Comparative Analysis of Chemical Components of Purified Essential Oil from Nilam Plants using Gas Chromatography

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ABSTRACT

This study aimed to determine the chemical components of the patchouli oil. Patchouli oil is one of the export commodities that have high economic value for Indonesia. In general, patchouli oil obtained from the hydrodistillation of patchouli leaves. Most industries are still using patchouli oil refiners made by ferrous metal. The rust will dissolve in patchouli oil obtained and led to the resulting of dark oil and patchouli aroma becomes lower. The main purpose of this research is to improve the quality of patchouli oil by the purification process technologies after oil refining process. In this research the purification of the impure and crude oil can be carried out using adsorption process with bentonite. Purification results with UV-VIS spectrophotometer showed that the activation energy at a wavelength of 510 nm-550 nm with 3.9 x 10\textsuperscript{-19} Joules. GC (Gas Chromatography) analysis showed that there are 13 components from patchouli oil, the 6 dominant peaks were compounds of patchoul alcohol (29.64%), delta-guanyne (23.26%), alpha-guanyne (21.9%), alpha-patchouline (4.24%), pogostol (4.15%), palustrol (4.00%), beta-pinene (3.9%). Based on the physical properties, the main constituent component content, and the Fe\textsuperscript{2+} content, refined patchouli oil meets the requirements of the Indonesian National Standards.

Keywords: GC, patchouli oil, oil refining.

INTRODUCTION

Patchouli oil is one of the export commodities that have high economic value for Indonesia. Indonesia is the largest country that supplied patchouli oil in the world market, and nearly 70% of total world oil demand patchouli from Indonesia. China is the other country where produce patchouli [1]. Further types of varieties patchouli plants is Pogostemon cablin benth, which contain patchoulol and pogostol as a principal component, actually from Philippines who then evolved into Malaysia and Indonesia [2,20]. It can produce essential oil which important for perfume industry, used to afford a base and a lasting character to a fragrance [16,17,18].

One of the challenge was faced by the industry is the quality of patchouli oil in Indonesia, because Indonesian patchouli oil often blended with vegetable oil or other oils. This resulted from the Indonesian patchouli oil valued cheaper than patchouli oil produced from other countries such as India [3]. To prevent fabrication against patchouli oil purity required efforts from many parts. One effort that can be conducted is to improve the quality of patchouli oil. Bentonite is one alternative material that can be used as an adsorbent for the purification process of patchouli oil. The use of bentonite as adsorbent in patchouli oil can
absorb impurities in the patchouli oil. Bentonite use oil refining, will improve the quality of patchouli oil and can improve competitiveness with other countries [4]. The advantages of activation process are increasing the surface area of bentonite grains in order to capable of absorption for impurities, suspended matters, and sediment of patchouli oil, replacing some of cations such as calcium, sodium, and potassium with hydrogen ions in the material lattice structure, and removing the cations of aluminium, iron, magnesium from lattice structure, which create micro cavities in the material [14].

Distillation techniques conducted by craftsmen of patchouli oil in Kuta Village Pemalang District has not been properly, so patchouli oil is produced by the quality of the crude [5]. In addition, the handling of the results after the production has not been done optimally, such as the separation of oil after refining process, containers which are used, improper storage, so processes will be undesirable for oxidation, hydrolysis or polymerization. Typically the oil produced will look darker and blackish in color or slightly greenish due to contamination of the metals Fe and Cu, which will affect the physical properties of oil chemistry. Quality or essential oil is determined by the natural characteristics of oil [6].

To improve the low quality of oil contaminated dark colored metal ions, oil can be done but with adsorption methods using bentonite more effective. Purification of clove oil with absorbent bentonite as the best metal is better than charcoal purification zeolite and clove oil with activated charcoal 5% and 5% with bentonite. The result was oil purity can be reached 75.58% while the active charcoal only 2.7%. Physically oil color purified with bentonite brown while with activated charcoal remains black. As a result of contamination with chelation do in a way, but with adsorption methods using bentonite over clove oil refining. Bentonite as an absorber has better metal rather than charcoal active and zeolite [7]. The result with bentonite purity while with the oil can remain active charcoal black [8]. According to Netty et.al., bentonite which has activated with hydrochloric acid is more active to absorb the waste and other unnecessary substance [11]. The downward tendency of such bentonites could be overcome by the process of activations with acids (HCl, H₂SO₄, and HNO₃) to produce the bentonites with higher absorption ability [12]. Acid treatment was very important in order to increase the acidity of pillar material and thus its catalytic activity and present as mesopores which exhibited a significantly smaller pore volume than the other pillar bentonites [13,15].

EXPERIMENT
Materials and Instruments

Materials used were bentonite, patchouli oil, hydrochloric acid. Instruments used in this research were the means of glassware, analytical balance Metter Toledo, GCA Corp, furnace, magnetic stirrer, Atomic Absorption Spectrophotometer (AAS) Perkin Elmer Analyzer 100, Gas Chromatography (GC) Agilent 6820, and Spectronic 20 1420 Shimadzu.

Purification Procedure

Patchouli oil purification consists of two stages. The first stage was the activation of bentonite which has size of 200 mesh was added hydrochloric acid at a concentration of 0.5 M, then stirred for 24 hours, washed with hot water, raffinate (reduced extraction) dried at a certain temperature (100-150 °C) for 1 hour, crushed and sieved to 100 mesh size. Furthermore, the second phase was the oil refining process includes patchouli leaves. Patchouli crude oil prepared with a certain amount added to the activated bentonite adsorbent with a certain weight. The mixture was stirred for 2 hours using a stirrer and let stand until precipitation. Raffinate was separated from the filtrate, retrieved pure patchouli oil.
Assessment of Results Purification

Assessment results patchouli oil refining was based on the level of clarity after purification expressed in absorbing efficiency, the content of iron (Fe) after the purification process, and the content of the main component in patchouli oil after purification. Clarity measurements were carried out by means of UV-VIS spectrophotometer at specific wavelengths. Determination of iron (Fe) content was used atomic absorption spectrophotometer (AAS). Patchouli Alcohol concentration measurement was performed by gas chromatography (GC).

