

Quantitative Analysis of Peroxide Value in Virgin Coconut Oil by ATR-FTIR Spectroscopy

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Abstract: Oxidation of fats and oils is an important indicator for performance and shelf life of oils. As other vegetable oils, virgin coconut oil (VCO) is not susceptible to lipid oxidation. Thus, a rapid method for quantitative analysis of peroxide value in VCO was developed in this study using Fourier transform infrared (FTIR) spectroscopy coupled with attenuated total reflectance (ATR). Thirty training samples of VCO were subjected to oxidative condition in convection oven at temperature of 70°C up to 20 days to accelerate the lipid oxidation process. The peroxide values were determined periodically using the standard method of American Oil Chemists' Society (AOCS) and then analyzed with FTIR spectroscopy. Calibration model using partial least square (PLS) was developed by studying the spectral features for regions that correlated with peroxide value content (absorption of oxidation compounds band near 988 to 900 cm^{-1}) and validated by removing one sample at a time. A linear calibration curve was obtained for the actual value against FTIR predicted value which yields an equation of $y = 1.0398x + 0.0468$ and satisfactory results of root mean square error of prediction (RMSEP) of 0.4978 and correlation coefficient (R^2) of 0.9826. Thus, FTIR spectroscopy with PLS regression can serve as important tools for determining the peroxide value in VCO. Application of FTIR is rapid, accurate and environmental friendly compared to the conventional chemical analyses.

Keywords: FTIR, oxidation, peroxide value, virgin coconut oil.

INTRODUCTION

Virgin coconut oil (VCO) is considered to be one of the functional food oil due to its valuable therapeutic value [1]. Thus, its production is increasing especially in tropical countries. Though the increased in the production quantity shows a positive sign, it is important to ensure that the quality of the oil is preserve in order to obtain the full benefits from the oil.

The peroxide value is a measure of the concentration of peroxides and hydroperoxides forms in the initial stage of lipid oxidation. The number of peroxides present in vegetable oils reflects its oxidative level and thus its tendency to become rancid [2]. In addition, VCO is normally packed in transparent plastic bottles. During prolonged storage or display at retailers, VCO may undergo quality deterioration. Thus peroxide value is a very important quality parameter in VCO analysis and efficient method to measure the peroxide value content in VCO is called for.

The official wet chemistry method used to measure peroxide value in virgin coconut oil is the standard method of American Oil Chemists' Society. However, the method is time consuming and labour intensive despite being relatively simple. The use of infrared spectroscopy has been suggested as alternative method to determine the peroxide value in vegetable oils. Fourier transforms infrared spectroscopy

which employs the mid infrared region of electromagnetic spectrum from 4000 to 400 cm^{-1} . The ease feasibility of using FTIR is due to rapid technique (2 minutes) and reduces the use of toxic solvents [3]. FTIR has been reported for use of quantification of various oil parameters including peroxide value. Peroxide value has been determined using FTIR in palm oil [4], canola oil [3]; sunflower, olive, rapeseed and safflower oil [5]. Thus, this paper focuses on the development method to determine the peroxide value in VCO using FTIR with attenuated total reflectance (ATR) in conjunction with partial least square (PLS) statistical analysis.

MATERIALS AND METHODS

Materials

Virgin coconut oil was obtained from Kelantan Biotech Corporation. All chemicals and reagents used were of analytical grade.

Chemical Analysis

Thirty training samples of VCO were subjected to oxidative condition in convection oven at temperature of 70°C up to 20 days to accelerate the lipid oxidation process. The peroxide values were determined periodically using the standard method of American Oil Chemists' Society (AOCS, Cd 8-53) [6]. Analyses were carried out in triplicate.

Spectra Collection

The FTIR measurement was done using Bruker Tensor 27 spectrometer (BRUKER, Karlsruhe, Germany) equipped with flow through horizontal ATR accessory. Drops of oil

