Fourier Transformed Infrared (FTIR) spectroscopy analysis of patchouli essential oils based on different geographical area in Aceh

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Abstract. Studies on the quality difference between oils in various provinces have been conducted with varied results, especially between Acehnese Patchouli and Javanese Patchouli. However, studies on quality differences of Acehnese Patchouli based on geographic differences have never been carried out, thus, still leaving a big mystery in determining whether geographical differences such as coordinates and height from sea level produce different quality. The purpose of this study was to determine the effect of geographic location (coordinates and height of water MASL) of the patchouli cultivations on oil quality by conducting Principal Component Analysis (PCA) on the FTIR spectrum of patchouli oil from 3 different districts, namely South Aceh, Aceh Tamiang and South-West Aceh. The results indicate a water content difference as it is close to the O-H group wave number, which usually indicates the presence of Patchouli alcohol. The PCA analysis results show that there is a very significant difference between patchouli oil from South Aceh and Aceh Tamiang and South-West Aceh, caused by the height and patchouli variety difference. The PCA method validation is also quite reliable, which is proven by an explained variance plot.

1. Introduction

Patchouli plants have been known for thousands of years in China and India. Patchouli oil produced from the distillation of the patchouli plant has been used for hundreds of years in Traditional Chinese Medicine (TCM). Botanically, the two known species are Pogostemon cablin and Pogostemon heynanus [1]. Past studies on these two patchouli species have produced almost the same main chemical components but have different compositions of each compound [2]. PogostemonHeynanus has a lower patchouli alcohol content compared to Pogostemoncaablin but has a higher alphacaryophyllene content [3].
Studies on the chemical components formed between these two species have been widely carried out. Aceh is one of the provinces in Indonesia famous for Patchouli since the colonialism era in 1800[4]. The Dutch trade alliance has been trading patchouli leaves from Aceh to foreign countries ever since. Aceh is even known as a patchouli oil-producing area with excellent quality, as indicated with one of the main and most important contents of the oil, i.e., patchouli alcohol, which was found to have the highest content in Aceh [5].

For hundreds of years, the Patchouli planted in Aceh was the Pogostemon cablin Benth species. This species has three varieties that are cultivated by farmers, namely Sidikalang, Lhokseumawe, and the Tapak Tuan varieties [2]. Past research has identified the differences between these three varieties, both in terms of yield and from aspects of chemical composition. In general, the chemical content of patchouli oil derived from Pogostemon cablin Benth consists of sesquiterpenes, phenolic compounds, and a small portion of alkaloids, as shown in Table 1 below.

Table 1. Common chemical components found in patchouli oil.

| No | Constituents                  | Concentration range (%) | Reference |
|----|-------------------------------|-------------------------|-----------|
| 1  | α-Pinene                      | 0.01-0.3                | [6]       |
| 2  | β-Pinene                      | 0.02-1                  | [7]       |
| 3  | Limonene                      | 0.01-0.3                |           |
| 4  | δ-Elemene                     | 0.01-1.9                |           |
| 5  | β-Pachoulene                  | 0.03-12                 | [8]       |
| 6  | β-Elemene                     | 0.18-1.9                |           |
| 7  | Cycloseychellene              | 0.02-0.8                |           |
| 8  | (E)-β-Caryophyllene           | 0.75-6.8                | [9,10]    |
| 9  | α-Guaiene                     | 2.9-23                  | [11,12]   |
| 10 | Seychellene                   | 2.3-13                  | [8,13]    |
| 11 | α-Humulene                    | 0.05-2                  |           |
| 12 | α-Patchoulene                 | 1.2-13                  | [14,15]   |
| 13 | Germacrene D                  | 0.0-0.2                 | [1,2,16]  |
| 14 | Aciphyllene                   | 0.7-4.2                 | [17]      |
| 15 | α-Bulnesene                   | 2.9-23                  | [13,15]   |
| 16 | Norpatchoulenol               | 0.11-4.0                | [12,18]   |
| 17 | Caryophyllene oxide           | 0.0-4.6                 | [19,20]   |
| 18 | Pogostol                      | 0.2-6.2                 | [13,20]   |
| 19 | Patchoulol                    | 11-72                   | [11,13,14,18]|
| 20 | Pogostone                     |                         | [10,12]   |

Aceh patchouli is known to have better quality than that of Java, Sulawesi, and other regions. Meanwhile, Aceh also has a variety of patchouli oil cultivation and refining locations under different conditions, such as rainfall and height from sea level.

