Comparison of the separation process of crude citronella oil using vacuum fractionation distillation on a pilot plant scale and laboratory scale

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Abstract. Crude citronella oil contains a mixture of components such as a group of hydrocarbon monoterpenes compounds, oxygenated monoterpenes, and sesquiterpenes. Therefore, it has low economic value and low functional value. A single component with high purity can be obtained through chemical and physical properties analysis. Based on the physical properties of the constituent components of citronella oil, the boiling points of each component are quite adjacent so that a single component can be separated by the fractionation distillation process. This study aims at determining the optimum condition (temperature, pressure, and reflux ratio) of a pilot plant scale fractionation with 8 meters of the column and the capacity of 200kg (raschig ring packing; temperature range 115-118°C and 118-121°C, reflux ratio 4:1 and 2:1) and comparing it to the laboratory scale (raschig ring packing; temperature range 115-118°C and 118-121°C, reflux ratio 2:1). Although the laboratory scale of fractionation distillation produced good quality rhodinol with 85% purity, the scale-up version of the pilot plant scale still cannot be occupied. For the citronellal fraction, both fractionation distillation process produced poor quality with only 50% purity. This occurred due to the different dimensions that lead to a higher pressure drop. A higher pressure drop will change the optimum temperature conditions.

1. Introduction
Crude citronella oil contains a mixture of components such as a group of hydrocarbon monoterpenes compounds, oxygenated monoterpenes, and sesquiterpenes that caused it has low economic value and low functional value [1]. According to international market standards, citronellol content and the total amount of alcohol must be higher than 35%. Mix citronellol and geraniol (commonly called as rhodinol), as well as geraniol and citronellol are used as an air freshener, tissue, soap, and cosmetics. Therefore, one of the efforts that can be made to increase the economic value of citronella oil is by increasing the levels of rhodinol contained in citronella oil [2].

A single component with high purity can be obtained through chemical and physical properties analysis. Based on the physical properties of the constituent components of citronella oil, the boiling points of each component are quite adjacent so that the fractionation distillation process can separate a
single component. Fractionation distillation is a physical separation process that uses the difference in the boiling points of the components in the mixture [3].

The laboratory-scale of a fractionated distillation of crude citronella oil in Institut Atsiri has been done [4]. Crude citronella oil is fractionated with 2 meters of the column and the capacity of 20kg (raschig ring packing; temperature range 115-118°C and 118-121°C, reflux ratio 2:1). The result of the fractions is pretty impressive. The optimum condition data from vacuum fractionation distillation on a laboratory scale is used for the pilot plant scale operation. The pilot plant scale fractionation uses 8 meters of the column and the capacity of 200kg (raschig ring packing; temperature range 3°C, reflux ratio 4:1 and 2:1). The fraction resulted from pilot plant scale vacuum fractionation distillation then is compared to the laboratory scale.

2. Materials and Methods
This research is conducted from August 2019 – March 2020 in Institut Atsiri, Universitas Brawijaya. The citronella oil is from Trenggalek Regency (Mahapengiri type). Before the fractionation process, the raw material must be examined of its composition using GC-MS in the Life Science Central Laboratory (Laboratorium Sentral Ilmu Hayati/LSIH), Universitas Brawijaya.

Both fractionation systems use the same process condition. The process condition is: pressure 30-40 mmHg, 3°C range of temperature (107-110 °C, 111-114 °C, 115-118 °C, 119-122 °C, 123-126 °C, 127-130 °C) and reflux ratio 2:1. The fractionation process is ended when the residue in the raw material tank is about 30±5% of the beginning. The fractionation process time was fluctuating, depending on the mass of the raw material. The temperature range was increased if no more distillate produced after 30 minutes. After the fractionation process, the product was examined again using GC-MS for chemical composition.

2.1. Laboratory scale operation of fractionation distillation
The laboratory-scale fractionation distillation diagram is illustrated in Figure 1. The laboratory-scale of column height is 2 meters with 1-inch Raschig ring random packing. The capacity of raw material tank is a maximum of 20 kg. For this research, the citronella oil used is 18kg. There is a screw valve in the three ways of equipment leading to the main condenser to adjust the reflux ratio. There are 3 condensers: the main condenser, the first vertical condenser functions to avoid excess oil entering the vacuum pump and the second condenser to cool down the distillate before ejection. The cooling process in the condenser is not monitored. However, the temperature in the inlet of the main condenser and the raw material tank is monitored well. The temperature controller is only used to control the heater. The pressure is also not controlled but monitored well. The pressure is adjusted manually through the vacuum pump.

