/10.1016/j.foodchem.2010.10.04.

[35] A. Serjouie, C.P. Tan, H. Mirhosseini, Y.B.C. Man, Effect of vegetable-based oil blends on physicochemical properties of oils during deep-fat frying, Am. J. Food Technol. 5 (5) (2010) 310–323, https://doi.org/10.3923/ajft.2010.310.323.

[36] P.K. Nayak, U. Dash, K. Rayaguru, K.R. Krishnan, Physio-chemical changes during repeated frying of cooked oil: a Review, J. Food Biochem. 40 (3) (2016) 371–390, https://doi.org/10.1111/jfbc.12215.

[37] L.S. Jurid, S.I. Zubairi, Z.M. Kasim, I.A.A. Kadir, The effect of repetitive frying on physicochemical properties of refined, bleached and deodorized Malaysian tenera palm olein during deep-fat frying, Arab. J. Chem. 13 (7) (2020) 6149–6160, https://doi.org/10.1016/j.arabjc.2020.05.015.

[38] M. Maskan, Change in colour and rheological behaviour of sunflower seed oil during frying and after adsorbent treatment of used oil, Eur. Food Res. Technol. 218 (1) (2003) 20–25, https://doi.org/10.1007/s00217-003-0807-z.

[39] Y.B.C. Man, W.R.W. Hussin, Comparison of the frying performance of refined, bleached and deodorized palm olein and coconut oil, J. Food Lipids 5 (3) (1998) 197–210, https://doi.org/10.1111/j.1745-4522.1998.tb00120.x.

[40] M.C. Dobarganes, G. Márquez-Ruiz, in: E.G. Perkins, M.D. Erickson (Eds.), Dimeric and Higher Oligomeric Triglycerides, Deep Frying. Chemistry, Nutrition and Practical Applications, AOCS Press, Illinois, 1996, pp. 89–111.

[41] K.S. Yu, H. Cho, K.T. Hwang, Physicochemical properties and oxidative stability of frying oils during repeated frying of potato chips, Food Sci. Biotechnol. 27 (3) (2018) 651–659, https://doi.org/10.1007/s10068-017-0292-y.

[42] N. Kishimoto, A. Kashiwagi, Reducing the formation of acrolein from linolenate-rich oil by blending with exra virgin olive oil during repeated frying of food at high temperatures, Food Sci. Technol. Res. 24 (6) (2018) 1017–1020, https://doi.org/10.3136/fstr.24.1017.

[43] Y. Liu, J. Li, Y. Cheng, Y. Liu, Effect of Frying Oils' Fatty Acid Profile on Quality, Free Radical and Volatiles over Deep-Frying Process: A Comparative Study Using Chemometrics, vol. 101, Lwt Elsevier Ltd, 2019, https://doi.org/10.1016/j.lwt.2018.11.033.

[44] E.P. Kalogianni, T.D. Karapantsios, R. Miller, Effect of repeated frying on the viscosity, density and dynamic interfacial tension of palm and olive oil, J. Food Eng. 105 (1) (2011) 169–179, https://doi.org/10.1016/j.jfoodeng.2011.02.021.

[45] S. Debnath, N.K. Rastogi, A.G. Krishna, B.R. Lokesh, Effect of frying cycles on physical, chemical and heat transfer quality of rice bran oil during deep-fat frying of poori: an Indian traditional fried food, Food Bioprod. Process. 90 (2) (2012) 249–256, https://doi.org/10.1016/j.fbp.2011.05.001.

[46] H. Yalcin, O.S. Toker, M. Dogan, Effect of oil type and fatty acid composition on dynamic and steady shear rheology of vegetable oils, J. Oleo Sci. 61 (4) (2012) 181–187, https://doi.org/10.5650/jos.61.181.

[47] S.I. Zubairi, I.A. Ab Kadir, Z. Nurzahim, A. Lazim, Evaluation of poly (L-lactic acid) (PLLA) rapid indicator film on deterioration degree of Refined, Bleached and Deodorised Malaysian Tenera palm olein oil (RBDPO) during long-term repetitive deep-fat frying, Arab. J. Chem. 15 (4) (2022), 103726, https://doi.org/10.1016/j.arabjc.2022.103726.

