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Determination of Iodine Value of Palm Oils Using Partial Least Squares Regression-Fourier Transform Infrared Data

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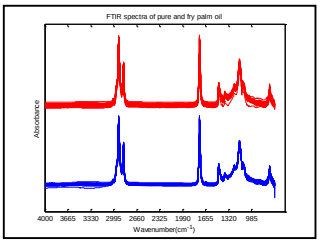
Graphical abstract



Abstract

This paper shows the determination of iodine value (IV) of pure and frying palm oils using Partial Least Squares (PLS) regression with application of variable selection. A total of 28 samples consisting of pure and frying palm oils which acquired from markets. Seven of them were considered as high-priced palm oils while the remaining was low-priced. PLS regression models were developed for the determination of IV using Fourier Transform Infrared (FTIR) spectra data in absorbance mode in the range from 650 cm^{-1} to 4000 cm^{-1}. Savitzky Golay derivative was applied before developing the prediction models. The models were constructed using wavelength selected in the FTIR region by adopting selectivity ratio (SR) plot and correlation coefficient to the IV parameter. Each model was validated through Root Mean Square Error Cross Validation, *RMSECV* and cross validation correlation coefficient, R^2_{cv}. The best model using SR plot was the model with mean centring for pure sample and model with a combination of row scaling and standardization of frying sample. The best model with the application of the correlation coefficient variable selection was the model with a combination of row scaling and standardization of pure sample and model with mean centering data pre-processing for frying sample. It is not necessary to row scaled the variables to develop the model since the effect of row scaling on model quality is insignificant.

Keywords: Palm Oils; PLS; FTIR; iodine value; SR plot

Abstrak

Kajian ini menunjukkan penentuan nilai iodin (IV) minyak sawit asli dan goreng menggunakan regresi kuasa dua kecil separa (PLS) dengan aplikasi kaedah pemilihan pemboleh ubah. 28 sampel terdiri daripada minyak sawit asli dan goreng diperolehi daripada pasaraya. Tujuh daripadanya dikelaskan sebagai minyak sawit mahal sementara selebihnya adalah minyak sawit murah. Model-model regresi PLS dibina untuk penentuan IV menggunakan data spektra inframerah fourier transformasi (FTIR) dalam unit serapan di jalur antara 650 cm^{-1} to 4000 cm^{-1}. Derivatif Savitzky Golay telah diaplikasi sebelum membina model ramalan. Model-model dibina menggunakan jalur dipilih dalam rantau FTIR dengan menggunakan plot nisbah pemilihan (SR) dan pekali korelasi kepada parameter IV. Setiap model disahkan melalui kuasa dua akar min validasi, *RMSECV* dan pekali korelasi validasi silang, R^2_{cv}. Model terbaik menggunakan plot SR adalah model dengan min berpusat untuk sampel asli dan model dengan kombinasi baris berskala dengan standardisasi untuk sampel goreng. Model terbaik dengan aplikasi pemilihan pemboleh ubah pekali korelasi adalah model dengan kombinasi baris berskala dan standardisasi untuk sampel asli dan model dengan data pre-proses min berpusat untuk sampel goreng. Tidak perlu untuk menskalakan baris pemboleh ubah untuk membina model memandangkan kesannya terhadap kualiti model adalah tidak ketara.

Kata kunci: Minyak sawit; PLS; FTIR; nilai iodin; plot SR

1.0 INTRODUCTION

Frying is a very popular food preparation at home and in fast-food restaurants. The method is fast, convenient and gives the fried foods desirable flavor, color and crispy texture. However, continuous usage at high temperature and in the presence oxygen and water, promotes thermal oxidation, polymerization and hydrolysis reaction. As a result, the flavour and colour of the fried food will be affected and also producing undesirable constituents which may be harmful to health [1]. Recently, there were an increasing number of cases reported regarding to used oil have been reprocessed and sold as a new with lower price to the consumers [2]. Due to consumer health and social care importance, reliable technique which provides rapidity and

accuracy is crucial especially for the quality assessment of the cooking oil before and after market penetration.

Several techniques has been used to asses oil quality, such as colorimetric reactions, iodine and saponification value determination, density viscosity, refractive index, and ultraviolet absorbance [3]. In this study IV was used as a principal indicator of the cooking oil quality which specifically measures the unsaturation of oils and fats. Based on the previous researches, IV usually was determined by titration methods. The conventional method of titration in determining IV is ineffective because it uses highly toxic, carcinogenic and environmentally unfriendly chemicals [4]. The method is complex, time consuming, and laborious [3, 5]. Through the titration method, the obtained result is unreliable because the result is depending on the skills of the analyst [6]. Traditional chemical methods practicing in the analysis of frying oil quality are not acceptable to on-line measurement [7].