2.2. Fractionation distillation pilot plant scale
The pilot plant scale fractionation distillation scheme is shown in Figure 2. The scaling-up process of this fractionation distillation is based on the raw material tank. The raw material tank for the pilot plant scale is 200kg and it filled up until 180kg of crude citronella oil. Although the maximum capacity of the raw material is 10 times bigger than the laboratory scale, the column height is not 10 times higher which is 20 meters. The column height is 8 meters. The designer team of the scale-up project thought about the economical aspect and the availability of the resources. The raw material tank is now equipped with a propeller to allow the oil to have more contact with the heat source. The heating process is used for oil heater. The oil in the oil heater source tank will be heated and the oil heater will be circulated in the jacket of the raw material tank. The pilot plant scale of column height is 8 meters with 1-inch Raschig ring random packing. There are 3 condensers: the first condenser in the half of the column to trap the heavy key component, the second condenser on the top of the column to trap the light key component and the last condenser is the smaller condenser below the first condenser to cool down the distillate. All the cooling process in the condenser including the temperature of the chiller is now monitored and controlled well. All the condition process is monitored using HMI monitoring.
system, so does the vacuum pump. All the control is automatic and it can be done using the HMI monitoring system. There are four distillate tanks: before citronellal component tank, citronellal component tank, trans tank and the rhodinol tank.

**Figure 1.** Schematic diagram of laboratory-scale fractionation distillation.

**Figure 2.** Fractionation distillation pilot plant scale diagram.
3. Results and Discussion

3.1. Chemical composition of crude citronella oil

Based on the analysis of the raw materials by using the GCMS, it is known that the retention time of each constituent component of citronella oil is quite close to each other. This shows the proximity of the boiling points of each component of the citronella oil. Apart from that, the retention time also shows the order of the boiling points of the constituent components of citronella oil, where the higher the retention times that the components have, the higher the boiling points as shown in Table 1.

Table 1. Composition of crude citronella oil.

| No | Fraction   | Compound          | Retention Time | Boiling Point (ºC) | % Content | % Total |
|----|------------|-------------------|----------------|--------------------|-----------|---------|
| 1  | Before     | Citronellal       | 5,971          | 176                | 7,23      | 18,21   |
| 2  | Citronella | Ocimene           | 6,205          | 177                | 4,08      | 18,21   |
| 3  |            | Octatriene        | 7,475          | 178                | 6,90      | 18,21   |
| 4  | Citronellal| Citronellol       | 7,927          | 208                | 27,42     | 27,42   |
| 5  |            | Citronellol       | 9,109          | 225                | 11,25     | 18,21   |
| 6  | Rhodinol   | Neral             | 9,342          | 225                | 0,62      | 43,55   |
| 7  |            | Geraniol          | 9,555          | 230                | 31,68     | 43,55   |
| 8  |            | Citral            | 9,781          | 225                | 1,21      | 43,55   |
| 9  |            | Citronellal acetate| 10,942  | 240                | 1,57      | 43,55   |
| 10 |            | Elemene           | 11,656         | 251                | 0,62      | 43,55   |
| 11 |            | Aromandrene       | 12,099         | 259                | 1,10      | 43,55   |
| 12 | Heavy      | Germacrene        | 12,236         | 279                | 0,75      | 43,55   |
| 13 |            | Methyl trans-     | 12,997         | 270,5              | 3,24      | 43,55   |
|    |            | isoeugenol        |                |                    |           |         |
| 14 |            | Elemol            | 13,778         | 289                | 1,74      | 43,55   |
| 15 |            | 1,3-              | 14,200         | 324                | 0,58      | 43,55   |

From the data of the boiling point sequence of the components and the grouping of component fractions target, then the design and condition of the separation process by fractionated distillation play an important role to produce components with higher purity. Distillation is the process of separating a mixture based on differences in the boiling points of the components in the mixture. A mixture of liquid-liquid components which are mutually soluble and volatile, but have different boiling points and vapor pressure can be separated by distillation [5]. The difference between fractionated distillation and simple distillation is the presence of a fractionation column. In the fractionation column, there are many stages of liquid-vapor equilibrium, so that the component with the lowest boiling point will reach the top of the column first compared to the component with a high boiling point. This process will be ongoing continuously so that it will get the single components gradually [6].

