Rapid detection of patchouli oil mixed by coconut oil using NIRS technology and chemometrics method

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Abstract. Aceh patchouli oil is sometimes mixed with various oils for profit resulting in the low quality of patchouli oil. This low quality caused Aceh patchouli oil to depress its selling price. The main objective of this study is to develop NIRS technology to investigate the authenticity of patchouli oil mixed with coconut oil using Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA) methods. This present study uses 6 kinds of sample treatment namely pure oil and mixed oil with a total of 42 samples for calibration and 18 samples for validation. The results showed that NIRS Technology with PCA and LDA methods provides a solution opportunity to solve the problem of counterfeiting patchouli oil with coconut oil. The PCA method successfully obtained a classification model that was able to provide a clear visual appearance to distinguish between pure patchouli oil and a mixture of patchouli oil and coconut oil. Meanwhile, the LDA method successfully obtained a validated classification model with the number of errors 1 out of 18 independent validation samples to distinguish between pure patchouli oil and non-patchouli oil.

1. Introduction
Patchouli oil is an essential oil obtained from the leaves and stems of patchouli by distillation. Patchouli oil is commonly used as an important component in the cosmetic, perfume, and soap industry which is difficult to replace by synthetic substances because it is very instrumental in determining the strength properties and fragrance resistance. Among patchouli oil in Indonesia, Aceh Patchouli oil (Pogostemon Cablin, Benth) is the world's best patchouli oil that can produce patchouli crude oil with a patchouli alcohol (PA) content above 30%. Until now, Aceh patchouli oil is needed as a blending material for other regional patchouli oil in Indonesia. The uniqueness of Aceh patchouli has also gained geographical indication protection from the Ministry of Law and Human Rights of the Republic of Indonesia. [1-3].

Indonesia’s patchouli oil exports are usually carried out to various countries such as France, Singapore, United States, United Kingdom, Germany, India, Spain and Netherlands. Indonesia is a
supPLIER of 90% of the world's patchouli oil needs and 30-40% of it comes from Aceh. Although Nilam Aceh is one of the largest foreign exchange producers for the country, but patchouli farmers' life has not improved significantly. Added value of patchouli commodity is not enjoyed by the local community even though Aceh is a production center for global patchouli and 100% of Aceh's patchouli land is a smallholder plantations spread almost throughout Aceh province. Data records, Aceh province is the poorest province in Sumatra island and ranked 5th poorest in Indonesia. [4-5].

One of the reasons for the low added value of patchouli commodity to the income of the Acehnese people is because the community's patchouli oil is considered problematic in its authenticity, especially when raw materials are scarce. The addition of certain ingredients both in the distillation process and in the further process[3]. Patchouli oil is commonly mixed with fatty oils (e.g. palm oil, coconut oil, duck oil), kruing oil, brake oil, kerosene, pentine oil and some organic solvents. This is certainly very depressing the selling price of oil in the community due to oil quality which is considered low. This low quality causes patchouli oil to not be used directly by the patchouli oil derivative products industry such as perfume industry, cosmetics, aroma therapy without further processing [6-7].

One of the main keys to increasing the selling value of Aceh patchouli is the controlling process of patchouli oil authenticity. Rapid and efficient quality detection can be realized through the development of Near Infrared Reflectance Spectroscopy (NIRS) technology. NIRS has become one of the most promising non-destructive methods and can be used for various material analysis. The advantages that can be achieved are simple samples preparation, rapid detection process, and environmental friendly because no chemicals are used. More importantly, NIRS has the potential to determine multiple quality parameters simultaneously. Through the development of chemometrics methods, NIRS technology capabilities became more popular and attracted a lot of attention from researchers in the food field. Components with a concentration percentage of 0.1% can be detected and evaluated using NIRS [8].

