Separation Process of Citronellal and Rhodinol from Citronella Oil using Vacuum Fractionations at Pilot Plant Scale

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Abstract: The aim of this work was to separate major components from citronella oil using vacuum distillation fractionation method. Operating condition that used in this study is vacuum pressure 10-30 mmHg. This process depends on the pressure and temperature of the system, as well the physical and chemical characteristics of the components to be separated.Based on GC-MS analysis of Citronella Oil is known that citronellal, citronellol, and geraniol has yielded 7,42%; 11,25%; and 31,68%, respectively. Fractional distillation under reduced pressure can isolate major component like limonene,citronellal,citronellol and rhodinol with higher purity 55.56%; 25.57%; and 46.19%, respectively.

1 INTRODUCTION

Essential oils are secondary metabolites that contain a mixture of terpenes and other complex volatile compounds produced from living organism. Essential oils have widely used as raw material for medicine , cosmetics, perfume and flavor fragrance agent (Almeida et al., 2018). The potential components of essential oil which generally consist of oxygenated compounds is very important to determine quality of essential oil and widely used as starting materials for flavor and fragrance industry.

Potential of essential oils in Indonesia is very large, but to supply the demand of its downstream industry, Indonesia should to import essential oils in the form of pure oils which contain high purity potential components.This fact show that the separation of the potential compounds in essential oils is a step that needs to be done to improve the purity of potential components that are needed by many industries.

Separation technique of potential components of essential oils can be carried out through chemical or physical processes.Separation of the components of essential oils by chemical processes can be done by adding chemical reagents that are selective to the desired compound, while physical separation can be done based on the physical properties of each compounds that can be done by fractionation distillation method. Fractionation distillation is a physical separation process that uses the volatility of different components in a mixture. The advantages of the fractionation distillation method can be used to separate components that have adjacent boiling points (Budiman, 2016).

Process of separation in fractionation distillation occurs due to contact and equilibrium between vapor and liquid in the fractionation coloumn (Ibrahim, 2014). According to Kister (1992) the main factors that influencing the effectiveness of the separation occuring in the fractionation process are design of fractionation coloumn and operating conditions. Therefore, optimization of the separation process is needed that can provide the most optimal operating conditions like temperature operation, so that contact between liquid and vapor takes longer to produce high purity compounds. The fractional distillation is one of unit operation that aims the separation of two or more substances using vacuum state by the volatility difference between them. This process depends on the pressure and temperature of the system, as well the physical and chemical characteristics of the components to be separated (Eden, 2018).

Citronella oil is the essential oil from citronella grasses (*Cymbopogon winterianus*) from Java Island, Indonesia. One part of Indonesia which is abundant

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of raw essential oil source especially citronella oil in Central Java. Central Java has the potential production of essential oils are quite large. The oil is used extensively as a source of perfumery chemicals such as citronellal, citronellol, and geraniol. These compounds are used extensively in soap, candles and incense, perfumery, cosmetic, and flavoring industries throughout the world (Eden, 2018).

This research will focus on the isolation of citronellal and rhodinol compounds using vacuum fractionation distillation by studying its optimum operating conditions in several parameters for the pilot plant scale.

2 MATERIAL AND METHOD

2.1 Material

The main raw material in this research are citronella oil from Institut Atsiri Brawijaya University. The main equipment used is vacuum distillation fractionation capacity 20kg that consists of reflux column, mixer, condenser, tank product that all part connected to a vacuum pump, and another equipment are analytical balance, bottle glass, gas chromatography mass spectrometry, refractometer.

2.2 Method

2.2.1 Characterization of Chemical Compounds of Citronella Oil

The first stage of this research is characterization of chemical compounds of citronella oil. The composition of chemical compounds contained in the raw material of citronella oil used as reference basis for each compound that will taken.

