

Fluorescence spectroscopy for analysing deterioration of palm olein in batch deep-fat frying

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Abstract

Palm olein has been commercially used as frying medium in batch deep-fat frying. During frying, the oil usually deteriorates due to the exposure to high temperature. In this study, a fluorescence spectroscopy technique was applied to monitor the deterioration of refined, bleached, and deodorized palm olein (RBDPO) in batch deep-fat frying. 22.5 kg of French fries were used as the frying material. In 30 batches, the french fries were intermittently fried at $185 \pm 5^\circ\text{C}$ for eight hours a day over five consecutive days capturing 40 hours. The fluorescence intensity of the RBDPO was recorded with excitation at 390 nm and resulting emission of 465 nm. The fluorescence intensity of the RBDPO over five days of frying decreased considering the wavelength range of emission 430-640 nm and excitation 360-430 nm. The decreased in intensity of fluorescence emission and excitation spectra were inversely correlated with the FFA content of the oil samples. This study demonstrates the potential of fluorescence spectroscopy in monitoring the deterioration of RBDPO during batch deep-fat frying.

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Introduction

Deep frying is known to be the process of cooking food product by completely immersed it into hot oil at the temperature between 150 to 200°C. In this process, oil plays an important role during frying as it acts as heat transfer medium, and becomes a component of the final food product (Navas *et al.*, 2007). Complex chemical changes take place during the process (Gertz, 2000). However, conditions with high amplitude of temperature and cooking time contribute to undesirable reactions.

Reusing frying oil repeatedly is a common practice in the household and in commercial sector. This is due to the lack of awareness in the household about harmful effect of the re-used oil as well as the commercial self-interests in the private sectors to reduce the cost of raw materials (Azman *et al.*, 2012). Repeatedly heated frying oil may be harmful to human health and contribute to chronic disease like hypertension and formation of atherosclerosis (Soriguer *et al.*, 2003; Adam *et al.*, 2008; Leong *et al.*, 2012).

Conventional chemical and instrumental methods to determine oil quality such as manual titration

(Saad *et al.*, 2007), column chromatography (Ahmad, 2014), wet chemical analysis, gas chromatography (Kuntom *et al.*, 2005) and high performance liquid chromatography (HPLC) (Hein and Isengard, 1997), are usually time consuming, involve large volume of potentially harmful solvent and require expertise to carry out such analysis. There are some current technical approaches proposed by researchers in determining the edible oil quality such as nuclear magnetic resonance (NMR) analysis (Agiomyrganaki *et al.*, 2010), differential scanning calorimetry (DSC) (Abdulkarim *et al.*, 2008), near-infrared (NIR) spectroscopy (Ng *et al.*, 2011) and fourier transform near infrared (FTNIR) spectroscopy (Chen *et al.*, 2015). Some of these methods showed their potential to replace the time consuming conventional methods, but still need more studies on its feasibility and commercialisation.

Recently, fluorescence spectroscopy was used to determine vegetable oil quality as it offers high sensitivity, simplicity and selectivity which are essential for chemical analysis (Sikorska *et al.*, 2012). There are some papers discussed about the potential of fluorescence spectroscopy in the analysis of oil quality and published over the years (Cheikhousman

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et al., 2005; Tena *et al.*, 2009; Guzmán *et al.*, 2015). Fluorescence spectroscopy was used in the study done by Cheikhousman *et al.* (2005) and Tena *et al.* (2009) to monitor the quality of oil under thermal stress. Cheikhousman *et al.* (2005) used fluorescence spectroscopy to investigate the quality of extra virgin olive oil under heat treatment. They found that fluorescence intensity have relation with the vitamin E and polyphenol content in the olive oil because fluorescence intensity decreased with the decreased of vitamin E and polyphenol content during heating. They also found that the changes in intensity of fluorescence excitation spectra were inversely correlated with hydroperoxides content (oxidation product) formed in the oil. This study indicated the ability of fluorescence spectroscopy in monitoring deterioration of extra virgin olive oil under thermal stress.

Later, Tena *et al.* (2009) in their study found that fluorescence intensity of extra virgin olive oil was decreased during heating and it may associated with the decreased of natural antioxidant in edible oil (vitamin E and phenols). Another study done by Guzmán *et al.* (2015) investigate the correlation between fluorescence emissions with the olive oil quality parameter; K270. They used fluorescence spectroscopy technique combined with multivariate analysis and found good correlation with the root mean square prediction error (RMSPE) of 0.08 and correlation coefficient, R^2 of 0.92. With the information from the previous studies on the use of fluorescence spectroscopy in monitoring the quality of olive oil, it is interesting to use this technique for monitoring degradation of palm olein.

