Linear Discriminant Analysis (LDA) and Partial Least Square (PLS) of Chemometric in Mixture of Lard and Palm Oil-Based on Ftir-Spectroscopy Data

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Abstract. Oil as a basic food requirement is often misused by irresponsible individuals, such as lard mixed in palm oil. This is certainly detrimental to society. Indonesia which has a majority Muslim population will have a big influence on the authenticity of oil. FTIR can be an alternative way to distinguish authentic and mixed foods or oils. The purpose of this study is to find out the difference between lard, palm oil, and the mixture of both by using FTIR combined with LDA (Linear Discriminant Analysis) and PLS and find out how much the contribution of LDA and PLS in distinguishing mixed pig oil, palm oil and oil both. The results obtained showed that FTIR was less effective in distinguishing between samples so it was necessary to combine it with LDA and PLS. LDA processed with the stepwise method gives good grouping results. There are two discriminant functions obtained. The LDA data shows the first discriminant function that is obtained with a variance value of 99.3% and the second discriminant function with a variance value of 0.07%. The LDA data shows the first discriminant function that is obtained with a variance value of 99.3% and the second discriminant function with a variance value of 0.07%. PLS data shows good results, which can be seen in the R2 value and validation error value (RMSECV) and low calibration error (RMSE).

Keywords: FTIR · Chemometrics · LDA · PLS

1 Introduction

Food is one of the important necessities of humans. Food is needed for human survival. Major the population in Indonesia adhere to the Islamic religion which there are some food or food ingredients not pure will be a problem. For example, when making some food oil is the basic ingredient. Many cases involving lard mixed in palm oil. It is very influential in human health and spirituality.

In the world many institutions that oversee food circulation like WHO and FAO. In Indonesia, there is an institution like BPOM, LPOM, etc. But in society is not effective for implementation and needs more sophisticated technology [1].

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FTIR is an instrument that is used for chemistry analysis effectively, fast and accurate [2]. In progress, FTIR has sensitivity, high resolution, and speed to data acquisition. FTIR is instrument environmentally friendly and does not destroy samples.

Infrared Spectroscopy employed used fingerprint technique. Fingerprint technique works in order to two compounds have amount or same peak intensity in infrared spectrum region. So it can distinguish some oil samples [3].

Chemometric is a chemical study that connects data from chemical research using statistical and mathematical methods [3].

The Chemometrics technique is easy to analyze the data obtained from the spectrum. The advantage of chemometrics analysis is to analyze infrared spectrum from samples research and connect spectrum profile which contains information in samples [4].

LDA analysis (*Linear Discriminant Analysis)* and PLS (*Partial Least Square*) is one part of the chemometric analysis needed to analyze fat and oil.

LDA is one of the chemometric analyses by a multivariate technique that is used to separate or merge samples. This method will find discriminant that can separate objects whose characteristics are known. Aim of classification object is to grouping object in two or more group which matches the characteristics that have been determined [5].

LDA has the main point for find Linear Discriminant Function (LDF) that used equation [6]:

$$Y = a_1X_1 + a_2X_2 + \ldots\ldots\ldots a_nX_n \tag{1}$$

Measure original n value from every object combine with Y value until data can reduction from n dimension into one or two dimensions. Objects in the same group have the same Y value and Object in the different groups have different Y values [6].

PLS regression is a sophisticated multivariate analysis technique, the function increase for quantitative infrared analysis. PLS is used for multivariate calibration because of the quality of calibration and ease of application [7].

PLS regression uses a least square algorithm that connects two matrices. Spectra data in X matrices and referent value in Y matrices. PLS combined FTIR to extract information that comes from complex spectra containing overlapping peaks and noise from the device [4].

Spectrum data used calibration model must completely term R2 value, RMSEC (Root Mean Standart Error of Calibration), RMSECV (Root Mean Square Error Cross Validation) as quantitative analysis.

RMSEC value function for evaluated there is an error when calibration. RMSEC value counted use [8]:

$$\text{RMSEC} = \sqrt{\frac{\sum_{i=1}^{n}(actual - calculated)^2}{N - f - 1}} \tag{2}$$

"actual" value shows concentration selected, while "calculated" shows spectra data value. N is the number of samples and first number factor use in the calibration model [8].

2 Methods

This research is a type of experimental research to distinguish between palm oil and lard and a mixture of both using FTIR that combined with LDA and PLS analysis.