Studies on the chemical composition of Aceh patchouli based on geographic differences have never been carried out. Thus it is crucial to see whether geographical differences such as coordinates and height from sea level give different qualities. Several instrumental methods have been widely used to identify the chemical composition on organic substances, such as Uv-Vis [21–23], laser [24,25], Mass Spectrometry [26–29], FTIR [30,31], and even image processing [32]. Functional group analysis using Fourier Transform Infrared Spectroscopy (FTIR) is a promising analysis technique to authenticate essential oils because it uses a fingerprint analysis approach. Essential oil fingerprint analysis was used for a qualitative approach, including authenticating plant species and assessing their quality [33]. One indicator in this study was to see the difference in the FTIR spectrum of patchouli oil from different geographic locations. In general, the main reference to identify differences in functional groups of FTIR absorption was based on some peaks seen in particular wavenumber with a specific
intensity value. However, the complex spectra produced by FTIR analysis required the statistical method which can solve the complex data [34–37]. Principle Component Analysis (PCA) is the fit method for this purpose by classifying the data based on the similarities or differences [38,39]. This reference is expected to identify differences in chemical composition based on geographic differences in Patchouli oil [40].

2. Materials and methods
2.1. Materials and samples
This study used patchouli oil samples of *Pogostemon cablin* Benth species taken in 3 districts with varying geographic locations based on differences in coordinates and height from sea level. The samples came from the Regency of South Aceh, Aceh Tamiang, and South-West Aceh, with five sample points that were taken for each district. The distribution of sampling points in each district is shown in Table 2.

| Regency       | Coordinate     | Height (MASL) |
|---------------|----------------|---------------|
| South Aceh    |                |               |
| Point 1       | 3.150787, 97.387019 | 32.7         |
| Point 2       | 3.246224, 97.298007  | 363          |
| Point 3       | 3.105984, 97.403731  | 241          |
| Point 4       | 3.057648, 97.328140  | 25.8         |
| Point 5       | 3.216805, 97.381108  | 39.9         |
| South-West Aceh|                |               |
| Point 1       | 3.955137, 96.801492  | 15.6         |
| Point 2       | 3.756932, 96.779986   | 9.0          |
| Point 3       | 3.843926, 96.760195   | 18.9         |
| Point 4       | 3.792979, 96.637504   | 23.1         |
| Point 5       | 3.874802, 96.610691   | 84.6         |
| Aceh Tamiang  |                |               |
| Point 1       | 4.325478, 97.852359   | 66.9         |
| Point 2       | 4.329639, 97.831961   | 69.6         |
| Point 3       | 4.331321, 97.953951   | 91.2         |
| Point 4       | 4.290266, 97.977026   | 66.6         |
| Point 5       | 4.337483, 97.887003   | 44.1         |

2.2. Measurement by FTIR and Principal Component Analysis (PCA)
The analytical equipment used was FTIR Shimadzu Model IR Prestige 21, 2012. The analysis was carried out at the Environmental Laboratory of the Chemical Engineering Department, Syiah Kuala University. The analysis was performed over a wavenumber range of 4,000-500 cm\(^{-1}\). The measurement results were tabulated with Microsoft Excel version 365, and the FTIR spectrum for wavenumber (cm\(^{-1}\)) versus transmittance was plotted. Principal component analysis (PCA) was performed using Unscrambler software version 10.4. The output obtained from the PCA analysis results is the Score Plot and Loading Plot, which can be used to see the effect of several variables on the chemical differences of patchouli oil from three different locations.

3. Results and discussion
3.1. Functional group identification using FTIR
Fourier transformed infrared spectroscopy is one of the most widely used techniques in the identification of functional groups in a mixture of chemical compounds. Figures 1a to 1c show the presence of an infrared spectrum and certain absorption bands observed in Patchouli Oil between 4000-500 cm. In general, 20-30 chemical components are often found in patchouli oil, although past
studies show that the number of chemical components in patchouli oil can reach more than 50 compounds [16]. All of the chemical compounds in Patchouli Oil have various compound groups such as Sesquiterpene hydrocarbons (SQHCs), Aciphyllene, α-Copaene, Cycloseychellene, γ-Patchoulenene, η-Selinene, Oxygenated sesquiterpenes, Norpatchoulenol, Nortetracyclopatchoulol, Pogostol, Selinane SQHCs, Sesquiterpene ketones, Pogostone, Eugenol, benzaldehyde and cinnamic aldehyde [43,44]. These various groups of the compounds produce tens of chemical components whose existence varies depending on the location of cultivation [43,44]. However, generally, the types of bonds that produce molecular vibrations in patchouli oil occur in the form of stretching OH at 3505 cm⁻¹, which comes from the alcohol group compound and displays an abundance of Patchouli alcohol (the essential component used in the perfume industry). The spectrum also showed vibratory stretching at 1635 cm⁻¹, confirming the presence of C = O carbonyl aldehyde. This proves that patchouli oil is rich in aldehyde compounds [45].