Analysis use Gas Chromatography (GC)

Samples of patchouli oil as much as 1 mL was injected in gas chromatography spectrophotometer mass (type Shimadzu GC-MS-QP2010) with operating conditions as follows: type column used HP-5ms, the column temperature set at 80 °C for 30 minutes and the speed of temperature rise an increase of 50 °C min up to a temperature of 200 °C and left for 25 minutes. The injector temperature detector temperature was conducted at 310 °C simultaneously. The carrier gas used is helium. It used FID (Flame Ionization Detector) as a detector.

RESULTS AND DISCUSSION

Patchouli oil obtained from the village of Kuta Village, Pemalang district during the observation was taken to Semarang which analyzed by UV-Vis Spectrophotometer, Atomic Absorption Spectrophotometer (AAS), Gas Chromatography (GC). Bentonite analyzed by Fourier Transform Infrared (FTIR) Spectroscopy. The results of spectroscopic analysis for bentonite presented Figure 1.

![Figure 1. The spectra of bentonite](image)

The main absorption peak-absorption on bentonite at wavenumber 3626.17 cm\(^{-1}\), 3448.72 cm\(^{-1}\), and 1635.64 cm\(^{-1}\). At the peak of 3626.17 cm\(^{-1}\) showed the stretching vibration of O-H which is located on a layered octahedral bound to Al [9] while decreasing states that the absorption peak at 3626.17 cm\(^{-1}\) showed the vibration H-O-H of water molecules on the structure of interlayer bentonite. In addition, the absorption peaks exhibited in 3448.72 cm\(^{-1}\) showed the vibration of O-H corresponding to the absorption peak at 1635.64 cm\(^{-1}\).
**Table 1.** The absorbance at 510 -550 nm of patchouli oil

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Patchouli oil before purification (A)</th>
<th>Patchouli oil after purification (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>510</td>
<td>0.654</td>
<td>0.740</td>
</tr>
<tr>
<td>520</td>
<td>0.510</td>
<td>0.575</td>
</tr>
<tr>
<td>530</td>
<td>0.410</td>
<td>0.466</td>
</tr>
<tr>
<td>540</td>
<td>0.329</td>
<td>0.385</td>
</tr>
<tr>
<td>550</td>
<td>0.277</td>
<td>0.333</td>
</tr>
</tbody>
</table>

Based on the calculations, the activation energy at a wavelength of 510 nm in 3.9 x 10^{-19} Joule which showed in Table 1 revealed that the maximum wavelength obtained at a wavelength of 510 nm. This table also shows that the greater the absorbance value indicates adsorption reactions that occurred more reactive.

**Content Analysis of Fe^{2+} with Atomic Absorption Spectrophotometer**

**Table 2.** Results of Fe^{2+} content test of patchouli oil by Atomic Absorption Spectrophotometer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe^{2+} contents (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before purification</td>
<td>24.960</td>
</tr>
<tr>
<td>After purification</td>
<td>23.001</td>
</tr>
</tbody>
</table>

Judging from the quality requirements standards in accordance with SNI’s qualification for patchouli oil, patchouli oil before and after purification is feasible quality. The Fe^{2+} content shown in Table 2, it have been under the maximum allowable limit (maximum of 25), but the iron content in the samples after the patchouli oil purification lower than patchouli oil samples before purification.

![Figure 2. Chromatogram patchouli oil before purification](chart.png)
Gas Chromatography (GC) Analysis of samples

Table 3. Patchouli Oil Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Patchouli oil before purification (%)</th>
<th>Patchouli oil after purification (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Patchouli alcohol</td>
<td>29.64</td>
<td>36.11</td>
</tr>
<tr>
<td>Delta-guanine</td>
<td>23.26</td>
<td>13.26</td>
</tr>
<tr>
<td>Apha-guanine</td>
<td>21.90</td>
<td>13.26</td>
</tr>
<tr>
<td>Alpha-patchouline</td>
<td>4.24</td>
<td>3.04</td>
</tr>
<tr>
<td>Pogostol</td>
<td>4.15</td>
<td>-</td>
</tr>
<tr>
<td>Palustrol</td>
<td>4.00</td>
<td>-</td>
</tr>
<tr>
<td>Beta-pinene</td>
<td>3.90</td>
<td>-</td>
</tr>
</tbody>
</table>

Analysis with Gas Chromatography (GC) revealed that main component of essential oil from nilam plant before purification is patchouli alcohol (29.64%) and after purification is patchouli alcohol (36.11%). This result much higher than result according to [11] which used activated bentonite H$_2$SO$_4$ and also exhibited higher result as compared to patchouli plant performance test which used extraction were carried out at temperature of 50 °C and pressure of 14 MPa by 32.23% [19].

![Figure 3. Chromatogram patchouli oil after purification](image)

![Figure 4. Comparison of patchouli oil before (left) and after (right) taking purification process.](image)
CONCLUSIONS
The study results patchouli oil purification by adsorption using bentonite it can be concluded that changes color from dark brown patchouli oil and discolored be light yellow. Fe metal ion removal percentage in patchouli oil with bentonite appropriate quality standards of patchouli oil SNI 06-2385-2006, and main component in patchouli oil is patchouli alcohol.

REFERENCES