

Quality Assessment of Fried Palm Oils using Fourier Transform Infrared Spectroscopy and Multivariate Approach

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Palm oil is one of the important commodities of Malaysia and is superior for frying due to its high oxidative stability and high content of unsaturated fatty acids. The quality of frying oil will decrease with time and repeated cycles of frying, and may subsequently affect the safety of the food. Several parameters such as peroxide value (PV) and conjugated diene value (CDV) have been used conventionally to monitor the quality of edible oils. In this study, Fourier Transform Infrared (FTIR) spectroscopy was used to evaluate the quality of palm oils after repeated cycles of frying. FTIR spectra were recorded from 4,000 to 400 cm^{-1} , and analysed using multivariate data analysis (MVA) to select important spectral regions and identify clustering pattern among samples. FTIR frequencies at 1,744 and 2,922 cm^{-1} were found to be the most discriminating variables influencing the separation between fresh and used frying oils. The correlations between peak areas at 1,744 and 2,922 cm^{-1} with PV and CDV values were also determined, yielding linear regression models with high correlation coefficient, R^2 . The results demonstrate that FTIR can be used as a rapid, reliable and accurate analytical method for the quality assessment of frying oils.

1. Introduction

Palm oil is one of the most abundant oils used in the society and is a native of equatorial West Africa. Palm oil is obtained directly from the flesh of the fruit which is making it easier to extract compared to other oils that are obtained from the seeds. Evidence obtained from Egyptian tombs shows that palm oil was used in food for over 5,000 years ago (Friedel, 1987). This already proves that palm oil has a long history of food use because of its easy extraction and production. Palm oil also has the highest growth among vegetable oils especially in Southeast Asia, because it has the highest productivity of all vegetable oils, at 5 t oil/ha, compared with 0.30 for soybean oil, 0.37 for rapeseed oil and 0.42 for sunflower oil (Gunstone, 2001).

Palm oil and its products belong to one of the most demanded oils used for the preparation of fried foods. This is due to its relatively cheap price and it can be obtained in large amounts with high oxidative stability, and hence results in high quality and tasty foods (Berger et al., 1991). Its high oxidative stability at high temperatures is due to its natural antioxidants and its moderate content of polyunsaturated fatty acids (Gunstone, 2001). The oil meets the requirements of the consumer and producer of fried food.

During frying process, the hot oil serves as a heat exchange medium at which the heat being transferred to the food being fried. When the time passes, it leads to darkening of the oil. This is due to the oil degradation which involves the heat, air and moisture to which the oil is exposed to, leading to oxidation, hydrolysis and polymerisation (Gebhardt, 1996). It is very important to monitor the free fatty acids, peroxide value, iodine value, conjugated diene and conjugated triene values which are linked to oil degradation process (Talpur et al., 2014).

In this study, frying experiments of French fries in palm oils were conducted repeatedly and the oil parameters were measured. Two of the oil parameters which are peroxide value and conjugated diene value were selected as a representative conventional quality measurement in addition to spectral analysis using Fourier Transform Infra-Red (FTIR) spectroscopy. FTIR has been proven to be fast, easy and environmental friendly as the sample preparation is very easy and often no sample preparation is needed (van de Voort et al., 2001).

FTIR used in combination with multivariate data analysis have allowed for a rapid evaluation of a large volume of spectral data for quality control.

2. Materials and Methods

2.1 Frying procedure

French fries and palm oil were purchased from the local market. The frying process was carried out in an electrical deep fryer with a temperature controller using 2 kg palm oil. When the oil reached 170 °C, 100 g of frozen French fries was placed into the hot oil for one frying cycle. Frying was done for 10 minutes for each cycle, with two frying cycles conducted within 1 h. A total of 10 frying cycles were performed using the same frying oil. After every frying process, 10 mL of oil was collected and cooled at room temperature. The collected samples were kept in capped amber bottles and stored in a refrigerator to protect from deterioration until further analysis. The volume of oil was not replenished and was reused for the entire frying process.