Palm olein is one of the palm oil products derived from fractionation of palm oil after crystallization at controlled temperature (Ahmad, 2014) and it appears in the form of liquid. The fractionation process caused lower melting point (22–24°C) in the palm olein, resulting in no greasy or waxy of food fried in this oil (Matthäus, 2007). Palm olein offers many advantages that make it a gold standard of frying oil. The advantages that palm olein could provide as a frying oil are a decent resistance to oxidation, it does not produce offensive odor, does not have linolenic acid and produce a good nutritional composition which free of trans fatty acids with the presence of tocopherols in its composition (Ahmad, 2014). Popularity of palm olein in frying industry has been increased since in the early 1980's (Ismail, 2005). The stability against oxidation and rancidity (Siddique *et al.*, 2010) with the presence of tocopherols and carotenoids making palm olein often known as heavy duty frying oil (Nallusamy, 2006).

In this study, fluorescence spectroscopy method was proposed in determining palm olein deterioration during frying. This study aims to explore the possibility of applying fluorescence spectroscopy to monitor deterioration of refined, bleached, and deodorized palm olein (RBDPO) in batch deep-fat frying process. Our interest is to ascertain whether fluorescence spectra contain information for this purpose before entering the expensive chemical reference analysis for the development of frying oil quality monitoring.

Material and Methods

Material

RBDPO (Besetia, Products Sdn Bhd) and French fries (Star Farm Sdn. Bhd.) were purchased from a local supermarket. Deep frying of French fries was carried out using a stainless steel table top gas fryer (Berjaya Steel Product Sdn. Bhd., model GDF-12) equipped with fry pot of eight kg capacity and thermostat control.

Frying protocol

At the start of frying, eight kg of RBDPO was filled into the fryer and the oil were heated at $185 \pm 5^\circ\text{C}$ for one hour to allow it equilibrate at this temperature (Bansal *et al.*, 2010). An intermittent frying was carried out at $185 \pm 5^\circ\text{C}$ for eight hours a day over five consecutive days (a total heating of 40 hours). Each day, 30 batches of French fries, 150 g per batch were fry for four minutes with intervals of 10 minutes. Every five batches of frying, 150 g of oil were collected, filtered, flushed in nitrogen and stored at -20°C for further analysis. In total, 6 samples (900 mL) of oil were collected each day. At the end of frying, the oil was removed from the fryer and weight to determine the amount of fresh oil needed to top up the oil to its initial level for the next day of frying (Warner and Knowlton, 1997; Petukhov *et al.*, 1999; Abdulkarim *et al.*, 2008). The frying experiment was done in the laboratory with closed environment and replicates three times.

Fluorescence measurement

Since the application of fluorescence spectroscopy to palm olein is relatively new, we do several testing by measuring the fluorescence emission and excitation spectra to identify which wavelength give useful information on fluorescence intensity of palm olein. Therefore, in this study, fluorescence intensity for emission spectra was recorded at two excitation wavelength, 390 nm and 425 nm. While, fluorescence intensity for excitation spectra was collected at three

emission wavelength, 330 nm, 465 nm and 520 nm.

Fluorescence measurements were carried out using fluorimeter (LS55, Perkin Elmer, USA), with manufacturers software to collect and store the spectra (FL Winlab Version 4.00.02, Perkin-Elmer, Inc, Norwalk, CT, USA). This instrument was equipped with a xenon lamp and two grading monochromators each for excitation and emission. The excitation and emission slit was set to 10 nm and 5 nm, respectively. The undiluted oil samples were centrifuged (MiniSpin plus, Eppendorf AG, Germany) in order to separate solid particles and then the oil was transferred into a disposable plastic cuvette. Then, the disposable plastic cuvette was put in the cuvette holder inside the fluorimeter. The fluorescence measurement process was illustrated in the Figure 1.

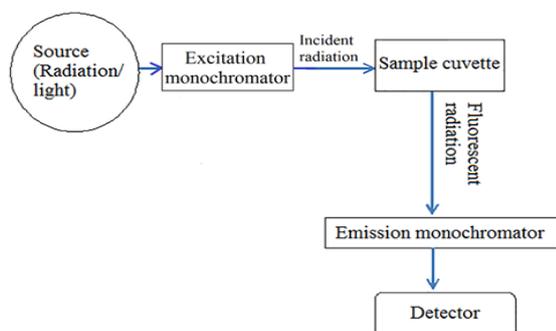


Figure 1. Schematic diagram on fluorescence measurement process

FFA analysis

The analysis of FFA for frying oil (RBDPO) samples were carried out using official MPOB Test Methods p2.5: 2004 (Kuntom *et al.*, 2005).