Numerous studies have been carried out to investigate and apply NIRS for patchouli oil that has now been developed for the characterization of patchouli oil extract [9] suspects the value of patchouli alcohol using PLS method [10], research to analyze the origin of the patchouli region [11] and research to suspect the authenticity of patchouli oil mixed with palm oil, distance oil [12-13]. From these studies it can be seen that NIRS technology can be used to help improving patchouli oil quality. Therefore the main objective of this study is to develop NIRS technology to suspect the authenticity of patchouli oil mixed with coconut oil using PCA and LDA methods.

2. Materials and methods

2.1. Oil samples treatments

This study used 2 types of oil namely patchouli oil (in the form of crude oil) and coconut oil. Furthermore, the two oils are made 6 kinds of treatments namely 100% pure patchouli oil (MN), 100% pure coconut oil (MK), a mixture of patchouli and coconut oil with a ratio of 50% : 50% (Mix50), a mixture of patchouli and coconut oil with a ratio of 75% : 25% (Mix75), a mixture of patchouli and coconut oil with a ratio of 80% : 20% (Mix80) and a mixture of patchouli and coconut oil with a ratio of 95% : 5% (Mix95). Each treatment is created 10 replays in which 7 replays will be used as calibration data and 3 replays as independent validation data. In total, there will be 42 calibration samples and 18 validation samples.

2.2. Diffuse reflectance infrared spectra acquisition

NIR spectra data of all samples were acquired using a self developed FT-IR IPTEK T-1516. The NIRS spectrum generated by this tool generally in accordance with commercial NIRS tool standards. However, it is necessary to pay attention to the frequency and energy requirements (optical gain, number of scans and resolution) in the process of retrieving the spectrum in order to produce a good spectrum. Self developed PSD NIRS i16 can emit light waves in a wavelengths range between 1.000 nm to 2.500 nm (4.000 – 10.000 cm⁻¹) and controlled by Thermo Operation® software. NIRS spectrum can be
obtained by configuring the workflow which is built using integrated Thermo Operation ® software. Workflow creation is done with settings to set the tool to work [14].

In this present study, the instrument is set with 32 scans, 2.0 cm⁻¹ resolution, and 4x optical gain so that it can acquire the diffuse reflectance spectrum of the sample. Then the tool averaged the results and saved the scan results in two different file formats. i.e. *.SPA dan *.CSV.

2.3. Image segmentation
NIRS spectrum obtained will be carried out validity test by checking the presence of outlier data using PCA method combined with Hotteling $T^2$ ellips method. Furthermore, a classification model will be created using PCA method to visually view the results of the grouping and use the LDA method to measure its classification success rate. Classification models using the LDA will then be validated using the independent data that has been set up.

3. Results and discussion

3.1. Spectra features and analysis
NIRS spectrum for oil samples are acquired at wavenumbers of 4.000-10.000 cm⁻¹. The NIRS spectrum is formed due to the absorption of NIRS light by materials resulting in molecules vibrating then forming the peaks and valleys of the spectrum. Figure 1 is a spectrum of patchouli oil and coconut oil that has been averaged aims to make it easier to interpret the presence of chemicals at certain wavelengths.

![Figure 1. Patchouli oil and Coconut Oil Typical Spectrum](image)

Based on Figure 1 it can be seen that the typical two oil spectrums look very similar, this is in accordance with previous research which states that the composition of coconut oil is very similar to patchouli oil and can mix perfectly with patchouli oil. Therefore, coconut oil is most commonly used as a mixture of patchouli oil [15].

However, when viewed in more detail it is obtained that pure patchouli oil and pure coconut oil have little difference at the height of the peaks and depth of the valleys spectrum that form. The difference was mainly for the patchouli alcohol peak that is dominant in patchouli oil and the fat peak that is dominant in coconut oil.
3.2. Outlier test

Outlier data is a different data than other data that can interfere the process of processing information. Outlier data were detected using PCA and Hotelling $T^2$ ellipse method. The data is indicated by its presence outside the ellipse line. Examination of outlier data in this study can be seen in Figure 2.

