

Prediction of chemical contents of cooking oil using near-infrared spectroscopy

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Abstract

Near-infrared (NIR) spectroscopy can be an alternative method that is faster and more accurate in monitoring the deterioration of cooking oil quality compared to chemical methods. This study aimed to assess NIR spectroscopy for monitoring the quality change of cooking oil that was used repeatedly, to determine the best spectra data pre-treatment and the number of main factors of partial least square (PLS) for prediction of the quality of cooking oil. Cooking oil samples were produced 0-15 times in the frying process using the double layer of the fryer so that there were variations in quality at each stage of frying with a total of thirty-two samples. Transflectance of cooking oil was measured by fourier transform NIR spectrometer at the wavelength of 1000-2500 nm. Peroxide number and free fatty acid content as the main chemical content of cooking oil parameters were determined by chemical method. Some spectra pre-treatments were applied and the calibration between NIR data and chemical data was carried out using PLS. The best calibration was selected based on the highest correlation coefficient (r), the lowest standard error of calibration (SEC), and the lowest standard error of prediction (SEP). The best accurate prediction of peroxide number was obtained by absorbance spectra with detrending pre-treatment at a PLS factor of 7 with a r value of 0.93, SEC of 0.17%, and SEP of 0.16%. Meanwhile, free fatty acid (FFA) content was original absorbance spectra at 8 factors of PLS with a r value of 0.94, SEC of 0.016%, and SEP of 0.019%. These results indicated that NIR spectroscopy can be used to monitor the quality change of cooking oil.

1. Introduction

Cooking oil is widely used by consumers to process food because it can conduct heat, provide taste, change texture and color, increase nutritional value, and does not require a long time to implement (Anwariyah *et al.*, 2018). Cooking oil demand makes the price high. The increasing price of cooking oil encourages people and business actors to reuse cooking oil repeatedly and even turn black. Using cooking oil at a temperature of 160-180°C can result in a complex degradation reaction in the oil and change the color of the oil, decrease the quality of the oil, reduce the quality of fried food and cause harmful effects on health (Devi and Ulfah, 2021). Therefore, it is necessary to monitor the quality of

cooking oil evaluated from several parameters, including peroxide number and free fatty acid content.

The evaluation of cooking oil quality is generally carried out by chemical methods. However, the method is quite expensive and takes a long time, thus it is not suitable to monitor the quality change of cooking oil quickly and in real time. Technologies that can be used to determine the quality of products quickly and in real-time are NIR spectroscopy technology (Mahanama, 2020), fluorescence fingerprint (Mala *et al.*, 2015), and FTIR (Fourier Transform Infrared) spectroscopy (Lim *et al.*, 2018). NIR spectroscopy can be implemented in the production process for process monitoring or used in

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laboratories to check quality which can be completed in less than one minute (Mahanama, 2020). Additionally, it allows multiple analyses from a single sample without harm to the product. The use of NIR spectroscopy is more environmentally friendly, cost-effective and fast. Irfan *et al.* (2020) applied NIR spectroscopy to detect adulteration of pure palm oil with palm oil added with recycled cooking oil using the principle component analysis (PCA) method to analyze the main components. It shows that NIR spectroscopy successfully classified the palm oil sample added with a concentration above 15% with an accuracy of 100%. Kaufmann *et al.* (2022) identified the authenticity of coriander oil adulterated with palm oil, canola oil, and soybean oil, which obtained a determination coefficient (R^2) of more than 0.98 with an RPD value of 7.1 using PLS calibration.

Efforts to maintain the quality of cooking oil can be made by developing a double layer developed by researchers and engineers at the Center for Agro Industry (BBIA), Indonesia. To monitor the decline in oil quality in the development of these tools, a technology is needed that can predict the quality of chemical content quickly, non-destructively and efficiently. This study aimed to assess NIR spectroscopy for monitoring the quality change of cooking oil that is used repeatedly in the double layer of the fryer and to determine the best NIR data pre-treatment and the number of main factors of PLS for predicting the quality of cooking oil quickly and accurately.

2. Materials and methods

2.1 Materials

The material was cooking oil obtained from frying nuggets and vegetable tempura using a double-layer fryer developed by BBIA researchers. Frying with cooking oil was done separately for each ingredient by using a double layer which requires 18 L of palm cooking oil at 170°C for about 10-15 mins until the fried ingredients' color changed to brownish-yellow. About 30-50 mL of the cooking oil was collected, cooled to room temperature and stored in dark glass bottles until used for analysis.

