The effect of material amount in distillation tank to chemical composition of citronella oil (Cymbopogon nardus L. Rendle)

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Abstract. The need for essential oils such as citronella oil, has increased along with the development of modern industries such as perfume, cosmetics, food, aromatherapy, and medicine industries. In the recent year, the volume of essential oil export is decreased, this due to quality issues. The purpose of this study was to determine the chemical composition of citronella oil using GC-MS (Gas Chromatography-Mass Spectroscopy) method using different amount of material in the refining tank of distillation (A = 40 kg; B = 50 kg; C = 60 kg; D = 70 kg; and E = 80 kg). The results showed that the highest percentage of citronella oil was found in A method when compared to the other method. The oil resulted, contain three main components namely citronellal (41.97%), geraniol (18.89%), and citronellol (12.91%). This research concludes that the more the amount of raw material in the refining tank will decreases the percentage of three main components (citronellal, geraniol, and citronellol) of oil resulted.

1. Introduction

Citronella oil is a commodity that has strong competitiveness and a good market in foreign markets [1]. The demand for essential oils is increases each year along with the development of modern industries such as perfume, cosmetics, food, aromatherapy, and medicine industries [2]. However, the volume of essential oil exports in recent years has decreased. In 2012, the volume of essential oil exports reached 4,938.54 tons with a value of US $ 17,432.76 and in 2017 dropped to 111.40 tons with a value of US $ 5,777.18 [3].

In the Dutch colonial era, Indonesia was known as the largest producer of citronella, but nowadays its production is behind to China and Vietnam. Currently, the world citronella oil consumption reaches 2,000–2,500 tons per year. The demand for essential oils is quite large because the market demand is increase by 3–5% per year. In the other side Indonesia is only able to provide 700 tons for citronella oil per year [4].

Indonesian citronella oil on the world market is known as "Java Citronella Oil" [5]. This oil is belongs to essential oil types which obtained by distilling the leaves of Andropogon nardus de jong (Citronella) plant. This plant is easy to cultivate, does not require special treatment, able to improve soil structure and also could be use for critical land conservation. The essential compounds of citronella oil also known to have potential to be antibacterial [6]. One of area that currently developing Citronella plantation and produces its essential oil is Pasaman in West Sumatra Indonesia [7]. Regarding the price, citronella oil is ranged forin 150,000 to 360,000/kg IDR and its fluctuative.
Based on the field observations in Sub-District of Padang Sarai, Lubuksikaping District, commonly, the community conduct citronella distillation for 2 hours. This method able to produce an average yield of 0.7% and can be done 3 times a day, meanwhile a refining method for 4 to 5 hours only gets an additional yield for 0.14–0.15%. The results of Ermaya’s, et al [8], reported that the highest yield of citronella oil, 1.92%, was obtained from 3 days withering time and 4 hours distillation time. Farmers have habit to compacting material in the tank during distillation process. For a 200 liter distillation tank, farmers estimate that the tank can hold 60 to 70 kg of fresh leaf material. Farmers assume that the more amount of leaves in the tank, they will get more oil produced. Not many farmers know that the density and arrangement of material in the tank can affect the yield and oil quality, then the result is not optimal.

The yield of citronella oil can be improved by conditioning and pre-treating of raw materials such as withering. Withering before distillation affects the quality of citronella oil. Highest yield of citronella oil obtained from withering time 3 × 24 hours [8]. The quality of refined essential oils can be affected by preliminary treatment, processing, and post-extraction treatment. One factor that affects the quality of essential oils in the processing is the amount of material or density of the distillation tank. Based on the description above, the purpose of this study was to know the effect of amount of material inside the distillation tank, to the chemical components of resulted citronella oil.

2. Methodology
Five different amount of material (raw grass), as treatment, in the refining tank namely A = 40 kg; B = 50 kg; C = 60 kg; D = 70 kg; and E = 80 kg were applied in this study. The production of essential oil was carried out in the citronella plantation of Padang Sarai Sub-District, Lubuksikaping District, Pasaman Regency, and Laboratory of Agricultural Product Technology in Universitas Ekasakti. Sample testing for resulted oil was carried out at the DKI Jakarta Provincial Health Laboratory.

The traditional distillation device with capacity of 200 liters was employed in this study. The distillation tank able to hold approximately 60–70 kg of raw material. The distillation system consists of a boiler, cooler (condenser), and separator. Other necessary glassware such as measuring cup, dropper, test tube and etc also prepared in this study. Citronella oil appearance as the result of different treatment can be visually observe in Figure 1. The GC-MS instrument that used in this study has the following specifications: Agilent Technologies 7,890 Gas Chromatograph with AutoSampler and 5,975 Mass Selective Detector and Chemstation data system. Column: HP INNOWAX. Capillary Column Length (m) 30 × 0.25 (mm) ID × 0.25 (μm) Film Thickness. Carrier gas: Helium. Column mode: Constant Flow. Flow Column: 0.6 mL/minute. Injection volume: 1 μL.