[48] W. Sunisa, U. Worapong, S. Sunisa, J. Saowaluck, W. Saowakon, Quality changes of chicken frying oil as affected of frying conditions, Int. Food Res. J. 18 (2) (2011) 615–620.

[49] D. Yang, G. Wu, Y. Lu, P. Li, X. Qi, H. Zhang, X. Wang, Q. Jin, Comparative analysis of the effects of novel electric field frying and conventional frying on the quality of frying oil and oil absorption of fried shrimps, Food Control 128 (2021), 108195, https://doi.org/10.1016/j.foodcont.2021.108195.

[50] S. Karakaya, S. Simsek, Changes in total polar compounds, peroxides value, total phenols and antioxidant activity of various oils used in deep fat frying, J. Am. Oil Chem. Soc. 88 (2011) 1361–1366, https://doi.org/10.1007/s11746-011-1788-x.

[51] T.M. Tengku-Rozaina, E.J. Birch, Physicochemical characterisation and oxidative stability of refined hoki oil, unrefined hoki oil and unrefined tuna oil, International Journal of Food Science & Technology 48 (11) (2013) 2331–2339, https://doi.org/10.1111/ijfs.12222.

[52] Codex Alimentarius, Standard for named vegetable oils codex stan 210-1999, Codex Alimentarius 1–13 (1999).

[53] Y. Kamisah, S. Shamil, M.J. Nabillah, S.Y. Kong, N.A.S. Hamizah, H.M.S. Qodriyah, M.F. Nur Azlina, A. Azman, K. Jaarin, Deep-fried keropok lekors increase oxidative instability in cooking oils, Malays. J. Med. Sci. : MJMS 19 (4) (2012) 57–62. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3629680/.

[54] P.E. Ebong, D.U. Owu, E.U. Isong, Influence of palm oil (Elaesis guineensis) on health, Plant Foods Hum. Nutr. 53 (3) (1999) 209–222, https://doi.org/10.1023/A:1008089715153.

[55] K. Jaarin, N. Masbah, Y. Kamisah, Chapter 10—heated oil and its effect on health, in: A.M. Holban, A.M. Grumezescu (Eds.), Food Quality: Balancing Health and Disease, Academic Press, 2018, pp. 315–337, https://doi.org/10.1016/B978-0-12-811442-1.00010-9.

[56] A.C. Godswill, I.O. Amagwula, I.S. Victory, A.I. Gonzaga, Effects of repeated deep frying on refractive index and peroxide value of selected vegetable, oils 4 (4) (2018).

[57] N. Zhang, Y. Li, S. Wen, Y. Sun, J. Chen, Y. Gao, A. Sagymbek, X. Yu, Analytical methods for determining the peroxide value of edible oils: a mini-review, Food Chem. 358 (2021), 129834, https://doi.org/10.1016/j.foodchem.2021.129834.

[58] T. Xu, J. Li, Y.W. Fan, T. Zheng, Z.Y. Deng, Comparison of oxidative stability among edible oils under continuous frying conditions, Int. J. Food Prop. 18 (7) (2015) 1478–1490, https://doi.org/10.1080/10942912.2014.913181.

[59] R. Mishra, H.K. Sharma, Effect of frying conditions on the physico-chemical properties of rice bran oil and its blended oil, J. Food Sci. Technol. 51 (6) (2014) 1076–1084, https://doi.org/10.1007/s13197-011-0602-y.

[60] E. Tabee, M. Jägerstad, P.C. Dutta, Frying quality characteristics of French fries prepared in refined olive oil and palm olein, JAOCS (J. Am. Oil Chem. Soc.) 86 (9) (2009) 885–893, https://doi.org/10.1007/s11746-009-1417-0.

[61] A. Sebastian, S.M. Ghazani, A.G. Marangoni, Quality and safety of frying oils used in restaurants, Food Res. Int. 64 (2014) 420–423, https://doi.org/10.1016/j.foodres.2014.07.03.