2.2 Tools

The tool used is a unit of NIR spectrometer type NIRFlex N-500 (Buchi, Switzerland) which has been connected to a computer device, a 10 cm diameter petri dish as a sample container when measuring spectra data and the software used is the Unscrambler X 10.4 and Microsoft Office Excel for data processing and analysis. A double-layer fryer was used to produce cooking oil samples from frying nuggets and vegetable tempura from 0-15 times the frying process.

2.3 Transflectance measurement

The 20 mL of cooking oil was put into a petri dish and transflectance of samples was measured by a spectrometer type NIRFlex N-500 (BUCHI Labortechnik AG Switzerland) at the wavelength of 1000-2500 nm. To minimize error, each measurement was repeated 3 times. A total of 32 samples were subjected to transflectance measurement.

2.4 Determination of chemical content of cooking oil

The measurement of the peroxide number was carried out using the iodometric titration method by weighing 5 ± 0.05 g of cooking oil sample, putting it into a 250 mL Erlenmeyer. After that 12 mL of chloroform and 18 mL of acetic acid were added. Then 0.5 mL of saturated KI solution, 30 mL of distilled water, 0.5 mL of 1% starch were added, and titrated with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ until the solution color changes from blue and begins to disappear (Firestone and Yurawecz, 2002).

Measurement of free fatty acids was carried out using the titration method by weighing 5 ± 0.2 g of the oil sample, then putting it into a 250 mL Erlenmeyer. After that 50 mL of neutral alcohol and 2 mL of phenolphthalein indicator (PP) were added, and then titrated using 0.1 N NaOH until the color changes to a light pink color that does not disappear for 30 s (Firestone and Yurawecz, 2002).

2.5 Transformation of transflectance

Data obtained from the measurement of the NIRFlex N-500 wavelength 1000 - 2500 nm in the form of transflectance was transformed to absorbance to make linearization correlation between NIR data and chemical content of cooking oil using equation 1.

$$X = \log \frac{1}{Tr} \quad (1)$$

Where X = absorbance and Tr = transflectance.

2.6 Near-infrared spectra pre-treatment

The data generated from the NIR spectrometer consists of noise related to radiation scattering from the samples surface, cause the baseline shift of spectra, and overlapping absorption wavelength (Oliveri *et al.*, 2018; Benes *et al.*, 2020). Pre-treatment was carried out to reduce noise, enhance spectra peak, and reduce overlapping absorption wavelength so the NIR prediction be more accurate. The pre-treatment methods used are normalization, standard normal variate (SNV), multiplicative scatter correction (MSC) and de-trending (DT).

2.7 Calibration and validation

The calibration between NIR spectra and chemical content (peroxide number and FFA) was carried out using partial least squares (PLS). The number of samples used was 32, with intervals of 3 repetitions at different points, so the amount of data obtained was 96. The data in the NirCal software was divided by 2/3 of the total data is 64, into the calibration set and 1/3 of the total data is 32, into the validation set. Accuracy of calibration and validation were evaluated based on statistical parameters, which include correlation coefficient (r), Standard Error Calibration (SEC), Standard Error Prediction (SEP), Coefficient of Variation (CV), and Ratio of Prediction to Deviation (RPD) (Andasuryani *et al.*, 2013).

3. Results and discussion

3.1 Chemical content in cooking oil

The results of the chemical content of cooking oil that was used repeatedly using a double layer are shown in Table 1.

During the frying process, various reactions such as oxidation, hydrolysis, polymerization, and metal reactions will occur, which affect the quality of edible oil. The frying media, oil, continuously degenerate when exposed to high temperature, oxygen and moisture. This leads to physical and chemical changes including the formation of hydrolysis products such as free fatty acids (FFAs) which are associated with undesirable darkening in color, off-flavoring and a lowering of the smoke point (Bazina and He, 2018). These resulted in the generation of FFAs, aldehydes, ketones, acids, and many other products (Fritsch, 1981).

When food is fried in heated oil, the moisture forms steam, which evaporates with a bubbling action and gradually subsides as the foods are fried. Water, steam, and oxygen initiate the chemical reactions in the frying oil and food. Water, a weak nucleophile, attacks the ester linkage of triacylglycerols and produces di- and monoacylglycerols, glycerol, and free fatty acids. Free fatty acid contents in frying oil increase with the number of fryings (Chung *et al.*, 2004).

