Rapid determination of patchouli oil quality as a tropical plant using infrared technology

Zulfahrizal *1,3, Syaifullah Muhammad 2,3, A A Munawar 1,3

1 Agricultural Engineering Department, Syiah Kuala University, Darussalam-Banda Aceh 23111, Indonesia
2 Chemical Engineering Department, Syiah Kuala University, Darussalam-Banda Aceh 23111, Indonesia
3 ARC PUI-PT Nilam Aceh, Syiah Kuala University, Darussalam-Banda Aceh 23111, Indonesia

*Email: zulfahrizal@unsyiah.ac.id

Abstract. Patchouli alcohol (PA) content is an important indication in the world patchouli oil trade. Testing the PA content of patchouli oil usually takes a long time and expensive, so that it greatly inhibits the activity of buying and selling patchouli oil in the community. Therefore the main objective of this study is to develop NIRS technology to estimate the PA content in Aceh patchouli oil purified rapidly and appropriately using PLSR and PCR methods. The sample in this study was patchouli oil which was purified into 20 types based on PA content. Laboratory test using GC-MS. Near infrared (NIR) spectrum of Patchouli oil samples were acquired and recorded using self-developed FT-IRIPTEK T-1516. The results showed that NIRS technology with PLSR and PCR methods provides a solution to solve the problem of PA content prediction in Aceh’s patchouli oil. SNV pretreatment is proven to improve prediction accuracy and robustness of the prediction model that built. The PLSR-SNV method succeeded in obtaining a prediction model that was categorized as very good model performance, while PCR-SNV method succeeded in obtaining a prediction model that was categorized as good model performance.

1. Introduction

Patchouli oil is 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. Patchouli Oil from Aceh (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, Patchouli oil from Aceh is needed as a blending material for other regional patchouli oil in Indonesia. The uniqueness of Aceh’s patchouli has also gained geographical indication protection from the Ministry of Law and Human Rights of the Republic of Indonesia [1, 2, 3].

Indonesia’s patchouli oil exports are usually carried out to various countries. Indonesia is a supplier of 90% of the world's patchouli oil needs and 30-40% of it comes from Aceh. Although patchouli from Aceh is one of the large foreign exchange earners for the country, but Added value of patchouli commodities is not enjoyed by Acehnese people, which is the production center for world
patchouli. Data records, Aceh province is the poorest province in Sumatra island and ranked 5th poorest in Indonesia [4, 5].

Indonesia is the world's largest supplier of patchouli oil needs, but both the volume and price of essential oil (especially national patchouli oil) are declining sharply at the moment so that Indonesia's position began to be threatened by China, India and Vietnam. Especially in Aceh, data in 2018 showed Aceh has the second highest patchouli productivity in Indonesia with the third largest patchouli land in Indonesia (2,240 ha) and production of 460 tons per year. Unfortunately, most of Aceh's patchouli oil is produced by farmers and refiners with varying PA content, high acid content, charred smell and high impurity content so that it is dark and turbid in color. This low quality causes the selling price of people's patchouli oil to be relatively cheap and cannot be used directly by the patchouli oil derivative product industry without advanced treatment process [5, 6].

Therefore, quality control of patchouli oil, especially the PA content of patchouli oil, is one of the main keys to increase the patchouli oil value. Methods of determining rapidly and appropriately needed to produce high quality standard patchouli oil commodities required by consumer countries. Patchouli oil quality estimation is usually carried out through laboratory tests using the acidimetric method or by using Gas Chromatography – Mass spectroscopy (GC-MS). This chemical method takes a long time, expensive and can cause environmental pollution. Thus, it is not suitable to be applied in industries that require rapid and non-destructive methods to analyze oil quality.

Rapidly and efficiently prediction of agriculture materials quality 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, including in agriculture. 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 [7].