![Figure 1. Distillation product of citronella oil](image-url)
conditions. This basis is used for identification. From the area of the curve peak area or the height of the curve peak, the component components can be determined quantitatively [9].

Right, before GC-MS equipment is employed, there is a calibration treatment with the following procedure: a row of the solution is made. After that, the solution is injected with the same volume into the injection site. The calibration line is drawn from the chromatogram, with the heavy substance on the horizontal axis, and the curve peak height or peak area of the curve on the vertical axis. Substance solutions are made as they appear in each monograph. From the chromatogram obtained with the same conditions as to how to obtain a calibration line, the area of the curve's peak area or the height of the curve's peak is measured. The amount of substance is calculated using a calibration line. In this way of working, all must be done in constant conditions. The instrument GC-MS can be observed in Figure 2.

3. Results and discussion
In this study, citronella oil from *Cymbopogon nardus* L. Rendle grass is extracted using hot steam method. The final process of steam distillation is condensation and separating liquid form which is a mixture of oil and water vapor. The difference in density between citronella oil and water makes it possible to separate them with the right instruments [10].

The identification of citronella oil components with five treatment then carried out by Gas Chromatography-Mass Spectroscopy (GC-MS) method. This method employed to identify the oil compounds, both on the component and mixture component [11]. This GC-MS method has the advantage of identifying molecular structure based on its molecular mass fragmentation [12]. In addition to identifying compounds, the GC-MS method also functions to separate components from a mixture, especially for essential oils [13]. Analysis using GC-MS showed that essential oils from citronella contained 11 organic compounds for treatment A and D; 12 organic compounds for treatment B and E; and 14 organic compounds for the treatment of C. Citronellal, geraniol, and citronellol are the three main compounds contained in five treatments and have percentage above 10%. Some of these components are classified as monoterpenoids, fatty acid esters, sesquiterpenoids, and allylbenzene. The quality of citronella oil is determined by the three main components mentioned above [14].

Citronellal (C10H16O) is a monoterpenoid which is reported as the main component of essential oils in various aromatic plant species. Citronellal is usually used in the perfume, cosmetics, and soap industries because of its distinctive aroma [15]. In this study, citronellal was the compound that had the highest percentage in all treatments.
Geraniol (C_{10}H_{18}O) is a commercially important terpenoid alcohol found in essential oils from several aromatic plants. This compound is one of the most important molecules in the aroma and taste industry. In addition to the scent of her perfume, geraniol is known to have insecticidal and repellent properties and is used as a natural pest control agent with low toxicity [16]. In this study, geraniol was the second-largest component of all treatments.

Citronellol (C_{10}H_{20}O) is one of the essential oil components of several medicinal plants used in traditional medicine as antihypertensive [17]. Several pharmacological properties such as antibacterial, antifungal, antispasmodic, and anticonvulsant activities have been described and are present in citronellol [18]. Citronellol is the third main component in all treatments.

The composition of chemical compounds contained in the citronella oil with treatment A (40 kg of raw material) was showed in Table 1. Citronellal, geraniol, and citronellol are three major components in the citronella oil on treatment A with the percentage succession: 41.97, 18.89, and 12.91%. Citronella oil that was available in the market contains the compounds of citronellal 32–42%, geraniol 10–12%, and citronellol 2–4% [1, 19]. Thus, citronella oil obtained by treatment A has a higher compound content than market citronella oil, in terms of geraniol and citronellol contents.

| No | Chemical components (%) | Treatment |
|----|-------------------------|----------|
|    |                         | A        | B        | C        | D        | E        |
| 1  | Citronellal             | 41.97    | 41.72    | 41.53    | 40.85    | 39.22    |
| 2  | Geraniol                | 18.89    | 18.81    | 18.34    | 18.29    | 17.97    |
| 3  | Citronellol             | 12.91    | 12.62    | 12.44    | 12.44    | 12.29    |
| 4  | Geranyl acetate         | 6.13     | 5.41     | 6.08     | 6.22     | 6.31     |
| 5  | Citronellyl butyrate    | 4.18     | 3.92     | -        | -        | 4.25     |
| 6  | 2,6-Octadiene, 2,6-dimethyl- | -     | -        | 4.15     | -        | -        |
| 7  | D-Limonene              | -        | 3.63     | 3.61     | 3.74     | 3.37     |
| 8  | Hedycaryol              | -        | -        | -        | -        | 3.09     |
| 9  | β-Cubene                | -        | -        | -        | 2.98     | -        |
| 10 | Elenol                  | -        | -        | -        | 2.31     | -        |
| 11 | Germacrene D            | 3.66     | 2.97     | 1.37     | -        | -        |
| 12 | Elemol                  | 2.27     | 2.33     | 2.3      | -        | -        |
| 13 | Germacrene              | -        | -        | 1.55     | -        | -        |
| 14 | Germacrene D-4-ol       | 1.45     | 1.59     | 1.44     | 1.5      | 1.68     |
| 15 | Eugenol                 | 1.15     | 1.17     | 1.17     | 1.21     | 1.19     |
| 16 | α-Cadinol               | 1.11     | 1.08     | 1.13     | 1.13     | 1.65     |
| 17 | Citral                  | -        | -        | -        | -        | 1.13     |
| 18 | (-)-β-Elemene           | 1.04     | 1.03     | 1.02     | 4.27     | 1.11     |

