Evaluation of Frying Oil Quality Using VIS/NIR Hyperspectral Analysis

Samira Kazemi, Ning Wang, Michael Ngadi, Shiv O. Prasher
Department of Bioresource Engineering, McGill University, Ste Anne-de-Belleveue, Quebec, Canada. Email: ning.wang@mcgill.ca

ABSTRACT

Traditional chemical methods of analyzing frying oil quality are time-consuming and not amenable to on-line measurements. The main objective of this study was to evaluate quality changes of heated based on visible/near infrared spectral analysis using a hyperspectroradiometer. The reflectance spectra of the heated oils were analyzed within a range of 400 to 1750 nm. Acid value, total polar component, and viscosity of oil samples were used as indicators of different quality levels of oil. Partial Least Squares calibration models were developed for quantitative evaluations of these parameters. The $R^2$ and Root Mean Square Error (RMSE) for each prediction were calculated to assess the prediction capability of calibration models. The study demonstrated that using the established calibration models, quality parameters could be predicted with $R^2$ values over 0.92.

Keywords: Spectroscopy, fatty acid, viscosity, Total polar component, Partial Least Squares Method, Multivariate Statistical Analysis

1. INTRODUCTION

Fried food industry is one of the largest industries in North America. Deep fat fried products are popular due to their unique flavor and texture characteristics. During frying, oil is subjected to prolonged periods of heating at high temperatures of about 180ºC in the presence of air and water. This leads to a wide range of complex chemical reactions categorized as thermal oxidation, hydrolysis, and polymerization. Undesirable constituents and off-flavors are developed in frying oil due to these chemical reactions (Innawong et al., 2004a). Therefore, the quality of the frying oil is critical factors to keep high quality fried products.

The rate of oil degradation during frying is influenced by several factors including the temperature of frying, exposure to air, stability of the oil against oxidation, and the moisture content of the fried food (Orthoefer, 1988). The frying industry is constantly seeking for new frying oils that are stable and impact desired characteristics to fried products. Thermal stability of the frying oil is related to the level of hydrogenation. The oxidative stability of the frying oil will increase with increased degree of hydrogenation. Thus, hydrogenated oils are widely used in the industry. However, during the hydrogenation process trans fatty acids are generated which, are associated with increased risk of hazards to human health. This fact has become a major concern for the use of hydrogenated oil in the fried food industry. Recently, as an alternative to hydrogenated frying oil, partially hydrogenated oils with less degree of unsaturation are increasingly adopted.

Degradation of oil during frying is followed by changes in free fatty acid (FFA) level, color, and viscosity, and by an increase in the number of polar molecules as a result of thermal and oxidative breakdown of the hydrocarbon chain in the oil (Innawong et al., 2004b). It is vital that the quality of frying oil is monitored closely in order to maintain appropriate quality of frying oil and fried food. Some food service restaurants evaluate oil quality from subjective parameters such as visual and odor characteristics (Moreira et al., 1999).

Traditional thermal methods for evaluating degraded oil quality (physical and chemical), such as measurement of total polar compounds (TPC), FFA, carbonyl value, and viscosity, are tedious, time consuming, and not amenable to on-line assessment. Highly increasing consumption of edible oils in deep-fat frying industry entitles the need for rapid, accurate, and cost-effective techniques of oil quality control.

Many studies have been conducted to investigate potentials of spectroscopic methods to determine quality parameters in edible oils, such as determination of trans fat content and peroxide value of edible oil using Fourier Transform near-infrared spectroscopy (FT-NIR) (Li et al., 2000a; Li et al., 2000b). Innawong et al. (2004a) used the spectra within the range of 4000-850 cm\(^{-1}\) with a FTIR attenuated total reflectance spectroscopy (FTIR-ATR) to differentiate among good, marginal, and unacceptable oils. Near-infrared spectroscopy instruments are also recognized as effective tools for quality control in food industry due to their fast and non-destructive measurement, no requirement for using hazardous reagents and solvents, and more flexible sample handling.

The goal of this study was to investigate feasibility of the VIS/NIRS techniques for rapid, quantitative evaluations of quality parameters for hydrogenated and non-hydrogenated oil that have gone through heating cycles. The specific objectives of this study were:

1. To establish VIS/NIRS calibration models to predict acid value, viscosity, and total polar components of heated oils,
2. To select the best wavelength regions for predicting the three quality parameters, and
3. To test and validate the prediction accuracy of the developed calibration models.