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 [8], predict the value of alcohol patchouli with alcohol meter as a comparison test tool [9], research to analyze the origin of the patchouli region [10], and research to suspect the authenticity of patchouli oil mixed with palm oil, castor oil, and coconut oil [11, 12, 13]. From these studies it can be seen that NIRS technology can be used to detect patchouli oil quality. Therefore, the main objective of this study is to develop NIRS technology to estimate the PA content in Aceh patchouli oil purified rapidly and appropriately using PLSR and PCR methods.

2. Materials and methods

2.1. Sample Treatment
Patchouli oil in the form of crude oil purified using rotary vacuum evaporator to obtain fractionated oil with three levels of patchouli alcohol content. Then all three were tested using GC-MS to find out the content of patchouli alcohol. Furthermore, by mixing the three oils above, 20 new patchouli oil variants are made based on PA content. All oil variants are bottled for further spectrum acquisition.

2.2. NIR Spectrum Acquisition
Near infrared (NIR) spectra data of Patchouli oil samples were acquired and recorded using 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 FT-IR IPTEK T-1516 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. Then the tool averaged the results and saved the scan results in two different file formats. i.e. *.SPA dan *.CSV [14].

2.3. Spectrum Validation Test
Nutmegs The NIR spectrum obtained will be carried out a validity test by checking the presence of outlier data. Principal Component Analysis (PCA) was firstly applied to the untreated raw spectra in order to explore the spectra in details and detect outliers by subjecting Hotelling $T^2$ ellipse. It used to define statistical boundaries assuming a normal distribution of scores of the PCA. The data used in this study is data that is inside the ellipse line, if it is outside the ellipse line, then the data is marked as outlier data and removed [15].

2.4. Spectrum Pre-treatment
Prior to calibration model development, The NIR spectrum for all patchouli oil samples was first carried out with spectrum pre-treatment. According to Mouazen et al., Spectrum pretreatment was performed to eliminate noise and spectra scattering in the spectrum so that resulting prediction model will be more accurate [16].

In this study, we employed Standard Normal Variate (SNV) method to enhance spectral data and investigated the impact of this correction method on the prediction performance. Zulfahirzal 14) said that Standard Normal Variate (SNV) is a good choice to pre-process and enhance spectra data. Spectra correction tends to remove spectral noises due to light scattering, sensor curvature, over-heated effects, and multiplicative effects. SNV standardizes each spectrum using only data from that spectrum, not using the average spectrum from each set [17].

2.5. Prediction Models
The main part of NIRS applications is to establish models used to predict desired quality parameters simultaneously of patchouli oil samples through a process called as calibration. Prediction models in this study were established using two different regression approaches namely Principal Component Regression (PCR) and Partial Least Square Regression (PLSR). Comparing PLSR with PCR is much done by researchers therefore comparing PLS and PCR is very interesting. According to literature, PLSR and PCR methods used for linear data. The PLSR method is the most widely used and has been recognized for its advantages in generating a better prediction results. PLS is a method that reduces the dimensions of data, to find the most relevant factors in predicting and interpreting data. PLS reduces the impact of many predictors that are irrelevant to data diversity. Predictor errors are improved by means of cross-validation. PLS seeks to find the best correlation between reference and infrared spectrum data during transformation to latent variables (LVs) in the regression process. The PCR method uses a data reduction approach to reduce the number of variables. PCR combines the analysis of the main components of the spectrum with multiple linear regression (MLR) in designing quantitative models for complex samples. PCR converts spectral data into latent variables without involving references [18, 19, 20].

3. Results and discussion

3.1. Patchouli Oil Spectrum
NIRS spectrum for oil samples are acquired at wavenumbers of 1000-2500 nm with the best settings on 32 scans, 2.0 cm$^{-1}$ resolution, and 4x optical gain. According to theory, oil NIRS spectrum is formed due to the absorption of NIRS light by oils resulting in molecules vibrating then forming the peaks and valleys of the spectrum. The NIR spectrum of oil can indicate the presence and organic content as a result of the interaction of electromagnetic wave radiation with patchouli oil. This interaction results in
bonding in materials such as C-H, O-H, N-H dan C-O to vibrate according to the magnitude of the given action. Vibration reactions that occur between these bonds are described in the form of spectral patterns whose magnitude varies depending on the sensitivity of that bond. Figure 1 shows the spectral features of Aceh patchouli oil.

