Effect of Column Length in Batch Vacuum Fractionation on The Distribution of Major Components of Citronella Oil (Cymbopogon winterianus)

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Abstract. The aim of this work was to assess the performance of a vacuum fractionation column length for fractions composition of major components of citronella essential oil. This study used column lengths of 1 m and 2 m. The column packing raschig ring-shaped cylinder with height 1.8 cm and diameter 1.5 cm. The column is filled as much as 75% of the length of the column. Fractions from column top, middle and residue were analyzed by gas chromatography-mass spectrometry (GC/MS). The major components of citronella oil were citronellal (31.63%), citronellol (17.62%) and geraniol (10.92%). The use of 2 m packaging column length in batch vacuum fractionation distillation produced highest citronella content was (88.43%) on top fraction. The highest citronellol content were (24.48%) and (32.17%) in the middle fractions column for 1 m and 2 m column lengths respectively, while the highest geraniol was 58.26% and 37.76% in the middle and residue fraction for 2 m column length, respectively.

Keywords: vacuum fractionation, length column, major component, citronella oil.

1. Introduction
Citronella oil obtained from hydrodestylation of the leaves of the citronella plant (Cymbopogon nardus) is composed of several tens of compounds, but the characteristic of the aroma is determined by two or three compounds. In the last three years Java lemongrass oil (C. winterianus) is one type of potential Indonesian essential oil with production reaching 700 - 800 tons per year. According to Lorenzo, et al (2000), citronella oil, C. winterianus Jowitt, which originated in the South Brazil region contained 31 components with the main components, namely citronellal, citronellol and geraniol with levels of 36.10%, 9.90% and 19.90% respectively [1], whereas according to Eden, et al. (2018), these three components in citronella oil from Java contain 21.59%, 7.43% and 34.27% [2].

Citronella oil is known as the most effective source of mosquito repellent insects, including Aedes aegypti and cattle ticks mainly caused by citronelal and geraniol components [3]. Even geraniol has a number of biological properties including antimicrobial, antioxidant and anti-inflammatory activities with insignificant toxicity [4].
Pure components and fractions of the essential oils often exhibit considerably stronger pharmacological properties and hence have a far larger commercial value than the essential oil itself. The price of fragrant citronella oil is much lower than for a single component. Citronellal, citronellol and geraniol with a purity above 85% have almost ten times the price. Meanwhile, according to Warsito, et al (2017) [5] the distribution of major and minor components of each kaffir lime oil fraction can be obtained using fractional distillation. The antioxidant activities of essential oils from parts of C. hystrix and the fractions produced by essential oil fractional distillation exhibited a combination of hydrocarbon monoterpenes and oxygenated monoterpenes [6].

Some efforts focused on producing pure components or oil fractions include using specific reagents for certain components, such as salting reactions with NaOH bases for components of eugenol in clove oil [7], salting reaction with NaHSO₃ for citronellal components in kaffir lime oil [6] and the formation of a complex with CaCl₂ to separate the geraniol component in the rodinol fraction of lemongrass oil [8].

Another approach uses separation techniques with super critical extraction methods [9] and fractionation distillation [2]. The major problems that are often encountered in the oil fractionation process are instability, oxidation and transformation of some of the components at the distillation temperature under atmospheric pressure [10]. Strategies to improve the quality of the distillate can be controlled by manipulating reflux ratio, pressure and column length. Almeida, et al (2018) use conditions: 18 trays, column holdup of 5%, 10 kPa to produce an eucalyptol fraction 98.89% from Eucalyptus globulus and 98.53% citronellal fraction from E. citriodora [11], while Eden, et al. (2018) in batch vacuum fractional of C. winterianus lemongrass oil using a stainless steel SUS 316 L reactor with a pressure at -76 cmHg and reflux ratios 5:1 capable of producing citronellal purity of 95.10%.

Another challenge in the batch vacuum fractionation application was fractionation of two components with a pressure at -225 °C and a reflux ratio of 9:1, while Eden, et al. (2018) in batch vacuum fractional of C. winterianus lemongrass oil using a stainless steel SUS 316 L reactor with a pressure at -76 cmHg and reflux ratios 5:1 capable of producing citronellal purity of 95.10%.

This research to study the effect of the length of the fractionated column packing filled glass material to determine the quality of the composition chemistry distillate produced.

