Robust fraudulence detection of patchouli oil plant using near infrared spectroscopy

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Abstract. This study aimed to apply the near infrared reflectance spectroscopy (NIRS) for a robust and fast detection method for fraudulence in patchouli oil plant. Pure patchouli oil sample and adulterated patchouli oil with ethanol were used as samples in this work. Spectral data in form of transmittance were acquired in wavenumbers range from 400 to 4000 cm$^{-1}$. A total of 60 patchouli oil were adulterated and mixed using six difference concentration of ethanol while 10 remaining patchouli oil samples were pure without mixed with other substances. Classification models of pure and adulterated patchouli oil samples were established using principal component analysis followed by cross validation approach. The results showed that the models can distinguish between pure and mixed patchouli oil with 100% accuracy with two principal components (PCs) of the PCA. Based on obtained results, it may conclude that NIRS approach can be used to determine and classify patchouli oil samples based on their purity and fraudulence with ethanol.

1. Introduction
Patchouli oil is an oil that is widely used as a fixative in perfumes. This function makes the demand for patchouli oil from Indonesia quite significant. Indonesia is the world's main producer of patchouli oil with a market share of 90%, the rest is supplied by China, Brazil and several other countries [1], [2]. Patchouli oil itself comes from tropical Southeast Asia, especially Indonesia and the Philippines. Patchouli oil contains patchouli alcohol which makes it unique from other essential oils [3].

The characteristic that is very important in oil production, including patchouli oil, is the aroma of patchouli alcohol (PA), because it is an indicator of the quality level of the original aroma and whether or not the patchouli oil is good. PA is the main constituent component that determines the quality of patchouli oil with levels not less than 30%. The PA level of patchouli oil has a significant effect on the quality of the aroma produced [4].

Product counterfeiting is a very interesting issue, both for food products and essential oils, especially patchouli oil. For consumers or producers, counterfeiting itself has advantages and disadvantages. Product counterfeiting usually mixes low value products with high value products. Patchouli oil which is very expensive is usually adulterated with palm oil or other substances. Patchouli oil refining that is carried out by the community still uses simple technology, corrosive tools and low efficiency. This affects the quality of the patchouli oil produced and the yield. The low efficiency and yields are
significant when converted into revenue received by both the refiner and the state. The loss of essential oil during the refining process can occur at several stages, including the pre-treatment stage, the refining process, and the separation or separation process [5]. Observations made on patchouli oil distillation show that the water in the separation process is cloudy and it is likely that the refined oil has not been separated completely, thus reducing the yield of patchouli oil. Near infrared spectroscopy (NIRS) is one of the most promising approach used to determine several quality parameters simultaneously in many agricultural products. In many current applications, the NIRS method is widely employed especially in sorting and grading process [6]. Numerous studies have been carried out regarding with the application of NIRS as a rapid and non-destructive method in agriculture and environmental studies [7]–[12]. This study aimed to apply the near infrared reflectance spectroscopy (NIRS) for a robust and fast detection method for fraudulence in patchouli oil plant. Pure patchouli oil sample and adulterated patchouli oil with ethanol were used as samples in this work.

2. Material and Methods
A total of 90 samples of pure and adulterated patchouli oils were used in this study. Spectral data in form of transmittance were acquired in wavenumbers range from 400 to 4000 cm$^{-1}$ for all respective samples. In addition, 60 patchouli oil were adulterated and mixed using six difference concentration of ethanol while 10 remaining patchouli oil samples were pure without mixed with other substances. Classification models of pure and adulterated patchouli oil samples were established using principal component analysis followed by cross validation approach [13], [14]. Moreover, optimum and relevant wavenumbers for classification was determined by looking the loading plot derived from the PCA results. The highest peak and lowest valleys of the spectrum in the loading plot were marked as optimum and relevant wavenumbers.