2.1 Tools and Ingredients

Tools used for research include; Shimadzu brand FTIR spectroscopy for testing samples. PC devices are used to analyze LDA and PLS. Dropper pipettes are used to take samples. Beaker glass as a sample container. Stirrers are useful for homogenizing mixed samples. SPSS software for LDA analysis and Software Unscrambler X 10.4 for PLS analysis. The materials used in this study include lard and palm oil as samples. Water distillation, chloroform, Hexane, and acetone use when FTIR test.

2.2 Samples Preparation

Lard and palm oil and mixtures of both are used as samples. The sample will be divided into 5 with different concentrations which can be seen in Fig. 1.

2.3 FTIR Test

FTIR testing using FTIR Shimadzu brand. Spectra waves measured by FTIR use frequency 4000 cm−1- 400 cm−1. When the measurement is complete the plate is cleaned with hexane twice and acetone until no residual samples appear and dried using tissue. After the scan process is complete, a plot of FTIR spectrum will appear for each sample. From the spectrum plot, wave analysis and transmittance are generated from each sample [3].

2.4 Data Analysis

The first analysis is FTIR analysis to get the peak wave transmittance number. After getting the wave peak then the data will be used to analyze the LDA (using SPSS software) and PLS (using the unscrambler software).

3 Results and Discussion

The results of FTIR were obtained in the form of graphs of wavelength and transmittance plots. Wavelength shows the vibration of the chemical structure of the sample and transmittance shows a linear correlation with concentration.

Based on Fig. 2. FTIR results from the five samples at wave number 400 to 4000 cm^{-1}. Where the X-axis is a wave number and the Y-axis is transmittance.

produced by all samples show the same results, only differing in intensity.

The most significant difference occurs when at wavenumbers 910 cm^{-1} and 1099 cm^{-1}. In the sample of lard and pure palm oil, some differences can be seen from the peaks wave produced. In lard, the wave crest appears while in palm oil does

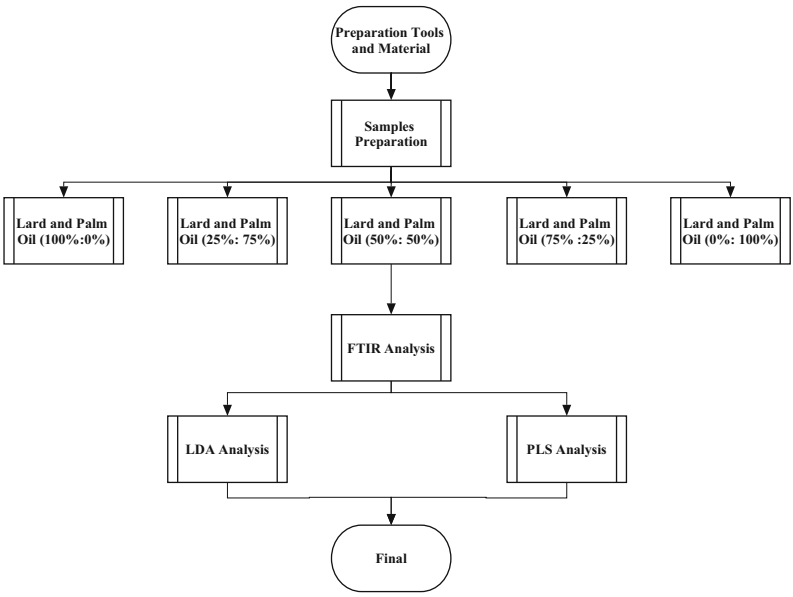

Fig. 1. Research Flow

not appear. In peak wave, there is rocking vibration which shows the functional group = CH from trans olefin isolation.

At 1099 cm^{-1} wavenumber in the lard and palm oil samples do have peaks, but the peaks produced by palm oil tend to be weaker than lard. This peak occurs due to the relationship of ether in triacylglycerols.

Another peak that appears in the results of the FTIR spectrum is 721 cm^{-1}. This wavenumber shows bending vibration overlapping which shows the Methylene-CH_2 functional group.