2. MATERIALS AND METHODS

2.1 Oil sample Preparation

Hydrogenated and non-hydrogenated canola oils were obtained from a local supplier (Canbra Foods Ltd., Lethbridge, AB). The hydrogenated and non-hydrogenated oils were blended in the ratios (w/w %) of 0:100 (i.e. non-hydrogenated oil), 40:60 and 80:20 to form three mixtures of oil samples. All the oil samples were heated at 190ºC in a domestic fryer on a 9 hrs per day cycle for a total time of 72 hrs. The temperature of the oil was controlled automatically by a controller (Model 689000-01, Eutech Instrument Pte Ltd., Singapore). Samples of 200 ml were collected at the end of each daily heating cycle and kept at 4ºC before used for chemical analysis and spectral collection.
2.2 Chemical Tests

Three major quality parameters of each oil sample, free fatty acid value, viscosity, and total polar compounds, were measured and used as indicators of oil quality.

The TPC of the samples was determined according to the AOCS official method, Cd 20-91, by column chromatography (AOCS, 1989). The efficiency of fractionation was assessed by the thin layer chromatography and results were reported in percentage of polar compounds (m/m).

Acid value of samples was measured according to the AOCS official method, Cd 3a-63, by alkaline titration. The acid value was reported in milligrams of KOH per gram of sample (AOCS, 1989).

Viscosity of samples was measured using a controlled stress/shear rheometer with coaxial concentric cylinder with a built-in peltier plate (Advanced rheometer, AR 2000, TA Instruments Inc., Leatherhead, UK) at 40°C. Viscosity readings were reported in Pa.s.

2.3 Spectral Collection

Spectral data were collected using a portable hyper-spectroradiometer (FieldSpec® Pro, Analytical Spectral Devices, Boulder, Colorado, USA), which measured reflectance spectra in a wavelength range of 350-2500 nm and a spectral resolution of 3 nm.

During spectral measurement, a Petri dish filled with an oil sample (40ml) was placed underneath the fiber bundle of the FieldSpec® Pro with a distance of 20 cm. The distance was calculated based on the field of view of 18° of the fiber bundle. A DC regulated fiber-optic illuminator (Fiber-Lite PL900-A, Dolan-Jenner Industries Inc, MA, USA) was used as a light source. Two fiber-optic light-guiding branches were mounted on a test frame to guide light to the sample. Figure 1 shows the test platform for spectral data collections.

Light reflected from the sample was collected by the fiber-optic bundle and sent to the FieldSpec® Pro for intensity measurement. A white reference panel with approximately 100% reflectance across the entire spectrum was used as a reference standard. At each wavelength reading, a ratio between the light intensity from the sample and the white reference was calculated. The View Spec Pro software (Analytical Spectral Devices, Boulder, Colorado, USA) was used for instrument control and computation. All spectra (350-2500 nm) were recorded and stored in a PC. The reflectance was normalized to the range of 0 to 1.

2.4. Calibration and Data Analysis

Spectral analysis was conducted using GRAMS/AI v7.02 (Thermo Electron Corp., Salem, New Hampshire, USA). Due to significant noise were observed in the ranges of 350-400 nm and 1750-2500 nm, for all the spectra, only the spectral range of 400-1750 nm were used for calibration and data analysis. Out of a total number of 54 spectra, 36 were randomly selected to form a training set and were used to develop Partial Least Squares (PLS) calibration models. The remaining 18 spectra formed a validation set to verify the prediction capability of the calibration models.