3. Result and discussion
Transmittance spectra feature of pure pathcouli oil and adulterated with ethanol is presented in Figure 1. It can be seen that in certain wavenumbers, especially in the range form 2925 to 3514 cm$^{-1}$, the different between them is obvious. This probably due to the patchouli alcohol content that are changes due to the additional substances.

![Figure 1. Transmittance spectra feature of two pure and adulterated patchouli oil.](image-url)
Moreover, the spectra features seem to contain a lot of noises beginning at 650 cm\(^{-1}\). These noises are due to the transmittance occurred on other materials in increasing the frequencies. Therefore, for a better classification performances, we cut off the wavenumbers until 650 cm\(^{-1}\) respectively. Patchouli oil in patchouli plants is found in the roots, stems, twigs and leaves of the plant. Generally, the essential oil content in the roots, stems and twigs of patchouli is smaller (0.4-0.5%) than the essential oil content in the leaves (2.5-5.0%). We expected that these segmented wavenumbers could increase the prediction accuracy in terms of data classifications. The segmented spectrum from 650 to 4000 cm\(^{-1}\) is presented in Figure 2.

![Figure 2. Transmittance spectra in segmented wavenumbers of two pure and adulterated patchouli oil.](image)

The Patchouli (Pogostemon cablin Benth) is a type of essential oil-producing plant, known as patchouli oil. Patchouli belongs to the Labiatae tribe, the Lamiales in the Angiosperms class. Types of patchouli that have been known in Indonesia include Pogostemon cablin Benth. The classification result of pure and adulterated patchouli oil is shown in Figure 3.

![Figure 3. Classification based on PCA results of patchouli oil.](image)
Patchouli plant (*pogostemon cablin* benth) is one of the important essential oil producing plants, known as Patchouli Oil. This plant contains the main component of PA, which is a compound of the *sesquiterpen* group with the molecular formula C15H26O. The high PA content in patchouli oil means that the better the quality of the oil. Patchouli alcohol functions as a binder for fragrances so that the fragrance lasts longer. This plant has long been used in general in traditional Asian medicines, especially China, India, and Arabia, which is efficacious as an aprodisiac (strong medicine), anti-stress, and anti-septic, to relieve headaches and fever. While the oil is used as aromatherapy, perfume, to treat skin by accelerating skin regeneration, removing eczema and acne scars and insects. The influence plot derived from Hotelling T index and residuals is presented in Figure 4.

![Figure 4](image-url)

**Figure 4.** Influence plot derived from the PCA analysis

Patchouli oil contains patchouli alcohol which is the main constituent and is used as an indicator to determine the quality of patchouli oil, patchouli oil content reaches 50-60%. Patchouli alcohol has a tricyclic tertiary alcohol sesquiterpen compound, insoluble in water, soluble in alcohol, 11 ether or other organic solvents, has a boiling point of 280.37 oC and the crystals formed have a melting point of 56°C. Patchouli alcohol is the main constituent component that determines the quality of patchouli oil with levels not less than 30%.

Patchouli oil itself has a quality that is determined by several factors, both concerning cultivation and post-harvest. The determination of the quality standard for the results has been adjusted to the national quality standard, namely SNI number: 06-2385-2006. Increasing and developing the role of quality standardization assurance of results in the marketing of plantation production in the international community, the application of quality standardization of results, especially smallholder plantations, is increasingly required to implement ISO 9000, ISO 14000, HACCP (Hazard Analysis and Critical Control Points) and SPS (Sanitary and Phytosanitary Measure) quality standards. and Phytosanitary Measure so that they are able to compete in the international market.

4. Conclusion
This presented study aimed to apply the near infrared reflectance spectroscopy (NIRS) for a robust and fast detection method for fraudulence in patchouli oil plant. Classification models of pure and adulterated patchouli oil samples were established using principal component analysis followed by cross validation approach. Based on obtained results, it may conclude that NIRS approach can be used to determine and classify patchouli oil samples based on their purity and fraudulence with ethanol region.
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