Spectroscopic techniques such as FTIR, nuclear magnetic resonance (NMR) and fluorescence spectroscopy have been applied to overcome the problems. FTIR spectroscopy has emerged as an attractive alternative technique with its sample handling development which equipped with Attenuated Total Reflectance (ATR) [8]. FTIR-ATR has been preferred as a popular choice due to its rapidity and sensitive techniques with minimal sample handling [9]. Moreover, the acquisition of the spectral data can be obtained easily with a relatively small amount of sample and nondestructive leftover where the sample will remain intact after analysis. PLS regression of multivariate calibrations is one of the chemometrics approach and FTIR spectroscopic method combine with chemometrics is a powerful tool in monitoring oil quality. Chemometrics methods able to deal with multivariate data, including high co-linear spectral data [10]. Several publications have reported the application of chemometrics applied to FTIR spectral data in analyzing edible oils quality such as olive oil [11], soybean oil, sunflower oil, coconut oil [12] and palm oil [13].

The aim for this paper is to determine the IV parameter of palm oils using PLS model with SR plot and correlation coefficient as variable selection tool. The model then will be compared through *RMSECV* and R^2_{cv}. Savitzky-Golay smoothing data technique is applied where the derivative is obtained by fitting a polynomial to the point and some of its left and right neighbours. The fitted value are better than original because some noise has been removed [14]. In this study, the first derivative spectra with 21 gap point and 2 degree polynomial has been used to developed the model [15]. In the interpretation of PLS model using spectra profiles such as FTIR spectra, most of the variations are unrelated to the response *y*. The model is dominated by the orthogonal variation which uncorrelated to the response and representing the interferent factors. In this study, SR plot is used to reveal FTIR spectral region with both high explanatory and high predictive to the IV response to cope with the situation [16]. SR plot provide a bridge from co-variance-based target projection (TP) loadings to an interpretative measure independent of the differences in variance of the *x*-variables and with good sensitivity [17]. PLS model based on SR plot will be compared to the model with correlation coefficient that select the best region in constructing model based on the high positive or high negative correlation of spectra data to the response [18]. The best data pre-processing in developing the PLS model also was investigated. Four data pre-processing were applied which are standardisation, mean centring and combination of row scaling with both standardisation and mean centring.

2.0 EXPERIMENTAL

2.1 Materials

Palm oil samples were purchased from local markets around Negeri Sembilan. There are of 58 samples which are 28 types are pure palm oil and 28 types of frying palm oil. The sample was numbered with 1 to 28 for each type.

2.2 Dataset

The dataset consisted of *y*-response and spectra data. IV value of the samples is the y-response which was determined through titration method. While spectra data of the samples was recorded in absorbance mode at the spectral range from 650 cm^{-1} to 4000 cm^{-1} [13] with 4 cm^{-1} spectral resolution and 4 scan number using Perkin Elmer 100 FTIR Spectrometer. The Attenuated Total Reflectance (ATR) was used at sample station for sample handling. Background spectrum was first collected without sample placing on the ATR plate. The dataset was further analyzed using Matlab R2008a software.

2.3 Chemometrics Method

The dataset was pre-treated using Savitzky-Golay first derivative with 21 gap point and 2 degree polynomial. The derivative enhances the spectral resolution and removes baseline and background [19]. By means of variable selection procedure, SR plot and correlation coefficient, the most significant variables in FTIR region were selected and subjected for PLS modelling. Four data pre-processing were used in developing the PLS models which are standardisation, mean centring, combination of row scaling with both standardisation and mean centring. Standardisation and mean centring is the type of column scaling where all variables are ensured to have similar influence on the model developed [20]. Standardisation turn the variance of each variable to one and keep constant mean of the variables at zero while mean centring subtract each variables in a column with its mean resulting final column mean to be zero [21]. For row scaling, the sum of the squares for variables of a sample is set equal to one. The models were compared through *RMSECV* and R^2_{cv}. The predicted value of IV was plotted against the actual IV value.