Figure 1. Typical Patchouli Oil Spectrum

3.2. Classification Spectrum Validation Test Results
Spectrum validation test aims to find outlier data and discard it. Outlier data is a data that is different from other data and may interfere with the processing of information. The results of the spectrum validation test of 20 data can be seen in Figure 2.

Figure 2. Outlier Data Testing.

Based on Figure 2, it can be seen that all data are inside the ellipse. Since there is no data that are outside the ellipse line, it can be said that 20 data is valid and can be done next process.

3.3. Prediction Models of Patchouli Oil based on PA Content
There were two types of regression methods applied here: (i) Partial Least Square Regression (PLSR); and (ii) Principal Component Regression (PCR) method. Prediction model is built by regressing raw spectrum data as independent variable (X) and PA content (Y). The results of the prediction analysis for both are presented in Table 1.
Table 1. Prediction Performance for Patchouli Alcohol Content using PLSR and PCR approaches.

| Prediction model | Latent Variable | r     | $R^2$   | RMSEC  | RPD   |
|------------------|----------------|-------|---------|--------|-------|
| PLSR-raw         | 5              | 0.8981| 0.8065  | 4.9943 | 2.33  |
| PCR-raw          | 5              | 0.8662| 0.7503  | 5.6738 | 2.05  |

PCR: Principal Component Regression, PLSR: Partial Least Square Regression, r: Coefficient of Correlation, $R^2$: Coefficient of Determination, RMSEC: Root Mean Square Error Calibration, RPD: Residual Predictive Deviation.

It can be seen from Table 1 that NIRS seems feasible to be used as rapid and non-destructive method; even using un-enhanced spectrum, the PA content of patchouli oil can be predicted quite well using PLSR and PCR models with correlation coefficient (r) of 0.8981 and 0.8662, respectively. The coefficient of determination ($R^2$) based on the PLSR method was 0.8065, while a lower one ($R^2 = 0.7503$) was obtained by PCR one. According to literature [16], the value of $R^2$ between 0.66 – 0.81 indicates a prediction that is close to the quantitative prediction. The RMSEC value obtained was 4.9943 in PLSR but a slightly higher value was achieved through the PCR, namely 5.6738. That value can be said to be good because it is still smaller than the standard value of the actual data deviation of 11.68. Another option to assess the accuracy of the next calibration data is the Ratio Prediction to Deviation (RPD) value. According to literature [21, 22], RPD value between 2 – 3 indicates the model is classified as good performance model. In order to gain the accuracy and robustness of that prediction, both PLSR and PCR use 5 latent variables during calibration, as shown in Figure 3.

![Figure 3. Plot Data Calibration PA Content for PLSR and PCR on Raw Spectrum Data](image)

The PLS and PCR prediction models were then added with SNV pretreatment to increase the accuracy and robustness of the prediction models. The results of the prediction analysis for both are presented in Table 2.

Table 2. Prediction performance for patchouli alcohol using PLSR-SNV and PCR-SNV Approaches.

| Prediction Model | Latent Variable | r     | $R^2$   | RMSEC  | RPD   |
|------------------|----------------|-------|---------|--------|-------|
| PLSR-SNV         | 5              | 0.9408| 0.8852  | 3.8468 | 3.02  |
| PCR-SNV          | 5              | 0.9325| 0.8695  | 4.1011 | 2.84  |

PCR: Principal Component Regression, PLSR: Partial Least Square Regression, r: Coefficient of Correlation, $R^2$: Coefficient of Determination, RMSEC: Root Mean Square Error Calibration, RPD: Residual Predictive Deviation.