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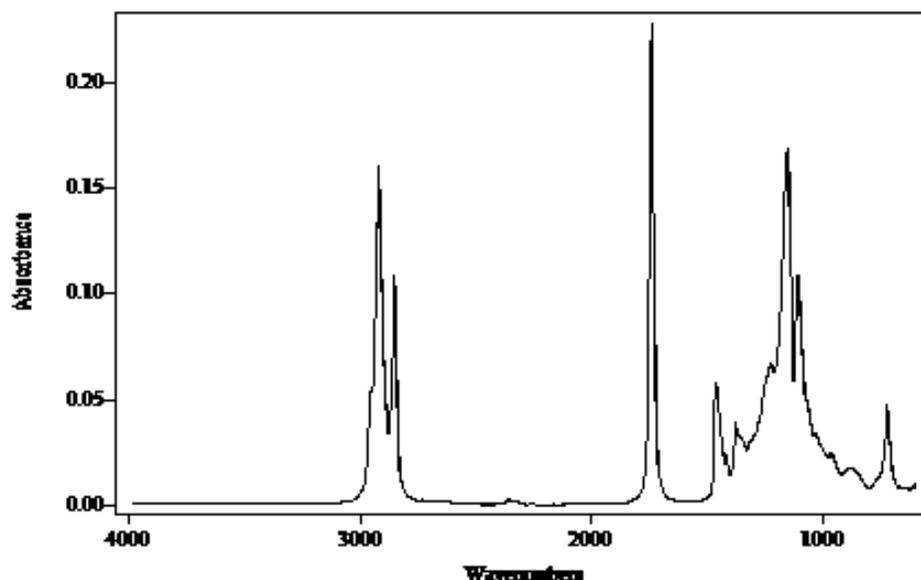


Fig. (1). FTIR spectrum of virgin coconut oil.

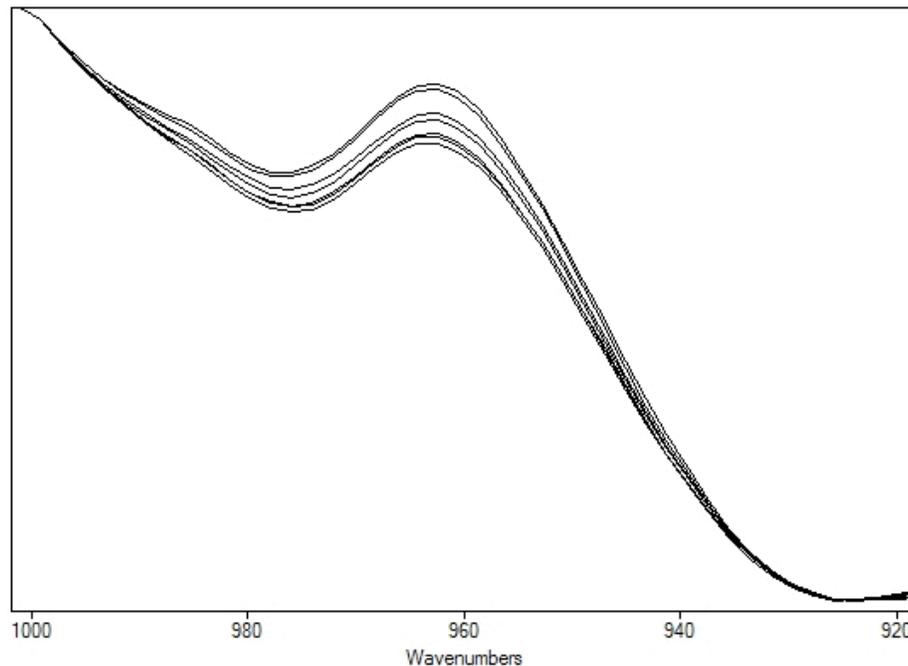


Fig. (2). Overlay spectra of virgin coconut oil at region 1000 to 920 cm^{-1} .

samples were placed in contact with the ATR. Single beam spectra in the range of 4000 to 650 cm^{-1} were obtained and corrected against the background to present spectra in absorbance unit. Spectra were obtained using 32 scans at 4 cm^{-1} resolution. Opus software (BRUKER, Karlsruhe, Germany) version 5.5 was used to operate the FTIR spectrometer and collect the spectra. The partial least square (PLS) calibration models that correlate between actual and predicted values of peroxide value was performed. The 'leave one out' cross validation was used to access the predictive accuracy of the calibration model.

RESULTS AND DISCUSSION

Fig. (1) shows the FTIR spectrum of VCO. One of the main feature of the spectrum is in the region of 3050 to 2800

cm^{-1} which was attributed to the absorbance of CH stretching vibrations (cis- $\text{CH}=\text{CH}$ -, $-\text{CH}_2$ -, CH_3 , CH_2/CH_3) [4]. The region between 1400 to 900 cm^{-1} is due to the stretching of C-O-C and CH bending [7]. The $-\text{C}=\text{O}$ stretching absorption of the triacylglycerol ester linkage can be observed in the region from 1800 to 1650 cm^{-1} . The region of 1500 to 1000 cm^{-1} is known as fingerprint region. The carbonyl absorption of the triacylglycerol linkage is observable at 1744 to 1739 cm^{-1} [8]. A band near 1238 cm^{-1} and 1163 cm^{-1} are related to the proportion of saturated acyl groups [9].