3.2. Distillate composition from laboratory scale of fractionation distillation

The result of the fractionation process of citronella oil using a laboratory scale of the fractionation distillation column is shown in Table 2. From Table 2, it is known that the component is volatilized far below their boiling point. In the light compound, there are 3 fractions before citronella is dominating. Limonene, ocimene and octatriene are distilled first in the temperature of 107-111ºC and 112-114ºC. A little bit of citronellal compound is already present before citronellal fraction along with octatriene. This phenomenon is happened due to the basic character of essential oil that easily volatilize even at room temperature. Citronellal composition in citronellal fraction is 81,5%. Citronella is evaporated at the temperature of 115-118ºC then optimized at the temperature of 119-122ºC. Citronellal concentration from citronella oil physically has been extracted through vacuum
fractionation distillation and obtained citronellal yields with a purity of 55.38% [7]. In other research, citronellal obtained from citronella oil through vacuum fractionation distillation with a purity of 91.3% under operating conditions with a reflux ratio of 5:1 and an operating pressure of 10 mbar [8]. So, it can be noted that the reflux ratio gives an important role to produce higher purity of citronellal. The citronellal fraction is greatly distilled with >80% of citronella purity. However, many companies of essential oil state that the minimum presence in the pure component if the major component is more than 85% [9]. It implies that the citronellal component in the citronellal fraction cannot be commercialized.

Table 2. Chemical composition of distillate from laboratory scale of fractionation distillation.

| No | Fraction       | Compound       | Set Point Material Temperature (ºC) | % Content | Total Mass (kg) |
|----|----------------|----------------|-------------------------------------|-----------|-----------------|
| 1  | Before Citronellal | Limonene       | 107-110                             | 33.28     | 1.66            |
| 2  | Before Citronellal | Ocimene        | 107-110                             | 35.8      |                 |
| 3  | Before Citronellal | Octatriene     | 107-110                             | 23.9      |                 |
| 4  | Before Citronellal | Limonene       | 111-114                             | 15.6      | 2.58            |
| 5  | Before Citronellal | Ocimene        | 111-114                             | 39.5      |                 |
| 6  | Before Citronellal | Octatriene     | 111-114                             | 19.91     |                 |
| 7  | Before Citronellal | Citronellal    | 115-118                             | 28.97     | 1.92            |
| 8  | Before Citronellal | Citronellal    | 119-122                             | 81.5      | 1.22            |
| 9  | Before Citronellal | Citronellol    | 119-122                             | 2.83      |                 |
| 10 | Rhodinol        | Geraniol       | 123-126                             | 48.55     | 1.57            |
| 11 | Rhodinol        | Geraniol       | 123-126                             | 15.81     |                 |
| 12 | Rhodinol        | Citronellol    | 123-126                             | 66.55     | 3.52            |

Citronellol and geraniol cannot be separated due to both boiling points are close and the mixture is called rhodinol. Rhodinol is showed up in the temperature of 123-126ºC and 127-130ºC. For the rhodinol aspect, the fraction that can be commercialized is residue with the composition of citronellol and geraniol is up to 85%. Unfortunately, rhodinol composition of citronellol and geraniol mixture is only 64%. In a research conducted by [10] produced 100% rhodinol (citronellol 42.98% and geraniol 57.02%) by using Column Chromatography Press. The other research conducted re-distillate rhodinol fraction twice from citronella oil. The rhodinol purity is only up to 67%. To produce greater rhodinol purity, it needs more post-treatment and isolation [11].

3.3. Distillate composition from pilot plant scale of fractionation distillation

The result of the fractionation process of citronella oil using the pilot plant scale of the fractionation distillation column is shown in Table 3. As Table 3 shown, it is similar to the fractionation distillation process that the component is volatilized far below their boiling point. In the light compound, there is only one fraction before citronella is dominating. Even in the previous citronellal fraction, the citronellal fraction is quite plentiful with 40% of citronellal. Citronellal composition in citronellal fraction is only 57.97%. In the trans fraction, Citronella is still presented with 46% purity along with citronellol and geraniol. Then rhodinol fraction is showed up in the temperature of 123-126ºC with the sum up of the mixture is only 66%. The citronellal fraction is poorly distilled with only 57% of citronella purity. In research conducted by [12], the citronellal is isolated through a vacuum fractionation distillation process, by varying the reflux ratio. The greater the volume of distillate that is accommodated, the lower the purity of the resulting citronellal because the compound which has a lower boiling point than the boiling point of the compound which wants to look like limonene which
is expected to be carried in the previous fraction, turns out to be carried along with the citronellal. The operating conditions that occurred in the fractionation distillation process must be adjusted to the properties and composition of the ingredients. The reflux ratio setting during the fractionation distillation process is determined by the composition of the light key component and the heavy key component in the material [13].