It is a well-known fact that palm cooking oil has the

most saturated bonds compared to other oils, which causes palm cooking oil to have many double bonds, and fatty acids having more double bonds are more reactive to oxygen, so they tend to be oxidized easily, while fatty acids that have single bonds tend to be more easily hydrolyzed. Both of these damage processes can reduce the quality of cooking oil (Suroso, 2013). Based on the data in Table 1, the more often the frying, the higher the peroxide value and free fatty acid content in the frying oil.

3.2 Spectra characteristics of cooking oil

The NIR absorbance spectra in the wavelength of 1000-2500 nm are shown in Figure 1. The peaks and valleys on the NIR spectra graph indicate the presence of the chemical content of the material. The spectra data for cooking oil showed that there were peaks and valleys in the wavelength of 1675-1744 nm and 2220-2497 nm. At this wavelength, there are molecular bonds that make up the compounds found in cooking oil. The compound or element in the material has a different absorption of radiation; this is used as an indicator of the chemical content of the material. Sánchez and Gomes (2018) reported the NIR absorption that appears was by the ether group at the wavelengths of 1660 nm and 2308 nm indicates that there is an aromatic C-H group, at a wavelength of 1730 nm, indicates that there are CH₃ and CH₂ bonds at a wavelength of 2350 nm stretches and deformations C=C-H. According to Lengkey *et al.* (2013), the peak absorption of free fatty acids is at a wavelength of 2200 nm, and the optimum absorption of O-H, C=O, and C-H atomic bonds are in the absorption region at a wavelength of 2100-2500 nm (Gauglitz, 2003). Free fatty acids are carboxylic compounds which are having a polar side, that is in the carboxyl group (-COOH) which also is electropositive (acid) (Rahayu *et al.*, 2014). The effect here is due to the high content of fatty acids with hydroxyl functional group, FFA has a high O-H functional group (Pietro *et al.*, 2020). The peroxide number, which describes the event of the formation of hydrogen peroxide, is the process of dissociation of H₂O molecules into O-H groups and H atoms (Zavodinsky *et al.*, 2018). Therefore, the higher the FFA value and peroxide number, the higher the content of OH groups. Based on the data in Figure 1, the

Table 1. Chemical content of cooking oil.

Parameter	Frying	Rate (%)	Average (%)	Standard deviation (%)
Peroxide number	0 - 5	0.610 - 1.559	1.107	0.363
	6 - 10	1.627 - 1.830	1.762	0.096
	11 - 15	1.830 - 2.034	1.965	0.097
Free fatty acids	0 - 5	0.107 - 0.196	0.145	0.034
	6 - 10	0.214 - 0.249	0.22	0.016
	11 - 15	0.266 - 0.267	0.267	0.004

optimum absorption of peroxides and free fatty acids was at a wavelength of 2200-2497 nm which was proven by their high absorption peaks.

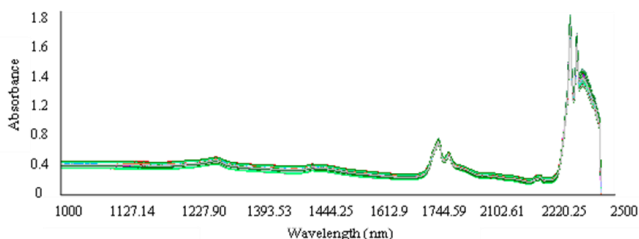


Figure 1. The absorbance spectra of cooking oil from 15 times frying.

3.3 Results of calibration and validation

The calibration and validation results with the PLS method are presented in Table 2. The PLS Method is a NIR data dimension reduction method to find the most relevant factors in predicting and describing the data. PLS usually produces a good model by using lower numbers in estimating the independent variable and the dependent variable showing a very high correlation which will be more effective in estimating (Ohyver, 2012; Benes et al., 2020).

Based on the specified value criteria (the highest of r , the lowest of SEC, SEP, and CV, the highest of RPD, and consistency in range of 80-110%), the best calibration to determine the content of peroxide is using pre-treatment of detrending at PLS factor 7 (r -value of 0.93, SEC of 0.17%, SEP of 0.16%, CV of 8.95%, and RPD of 2.32 and 107.35% consistency). For free fatty acids, the best calibration was obtained using original spectra at PLS factor 8 with an r -value of 0.94, SEC of 0.016%, SEP of 0.019%, CV of 10.18% and RPD of 2.93 and 88.30% consistency. The normalization method aims to reduce the effect of particle size by making the sample scale on a baseline based on area, mean, interval, maximum point, and unit vector. The normalization of spectra makes the reflectance value in a more extended range (Swierenga et al., 1999). The Standard Normal Variate (SNV) method is used to reduce the multiplication effect that causes slope changes and

(additive), which affects the baseline shift of the spectra. The Multiplicative Scatter Correction (MSC) method is used to compensate for additive-induced and multiplicative effects in spectra data induced by physical effects, such as non-uniform scattering across the spectra. The additive and overlap can be described by *De-trending (DT)* which aims to remove non-linear trends in the spectra (Sánchez and Gomes, 2018).