![Figure 1. FTIR spectrum for patchouli oil originating from South Aceh, South-West Aceh, and Aceh Tamiang Regency: (A) combined 15 points spectrum from three regencies; and (B) The spectrum of mean transmittance values for each regency. TS = sample point; AS = South of Aceh; ABD = Southwest Aceh; AT = Aceh Tamiang.](image)

A peak at 1445 cm⁻¹ indicates a stretching of C-H bonds in the alkane and a C = C stretching of the aromatic ring [46], and at the peak of 1373 cm⁻¹ is characteristic of the O-H bond of carboxylic acids [47]. Of the three spectrums observed in Figure 1, there is a band widening in the spectrum of patchouli oil originating from South-West Aceh, especially at 3500-3040 cm⁻¹. This symptom indicates an unusual abundance of H₂O because it is close to the O-H group wave number, which usually provides information on the presence of Patchouli alcohol [48]. When viewed visually, of the five oil samples from South-West Aceh Regency, three of them look cloudy and dark in color, which indicates that the patchouli oil contains impurities. However, this assumption still needs to be proven by the Principal Component Analysis (PCA) analysis results.

### 3.2. Principal Component Analysis (PCA)

PCA analysis of a spectrum of 15 samples from three regencies with different coordinates and height (MASL) is shown in Figure 2. The analysis results show that there is a qualitatively significant difference between patchouli oil in South-West Aceh Regency and Aceh Tamiang and South Aceh Regency. The principal component analysis also shows that three PCs represent 96% of the variance of the sample.
Figure 2. PCA analysis results of patchouli oil FTIR spectrum originating from 3 districts in Aceh, namely South Aceh, Aceh Tamiang, and South-West Aceh, (A) Score plot PC1 vs PC2; and (B) 3D score plot of PC1, PC2, and PC3.

PC1-PC3 respectively gave variance values of 80, 14, and 2%. The data are clustered based on the patchouli oil regency origin. Although the number of samples is still relatively small, there is a good separation between the sample groups and the PC1 axis. Findings show a closer similarity between patchouli oil in South Aceh and Aceh Tamiang, and it looks significantly different from patchouli oil from South-West Aceh. It is suspected that the height of the cultivation location affects the similarity of patchouli oil properties, as indicated by the average height of the sample locations, namely: South Aceh has an average height of 140.48; South-West Aceh with 30.24; and Aceh Tamiang with 67.68 MASL. It appears that the height of the Aceh Strait is closer to Aceh Tamiang, although geographically, it is closer to South-West Aceh. Another assumption is the factor of differences in planted patchouli oil varieties. South-West Aceh may plant different varieties of Patchouli from South Aceh and Tamiang. However, these findings need to be tested further with other chemometric methods such as Discriminant Analysis [2,33].

The results of the loading plot (selected from PC-2) shown in Figure 3a show that in the range of 3600-2600 cm\(^{-1}\), there is a widening of the band, which indicates a difference in the water content of the sample3[49]. It also appears that there is much information that needs to be explored in the range between 1600-650 cm\(^{-1}\). The analysis's repetition is an important consideration when analyzing, by carrying out a specific analysis only in that range to obtain a better band.

Figure 3. Loading plot of PCA analysis results (a) and Explained Variance (b) of the Aceh patchouli oil. The curve explained variance shown in Figure 3a provides information that the PCA model used in this study is classified as robust, indicated by the red curve (validation), which is always in the same direction as the blue curve.
4. Conclusion
There are indications of water abundance in an unusual amount because it is close to the O-H group's wavenumber, which usually provides information on the presence of the Patchouli alcohol compound. The PCA analysis results show that there is a significant difference between patchouli oil from South Aceh Selatan and Aceh Tamiang and South-West Aceh, due to the difference in height or differences in the varieties of Patchouli. The loading plot strengthens the suspicion of contamination by water. The PCA method validation is also quite reliable, which is shown by the explained variance plot.

5. References
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