[62] F. Esfarjani, K. Khoshtinat, A. Zargaraan, F. Mohammadi-Nasrabadi, Y. Salmani, Z. Saghafi, H. Hosseini, M. Bahmaei, Evaluating the rancidity and quality of discarded oils in fast food restaurants, Food Sci. Nutr. 7 (7) (2019) 2302–2311, https://doi.org/10.1002/fsn3.1072.

[63] A. Ismail, H.B. G. Bannenberg, Rice, E. Schutt, D. Mackay, Oxidation in EPA- and DHA-rich oils: an overview, Lipid Technol. 28 (3–4) (2016) 55–59, https://doi.org/10.1002/lite.201600013.

[64] A. Kaur, B. Singh, A. Kaur, N. Singh, Changes in chemical properties and oxidative stability of refined vegetable oils during short-term deep-frying cycles, J. Food Process. Preserv. 44 (6) (2020), e14445, https://doi.org/10.1111/jfpp.14445.

[65] G. Daniali, S. Jinap, P. Hajeb, M. Sanny, C.P. Tan, Acrylamide formation in vegetable oils and animal fats during heat treatment, Food Chem. 212 (2016) 244–249, https://doi.org/10.1016/j.foodchem.2016.05.174.

[66] H.R. Tavakoli, M. Naderi, S.M. Jafari, M.H. Naeli, Postmarketing surveillance of the oxidative stability for cooking oils, frying oils, and vanaspati supplied in the retail market, Food Sci. Nutr. 7 (4) (2019) 1455–1465, https://doi.org/10.1002/fsn3.982.

[67] Y. Halim, J. Natania, L. Halim, L. Soedirga, Yakhin, Physical and chemical characteristics of frying oil in Indonesia in a repeated frying model 8 (3) (2016) 583–589.

[68] S.A. Kamarudin, S. Jinap, R. Sukor, S.P. Foo, M. Sanny, Effect of fat-soluble anti-oxidants in vegetable oils on acrylamide concentrations during deep-fat frying of French fries, Malays. J. Med. Sci.: MJMS 25 (5) (2018) 128–139, https://doi.org/10.21315/mjms2018.25.5.12.

[69] M. Mohammadi, P. Hajeb, R. Seyyedian, G. Hossein Mohebbi, A. Barmak, Evaluation of oxidative quality parameters in imported edible oils in Iran, Br. Food J. 115 (6) (2013) 789–795, https://doi.org/10.1108/BFJ-Feb-2011-0035.

[70] A. Mariod, B. Matthäus, K. Eichner, I.H. Hussein, Frying quality and oxidative stability of two unconventional oils, JAOCS (J. Am. Oil Chem. Soc.) 83 (6) (2006) 529–538, https://doi.org/10.1007/s11746-006-1236-5.

[71] N. Kim, K.S. Yu, J. Kim, T. Lim, K.T. Hwang, Chemical characteristics of potato chips fried in repeatedly used oils, J. Food Meas. Char. 12 (3) (2018) 1863–1871, https://doi.org/10.1007/s11694-018-9800-x.

[72] M. Kurańska, J. Banaś, K. Polaczek, M. Banaś, A. Prociak, J. Kuc, K. Uram, T. Lubera, Evaluation of application potential of used cooking oils in the synthesis of polyol compounds, J. Environ. Chem. Eng. 7 (6) (2019), 103506, https://doi.org/10.1016/j.jece.2019.103506.

[73] E. Zahir, R. Saeed, M.A. Hameed, A. Yousuf, Study of physicochemical properties of edible oil and evaluation of frying oil quality by Fourier Transform-Infrared (FT-IR) Spectroscopy, Arab. J. Chem. 10 (2017), https://doi.org/10.1016/j.arabjc.2014.05.025. S3870–S3876.