Statistical analysis

The intensity of fluorescence emission and excitation spectra and FFA data were evaluated using SAS (Version 9.1, SAS Institute, Inc., Cary, NC, USA) and table calculation software (Microsoft Excel 2007, MS Corporation, Redmond, WA, USA). Analysis of Variance (ANOVA) and Duncan Multiple Range Test (DMRT) were carried out to determine the significant differences in the fluorescence intensity during five days of frying. Significant differences between fluorescence intensity and frying time were determined at the 5% probability level. Regression analysis was performed to evaluate the relationships between the changes in intensity of fluorescence emission and excitation spectra data with FFA content of RBDPO samples.

Results and Discussion

From two emission spectra and three excitation spectra collected, only emission spectra at excitation wavelength 390 nm and excitation spectra at emission wavelength 465 nm showed clear changes in fluorescence intensity during frying. These changes may related to the presence of tocopherols, compounds of vitamin E group (α -Tocopherol, α -Tocotrienol, γ -Tocotrienol, δ -Tocotrienol) in the palm olein (Berger, 2005) and formation of oxidation product (Kyriakidis and Skarkalis, 2000; Cheikhousman *et al.*, 2005; Tena *et al.*, 2009). Therefore, the fluorescence emission spectra at excitation 390 nm and fluorescence excitation spectra at emission 465 nm were discussed (Figure 2).

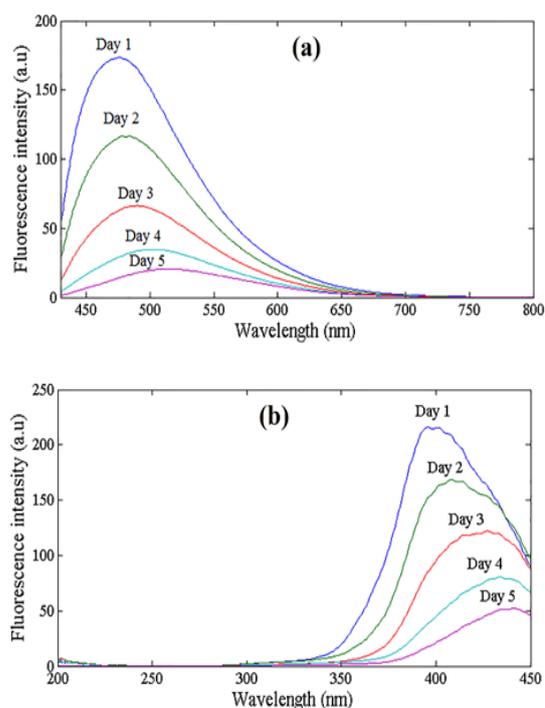


Figure 2. (a) Emission spectra at excitation 390 nm and (b) excitation spectra at emission 465 nm of RBDPO samples during five days of frying

Fluorescence emission spectra at excitation 390 nm curves showed one broad peak in the range of 430-640 nm (Figure 2a). Meanwhile, fluorescence excitation spectra at emission 465 nm curves exhibit systematic changes in intensity for each day of frying in the range of 395-425 nm (Figure 2b). Both spectra showed decreasing trend from the first to fifth day of frying. Results from ANOVA proved that frying cycles (Day) were highly significant in effecting the mean of fluorescence intensity for emission and excitation spectra ($P < 0.0001$; Table 1). Further investigation was done to compare the mean of fluorescence intensity using DMRT at prominent

peak of emission 525 nm and excitation 395 nm. This peaks may associated with oxidation products and vitamin E as presented in the previous study by Kyriakidis and Skarkalis (2000) and Sayago *et al.* (2004).

DMRT results showed that there were significant differences between the mean measured fluorescence intensity of RBDPO over five days of frying (Table 1). The mean measured fluorescence intensity of RBDPO from Day 1 to Day 5 at emission 525 nm were decreased from 109.04 to 20.08 a.u and 166.37 to 44.06 a.u at excitation 425 nm. Although, Duncan grouping showed no significant difference in some cases but the mean of fluorescence intensity between them was generally quite distinct.