2.2.2 Isolation Process of Citronellal and Rhodinol Compounds using Vacuum Fractionation

The process of isolation of citronellal and rhodinol compounds is carried out under vacuum pressure of 10-30 mmhg. Temperature of the vessel is set gradually appropriate to boiling point of each compound that contained on citronella oil. Temperature at the top of the fractionation column (T.head) connected with a thermocouple instrument to observe temperature change during isolation process. Distilate that produced at different temperatures are collected in different container. The temperature at the top column (T.Head) and temperature of raw material is recorded on each distillate that collected.

2.2.3 Analysis of Isolation Product of Citronella Oil

Distillate that obtained from each fraction produced in the fractionation distillation process is then analyzed to know purity level and refractive index of the component to determine quality of the pure compound that produced using Gas chromatography-Mass Spectrometry (GC–MS) .

3 RESULT AND DISCUSSION

Essential oil consist highly volatile substance that isolated by distillation from an odoriferous plant. Citronellal or rhodinol is the major component of the monoterpene fraction of citronella oil and gives the essential oil of citronella its characteristic lemon odor is also used in many chemical syntheses (Eden,2018). In this study, citronella oil is separated by distillation fractionation process to produce major compound of citronella oil like citronellal and rhodinol.

3.1 Physical Properties of Citronella Oil

Citronella oil was obtained by using steam distillation methods are pale yellow to yellow when freshly distilled. The physical properties of Citronella oil shown in Table 1.

Table 1. The Physical Properties Of Citronella Oil

Parameter	Result
Appearance	Oily Liquid
Color	Pale Yellow
Odor	Sweet,citrusy,woody
Refractive Index (20^{o}C)	1.467
Specific Gravity (25 ^{o}C)	0.88

3.2 Chemical Composition of Citronella Oil

According to the data of Gas Chromatography Mass Spectometry (GC-MS), citronella oil consist of terpenoid compounds as major components that show in table 2. The major components of Citronella Oil that used as raw material in this study are

citronellal,citronellol, and geraniol that has yield 27,42%,11,25% and 31,68% respectively. The chromatogram of citronella oil shown in Figure 1.

Tabel 2. Chemical Composition of Citronella Oil

Composition	Percent (%)
Limonene	7.23
Ocimen	4.08
Octatriene	6.90
Citronellal	27.42
Citronellol	11.25
Citral	0.62
Geraniol	31.68
Citronellyl Acetate	1.21
Cyclohexane	1.57
Germacrene	0.62
Benzene	1.10
Elemol	0.75
1,3-cyclopentadiene	3.24
Tricyclo hexane	1.74
Cyclopentadiene	0.58

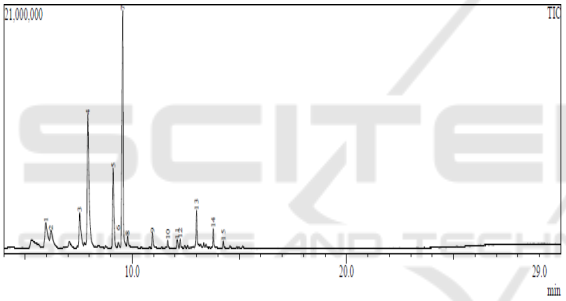

Figure 1: Chromatogram of Citronella Oil

3.3 Isolation of Major Component from Citronella Oil

Most terpenes such as citronellal, citronellol, and geraniol are thermally unstable,decomposing or oxidizing at high temperatures or the presence of light or oxygen. Therefore, separation of component active from citronella oil is needed a mode of vacuum condition to decrease temperature operation (Eden, 2018). According to Egi (2005), correlation between boiling point and pressure shown in Figure 2.

Theoritical approach of operating condition has been done through correlation of pressure with boiling point of the major components of citronella oil. According to the theoritical, operating conditions use pressure 10- 30 mmHg so the estimated boiling point of citronellal 84,8 – 107,95^{o}C, and rhodinol 107-133^{o}C. Table 3 shows that theoritical boiling point of each component of citronella oil in this study, slightly different with theoritic data.