2.2 FTIR analysis

FT-IR spectra were recorded using the IRTracer-100 (Shimadzu, Japan) equipped with an attenuated total reflectance (ATR) accessory. Drops of oil samples were placed on a measurement plate and measurements were taken at 40 scans and at a resolution of 2 cm⁻¹ with Happ-Genzel apodisation. After each measurement, the plate was carefully cleaned from any previous residues by wiping using acetone and hexane and dried with a soft tissue before filling in with the next sample. A proprietary Lab Solutions software (Shimadzu, Japan) was used for FTIR data collection and processing. All spectra were recorded from 4,000 to 400 cm⁻¹ and read as absorbance in triplicate before taking the averaged value.

2.3 Multivariate data analysis

Multivariate data analysis of FTIR spectra was performed using MetaboAnalyst 3.0 (Xia et al., 2015). Peak intensities were scaled to unit variance.

2.4 Determination of peroxide value (PV)

PV was determined according to the thiocyanate method. 0.01 g of oil sample was mixed in a disposable glass tube with 9.8 mL chloroform-methanol (7 : 3 v/v) in a vortex mixer for 2 - 4 s. Ammonium thiocyanate solution (50 µL, 30 % w/v) was added and the sample was then mixed in a vortex mixer for 2 - 4 s. Then, 50 µL of iron (II) chloride solution ([0.4 g barium chloride dihydrate dissolved in 50 mL H₂O] + [0.5 g FeSO₄•7H₂O dissolved in 50 mL H₂O] + 2 mL 10 M HCl, with the precipitate, barium sulphate, filtered off to produce a clear solution]) was added, and the sample was mixed in a vortex mixer for 2 - 4 s. After 5 min incubation at room temperature, the absorbance of the sample was read at 500 nm against a blank that contained all the reagents except the sample using a spectrophotometer.

To make the stock solution, 1 mL was taken from a 1 mg/mL iron (III) solution and diluted to 100 mL with the solvent. Next, six samples containing 5 to 30 µg iron (III) were made for calibration model. The peroxide value of the models was then calculated as milligram equivalents oxygen per kilogram oil (mEq O₂/kg-oil) using Eq(1) (Farhoosh and Moosavi, 2009).

$$PV = (\text{Corrected absorbance} \times m) / (55.84 \times W \times 2) \quad (1)$$

where, Corrected absorbance = absorbance of sample – absorbance of blank, m = slope of calibration curve, W = mass in gram of the samples taken, 55.84 = atomic weight of iron

2.5 Determination of conjugated diene value (CDV)

CDV was measured spectrophotometrically at 234 nm and read against HPLC grade hexane as blank. The oil samples were diluted to 1 : 600 with hexane. An extinction coefficient of 29,000 L mol⁻¹ was utilised to quantify the concentration of conjugated dienes formed during the frying process (Farhoosh and Moosavi, 2009).

3. Results and Discussion

3.1 FTIR spectra of palm oil samples

FTIR spectra show the existence of specific functional groups in the samples. Since all vegetable oils including palm oil have similar composition, the observed peaks are the same. All spectra from fresh and used palm oils demonstrated similar pattern with no distinguishable differences, except for the intensities or peak areas (Figure 1). Table 1 summarises the major peaks observed from palm oil samples.