3.0 RESULTS AND DISCUSSION

3.1 Determination of IV

Figure 1 showed the IV of 28 samples before and after frying process. After frying process, IV of the cooking oils was decreased due to more intensive thermo-oxidative transformation that occurred. The decrease in IV is believed due to destruction of double bond from oxidation, scission, and polymerization [22]. Designated sample number 3 and 19 which is consist of low-price type of palm oils resulted in substantial differences of IV after frying process, thus indicate that repetition frying of these cooking oil is inappropriate.

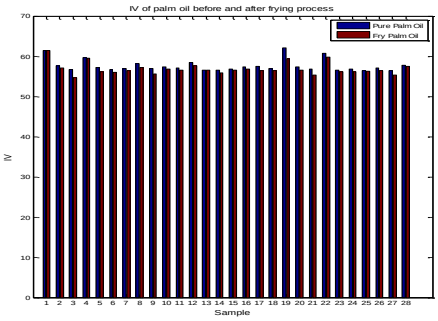


Figure 1 The IV of palm oils before and after frying process

3.2 Spectral Analysis

The changes in palm oils after being fried also can be seen in FTIR spectra. From the Figure 2, there are some changes between pure and frying FTIR spectra at region 3100 cm^{-1} to 2990 cm^{-1} and 1500 cm^{-1} to 1300 cm^{-1}. This is corresponding to *cis*–CH=CH- stretching and CH2 scissoring and CH3 symmetrical deformation respectively [4]. Previous study reported that C-H stretch in trans HC=CH region at 968 cm^{-1} is used to determine IV [23]. The FTIR spectra for both types of palm oils are almost similar since there are the similar functional groups of palm oils present in the samples.

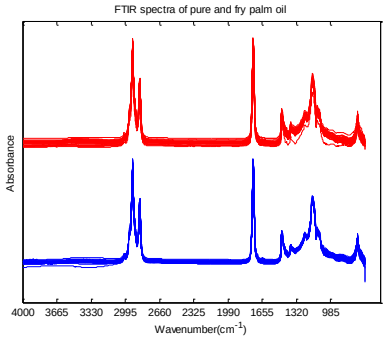


Figure 2 FTIR spectra of pure (blue) and frying (red) palm oils

3.3 PLS Regression Model

PLS regression model was developed to predict the IV of palm oils before and after frying with the application of SR plot and correlation coefficient as variable selection tools. PLS model with SR plot used the optimal PLS component from cross validation using all variables to obtain the regression coefficient, then the significant variables were selected after calculating the ratio between explained variance with residual variance by the target component. Figure 3 showed the SR plot of each model and the threshold has been made to select variables in constructing PLS model. The straight red line showed the threshold for each model based on the ratio calculated. The variables with SR above the threshold made were used to develop the model.

The models then were validated through *RMSECV* and R^2_{cv} where the lowest *RMSECV* and higher R^2_{cv} contribute to the best prediction model. Table 1 and 2 showed the performance of each PLS models using variables obtained from SR plot as variable selection for pure and frying sample respectively. From the table, the best model for pure sample is model with mean centring data pre-processing while for frying sample, the best model is model with row scaling and standardisation because of their lower *RMSECV* and higher R^2_{cv}. In predicting the IV, PLS model for frying sample is better since fewer optimal PLS component is needed in constructing the model compared to the model of pure sample.

Through the SR plot, discriminating variables will be selected based on higher SR representing more significant variables [24]. SR plot combines the possibility of using co-variance-based weights for the PLS/TP modelling and correlation-like model parameters for the interpretation and selection of influential variables. The SR plot has some similarity to a reproduced correlation coefficient, but display much more localized information due to the higher sensitivity of this ratio compared to the correlation coefficient [17]. Figure 4 showed the correlation coefficient between IV parameter and x-variables. The red line representing the threshold for selected variables, where the variables with correlation coefficient above than the threshold value were used to developed the models. Higher correlation values of variables represented greater importance to the IV.

Table 1 Model performance for pure sample using SR plot variable selection

Data pre-processing	*RMSECV*	R^2_{cv}	*RMSEC*	R^2_{cal}	Component	Number of variables
Standardisation	0.5704	0.9257	0.3581	0.9413	8	23
Mean centring	0.5658	0.9269	0.3574	0.9416	8	23
Row scaling and Standardisation	0.5572	0.9288	0.3435	0.9460	9	19
Row scaling and Mean centring	0.5596	0.9282	0.3461	0.9452	8	19