The PLS calibration method was used to decompose the spectra into a set of “variation spectra”, also called “factors”, that represented changes in reflectance within the spectral range. It performed the decomposition on both spectral and targeted parameter(s) simultaneously, so that the calibration models established are related directly to the parameters of interest. In this study, three parameters, acid value, viscosity, and total polar compounds of the oil samples, measured with the chemical analysis, were used as “constituent” data, and the spectra were used as the “spectral” data for training set. These spectra were preprocessed using mean centering and automatic baseline correction (Thermo Galactic, 2003). Mean centering was a process of calculating the average spectrum of the training set spectra and then subtracting the average spectrum from each individual spectrum. Same procedure was performed on the concentration values of each constituent. This enhanced the difference between samples in both spectral and constituent data by removing the mean from the data. Automatic baseline correction was chosen to remove the baseline effects from the spectra occurred during spectral collection. The PLS procedure yielded the calibration models, the optimal numbers of factors used in the calibration models, the feature wavelengths for predicting the constituents, and the predicted constituents for each sample in the training set. The optimal number of factors for establishing the calibration model was determined by the predicted residual error sum of squares (PRESS). The number of factors with the minimum PRESS value was considered the optimal. Beta coefficients were used to find the feature wavelength ranges (at peak or valley in the PLS Beta Coefficients plot) to predict the parameter of the interest in an oil sample. Eliminating the useless wavelength regions which had no or very less contribution to parameter prediction would simplify the calibration models and reduce the time for required computation. Also selected wavelength regions can be
used as a basis to design on-line systems with less cost. Concentration residuals, the difference between the actual and predicted concentration for samples, were used for outlier detection in a training set. The best calibration model was chosen with the highest $R^2$ values for the predicted parameters versus actual parameters obtained from cross validation. The Root Mean Square Error (RMSE) for both training and validation set were calculated for each constituent to evaluate prediction performance of the calibration model.

3. RESULTS AND DISCUSSION

3.1 Chemical Analysis

Figures 2, 3 and 4 show changes in acid value, viscosity and TPC, respectively, during heating for three types of oil samples, namely non-hydrogenated (0:100), 40% hydrogenated (40:60) and 80% hydrogenated (80:20). For fresh oil sample, the average initial (fresh) acid value was 0.1 mg KOH/g fat, whereas the average viscosity and TPC values were 36 mPa.s and 6%, respectively. The viscosity, TPC and acid values were in the typical range reported for fresh good quality vegetable oils (Danowska-Oziewicz and Karpiska-Tymoszczyk, 2004; Benedito et al. 2002; Goburdhun and Jhurree, 1995). Values of the quality parameters increased with heating time, indicating increased oxidation and polymerization. Quality of the non-hydrogenated oil changed more rapidly, as expected, compared to the oils with higher degrees of hydrogenation. This is attributed to the higher content of unsaturated fatty acids in the non-hydrogenated oil resulting higher oxidation during heating. Based on regulations in most countries, frying oil that has gone through heating cycles should be discarded when its TPC value reached 25% (Benedito et al., 2002). Results of chemical analysis demonstrated that the 0:100 and 40:60 oils reached the 25% TPC level within the 72h of frying at 190ºC used in this study. This would have occurred at even shorter time if the oil was used for frying foods. Therefore, in this study, different levels of oil quality from fresh to discardable stage, were generated. This would justify the applicability of the results of this study for quality determination of oils that have been used for frying foods.

![Figure 2](image-url) Changes in acid values during heating for three types of oil samples, namely non-hydrogenated (0:100), 40% hydrogenated (40:60) and 80% hydrogenated (80:20).

Figure 3 Changes in viscosity during heating for three types of oil samples, namely non-hydrogenated (0:100), 40% hydrogenated (40:60) and 80% hydrogenated (80:20).

Figure 4 Changes in total polar compounds during heating for three types of oil samples, namely non-hydrogenated (0:100), 40% hydrogenated (40:60) and 80% hydrogenated (80:20).

3.2. VIS/NIR Calibration

Figure 5, as an example, shows a reflectance spectrum of non-hydrogenated (0:100) canola oil within the range of 400-1750 nm. The differences among the reflectance spectra of the three types of oil samples were not significant visually, except for those in visible range (400 – 700 nm) due to color changes of the oil samples during heating.
3.2.1 Model 1: Calibration Model Using a Spectral Range of 400-1750 nm.

PLS calibration models were established to predict acid value, viscosity, and TPC with the number of factors of 9, 8, and 8, respectively. Results of the calibration are shown in Figure 6, 7 and 8. The acid value was predicted with a $R^2$ of 0.95 for the training set and RMSE of 0.0042 and 0.0111 for the training and validation sets, respectively. The viscosity was predicted with a $R^2$ of 0.91 for the training set and RMSE of 0.0005 and 0.0007 for the training and validation sets, respectively. The TPC was predicted with a $R^2$ of 0.98 for the training set and RMSE of 0.3080 and 0.7505 for the training and validation sets, respectively.