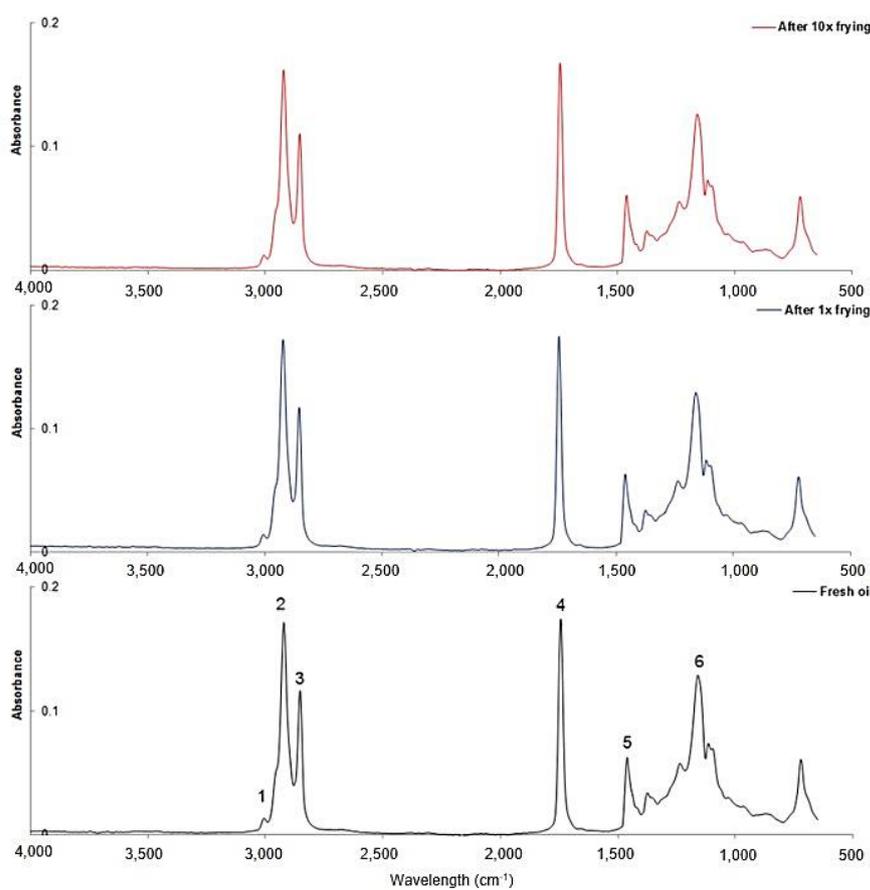


Figure 1: Representative FTIR spectra of fresh, 1-time and 10-times fried palm oil samples

Table 1: Major peaks observed from the FTIR spectra of palm oil samples

Peak no	Wavelength (cm ⁻¹)	Functional group	Reference
1	3,008	<i>cis</i> double bond of unsaturated fatty acids	(Talpur et al., 2014)
2	2,922	C–H stretching band from fatty acid hydrocarbon chain	(Silverstein et al., 1991)
3	2,853	C–H stretching band from fatty acid hydrocarbon chain	(Silverstein et al., 1991)
4	1,744	C=O stretching (ester) band	(Talpur et al., 2014)
5	1,461	bending vibrations of CH ₂ and CH ₃ aliphatic groups	(Silverstein et al., 1991)
6	1,160	stretching vibrations of the C–O ester group	(Talpur et al., 2014)

3.2 Peroxide value

Peroxide value (PV) is commonly used to determine the rancidity of a sample containing fat or oil subject to oxidation. PV shows the degree of oxidation in the substance and measures the amount of total peroxides as a product of primary oil oxidation. This value is a commonly used indicator of the shelf life of a product because an elevated peroxide value will accompany disagreeable odours. Fresh oils usually have peroxide values well below 10 mEq O₂/kg-oil (Egan et al., 1981), though it also depends on the type of oil and whether or not the oil has been refined since PV is greatly reduced by the refining process. A rancid taste is often just noticeable for peroxide values between 10 and 20. In this study, PV value for fresh palm oil was 0.20 mEq O₂/kg-oil, and increased to 1.48 - 5.78 mEq O₂/kg-oil after frying. As shown in Figure 2(a), the PV values reached a plateau after eight times of frying. This observation is consistent with previous reports indicating the instability of peroxides, which are formed during the early stages of oxidation and highly susceptible to further changes that results in the formation of secondary oxidation products. Previous study reported a decrease in the PV of oil samples after an initial increase (Che Man et al., 1999). In another study, the PV values of

vegetable oils were reported to be lower than 4.42 mEq O₂/kg-oil during the frying process and none of them were above the limit of 10 mEq O₂/kg-oil (Farhoosh and Moosavi, 2009).

3.3 Conjugated diene value

Conjugated diene (CDV) is formed as intermediates through a shift of double bond of polyunsaturated acids (PUFA). It is a representative index that can be used during frying to characterise the status of oxidation of edible oils (Houhoula et al., 2002). From Figure 2(b), it can be seen that CDV increased linearly with frying times. While Farhoosh (2009) reported that the content founds for conjugated diene of vegetable oils during the frying process ranged from 5 to 42 mmol L⁻¹, this study showed that the CDV values for fried palm oils are between 0.1 to 0.6 mmol L⁻¹, possibly due to the difference in the types of oil.