Table 2 Model performance for fry sample using SR plot variable selection

Data pre-processing	*RMSECV*	R^2_{cv}	*RMSEC*	R^2_{cal}	Component	Number of variables
Standardisation	0.7605	0.8539	0.5779	0.8425	3	186
Mean centring	0.7800	0.8446	0.6005	0.8299	3	283
Row scaling and Standardisation	0.6603	0.8922	0.4044	0.9229	4	273
Row scaling and Mean centring	0.7247	0.8675	0.5270	0.8690	4	252

Table 3 and 4 showed the performance of the model for pure and frying sample respectively. Based on tables below, it can be concluded that model for pure sample with row scaling and standardisation and model with mean centring data pre-processing for frying sample is the best model since they have low *RMSECV* and higher R^2_{cv}.Both SR plot and correlation coefficient resulting in fewer variables needed to develop the model rather than using all variables from the original data, thus enhance the efficiency of the prediction model. The resulting model performance also showed that there is no need to row scaled the variables to

develop the models since the effect on the *RMSECV* and R^2_{cv} is slightly small. After obtaining the best prediction model, the predicted and actual value of IV was plotted. Figure 5 showed the plot for each best PLS model with respective variable selection.

Based on the Figure 2, the characteristics of the palm oils through FTIR technique did not showed significant changes before and after being fried. Through the observation, the spectra looked similar to each other. Through the aid of the PLS method, the relevant information related to the IV was extracted. The linear combination between spectra data or variables with IV was found. Variable selection procedure in PLS model development showed that the significant variables needed to determine the IV before and after frying were different as showed in Table 1, 2, 3 and 4. From the tables, the variables selected in pure palm oils model are fewer than in fry palm oils model. This showed that more variables in FTIR region undergo changes related to the IV after the oxidation such as at 2872 cm^{-1} was formed corresponding to the production of CH_3.

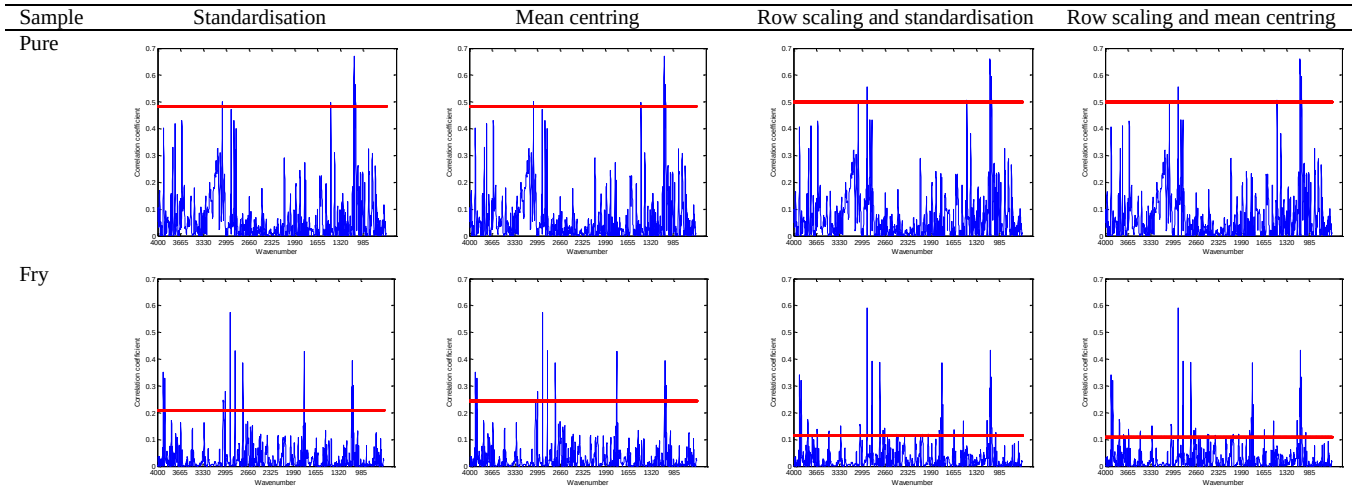


Figure 3 SR plot of each models with the threshold line to select significant variables