When the model was constructed using SNV pretreatment, prediction accuracy and robustness slightly increased and improved. According to Table 2, it can be seen that the correlation coefficient (r) of PLSR and PCR methods increases respectively at 0.9408 and 0.9325. A similar tendency was also occurred by the value of the coefficient of determination ($R^2$) presented by the PLSR ($R^2=0.8852$) and
PCR \( (R^2=0.8695)\). According to literature [16], \( R^2 \) value between 0.82 – 0.90 indicates a good prediction result because if the \( R^2 \) value is closer to zero, it is considered the better. Further, RPD index for PLSR and PCR also increased to 3.02 dan 2.84, respectively. The error value in the calibration (RMSEC) of the PLSR method was 3.8468 and PCR regression method was 4.1011. This can be also inferred that the resulted data was relatively good. According to literature [21], RPD value >3 indicates the model is categorized as very good model performance. There are still 5 latent variables used as shown in Figure 4.

![Figure 4](image)

**Figure 4**. Plot Data Calibration PA Content for PLSR and PCR on SNV Spectrum Data

NIR Spectrum acquiring process is very dependent on environmental conditions. Temperature and relative light factors affect the spectrum acquiring process. These factors can interfere with the accuracy and robustness of the prediction model. SNV pretreatment which is able to eliminate multiplicative interferences from scatter effects has been proven to be able to enhance prediction models and investigated the impact of this correction method on the prediction performance. In comparison, PLSR normally generated a better prediction results compared to PCR. PLSR method can simultaneously decompose the spectral data (X-variable) and the actual measured quality parameters data (Y-variable). It considers the relationship between the two in the decomposition, strengthen the corresponding calculation and ensuring the best correction model. The original work of PLSR is a linear method which assuming a linear relationship of the modelled quality parameters or concentrations as a function of the near infrared spectral data variations. Weak nonlinearities may be solved by increasing the number of factor or also known as latent variables (LVs) included in the PLSR. Whereas when compared to the PCR method, this method only converts spectral data into latent variables without involving actual measured quality parameters data.

4. Conclusions

The NIRS technology with PLSR and PCR methods provides a solution to solve the problem of PA content prediction in Aceh’s patchouli oil which is still an obstacle in the patchouli oil trade. SNV pretreatment is proven to improve prediction accuracy and robustness of the prediction model that built. The PLSR method combined with SNV pretreatment proved to be better than the PCR method combined with SNV pretreatment. The PLSR-SNV method succeeded in getting a prediction model that was categorized as very good model performance with a RPD value of 3.02 and a correlation coefficient value of 0.9408, a determination coefficient of 0.8852, an RMSEC of 3.8468 and 5 latent variables.

Acknowledgment

We would like to thank for all support to the division of research and community services (LPPM) Syiah Kuala University (USK), especially for research funding through the USK Superior Research (Penelitian Unggulan USK-PUU) research scheme 2021 (Number: 168/UN11/SPK/PNBP/2021).
References

[1] Swamy, M.K. and U. R. Sinniah. 2015. A Comprehensive Review on the Phytochemical Constituents and Pharmacological Activities of Pogostemon cablin Benth.: An Aromatic Medicinal Plant of Industrial Importance. J. Molecules. 20, 8521-8547.

[2] ARC Team. 2018. Penyusunan Master Plan, DED, UKL, dan UPL Sikim Nilam Kabupaten Aceh Jaya. Research report. Dinas Perindustrian dan Perdagangan Aceh dan LPPM Unsyiah.

[3] Waskitoaji, W. 2018. Kebijakan Ristekdikti dalam Sistem Inovasi Daerah. National Conference of Ristekdikti. Jatinangor, November 21 2018.

[4] Muhammad, S., E. Sufriadi, dan Ernawati. 2018. Penyusunan Masterplan Pengembangan Sentra Industri Kecil dan Menengah (SIKIM) Nilam Aceh Jaya. Community Service Report. Unsyiah.

[5] Lubis, Z. A. 2019. Kondisi Ekonomi Aceh dan Potensi Pengembangan Nilam. Forum Bisnis Klaster Inovasi Nilam Conference. Banda Aceh, 30 September 2019.

[6] Idris, A., M. Ramajura dan I. Said. 2014. Analisis Kualitas Minyak Nilam Produksi Kabupaten Buol. J. Akad. Kim. 3(2), 79-85.