[74] P. de la Mata, A. Dominguez-Vidal, J.M. Bosque-Sendra, A. Ruiz-Medina, L. Cuadros-Rodríguez, M.J. Ayora-Cañada, Olive oil assessment in edible oil blends by means of ATR-FTIR and chemometrics, Food Control 23 (2) (2012) 449–455, https://doi.org/10.1016/j.foodcont.2011.08.013.

[75] M.M. Radhi, E.A. Jaffar Al-Mulla, W.H. Hoiwdy, Effect of temperature on frying oils: infrared spectroscopic studies, Res. Chem. Intermed. 39 (7) (2013) 3173–3179, https://doi.org/10.1007/s11164-012-0830-4.

[76] H. Zhang, P. Jin, M. Zhang, L.Z. Cheong, P. Hu, Y. Zhao, L. Yu, Y. Wang, Y. Jiang, X. Xu, Mitigation of 3-Monochloro-1,2-propanediol ester formation by radical scavengers, J. Agric. Food Chem. 64 (29) (2016) 5887–5892, https://doi.org/10.1021/acs.jafc.6b02016.

[77] A. Rohman, Y.B.C. Man, Fourier transform infrared (FTIR) spectroscopy for analysis of extra virgin olive oil adulterated with palm oil, Food Res. Int. 43 (3) (2010) 886–892, https://doi.org/10.1016/j.foodres.2009.12.006.

[78] S.Y. Lee, F. Abas, A. Khatib, I.S. Ismail, K. Shaari, N. Zawawi, Metabolite profiling of Neptunia oleracea and correlation with antioxidant and α-glucosidase inhibitory activities using 1H NMR-based metabolomics, Phytochem. Lett. 16 (2016) 23–33, https://doi.org/10.1016/j.phytol.2016.02.014.

[79] S.M. Alshuiael, M.A. Al-Ghouti, Multivariate analysis for FTIR in understanding treatment of used cooking oil using activated carbon prepared from olive stone, PLoS One 15 (5) (2020), https://doi.org/10.1371/journal.pone.0232997.