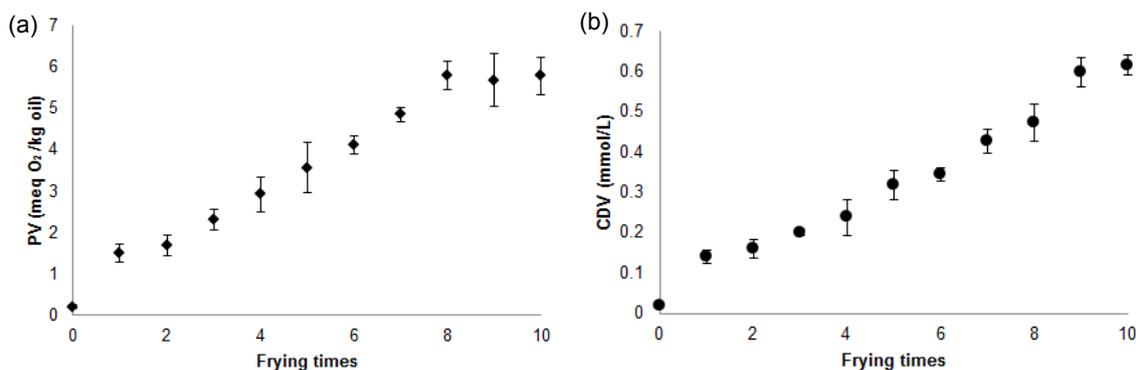


Figure 2: Changes in (a) peroxide values (PV) and (b) conjugated diene values (CDV) in palm oils during frying process

3.4 Principal component analysis

Principal component analysis (PCA) is a widely used method in multivariate data analysis, often used with spectral data that consist of thousand features that necessitate data reduction. In PCA, multi-dimensional data are reduced to several principal components (PCs) that best represent the data in low dimensions. The PCs are expressed in terms of percentage of variables explained. PC1 has the largest % variables explained, followed by PC2, PC3 and so on. In this study, full FTIR spectra of fresh and used frying oils were subjected to PCA to obtain important spectral regions that differentiate the samples and identify clustering pattern among different frying times. As a result, separation between fresh and used palm oils can be obtained from principal component 2 (PC2), which accounts for 9 % of the separation (Figure 3(a)). From the loading plot, two wavelengths were found to contribute to the separation between the two groups (Figure 3(b) and 3(c)), which are 2,922 and 1,744 cm⁻¹. The absorbance values for fresh oil at 2,922 and 1,744 cm⁻¹ are higher compared to used frying oils, with a decreasing trend in absorbance with increasing frying times (Figure 3(b) and 3(c)).

3.5 Comparison between conventional method and FTIR-MVA

To examine the feasibility of FTIR in the determination of palm oil quality during frying, the correlations between conventional method using PV and CDV with FTIR were determined. Based on PCA result, the peak area at wavelength 2,922 and 1,744 cm⁻¹ were chosen to derive the linear regression with PV and CDV values. The result is summarised in Table 2. Two types of data points were used, which are individual data points and averaged data points (n = 3). Higher correlation values were obtained when averaged data were used. In addition, the wavelength at 1,744 cm⁻¹ gave better linear regression compared to 2,922 cm⁻¹ and thus higher prediction ability of PV and CDV values. The high correlation values (R² > 0.9) indicates the potential of using FTIR as an alternative to PV and CDV measurement for the quality monitoring of frying oils. FTIR is a desirable method as it can measure directly without sample preparation, does not involve harmful chemicals, fast result within a few minutes, easy operation and reproducible spectral data. FTIR spectra may also be extended to derive the correlation with other oil parameters such as fatty acid content, iodine value and colour index, and thus developed into a single platform for quality analysis.

