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Fractionation of Java Citronella Oil and Citronellal Purification by Batch Vacuum Fractional Distillation

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Abstract. The aim of this work was to assess the performance of a vacuum fractionating column for the fractionation of Java Citronella Oil (*Cymbopogon winterianus*) and citronellal purification during batch mode operation at vacuum -76 cmHg and reflux ratios 5:1. Based on GC-MS analysis of Java Citronella Oil is known that citronellal, citronellol, and geraniol has yielded 21,59%; 7,43%; and 34,27%, respectively. Fractional distillation under reduced pressure and continued redistilled are needed to isolate the component of Java Citronella Oil. Redistilled can improve the purity, then distillate collected while the temperature changed. In the first distillate yielded citronellal with a purity of 75.67%. The first distillate obtained residue rhodinol product will then be carried back to separation into citronellol and geraniol. The purity of citronellol reached 80,65% purity, whereas geraniol reached 76.63% purity. Citronellal Purification resulting citronellal to 95.10% purity and *p*-menthane-3,8-diol reached 75.95% purity.

1 Introduction

Java citronella oil is the essential oil from citronella grasses (*Cymbopogon winterianus*) from Java Island, Indonesia. One part of Indonesia which is abundant of raw essential oil source especially citronella oil in Central Java. Central Java has the potential production of essential oils are quite large. Some essential oils produced from refining industry owned by the government, private and community sectors [1]. Java citronella oil is popularly known by its characteristic insect and mosquito repellent and used in perfumery, soaps, detergents, and industrial polishes [2,3]. 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. The oil of java citronella is composed mostly by monoterpenes (±80%) (major components being aldehydes and alcohols), although sesquiterpenes are also found. Citronellal, citronellol, and geraniol are the major terpenoids found in the Java Citronella Oil [2,4,5]. Citronella oil is also a plant-based insect repellent. These can be used as conventional mosquito repellents with little or no harmful effects [6]. Citronellal or rhodinal is the major component of the monoterpene fraction of citronella oil and gives the essential oil of citronella its characteristic lemon odor [7], is also used in many chemical syntheses [8]. Geraniol (3,7-dimethyl octa-trans-2, 6-dien-1-ol) oil, the main ingredient in the essential oil of ginger, lemon, lavender, orange, rose, palmarosa and other plants, is acyclic monoterpene alcohol [9]. Geraniol is a colorless, odor pleasant compound (aroma of roses) [2]. Citronellol (3,7-dimethyl oct-6-en-1-ol), an essential oil component of lemongrass, citronella grass, and also presents an odor of roses. It is used as a flavoring agent in food and beverages, fragrances, and an insect repellent [2, 10].

Most terpenes such as citronellal, citronellol, and geraniol are thermally unstable, decomposing or oxidizing at high temperatures or the presence of light or oxygen [11]. Therefore, separation of component active from java citronella oil is needed a mode of vacuum condition to decrease temperature operation. 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 [12]. Batch vacuum distillation works at mild temperatures and offers flexibility to operate with different oils in the same industrial plant. The main advantages of batch processes are the flexibility and versatility and also the possibility of working with small volumes, thus allowing performing raw material tests before large-scale processing [13]. The objective of this work is to evaluate the use of the batch vacuum fractional distillation to separate terpenoid compounds of the Java Citronella Oil. The Java Citronella Oil was isolated by using steam distillation from grasses of *Cymbopogon winterianus* plants collected in Boyolali District, Central Java, Indonesia.

2 Methods

2.1 Raw Material

Grasses of *Cymbopogon winterianus* was collected from Boyolali District, Central Java, Indonesia. This herb was selected, dried, and prepared for one day. Other chemicals were purchased from Merck.