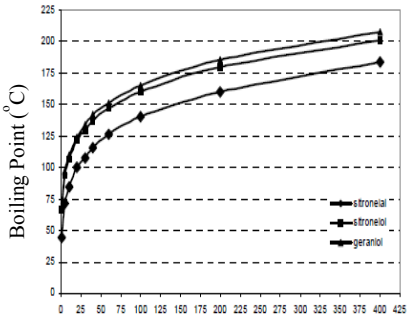

Figure 2: Correlation Between Presssure and Boiling Point

Table 3: Correlation of Temperature and Purity of Major Components

No	Components	Temperature(^{o}C)	Percent (%)
1.	Limonene	113-115	35.28
2.	Citronellal	116-118	55,56
3.	Citronellol	121-125	25,57
4.	Geraniol	121-125	46,19

3.4 Physical Properties of Citronellal and Rhodinol

Citronellal is responsible for the characteristic of odor in citronella oil. It has flavor citrus-like odor but seems to be less sweet and fruity than citral. Geraniol and citronellol that called rhodinol are known as the rose alcohols because of their occurrence in rose oils and also because they are the key materials responsible for the rose odor character in citronella oil. Each of active component has the characteristic of physical properties that shown in Table 4.

Table 4: The Physical Properties of Citronellal and Rhodinol from Citronella oil

Parameter	Citronellal	Rhodinol
Appearance	Oily Liquid	Oily Liquid
Color	Pale yellow	Colorless
Odor	Citrus,slightly sweet,green and aldehyde, strong	Sweet, rosy floral,citrus, soft
Refractive Index	1.466	1.4734

3.5 Chemical Composition of Major Component from Citronella Oil

Major components of Citronella Oil can obtained

through fractional distillation process.Identification of the major components fraction from citronella oil was carried out by gas chromatography-mass spectometry(GC-MS).In this study, we obtained purity of limonene 35.28%, citronellal 55.56%, citronellol 25.57% and geraniol 46.19%.The chromatogram of limonene,citronellal,and rhodinol shown in figure 3,4,5 respectively.

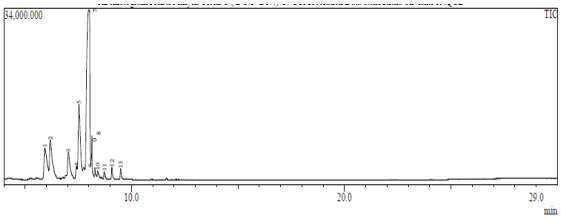

Figure 3: Chromatogram of Limonene

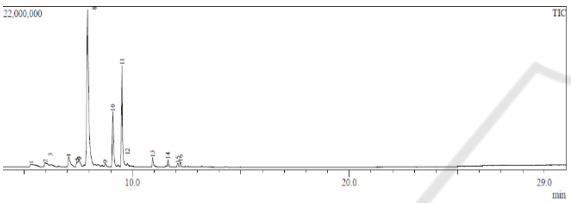

Figure 4: Chromatogram of Citronellal

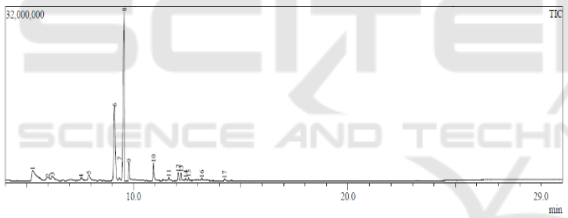

Figure 5: Chromatogram of Rhodinol

4 CONCLUSIONS

Citronella oil is containt major component are citronellal, citronellol, and geraniol with purity of 27.42%,11.25%,31.68% espectively.Vacuum fractional distillation using operating condition with pressure 10-30 mmhg that obtained increase purity of major components citronellal, citronellol, and geraniol are 55.56%; 25.57%; and 46.19%, respectively.

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