2. Materials and Method
2.1. Materials
Java citronella oil (C. winterianus) with index of refraction 1.457 and specific gravity of 0.902 g/mL obtained from Essential Oil’s Institute, Brawijaya University.

2.2. Methods

2.2.1. Batch Vacuum Fractionation Distillation from Citronella Oil. The vacuum fractionation distillation apparatus using Goel Scientific Glass Works LTD Merck with a 5 Liter spherical vessel. Fractionation column length of one meter (1 column) and two meters (2 columns) is filled with cylindrical raschig ring with a height of 1.8 cm and a diameter of 1.5 cm as much as 75% of the column length. The spherical vessel chamber is connected to a temperature controller to measure and regulate the temperature of the heater and a digital thermometer to regulate steam temperature, and a vacuum pump (TED PELLA, INC) which is connected with a vacuum gauge (vacuum) for vacuum processing and vacuum pressure measurement. The vacuum pressure used was 3 to 1 cmHg, with an operating time of 9 x 8 h for a sample of 2000 g of citronella oil. The process of storing fractionation results was carried out periodically approached based on the quantity displayed in the chromatogram which is balanced with the volume of each fraction. Fractions of the separation results were analyzed using GC-MS instrumentation.

2.2.2. Analysis of chemical composition of fractions and essential oil. The analysis of the fractions and essential oil produced was performed on Gas Chromatography-Mass Spectrophotometry (GC-MS) on Agilent 7890B (GC) and 5977B (MS). The column using a HP-5MS capillary column (30 m x 0.25 mm x 0.25 µm). Injector temperatures were set at 50 °C, the oven temperature was programmed from 50 – 260 °C and gradually increased at a rate of 5 °C/min. Helium was used as the carrier-gas
at 3.0 mL/min flowrate. Compound identification was based on GC peak areas by determining the percentage of fraction components, and MS spectra to determine m/z with using ionization energy of 70 eV and mass spectra with those of NBS75K library data of the GC–MS system.

3. Result and Discussion

3.1. The chemical composition of citronella oil
Based on the results of GC-MS analysis detected at least 25 compounds (Figure 1) which generally consisted of two groups were hydrocarbons monoterpene and oxygenated monoterpene. Three major components that determine the aroma of fragrant citronella oil are oxygenated monoterpene, which includes citronellal (31.63%), citronellol (17.62%) and geraniol (10.92%) and followed by components of citronellyl acetate esters (4.39%) and geranyl acetate (7.72%).

The peaks of the main components in a separate chromatogram from each other which indicate these components have significant boiling point differences. The main component with a smaller retention time has a lower boiling point, whereas the major component is always followed by a minor component which squeezes it. Minor components tend to be isomers of major components and their boiling points do not differ significantly, so they are quite difficult to be separated.

![Figure 1. Citronella oil chromatogram.](image)

3.2. Chemical composition of citronella oil fractions
Vacuum fractionation distillation as one way to overcome the process of separating a mixture of compounds, especially essential oils which contain many components that are not stable during the process, especially those that have high boiling points or are easily oxidized. In fractionation of essential oil liquids carried out in batch models, steam gradually discharges from the equilibrium of the liquid in the order of its boiling point, where the component having a lower boiling point evaporates first followed by a component with a higher boiling point. The vapor produced must be maintained in accordance with different groups of compounds and held in continuous column packaging. The pattern of the relationship between fractions and the volume of distillates in the use of each column is obtained as shown in Figure 2.

The temperature ranges in each fraction that occurs in the use of a longer column seems clearer, so that the difference in the amount of the volume of distillate produced differs significantly between the fraction of one and the other fraction.

The effectiveness of using a longer packaging column (2 m) is also evident from the results of the analysis of the composition of each fraction. The results of analysis by GC-MS, both top fraction, middle fraction and residue as shown in Tables 1, 2, and 3, respectively. The use of long column packaging (1 m), three main components of citronellal, citronellol and geraniol are scattered in each fraction, whereas in the use of column length (2 m) these components can be concentrated.
Figure 2. Relationship of fraction (temperature range) and volume of distillates for column length of 1 meter (1 m) and 2 meters (2 m).