The composition of the chemical components contained in essential oils with treatment B (the amount of raw material 50 kg in the refining tank) can be observed in Table 1. Citronella oil obtained by treatment B contains citronellal, geraniol, and citronellol with a percentage of 41.72, 18.81, and 12.62%, respectively. When compared with citronella oil treatment A, the percentage of three compounds decreased in the citronella oil treatment B. The increased amount of raw materials from 40 kg (treatment A) to 50 kg (treatment B) resulting in the decrease of citronellal, geraniol and citronellol percentage on citronella oil.

In Table 1, it can be observed the chemical composition contained in the citronella oil treatment C. Three main compounds contained in the citronella oil is generated by the amount of the raw material of 60 kg in the distillation tank (treatment C) is citronellal (41.53%), geraniol (18.34%), and citronellol (12.44%). The increase in the raw material amount on treatment C also caused a decrease in the levels of those three compounds. Citronella oil with treatment C contains citral with a percentage of 1.17%. This compound was not detected in citronella oils with treatment A and B. Citral, or 3,7-dimethyl-2,6-octadienal or lemonal is a pair or mixture of terpenoids with the molecular formula C_{10}H_{16}O. Citral is
one of the most important natural flavoring compounds that has a strong lemon aroma, widely used as an additive in foods, drinks, and cosmetics with high consumer acceptance [20].

The entire chemical components that make up the essential oil from treatment D can be seen in Table 1. As with the previous treatment, essential oil treatment D has Citronellal (40.85%), geraniol (18.29%), and citronellol (12.44%) as three main components. The content of these three compounds also decreased when compared with the previous treatment (A, B, and C). The raw material amount in treatment D as much as 70 kg has fulfilled 7/10 refining tank capacity. Reducing the space in this distillation tank results in obstruction of the streamflow from the water heater. This will result in the process of extracting essential oils from raw materials of citronella leaves is not optimal.

All chemical compounds contained in essential oils from treatment E can be observed in Table 1. From the sample of citronella oil obtained from all treatments, treatment E (amount of raw material 80 kg in a refining tank) has the lowest content of citronellal, geraniol, and citronellol, namely: 39.22%; 17.97%, and 12.29%, respectively. In treatment E, the capacity of the refining tank (100 kg) leaves only 20 kg of space after the raw material is added. This causes the stream distribution coming from the furnace of the water heater is not optimal so that the process of extracting essential oils from raw materials is also inhibited. So, the amount of three main compounds contained in citronella oil from treatment E was the lowest when compared to the other four treatments.

Increasing the amount of raw material in the refining tank caused the degradation of the levels of three main compounds (citronellal, geraniol, and citronellol) contained in citronella oil. The highest percentage of citronellal, geraniol, and citronellol were found in treatment A, with 40 kg of raw material in the refining tank. The decrease in the percentage of these three components is due to the amount of hot steam that is in contact with the raw material that has decreased with the increasing amount of raw material in the refining tank. Therefore, citronella oil with treatment E which has the highest amount of raw material (80 kg), containing citronellal, geraniol, and citronellol with the lowest percentage when compared with other treatments. Besides, the amount of raw material also affects the distribution of steam in the refining tank. Increasing the raw material amount causes a decrease in the distribution of water vapor in the refining tank. It also caused a decrease in the percentage of citronellal, geraniol, and citronellol contained in citronella oil. The comparison of citronellal, geraniol, and citronellol levels from the five treatments tested can be observed in Table 2.

In the steam-water distillation system, the steam that is initially formed will condense first. This condition happens continuously until it reaches a temperature equal to the boiling point of water, to achieve a constant temperature requires a longer time for the material that much. The greater amount of material in the tank causes contact with steam reduced because the greater the distance traveled and the obstacles experienced by the penetration of steam. The increase of distance and friction experienced by steam will result in lower refining speed that causes the resulting oil to be reduced.

The quality standard of citronella oil for export quality can be analyzed according to physical criteria, namely based on color, specific gravity, refractive index, or chemically, based on total geranial, total citronellal of at least 35%. The results showed that the total citronellal of the five treatments exceeded export quality. Low levels of geraniol and citronellol are usually caused by poor citronella species, in addition to poor maintenance of plants, and age of plants that are too old.

| Chemical Components | A    | B    | C    | D    | E    |
|---------------------|------|------|------|------|------|
| Citronellal         | 41.97| 41.72| 41.53| 40.85| 39.22|
| Geraniol            | 18.89| 18.81| 18.34| 18.29| 17.97|
| Citronellol         | 12.91| 12.62| 12.44| 12.44| 12.29|
4. Conclusion
The citronella oil from treatment A, contained highest levels of citronellal, geraniol, and citronellol, this quality was met with export quality. Increasing amount of raw material in the refining tank causes the decrease of the percentage of three main components (citronellal, geraniol, and citronellol).

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