Table 1. ANOVA and DMRT for the mean fluorescence intensities of RBDPO samples at prominent peak of emission and excitation over five days of frying

Peak (nm)	Treatment	P value	Mean of fluorescence intensity(a.u)
Emission 525	Day 1	<.0001	109.04 ^a
	Day 2		80.59 ^b
	Day 3		51.81 ^c
	Day 4		31.23 ^{cd}
	Day 5		20.08 ^d
Excitation 425	Day 1	<.0001	166.37 ^a
	Day 2		154.76 ^{ab}
	Day 3		120.64 ^b
	Day 4		75.18 ^c
	Day 5		44.06 ^c

*Duncan grouping with the same letter is not significantly different

The decreasing trend in the intensity of emission and excitation peak observed were expected due to the reduction of tocols (compounds of vitamin E) in RBDPO which closely related to the production of hydrolysis product in the oils like FFA (Yoshida *et al.*, 1992; Bansal *et al.*, 2010). Therefore, analysis of FFA was done to investigate their relationship with fluorescence intensity at prominent peak of emission 525 nm and excitation 425 nm.

Relationship between fluorescence intensity with FFA content

FFA content increased during frying from 0.08 to 0.36 % (Table 2). This similar to the result presented by Fauziah *et al.* (2000). They reported that FFA content of palm olein increased from 0.06% to 0.42% during batch frying of potato crisps. The process of frying was known to cause oxidative rancidity which increases FFA content in the oil (Choe and Min, 2007). The increased of FFA content during frying were inversely correlated with the change in intensity

of fluorescence emission and excitation spectra.

Thus, linear regressions were calculated to find the relationship between fluorescence intensity at prominent peak of emission 525 nm and excitation 425 nm with FFA content. Result from the linear regression analysis showed that the fluorescence intensity and FFA exhibit strong negative linear correlation with high coefficient of determination, R^2 (Figure 3). To summarize, linear regression analysis on our experimental data showed that fluorescence spectral data were significantly sufficient for monitoring deterioration of palm olein quality during frying.

Table 2. The mean of FFA over five days of frying

Treatment	Mean FFA (%)
Day 1	0.08 [*]
Day 2	0.14 ^d
Day 3	0.22 ^c
Day 4	0.30 ^b
Day 5	0.36 ^a

*Duncan grouping with the same letter is not significantly different

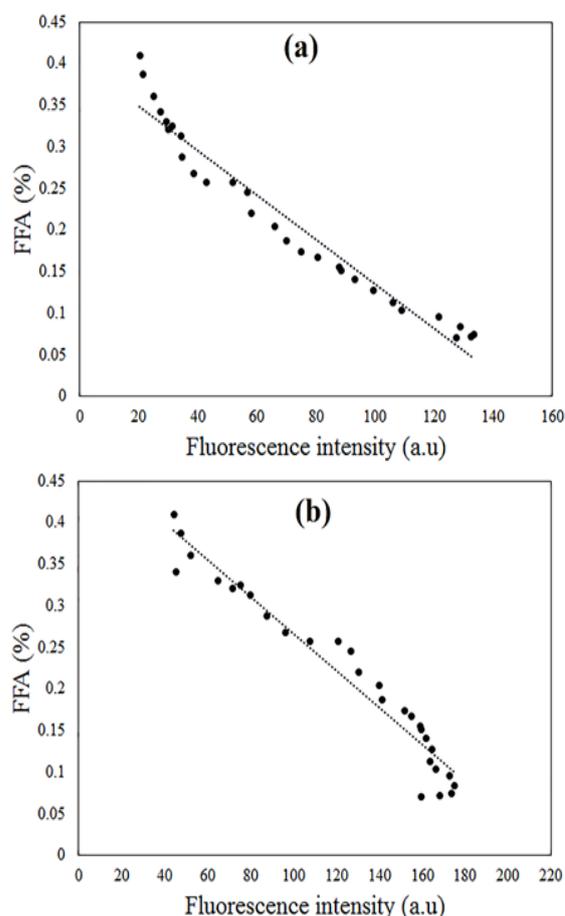


Figure 3 Relationship between fluorescence intensity with FFA of RBDPO samples at prominent peak of (a) emission 525 nm ($R^2=0.95$) (b) excitation 425 nm ($R^2=0.95$)

Conclusion

The present study was intended to use fluorescence spectroscopy to monitor the deterioration of palm olein during batch deep-fat frying. The intensity of fluorescence emission spectra (430-800 nm) and excitation spectra (200-450 nm) of RBDPO samples during batch deep-fat frying were collected at the excitation wavelength 390 nm and emission wavelength 465 nm, respectively. Fluorescence intensity for both spectra decreased over five days of frying which were inversely correlated with the FFA content of the oil samples. The results from this study demonstrated the potential of fluorescence spectroscopy measurements in the development of a sensing system for monitoring the deterioration of palm olein during batch deep-fat frying.

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