Table 1. Top Fraction Chemical Composition

| No | Components               | SI | Column (1 m) | Column (2 m) |
|----|--------------------------|----|--------------|--------------|
| 1  | Limonene                 | 95 | 15.42        | 0.27         |
| 2  | Ocimene                  | 97 | 2.94         | 0.06         |
| 3  | Linalool                 | 98 | 15.80        | 0.51         |
| 4  | Citronellal              | 97 | 23.26        | 88.43        |
| 5  | Citronellol              | 98 | 11.96        | 3.90         |
| 6  | Geraniol                 | 97 | 11.96        | 3.99         |
| 7  | Citronellyl acetate      | 96 | 2.49         | -            |
| 8  | Geranyl acetate          | 97 | 2.01         | -            |
| 9  | Trans β-Caryophyllene    | 97 | 3.02         | -            |

Table 2. Middle Fraction Chemical Composition

| No | Components               | SI | Column (1 m) | Column (2 m) |
|----|--------------------------|----|--------------|--------------|
| 1  | Isopulegol               | 97 | 2.93         | -            |
| 2  | Citronellal              | 97 | 15.4         | -            |
| 3  | Citronellol              | 98 | 24.48        | 36.38        |
| 4  | Geraniol                 | 97 | 21.64        | 58.26        |
| 5  | Citronellyl Acetate      | 96 | 7.13         | -            |
| 6  | Ciclosivosativenes       | 95 | 1.27         | 5.36         |
| 7  | Geranyl Acetate          | 98 | 6.67         | -            |
| 8  | β-Boubornene             | 95 | 3.07         | -            |
| 9  | β-Caryopiilene           | 97 | 7.17         | -            |
| 10 | α-Bergamotene            | 96 | 1.38         | -            |
Table 3. Residue Chemical Composition

| No | Components            | SI  | Percentage(%) |       |       |
|----|-----------------------|-----|---------------|-------|-------|
|    |                       |     | Column (1 m)  | Column (2 m) |
| 1  | Citronella            | 97  | 1.99          | -     |
| 2  | Citronelol            | 97  | 9.82          | -     |
| 3  | Geraniol              | 96  | 20.72         | 37.76 |
| 4  | Citronellyl acetate   | 96  | 4.20          | -     |
| 5  | Guaianicole           | 92  | 1.60          | -     |
| 6  | Gerani acetate        | 97  | 13.71         | -     |
| 7  | Methyl eugenol        | 94  | 1.24          | -     |
| 8  | Trans-β-Caryopillene | 96  | 3.30          | -     |
| 9  | Germacrene            | 95  | 2.52          | 5.68  |
| 10 | Methyl trans-isoeugenol | 95  | 4.11          | -     |
| 11 | α-Murolene            | 96  | 4.97          | -     |
| 12 | γ-Cadinene            | 94  | 2.35          | 15.26 |
| 13 | Citronellyl n-butyrate| 96  | 8.06          | -     |
| 14 | Elemol                | 90  | 11.81         | 8.25  |
| 15 | α-Cadinol             | 87  | -             | 5.46  |
| 16 | α-Cedrene             | 91  | 1.07          | -     |
| 17 | γ-eudesmol            | 91  | 1.18          | -     |

The use of a 2 m packaging column length produced citronellal major component purity increased significantly from 31.63% (in citronella oil) to 88.43% (in the top fraction), while with 1 m column length still mixed 11 components and levels of citronellal (23.26%), citronellol (11.96%) and geraniol (11.96%) (Table 1). Likewise, the 2 m fractionation column length was not found in the citronellal major component, while the geraniol component major has the highest purity or increased from 10.92% to 58.26% and citronellol increased from 17.62% to 36.38%, in citronella oil and in middle fraction respectively (Table 2), while the use 1 m packaging column length, major components was still mixed with 10 components. Furthermore, according to Table 3, geraniol component in the residue only 37.76% followed by four other components which have higher boiling points, while the use of 1 m column length in still contains citronellal major components (1.99%) mixed with 16 other components.

4. Conclusion
In the batch vacuum fractionation distillation, the use of 2 m packaging columns length filled with glass was more effective rather than 1 m packaging columns length to improve the quality of the purity of the major components of citronellal oil. Citronellal as a major component, its purity increased significantly from 31.63% to 88.43% in the top fraction, geraniol increased from 10.92% to 58.26% and citronellol increased from 17.62% to 36.38%.

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