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Application of near-infrared spectroscopy to characterize binary blends of palm and canola oils

Ogan Mba, Peter Adewale, Marie-Josée Dumont*, Michael Ngadi**

Department of Bioresource Engineering, Macdonald Campus of McGill University, 21,111 Lakeshore Road, Ste-Anne-de-Bellevue, Quebec H9X 3V9, Canada

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ABSTRACT

This work evaluated essential quality parameters of binary blends of vegetable oils using a rapid and non-destructive method namely Fourier transform near-infrared (FTNIR) spectroscopy. Crude palm oil and canola oil from different vendors were blended at different ratios to obtain 40 oil samples with wide ranges of iodine values (IV), free fatty acids (FFA) and peroxide values (PV). FTNIR spectra of these oil samples were acquired and used in the calibration and test validation steps. The IV, FFA and PV of the oil samples were analyzed by AOCS methods. The FTNIR spectra were correlated to the AOCS data using partial least squares (PLS) regression. Calibration models were developed after test validation. The chemometric models were further improved through spectral processing. The optimal models were first derivative and first derivative + straight line subtraction. For IV, coefficient of determination (R^2) = 0.98; root mean square error of prediction (RMSEP) = 2.54 and residual predictive deviation (RPD) = 6.11. The values for FFA were R^2 = 0.9927; RMSEP = 0.35 and RPD = 11.6. While the values for PV were R^2 = 0.9722; RMSEP = 0.49 and RPD = 6.4. The simultaneous characterization of the essential chemical quality parameters of vegetable oil blends by FTNIR spectroscopy is reported.

1. Introduction

Palm oil is extracted from the fleshy orange-red mesocarp of oil palm fruits *Elaeis guineensis*. It is a vegetable oil with a balanced composition of saturated and unsaturated fatty acids both in the crude and processed forms. Palm oil is important in the world's vegetable oil trade. It is mainly used for edible purposes such as in cooking, margarine production, deep-fat frying, shortening, ice creams and cocoa butter substitutes in chocolate. Palm oil is also used in soap and oleo-chemical industries (Barriuso et al., 2013; Schrøder et al., 2006). Oilseed rape species used to produce canola oil are from the *Brassica* genus in the *Cruciferae* family. The conversion from high erucic acid rapeseed (HEAR) to canola resulted in an oil with very low levels of saturated fatty acids (6%), high levels of the monounsaturated fatty acid where oleic acid is predominant (58–61%) and moderate levels of polyunsaturated fatty acids (36%) (Farag et al., 2010). It has been reported that blending vegetable oils improved nutrition and physical properties as well as the stability of the mixture of oils (Curvelo et al., 2011; Tyagi and Vasishtha, 1996). Oils are also blended to obtain the desired mix with appropriate fatty acid composition and effective antioxidants at minimum cost (Kochhar, 2000). To improve the handling properties of palm oil at low temperature, blending with canola oil and enzymatic modification improved the fluidity of the blend (Ramírez and Cava, 2005). Blending palm olein and canola oil has been used to produce lower linolenic acid, *trans* fat free margarine (Dinh et al., 2008); oil samples with increased levels of essential fatty acids, tocopherols, tocotrienols and improved frying stability (Zou et al., 2012). Rapid and online investigation and monitoring of the quality of binary blends of palm oil and canola oil during storage and application in foods is important to ensure the safety and functionality of the oil samples and the wholesomeness food products.

The current standard chemical methods such as AOCS, AOAC and IUPAC used to evaluate the quality of oils are among the most diversified ones for food safety and quality analyses (Du et al., 2012). Although some of the methods are relatively simple, others are complicated and require expensive instruments and hazardous chemicals. Each method targets only part of reactions; several methods are normally required to evaluate the quality of

Abbreviations: AOAC, Association of Official Analytical Chemists; AOCS, American Oil Chemists' Society; FFA, free fatty acid; FTNIR, Fourier transform near-infrared; IUPAC, International Union of Pure and Applied Chemistry; IV, iodine value; NIRS, near infrared spectroscopy; PCO, palm and canola oils; PLS, partial least square; PV, peroxide value; RMSEP, root mean square error of prediction; RPD, residual predictive deviation.

* Corresponding author. Tel.: +1 514 398 7776; fax: +1 514 398 8387.
** Co-corresponding author. Tel.: +1 514 398 7779; fax: +1 514 398 8387.
E-mail address: marie-josee.dumont@mcgill.ca (M.-J. Dumont).

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culinary oil. This makes the analyses of fats and oils costly and time consuming. The development and integration of rapid methods for accurately evaluating the quality of fats and oils is of significant importance in ensuring its safety and quality. In 2001, FTNIR was approved by the American Oil Chemists' Society (AOCS) as an official method for the determination of the iodine value of fats and oils (Azizian et al., 2007). Since then NIRS has gained importance as a tool for the investigation of vegetable oil samples. Using infrared and near-infrared spectroscopy in combination with different chemometric tools, adulteration of oil, such as extra virgin olive oil and palm oil, has been detected and quantified (Christy et al., 2004; Rohman and Man, 2010). The classification of oils with different geographic (Casale et al., 2010) and botanic (Yang et al., 2005) origin or quality parameters (Lankmayr et al., 2004) has been demonstrated. Furthermore, NIRS and single bounce attenuated total reflectance (SB-ATR) FTIR have been used for the quantification of fatty acids and triacylglycerides of different edible oils and partially hydrogenated vegetable oils (Dupuy et al., 2010; Galtier et al., 2007; Sherazi et al., 2009). Other non-destructive techniques for oil authentication and analysis are differential scanning calorimetry and electronic nose (Man and Rohman, 2013).