[7] Cen, H dan Y. He. 2007. Theory and Application of Near Infrared Reflectance Spectroscopy in Determination of Food Quality. J. Trends in Food Sci & Technol. 18:72-83.

[8] Sundrajan, S. and N. H. Abdurahman. 2019. Chemical Compound Characterizations of Patchouli Leaf Extract via GC-MS, LC-QTOF-MS, FTIR, and 1H NMR. Inter J. of Engineering Research & Tech. 8(6), 1054-1059.

[9] Zulfahrizal, A. A. Munawar, H. Meilina. 2019. Fast Quantitative Prediction of Patchouli Alcohol Content Using Near Infrared Reflectance Spectroscopy. 2nd International Conference of Essential Oils. Banda Aceh, 29-30 Oktober 2019.

[10] Idris, A., M. Ramajura dan I. Said. 2014. Analisis Kualitas Minyak Nilam Produksi Kabupaten Buol. J. Akad. Kim. 3(2), 79-85.

[11] Fahmi, Z., Mudasir dan A. Rohman. 2020. Attenuated Total Reflectance-FTIR Spectra Combined with Multivariate Calibration and Discrimination Analysis for Analysis of Patchouli Oil adulteration. Indonesian J. Chem. 20(1), 1-8.

[12] Zulfahrizal, S. Muhammad, A. A. Munawar, Mahlinda. 2020. Near Infrared Technology And Multivariate Analysis Approach For A Rapid Authentication Of Patchouli Oil. Int J of Scientific & Tech Research. 9(8), 145-149.

[13] Zulfahrizal, S. Muhammad, A. A. Munawar, Mahlinda. 2020. Rapid Detection of Patchouli Oil Adulterations by Near Infrared Spectroscopy. 2nd International Conference on Agricultural Technology, Engineering, and Environmental Sciences. Banda Aceh, 21-22 September 2020.

[14] Zulfahrizal, H. Meilina, A. A. Munawar. 2017. Rancang Bangun dan Pengujian Alat Sensor Portabel Berbasis NIR Spectroscopy untuk Prediksi Cepat Kualitas Biji Kakao Utuh. Postgraduate National. Banda Aceh, 12 April 2017.

[15] Mouazen, A., Maleki, M., De Baerdemaeker, J., Ramon, H. (2003). On-line measurement of some selected soil properties using a VIS-NIR sensor. Soil Tillage Res. 93. 13–27.

[16] Zulfahrizal. 2014. Pengembangan Metode Pengukuran Nondestruktif untuk Menentukan Mutu dan Fermentasi Biji Kakao Utuh Menggunakan NIR Spectroscopy. Thesis PhD. Institut Pertanian Bogor.

[17] Chen, J and X. Z. Wang. 2001. A New Approach to Near-infrared Spectral Data Analysis using Independent Component Analysis. J.Chem 113 : 1272-1277.

[18] Zulfahrizal, H. Meilina, A. A. Munawar. 2016. Estimasi Kandungan Lemak Pada Biji Kakao Utuh Secara Cepat dan Non-Destruktif dengan Menggunakan Teknologi NIRS. J. Otomasi Kontrol dan Instrumentasi. 8(1), 17-23.
[20] Hayati, R., Z. Zulfahrizal and A. A. Munawar. 2021. Robust prediction performance of inner quality attributes in intact cocoa beans using near infrared spectroscopy and multivariate analysis. J. Heliyon 7(2021) e06286.

[21] Nicolaï, B. M., K. Beullens, E. Bobelyn, A. Peirs, W. Saeys, K. I. Theron, dan J. Lammertyn. 2007. Nondestructive measurement of fruit and vegetable quality by means of NIR spectroscopy: A review. Postharvest Biology and Tech. 46(2), 99–118.

[22] Kusumiyati, Munawar A A and Suhandy D 2021 Fast, simultaneous and contactless assessment of intact mango fruit by means of near infrared spectroscopy AIMS Agric. Food 6 172–84