2.2 Steam Distillation Method

The essential oils were collected by the steam distillation method. The grasses of *Cymbopogon winterianus* were packed into the kettle sitting on a perforated plate above the boiling water. The essential oils were volatilized with boiling water at temperature 100°C for 6 hours or more. After the steam distillation process, the oil will be collected and separated used the separatory funnel which can be used to separate the immiscible liquids of two layers such as oil and water. The oils which have lighter density than water will be visible at the top of the separatory funnel. Wait for the water and oil separated completely and formed two layers and oil was collected. Solid of Na_2SO_4 was used to adsorb the residual of water that fused with the oil. The quantity of the oil determined according to the yield. The yields of essential oils were calculated using the formula:

$$\%\text{Yield} = \frac{\text{Weight of Oil (g)}}{\text{Weight of } Cymbopogon\ winterianus\ Grasses\ Taken\ \text{(g)}} \times 100\%$$

2.3 Batch Vacuum Fractional Distillation Method

The rhodinol, citronellol, geraniol, and *p*-menthane-3,4-diol oils (Figure 1) obtained by fractional vacuum distillation of java citronella oil (*Cymbopogon winterianus*) (distillate fractions DF-33 P = -76 cmHg R = 5:1).

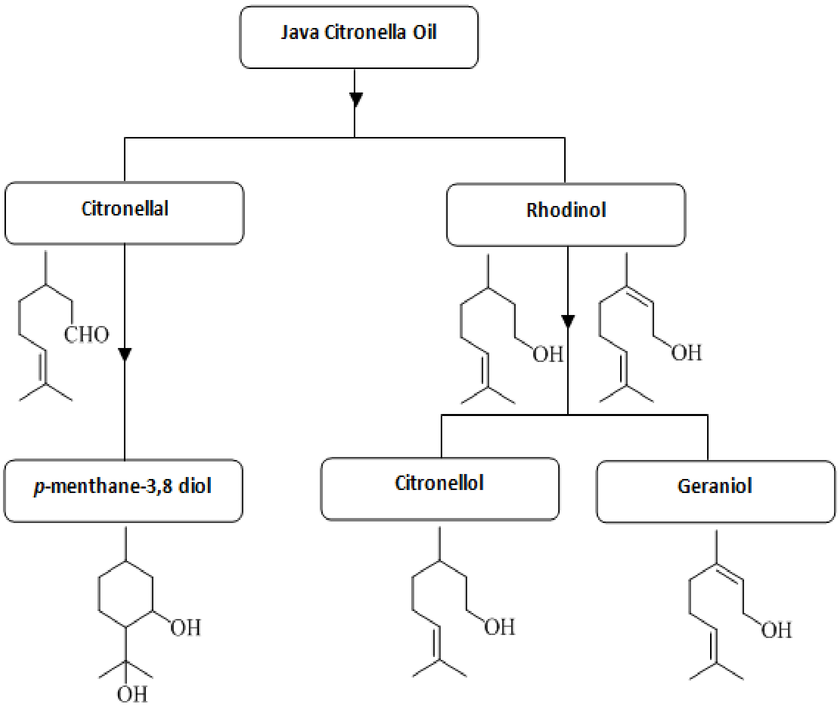

Figure 1.Fractional Distillation Mechanisms of Java Citronella Oil to produce Citronellal, Rhodinol, Citronellol, Geraniol, and *p*-menthane-3,4-diol Oils

The batch vacuum fractional reactor built in stainless steel SUS 316 L. The capacity reactor of 25 kg consists of reflux column, mixer, condenser, and tank product. All part connected to a vacuum pump (Figure 2).