Near Infrared Spectroscopy (NIRS) is an analytical technique using a source of emitting radiations of the known wavenumber 12,500–4000 cm^{-1} (wavelength 800–2500 nm). NIRS makes it possible to obtain a complete image of major organic components of the material being analyzed (Van Kempen, 2001). The principle behind the method is the absorption or reflection of different wavelengths of incident radiation, which depends on the chemical composition of the sample (Mlček et al., 2006). For the determination of the components in the samples, it is nevertheless necessary to perform an accurate calibration of the NIR spectrometer using an appropriate file of calibration standards of the known composition or using appropriate analytical methods known as the reference methods. The dependence of NIRS on reference methods is one of the major disadvantages. Other disadvantages include its low sensitivity to minor components and complicated interpretation of spectral data (Büning-Pfaue, 2003). The combination of NIRS and chemometrics can be applied to many foods and agricultural commodities and is widely used in the cereal, oilseed, dairy, pharmaceutical and other processing industries to predict the chemical composition of biological products with high accuracy. Both Fourier transform near-infrared (FTNIR) and Fourier transform infrared (FTIR) are fast and nondestructive methods which only require minimal or no sample preparation (Bala and Singh, 2013; Ferrer-Gallego et al., 2011; Rohman et al., 2010). FTNIR is an excellent tool in industrial quality assurance/quality control because it has large path length that permits analysis of more samples. It can pass through glass and plastic materials to analyze the samples inside. The spectrum gives accurate, precise and fast results in a few seconds. FTNIR has remote sampling capabilities. While mid-infrared spectroscopy makes use of fundamental vibrations, NIR spectroscopy uses overtones and combination bands. Combination bands are the sum of several fundamentals from different vibrations which contributes to high analysis repeatability and accuracy, meeting standard laboratory testing protocols. Thus, one single spectrum may contain qualitative and quantitative physical and chemical information (De Beer et al., 2011).

Concerning the analysis of edible oils, Li et al. (1999) have demonstrated the use of FTNIR spectroscopy for the determination of IV. They reported that even though the near-IR spectra show considerable variation for oils and fats of different origin, the near-IR signature for unsaturation (IV) in the second overtone region, 9100–7500 cm^{-1} (1333–1099 nm) is remarkably uniform for a wide variety of oils and fats. Sato et al. (1991) reported that NIRS absorption bands between 6250–5555.56 cm^{-1} and 4761.9–4545.45 cm^{-1} contain useful information regarding fatty acid compositions in various fats and oils. Man and Moh (1998) obtained an optimized calibration model for the free fatty acids of palm oil based on C=O overtone regions from 5504.41 to 4878.05 cm^{-1}. They reported that the best wavenumber combinations were 5313.5; 4975.12 and 4901.96 cm^{-1} (i.e. wavelengths of 1882; 2010 and 2040 nm). PLS calibration model for predicting the PV of triacylglycerols at levels of PV 10–100 was developed using the spectral region from 4710 to 4550 cm^{-1} (Dong et al., 1997). Li et al. (2000) further described the upgrading of the FTNIR PV method for the determination of PV in the range 0–10 PV based on the quantitation of triphenylphosphine oxide using the region 4695–4553 cm^{-1}.

Our research group has recently utilized FTNIR to evaluate and predict the iodine value and free fatty acid contents of animal fats waste and their binary blends (Adewale et al., 2014). The objectives of this work were to use FTNIR spectroscopy to evaluate and monitor the essential quality attributes of binary blends of palm and canola oils and determine which spectra preprocessing method gave the best fit model. The work focused on simultaneously evaluating iodine value (IV), free fatty acid (FFA) and peroxide value (PV) of the blend of oil samples. The NIR spectra of the oil samples were preprocessed to improve the PLS results. IV, FFA and PV were chosen for this evaluation because they are among the top most important chemical quality indices of fresh oil samples monitored by both food service and industrial frying operators (Chong, 2012). This study will assist rapid detection of quality of binary blends of vegetable oils in research and industrial applications.

2. Materials and methods

2.1. Sample collection and calibration standards

Crude palm oil and canola oil were purchased from different vendors in Montreal QC and Richmond BC, Canada. Analytical grade reagents were purchased from Fischer Scientific and J.T. Baker Co, New Jersey, USA. Forty samples of palm and canola oil blends and 3 replicates for each sample were used for the development of the calibration model. Total number of calibration spectra was 90 while the test validation spectra were 30. Blending palm and canola oil in different ratios (w/w) was done in order to obtain oil samples with a wide range of IV, FFA and PV. IV is a measure of degree of unsaturation determined by the Wij's method. It is expressed as the weight percent of iodine consumed by the oil in a reaction with iodine. The formation of FFA in lipids is due to the hydrolysis of the triacylglycerol and hydroperoxides decomposition in the presence of moisture and air. FFA was determined by dissolving a portion of the oil sample in hot ethyl alcohol and titrating against 0.25 M sodium hydroxide. Phenolphthalein was used as the indicator. PV is the most widely used analytical measurement of oxidative deterioration. The PV was a measure of the hydroperoxide content by iodine titration, using 0.01 M sodium thiosulphate. The IV, FFA and PV were determined in triplicates using the AOCS methods Tg 1–64, Ca 5a–40 and Ja 8–87 (Firestone, 2009). The data was used to develop the PLS calibration models for the prediction of the IV, FFA and PV of the blend of oil samples.

2.2. FTNIR spectral acquisitions

About 1.0 ml of each of the palm/canola oil (PCO) sample blend was pipetted into glass cuvettes (optical path length = 1 mm) and set into the sample compartment of the spectrometer. NIR spectra were acquired using a Bruker Optics MPA FTNIR Spectrometer. The spectrometer was equipped with the optics validation protocol (OVP), which is an instrument validation tool that includes comprehensive instrument test protocols and a PC workstation based