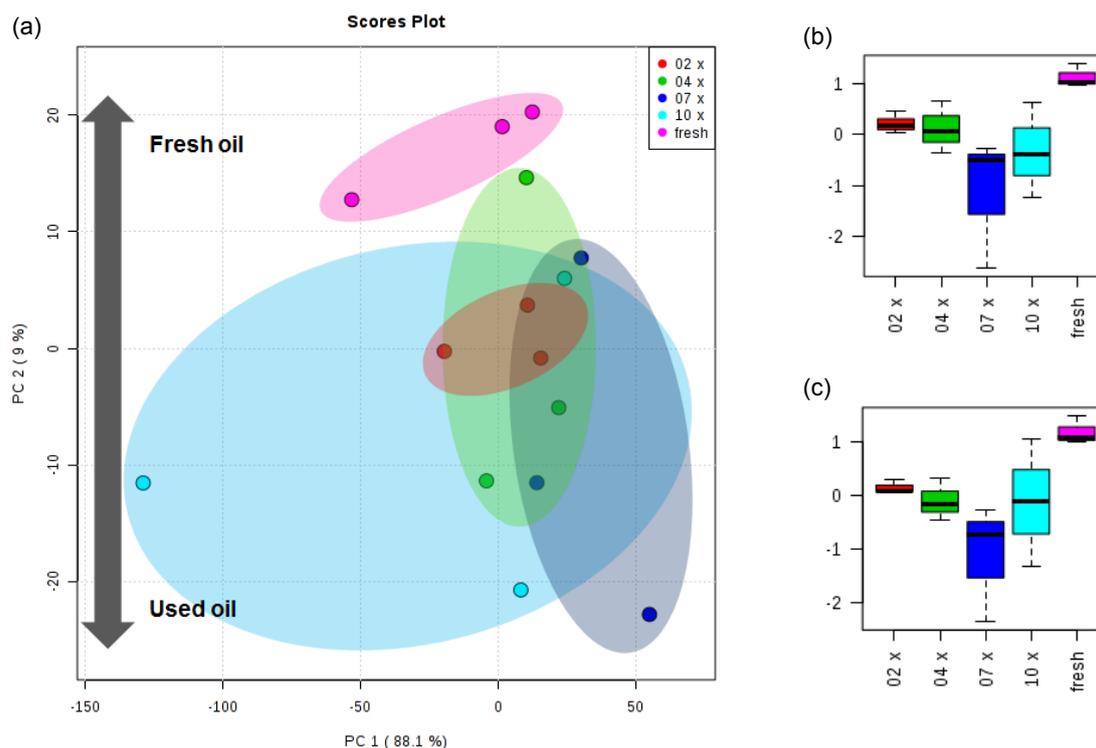


Figure 3: (a) Score plot of principal component analysis of full FTIR spectra from fresh and used palm oils; Loading values of different oil samples at (b) $2,922\text{ cm}^{-1}$ and (c) $1,744\text{ cm}^{-1}$

Table 2: Linear regression between peak areas at featured wavelength (x) and PV or CDV values (y)

Featured wavelength (cm^{-1})	PV				CDV			
	Individual		Averaged		Individual		Averaged	
	Linear equation	R^2	Linear equation	R^2	Linear equation	R^2	Linear equation	R^2
2,922	$y = -2.419x + 21.08$	0.420	$y = -5.968x + 47.65$	0.897	$y = -2.419x + 21.08$	0.420	$y = -0.511x + 4.08$	0.902
1,744	$y = -4.907x + 26.91$	0.679	$y = -9.250x + 48.14$	0.974	$y = -0.41x + 2.25$	0.670	$y = -0.784x + 4.09$	0.963

4. Conclusions

FTIR spectroscopy combined with multivariate data analysis was proven to be a fast and reliable alternative evaluation method for the stability and quality monitoring of frying oils. The effects of using palm oil for up to ten times were studied by comparing the peroxide and conjugated diene values with spectral analysis using FTIR. Through PCA modelling, the parameters and clustering patterns with identifiable features were obtained. FTIR frequencies at $2,922$ and $1,744\text{ cm}^{-1}$ were found to be the most discriminating variables influencing the separation between fresh and used frying oils. The absorbance values for fresh oil at $2,922$ and $1,744\text{ cm}^{-1}$ are higher compared to those of used frying oils, with a decreasing trend in absorbance with increasing frying times. Linear regression between peak areas at $2,922$ and $1,744\text{ cm}^{-1}$ with PV and CDV showed good correlations, implying the potential use of FTIR as a single platform quality assessment method.

Acknowledgments

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