[80] N.A. Ishak, N.I. Tahir, S.N. Mohd Sa'id, K. Gopal, A. Othman, U.S. Ramli, Comparative analysis of statistical tools for oil palm phytochemical research, Heliyon 7 (2) (2021), e06048, https://doi.org/10.1016/j.heliyon.2021.e06048.
[81] J.A. Westerhuis, E.J.J. van Velzen, H.C.J. Hoefsloot, A.K. Smilde, Multivariate paired data analysis: multilevel PLSDA versus OPLSDA, Metabolomics 6 (1) (2010) 119–128, https://doi.org/10.1007/s11306-009-0185-z.
[82] B. Worley, R. Powers, PCA as a practical indicator of OPLS-DA model reliability, Current Metabolomics 4 (2) (2016) 97–103, https://doi.org/10.2174/2213235X04666160613122429.
[83] C. Rombouts, L.Y. Hemeryck, T. Van Hecke, S. De Smet, W.H. De Vos, L. Vanhaecke, Untargeted metabolomics of coonic digests reveals kynurenine pathway metabolites, dityrosine and 3-dehydroxycarnitine as red versus white meat discriminating metabolites, Sci. Rep. 7 (1) (2017), 42514, https://doi.org/10.1038/srep42514.
[84] L.W. Khoo, S.F.A. Kow, M. Maulidiani, M.T. Lee, C.P. Tan, K. Shaari, C.L. Tham, F. Abas, Plasma and urine metabolite profiling reveals the protective effect of Clinacanthus nutans in an ovalbumin-induced anaphylaxis model: 1H-NMR metabolomics approach, J. Pharmaceut. Biomed. Anal. 158 (2018) 438–450, https://doi.org/10.1016/j.jpba.2018.06.038.
[85] A. Mediani, F. Abas, A. Khatib, M. Maulidiani, K. Shaari, Y.H. Choi, N.H. Lajis, ^{1}H-NMR-based metabolomics approach to understanding the drying effects on the phytochemicals in Cosmos caudatus, Food Res. Int. 49 (2) (2012) 763–770, https://doi.org/10.1016/j.foodres.2012.09.022.
[86] A.A.B. Sajak, A. Mediani, M. Maulidiani, N.S. Mohd Dom, C. Machap, M. Hamid, A. Ismail, A. Khatib, F. Abas, Effect of Ipomoea aquatica ethanolic extract in streptozotocin (STZ) induced diabetic rats via ^{1}H NMR-based metabolomics approach, Phytomedicine 36 (2017) 201–209, https://doi.org/10.1016/j.phymed.2017.10.011.
[87] M.A. Wheelock, E.C. Wheelock, Trials and tribulations of 'omics data analysis: assessing quality of SIMCA-based multivariate models using examples from pulmonary medicine, Mol. Biosyst. 9 (11) (2013) 2589–2596, https://doi.org/10.1039/C3MB70194H.
[88] K.M. Goh, Y.H. Wong, C.P. Tan, K.L. Nyam, A summary of 2-, 3-MCPD esters and glycidyl ester occurrence during frying and baking processes, Curr. Res. Food Sci. 4 (2021) 460–469, https://doi.org/10.1016/j.crfs.2021.07.002.
[89] B. Matthäus, F. Pudel, Mitigation of 3-MCPD and glycidyl esters within the production chain of vegetable oils especially palm oil, Lipid Technol. 25 (7) (2013) 151–155, https://doi.org/10.1002/lite.201300288.
[90] M. Shimizu, P. Weitkamp, K. Vosmann, B. Matthäus, Influence of chloride and glycidyl-ester on the generation of 3-MCPD- and glycidyl-esters, Eur. J. Lipid Sci. Technol. 115 (7) (2013) 735–739, https://doi.org/10.1002/ejlt.201200310.
[91] M. Xu, A. Thompson, B. Chen, Dynamic changes of 3-MCPD esters and glycidyl esters contents as well as oil quality during repeated deep-frying, LWT 153 (2022), 112568, https://doi.org/10.1016/j.lwt.2021.112568.
[92] A.K.K. Rahn, V.A. Yaylayan, What do we know about the molecular mechanism of 3-MCPD ester formation? Eur. J. Lipid Sci. Technol. 113 (3) (2011) 323–329, https://doi.org/10.1002/ejlt.201000310.
[93] W. Cheng, G. Liu, L. Wang, Z. Liu, Glycidyl fatty acid esters in refined edible oils: a review on formation, occurrence, analysis, and elimination methods, Compr. Rev. Food Sci. Food Saf. 16 (2) (2017) 263–281, https://doi.org/10.1111/1541-4337.12251.
[94] M.E. Di Pietro, A. Mannu, A. Mele, NMR determination of free fatty acids in vegetable oils Processes 8 (4) (2020) 410, https://doi.org/10.3390/PR8040410.
[95] Z. Song, Y. Wang, G. Li, W. Tan, S. Yao, A novel ^{1}H NMR spectroscopic method for determination of glycidyl fatty acid esters coexisting with acylglycerols, Eur. J. Lipid Sci. Technol. 117 (7) (2015) 918–925, https://doi.org/10.1002/ejlt.201400332.
[96] M.D. Guillén, A. Ruiz, High resolution ^{1}H nuclear magnetic resonance in the study of edible oils and fats, Trends Food Sci. Technol. 12 (9) (2001) 328–338, https://doi.org/10.1016/S0924-2244(01)00101-7.
[97] B. Nieva-Echevarría, E. Goicoechea, M.J. Manzanos, M.D. Guillén, The influence of frying technique, cooking oil and fish species on the changes occurring in fish lipids and oil during shallow-frying, studied by ^{1}H NMR, Food Res. Int. 84 (2016) 150–159, https://doi.org/10.1016/j.foodres.2016.03.033.
[98] R.C. Castro, D.S.M. Ribeiro, J.L.M. Santos, R.N.M.J. Páscoa, Comparison of near infrared spectroscopy and Raman spectroscopy for the identification and quantification through MCR-ALS and PLS of peanut oil adulterants, Talanta 230 (2021), 122373, https://doi.org/10.1016/j.talanta.2021.122373.