During thermal oxidation of VCO, several changes in the peak intensity were observed. The frequency for band 983 to 985 cm^{-1} were increased as the oxidation increased, reaching a maximum value near 988 cm^{-1} (Fig. 2). The band at 988 cm^{-1} is associated with presence of trans, trans and/or cism

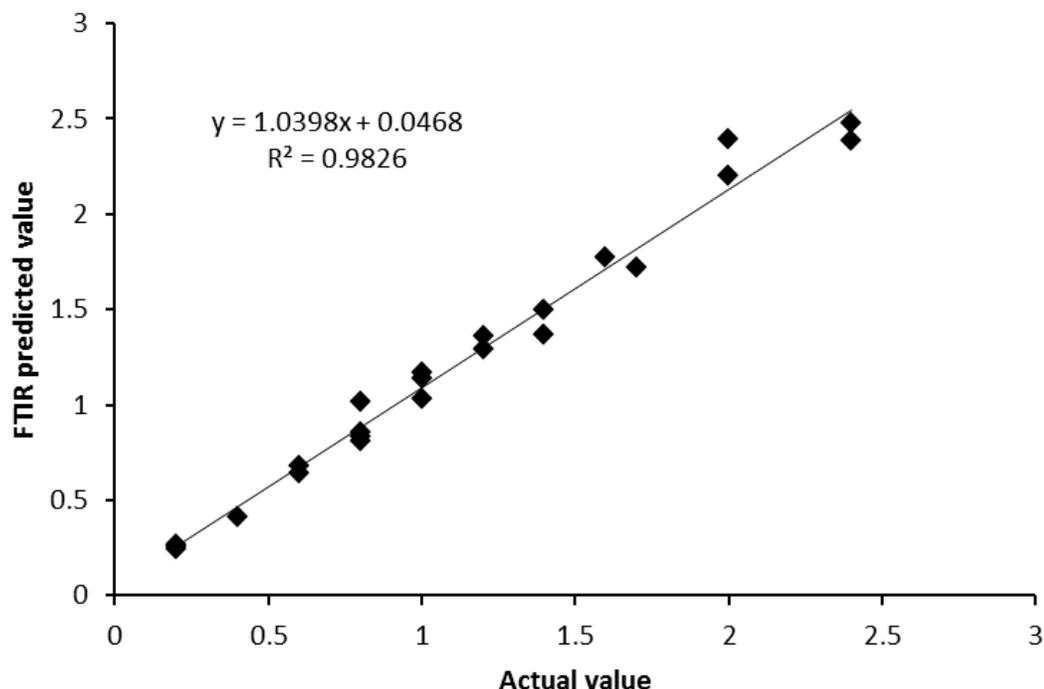


Fig. (3). PLS calibration model of actual versus predicted FTIR peroxide value.

trans-conjugated olefinic double bonds [10]. The band at 967 cm^{-1} is associated with the bending vibration of CH functional groups of trans-olefins [11]. Fig. (2) shows the increase in band 967 cm^{-1} as the oxidation advances. This band provided information about the gradual cis to trans isomerisation in the oxidized oil [12]. Thus, this band has been considered as indicator of oxidative stability.

The hydroperoxide bands have been reported at 3450 cm^{-1} , due to -OO-H stretching vibration of the oxidized methyl octadecadecionate [4]. The formation on hydroperoxide band however was not observable in this study. This hydroperoxide band can be interfered by other OH containing components such as free fatty acids [3].

The ability of PLS to mathematically correlate spectral changes to changes in the concentration of component of interest is being utilized in this study. The region of $988\text{-}900\text{ cm}^{-1}$ was selected for PLS calibration. Fig. (3) shows the PLS calibration model of the actual peroxide value determined by chemical method versus the FTIR predicted value in VCO. The slope indicates that there is linear relationship between FTIR predicted and chemically determined values with slope approaching to 1. The regression line equation obtained was $y = 1.0398x + 0.0468$ with coefficient of determination (R^2) equals to 0.9826. Validation was done by removing one standard at a time and satisfactory result of root mean error of prediction (RMSEP) of 0.4978 was obtained.

CONCLUSIONS

The present study shows that reliable prediction ability is obtained for determination of peroxide value using PLS. This indicates that FTIR combined with PLS can serve as a rapid powerful technique to determine the peroxide value in VCO than can be achieved using conventional methods.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

ACKNOWLEDGEMENTS

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