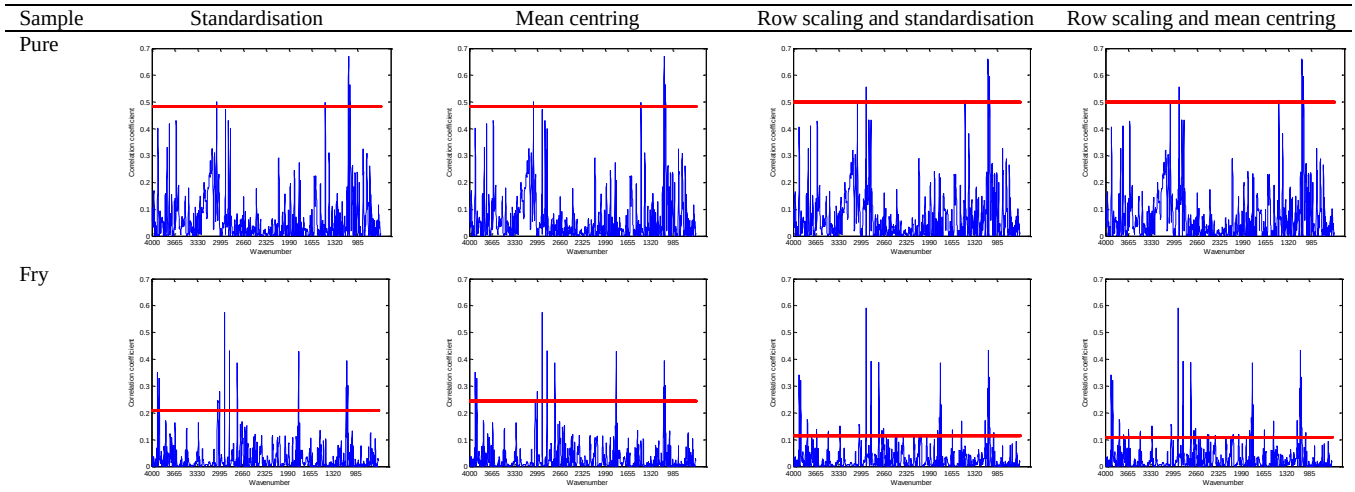


Figure 4 Correlation coefficient of each models with the threshold line to select significant variables

Table 3 Model performance for pure sample using correlation coefficient variable selection

Data pre-processing	*RMSECV*	R^2_{cv}	*RMSEC*	R^2_{cal}	Component	Number of variables
Standardisation	0.5704	0.9257	0.3581	0.9413	8	23
Mean centring	0.5658	0.9269	0.3574	0.9416	8	23
Row scaling and Standardisation	0.5572	0.9288	0.3435	0.9460	9	19
Row scaling and Mean centring	0.5596	0.9282	0.3461	0.9452	8	19

Table 4 Model performance for fry sample using correlation coefficient variable selection

Data pre-processing	*RMSECV*	R^2_{cv}	*RMSEC*	R^2_{cal}	Component	Number of variables
Standardisation	0.5951	0.9130	0.2508	0.9703	8	56
Mean centring	0.5784	0.9206	0.2199	0.9772	12	35
Row scaling and Standardisation	0.6789	0.8858	0.4247	0.9149	2	151
Row scaling and Mean centring	0.7406	0.8662	0.2557	0.9692	7	169

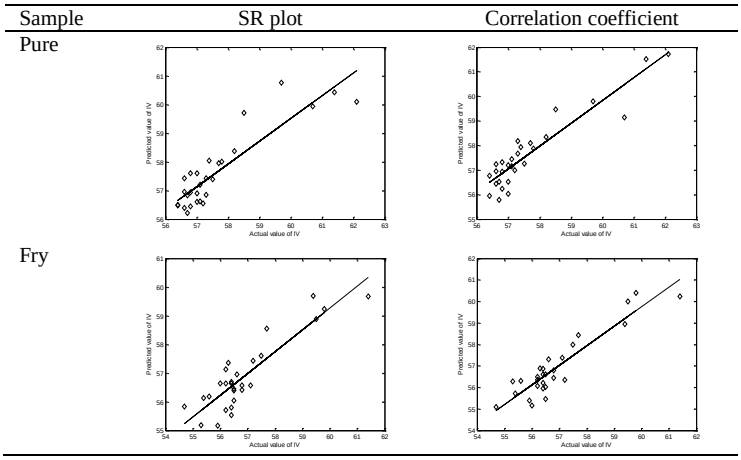


Figure 5 The predicted value versus actual value of IV for each best models

4.0 CONCLUSION

In this work, FTIR-ATR spectroscopy in combination of multivariate analysis (PLS regression) has been successfully used for determination of IV of palm oils. SR plot and correlation coefficient enhance the quality of the PLS model by isolating the most significant variables. On the other hand, different data pre-processing provide a different effect on the PLS model performance. Data pre-processing improves the quality of the PLS model, but it is not necessary to apply the row scaling to the data since the effect on model quality is small.

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