A wavenumber 1163 cm-1 and 1118 cm-1 there is a stretching vibration which shows the functional group C-O (ether). Wavenumber 1377 cm^{-1} has symmetric bending vibrations indicating the presence of a C-O ether functional group. At CH rocking (bending) 1417 cm^{-1} wavenumber from cis which is not substrate in an alkene. Wavenumber 1463 cm^{-1} has a CH_2 functional group from bending vibration. In areas with a wavelength of 1747 cm^{-1}, there is a high carbonyl absorption so that the peak produced is sharp and indicates a stretching vibration of the C = O Carbonyl functional group. At a wavelength of 2852 cm^{-1}, it shows the symmetric stretching vibration of the C-H (CH_3) Methylene functional group.[9]

The wavelength of 2924 cm^{-1} is the highest peak that is produced from all samples and indicated Stretching asymmetric CH2 functional groups. The peak wavelength of 3007 cm^{-1} uptakes of lard is higher than palm oil because the saturated fatty acid that content of lard is higher than palm oil. On that area, it shows the functional group Cis-olefinic C = H of Stretching vibrations [9].

Based on FTIR results, the lard spectrum shows higher absorption of palm oil because the content of linoleic and linolenic acids in lard is higher than in palm oil. The intensity

produced by lard is higher than palm oil. More oil containing a mixture of lard will produce high intensity and more oil containing a mixture of palm oil will produce short intensity.

3.1 LDA Analysis

The LDA analysis results in the form of a score plot (Fig. 3) after going through various stages. Scor plot comes from the discriminant function. In Fig. 3 the X-axis shows the first. Discriminant function and the Y-axis shows the second discriminant function. The final result of the LDA shows the value of the variant obtained from the first discriminant function, which is 99.7% and the value of the variant obtained in the second discriminant function is 0.03%.

From the results of the LDA analysis, there are several group groups. Blue indicates lard with a concentration of 100%, green color namely palm oil with a concentration of 100%, yellow color shows a mixture of lard and palm oil with a concentration ratio of 25%: 75%, purple color shows a mixture of lard and palm oil with a concentration ratio of 50%: 50%, red color which is a mixture of lard and palm oil with a concentration ratio of 75%: 25%. Mixed oil which has a pure oil concentration tends to approach more pure oil and vice versa.

These results indicate that the LDA is able to group the five oil samples. The first function of LDA is more dominant in distinguishing groups than the second discriminant function. The first discriminant function has a major contribution in distinguishing between samples. The two functions add up to 100%, so the LDA results show no information is missed when analyzing and the errors obtained are also small (Table 1).

Table 1. Functional Clusters of Absorbance Peak in FTIR Spectrum of Lard and Palm Oil.[9]

Frequency (cm)	Functional Groups	Vibration
3007 cm^{-1}	= C-H (*cis*)	*Stretching*
2922 cm^{-1}	-CH-H (CH_2)	*Stretching asymmetric*
2852 cm^{-1}	-C-H (CH_3)	*Stretching symmetric*
1740 cm^{-1}	-C = O (ester)	*Stretching*
1465 cm^{-1}	-C = H (CH_2)	*Bending*
1375 cm^{-1}	-C-H (CH_3)	*Bending symmetric*
1235 cm^{-1}	C-O ester (*stretching*)	
	-C-O	*Stretching*
1160 cm^{-1}	-CH2-	*Bending*
1117 cm^{-1}	C-O	*Stretching*
1098 cm^{-1}	C-O	*Stretching*
721 cm^{-1}	-CH = CH- (*cis*)	*Bending*