The value of r close to 1 identifies a strong result between the x -variable and the y -variable, so the estimation and validation are good. The resulting RPD value of 2-2.5 indicates that the prediction model built is considered quite good, and the RPD value in the range of 2.5-3 indicates that the prediction built is very good (Mouazen et al., 2005). The developed calibration using selected pretreatment along with selected PLS factor number can predict peroxide number and FFA accurately.

The plot of peroxide number and FFA predicted by NIR using the best calibration and that determined by chemical method (reference) was shown in Figure 2. The peroxide number predicted by NIR agrees very well with that of reference (Figure 2a). The FFA predicted by NIR also fits to FFA determined by the chemical method (Figure 2b). The standard errors (SEC and SEP) are also low close to 0, indicating that NIR prediction was accurate.

4. Conclusion

The NIR spectroscopy associated with selected pre-treatment of NIR absorbance at the wavelength of 1000-2500 nm and the number PLS factors method can be used to predict the chemical content of free fatty acids and peroxide numbers of cooking oil. The best accurate prediction of peroxide number was obtained by absorbance spectra with detrending pre-treatment at a PLS factor of 7 with a r value of 0.93, SEC 0.17%, and SEP 0.16%. Meanwhile, free fatty acid content was the original absorbance spectra at 8 factors of PLS with a r value of 0.94, SEC 0.016%, and SEP 0.019%. Measuring

Table 2. The calibration and validation results of the estimation of the chemical content of cooking oil using the PLS method.

Parameter	Pre-treatment	PLS factor	r	SEC (%)	SEP (%)	CV (%)	RPD	Consistency
Peroxide number (%)	Original	9	0.93	0.16	0.16	9.43	2.20	100.01
	Normalization	9	0.94	0.16	0.19	10.91	1.90	82.20
	SNV	8	0.93	0.16	0.17	9.67	2.15	94.54
	MSC	8	0.93	0.16	0.17	9.81	2.12	93.13
	DT	7	0.93	0.17	0.16	8.95	2.32	107.35
Free fatty acids (%)	Original	8	0.94	0.02	0.02	10.18	2.93	88.30
	Normalization	8	0.94	0.02	0.02	10.60	2.81	88.53
	SNV	7	0.94	0.02	0.02	10.57	2.83	91.12
	MSC	8	0.93	0.02	0.02	10.29	2.83	79.48
	DT	7	0.94	0.02	0.02	10.40	2.88	90.60

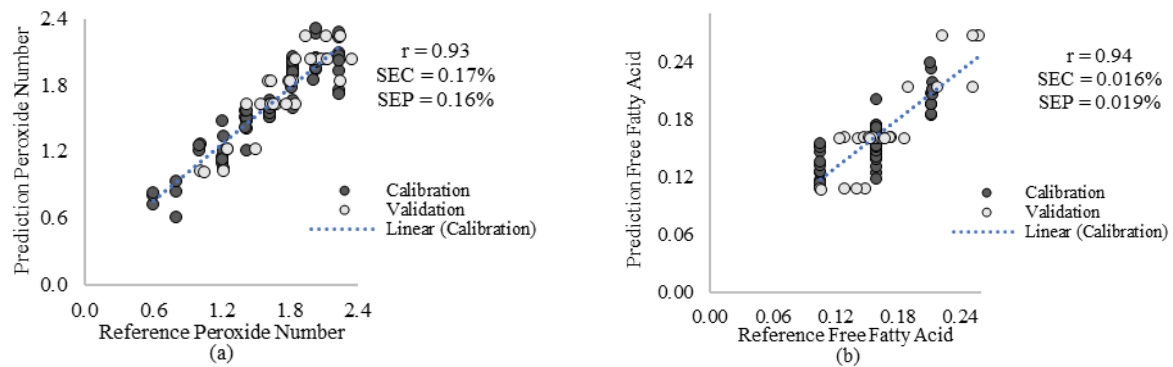


Figure 2. The plot of NIR prediction result of (a) peroxide and (b) free fatty acids.

the quality of repeatedly used cooking oil can be done quickly and accurately using NIR technology.

Conflict of interest

The authors declare no conflict of interest.

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