![Figure 2. Outlier Data Examination](image)

Based on Fig.2 it can be seen there are some data that are outside the ellipse line which can be predicted as outlier data. But, the proof needs to be done by erasing the data and then re-processed. In this study evidently the data that was outside the ellipse line was not outlier data but in the form of lever data. This can be proved after deleting the data that happens even more data comes out of the ellipse line. Therefore all data totaling 60 can be considered valid and can be used all of them for further processing.

3.3. PCA classification

Data processing using PCA method aims to make it easier to visually see the formation of data classification clusters. A good classification model, built using PCA method must have a latent variable (LV) smaller than 9. Classification results using PCA method can be seen in Figure 3.

![Figure 3. Analysis Results Using PCA Method](image)

As can be seen in Figure 3, the PCA forms 2 large classification clusters that are cluster consisting of pure patchouli oil (MN) and cluster consisting of other than patchouli oil (MK, Mix (50-50), Mix
(75-25), Mix (80-20) and Mix (95-5)). So it can be concluded that NIRS with PCA is able to distinguish pure patchouli oil from coconut oil to the limit of the coconut oil mixture of 5%.

Furthermore, loading plot analysis of test results will be carried out using PCA method. The loading analysis of PCA described the potential and relevant wavelength which aims to determining the most dominant substance that forms the PCA classification results. The presence of these substances can be seen from the dominant vibrations display which are formed from the loading plots obtained. Results of loading plot analysis was present in Figure 4.

**Figure 4. Loading Plot Results**

As shown in Figure 4 can be seen there are 3 main vibrations formed, so it can be said that it is the vibration of the dominant substance that affects the PCA classification process. If the wavelengths are traced, it can be assumed that these substances are fat and PA. This is in line with research that says coconut oil is identical to high fat content [15] and patchouli oil is identical to high PA levels [9].

3.4. LDA classification

Data processing using LDA method aims to make it easier to see the success rate of classification models. Classification results using LDA method was presented in Figure 5.

**Figure 5. LDA Classification Result**
Based on Fig. 5 it can be seen that the LDA successfully detected 6 kinds of sample treatment. Of the 6 treatments, LDA succeeded in making a classification of 66.67%. Furthermore, validation test are carried out by entering independent data into the LDA model that has been generated. In detail the validation results using data independent of LDA classification model can be seen in Table 1.

| No | Class       | Actual     |
|----|-------------|------------|
| 1  | MN          | MN         |
| 2  | MN          | MN         |
| 3  | MN          | MN         |
| 4  | Mix (50-50) | MK         |
| 5  | Mix (50-50) | MK         |
| 6  | Mix (80-20) | MK         |
| 7  | MK          | Mix(50-50) |
| 8  | Mix (50-50) | Mix(50-50) |
| 9  | Mix (50-50) | Mix(50-50) |
| 10 | MK          | Mix(75-25) |
| 11 | Mix (50-50) | Mix(75-25) |
| 12 | Mix (50-50) | Mix(75-25) |
| 13 | Mix (80-20) | Mix(80-20) |
| 14 | Mix (80-20) | Mix(80-20) |
| 15 | Mix (80-20) | Mix(80-20) |
| 16 | Mix (80-20) | Mix(95-5)  |
| 17 | MN          | Mix(95-5)  |
| 18 | Mix (80-20) | Mix(95-5)  |

Based on Table 1 it can be seen that the LDA classification model still performs 8 errors in detecting 18 independent data for 6 kinds of sample treatments. However, the LDA method successfully obtained a validated classification model with the number of errors 1 out of 18 independent validation samples to distinguish between pure patchouli oil and non-patchouli oil.

4. Conclusions
NIRS technology with PCA and LDA methods provides a solution opportunity to solve the problem of counterfeiting patchouli oil with coconut oil which has remained an obstacle in the patchouli oil trade. The PCA method successfully obtained a classification model that was able to provide a clear visual appearance to distinguish between pure patchouli oil and a mixture of patchouli oil and coconut oil. Meanwhile, the LDA method successfully obtained a validated classification model with the number of errors 1 out of 18 independent validation samples to distinguish between pure patchouli oil and non-patchouli oil.

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