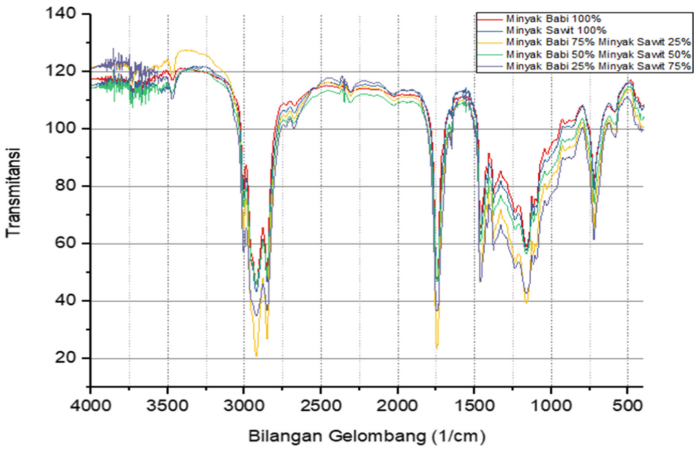

Fig. 2. Results FTIR Spectrum All Samples

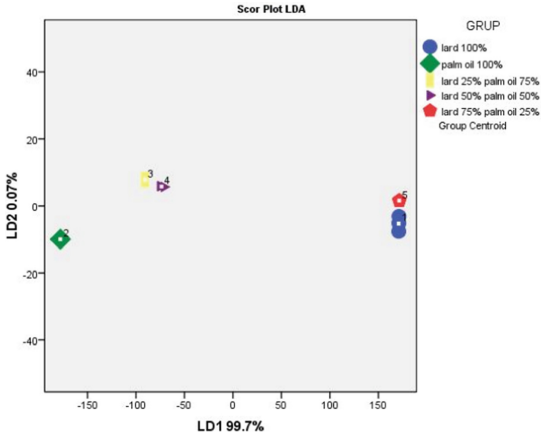

Fig. 3. Scor plot LDA

3.2 PLS Analysis

The results of PLS regression can be seen in Fig. 4 and Table 2. The used in PLS are Factors, Loadings, and Scores. PLS uses free variable data as X and non-independent variable data as Y. The X and Y matrices will be calculated for the suspension value and make a regression of the two values.

PLS regression shows the results seen from the validation error value (RMSECV) of 3.85 and the calibration error value (RMSE) of 0.64. Based on these data the PLS analysis is good, it can be seen from the R2 value which is close to 1 and the low validation error value (RMSECV), and the calibration error value (RMSE).

The selected spectrum data is based on the best predictive ability if the correlation value R2 is large and the error values of RMSEC and RMSECV are getting smaller.

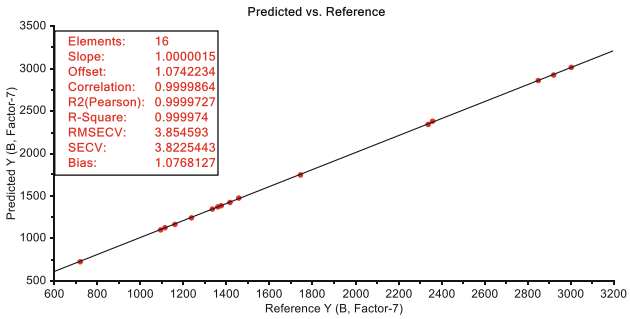

Fig. 4. Results PLS Analysis

Table 2. Value of PLS Analysis Results

	Validation	**Calibration**
R2	0,99	0,99
Correlation	0,99	0,99
RMSECV	3,85	-
RMSE	-	0,64
SECV	3,82	-
Bias	1,07	-

4 Conclusions

FTIR results show there is a difference between pig oil, palm oil, and a mixture of both. But it will be difficult and long to analyze it. FTIR will be better when combined with LDA and PLS chemometric analysis. The LDA results show good results which can group the five samples while the PLS results also show good results which can be seen from the value of calibration errors and a little validation.

References

1. L. Hilda, Analisis Kandungan Lemak Babi dalam Produk Pangan di Padangsidimpuan secara Kualitatif dengan Menggunakan Gas Kromatografi (GC). 2014;1–15.
2. A. Rohman, Y.B.C. Man, Potential Use of FTIR-ATR Spectroscopic Method for Determination of Virgin Coconut Oil and Extra Virgin Olive Oil in Ternary Mixture Systems. 2011;155–62.
3. Y.B. Che Man, A. Rohman, T.S.T. Mansor, Differentiation of lard from other edible fats and oils by means of Fourier transform infrared spectroscopy and chemometrics. JAOCS, J Am Oil Chem Soc. 2011;88(2):187–92.
4. H. Lukman, I. Wulandari, Y. Retnaningtyas, Penentuan Kadar Flavonoid pada Ekstrak Daun Tanaman Menggunakan Metode NIR dan Kemometrik (Determination of Flavonoid in Leave Extracts Using NIR and Chemometric). 2016;4(1):8–13.

5. K. Fukunaga, Introduction to Statistical Pattern Recognition Second. Boston: Harcound Brace Jovanovich; 1990.
6. J.N. Miller, J.C. Miller, Chemometrics for Analytical Chemistry. Fifth edit. Analytical Chemistry. edinburgh gate: Pearson Education Limited; 2010.
7. M. Paye, A. Barel, Maibach H. Handbook of Cosmeutical Science and Technology. 2001.
8. P. Liang, H. Wang, C. Chen, F. Ge, D. Liu, S. Li, et al. The Use of Fourier Transform Infrared Spectroscopy for Quantivication of Adulteration in Virgin Walnut Oil. 2013;2013.
9. M.D. Guillén, N. Cabo, Characterization of Edible Oils and Lard by Fourier Transform Infrared Spectroscopy. Relationships Between Composition and Frequency of Concrete Bands in the Fingerprint Region. 1997;74(10):1281–2.