In the rhodinol fraction, there was the companionship of citronellal. The citronellal cannot be effectively separated based on the presence in every fraction including in residue. Rhodinol fraction is also not greatly separated. It implies that the citronellal and rhodinol component in the citronellal fraction cannot be commercialized based on The Good Company [9] standard, one of the distributors of essential oils compound. Djafar and Hidayati [14] is also conducted the rhodinol purification by fractionating lemongrass oil. The rhodinol production was only 28%, far below this research.

| No | Fraction     | Compound       | Set Point Material Temperature (°C) | % Content | Total Mass (kg) |
|----|--------------|----------------|------------------------------------|-----------|-----------------|
| 1  | Before Citronellal | Limonene       | 111-114                            | 39,8      | 15,2            |
|    |               | Citronellal    |                                    | 40,06     |                 |
| 3  |               | Limonene       |                                    | 6,89      |                 |
| 4  | Citronellal   | Citronellal    | 115-118                            | 57,97     | 26,1            |
| 5  |               | Citronellol    |                                    | 9,29      |                 |
| 6  |               | Geraniol       |                                    | 12,54     |                 |
| 7  |               | Citronellal    |                                    | 46,7      |                 |
| 8  | Trans         | Citronellol    | 119-122                            | 13,29     | 11,8            |
| 9  |               | Geraniol       |                                    | 20,15     |                 |
| 10 |               | Citronellal    |                                    | 7,99      |                 |
| 11 | Rhodinol      | Citronellol    | 123-126                            | 18,62     | 134             |
| 12 |               | Geraniol       |                                    | 48,06     |                 |
| 13 |               | Citronellal    |                                    | 8,14      |                 |
| 14 | Residue       | Citronellol    | 127-130                            | 8,97      | 12,9            |

3.4. Composition comparation

The comparison between laboratory scale and pilot plant scale fractionation distillations are based on the citronellal and rhodinol fractions. This is due to the similarity of a major component inside each fraction and most profit-oriented fraction from citronella oil. The composition comparison is shown in Figure 3.

In the citronellal fraction, laboratory-scale fractionation distillation had more citronellal component than the pilot plant. In the pilot plant scale, there was limonene. The other component like citronellol and geraniol in pilot plant scale is also greater than in the laboratory scale. It can be noted that the separation process in the pilot plant scale is not as successful as the laboratory-scale even when the process condition is perfectly similar. This occurred due to differences in the dimensions of the raw material capacity and the height of the fractionation column. Even if the packing inside the column is the same, but height differences can lead to different results. The higher the fractionation column, the higher the pressure drop. If the pressure drop is high, it will change the optimum temperature condition [13]. In the pilot plant scale, the pressure drop is higher than on the laboratory scale. This made the setpoint temperature shifted. When the pilot plant scale’s setpoint temperature was the same as the laboratory scale’s set point temperature, the product is not as great as the laboratory scale. So the dimension difference can not compensate for process condition.
3.4.1. Citronellal fraction chemical composition.

3.4.2. Rhodinol fraction chemical composition.

**Figure 3.** Chemical composition of each fraction: laboratory scale vs pilot plant.

Rhodinol fractions in both fractionation systems are almost the same. Both citronellal and geraniol are in the same range as 10-15% and 48% respectively. However, the sum-up of the mixture is not exceeded 85% which cannot be commercialized in accordance with the International system for categorization of a pure component. Even in the pilot plant scale, the citronellal is still present. Warsito *et al.* [15] conducted a research on the influence of column height with the distillate composition by varying 1 meter and 2 meters fractionation column with 1-in Raschig ring random packing. The result is rhodinol fraction is better produced with 2 meters column packing with 58% of geraniol. Silvianti [4] also studied about the impact of reflux ratio of distillation process: without reflux ratio and 2:1.
Reflux ratio 2:1 gave better purity and yield than without reflux ratio. At the reflux ratio (2:1) the purity and yield of citronellal and rhodinol were (81.5%; 6.6%) and (84.35%; 19.4%), respectively. Based on the related previous studies, it can be inferred that the column height and reflux ratio played a big role in the purity and yield of the distillate. Contrary to this research, higher column height meaning more number of packing and it gave better yield and purity. It appears so because the surface area is increased and gives the fraction more space to contact [16]. A higher reflux ratio also gives better purity of fractions [17]. However, some vacuum fractionation distillation still doesn't give better purity. To purify the fractions, it needs to re-distillate the fraction. Re-distillation of citronellal fraction from citronella oil has been done. The purity is increased from 75.67% of citronellal to 95.10% [18].

4. Conclusions
The separation process for laboratory scale and pilot plant scale must be adjusted to produce a higher quality of the pure component. Although the laboratory scale of fractionation distillation produced good quality rhodinol with 85% purity, the scale-up version of the pilot plant scale still cannot be occupied. For the citronellal fraction, both fractionation distillation process produced poor quality with only 50% purity. This occurred due to the different dimensions that lead to a higher pressure drop. A higher pressure drop will change the optimum temperature conditions.

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