![Figure 5. A reflectance spectrum of non-hydrogenated (0:100) canola oil within the range of 400-1750 nm](image)

![Figure 6. Predicted vs. actual acid value of the training and validation sets.](image)
3.2.2 Model 2: Calibration Models Using the Feature Wavelength Ranges

Based on the PLS Beta coefficient plot for each constituent, the common spectral regions of the most variations (named, feature wavelength ranges) were found in ranges of 450-550, 850-950, 1140-1180 and 1200-1300 nm. Variations in the visible region could be due to the color changes in oils heated for different times. Lankmary et al. (2004) studied the region of 410-445 nm to classify two categories of pumpkin seed oil according to their quality, namely accepted and rejected oil. Acceptable oils had higher peaks at 418 nm and lower peaks at 434 nm compared to rejected oils.

The second overtone of C-H stretching in various chemical groups such as –CH2, –CH3 and HC=CH is observed in the region of 1100-1300 nm (Hourant et al., 2000). The bands around 1180 nm have been assigned to the C-H stretching overtone in HC=CH structure of pure fatty acids containing cis double bonds (Sato et al., 1991). The region of 9100-7560 cm\(^{-1}\) (about 1098-1322 nm) was reported to contain information about the degree of unsaturation and was used for

Figure 7. Predicted vs. actual viscosity for the training and validation sets.

Figure 8 Predicted vs. actual total polar compounds for the training and validation sets.

quantitative determination of Iodine value of edible oils (Li et al., 2000a). Li et al. (2000a) related the region of 8975-7189 cm\(^{-1}\) (around 1114-1391 nm) to the trans content of edible oils. The bands of C=O also appeared at around 900 nm. The observed variations on PLS Beta coefficient plot within the feature wavelength ranges could be explained by the fact that the C=C bounds break down during thermal degradation of oil and cis double bonds transform to trans double bonds. Oxidation products with C=O group in their structure also were formed as a result of thermal oxidation.

The second calibration model was established using the reflectance within the feature wavelength ranges. With the similar procedures of previous calibrations, the cross-validation results for predicting acid value, viscosity, and TPC for three types of oil samples were shown in Figures 9, 10, and 11, respectively. With the training set, the acid value, viscosity, and TPC were predicted with \(R^2\) of 0.93, 0.92 and 0.92, and RMSE of 0.0190, 0.0011, and 1.4030, respectively. The RMSE of the validation sets for the acid value, viscosity, and TPC were 0.0183, 0.0008, and 1.3101, respectively.

![Graph](image)

Figure 9. Predicted vs. actual acid value using the PLS calibration models with the feature wavelength ranges.

Table 1 summarized the calibration models developed and corresponding cross-validation results for predicting the three quality parameters.

Table 1 Summarized results of PLS calibration models

<table>
<thead>
<tr>
<th>Calibration model</th>
<th>Training set</th>
<th>Validation set</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>RMSE</td>
</tr>
<tr>
<td></td>
<td>AV*</td>
<td>VI**</td>
</tr>
<tr>
<td>Model 1</td>
<td>0.93</td>
<td>0.91</td>
</tr>
<tr>
<td>Model 2</td>
<td>0.93</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Notes: * Acid value  ** Viscosity  *** Total polar component

4. CONCLUSIONS

The feasibility of using VIS/NIRS techniques to rapidly and quantitatively evaluate quality parameters for heated edible oils was investigated. The results show that with a fine resolution, the spectral reflectance of the oils can be used to effectively predict the three quality parameters, i.e. acid value, total polar compounds, and viscosity.

Partial Least Squares calibration models using a wavelength range of 400 – 1750 nm could track the changes of the three parameters of the heated oil samples with high accuracy. $R^2$ values obtained from the calibration models were 0.95 for acid value, 0.91 for viscosity and 0.98 for total polar compounds.

Four feature wavelength ranges, 450-550, 850-950, 1140-1180 and 1200-1300 nm, were selected. The $R^2$ values for predicting the three quality parameters were above 0.92. The feature wavelength ranges could be used as a basis to design on-line oil quality evaluation systems.

In summary, the VIS/NIR spectroscopy proved to be a useful and fast technique with the capability of simultaneous prediction of oil quality parameters. Once a calibration models is developed, prediction and analysis could be done within few minutes.

5. REFERENCES