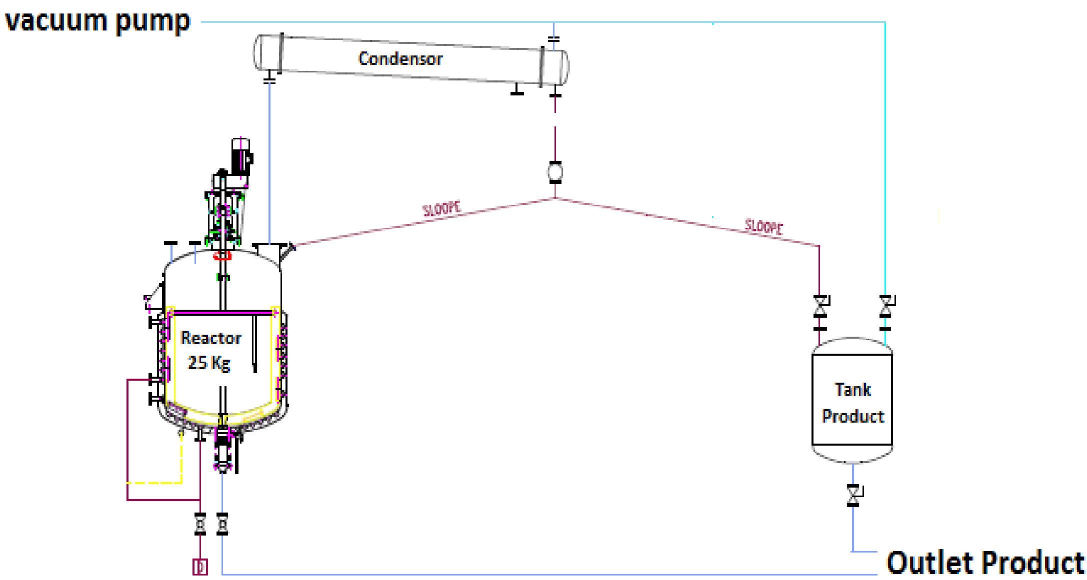

Figure 2.Batch Vacuum Fractional Distillation Reactor

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2.4 Physical properties

The specific gravity and refractive index of the Java citronella oil extracted from the *Cymbopogon winterianus* grasses, citronellal, rhodinol, citronellol, geraniol, and *p*-menthane-3,4-diol oils were measured. The specific gravity measured at 25°C and refractive index measured at 20°C.

2.5 GC/MS Analysis

Gas chromatography-mass spectrometry (GC–MS) analysis was carried out on an Agilent Technologies GC–MS instrument equipped with a GC 7890A gas chromatograph, an MS 5975C VL MSD mass spectrometer detector and provided with an HP-5MS capillary column. The data acquisition and data processing were performed using the MSD Chemstation E.01.01.335 (Agilent) software.

3 Result and Discussion

The term essential oil is used to refer to highly volatile substance isolated by steam distillation from an odoriferous plant of a single botanical species. This method is the favorite method for essential oil extraction process was steam distillation [14]. In this study, the java citronella oil from the grasses of *Cymbopogon winterianus* was extracted by the hot steam that applied in this method. The final of steam distillation process will be condensed and separated into the liquid form that was the mixture of oil and steam. The oils were less dense than water and could be separated using proper method and instruments.

3.1 Physical Properties of Java Citronella Oil

The java citronella oil was obtained from grasses of *Cymbopogon winterianus* by using steam distillation methods are pale yellow to yellow when freshly distilled. This essential oil yielded varied from 0.956% to 1.06% and shown in Table 1. The physical properties of java citronella oil shown in Table 2. They are only slightly soluble in water and dissolve fairly well in ethanol and mixed very well with vegetable oils, glycerol, and propylene glycol.

Table 1. The Yield of Java Citronella Oil (*Cymbopogon winterianus*)

Parameter	Java Citronella Oil				
	I	II	III	IV	V
Sample Weight (kg)	5.00	5.10	5.10	5.00	5.05
Content of Oils (g)	47.80	50.45	52.90	51.90	53.03
Yield (%)	0.956	0.989	1.04	1.04	1.06

Table 2. The Physical Properties of Java Citronella Oil (*Cymbopogon winterianus*)

Parameter	Java Citronella Oil				
	I	II	III	IV	V
Appearance	Oily liquid				
Color	Pale Yellow		Yellow		
Odor	sweet, warm floral, woody, citrusy				
Refractive Index at 20 °C	1.467	1.467	1.469	1.468	1.469
Specific Gravity at 25 °C	0.879	0.877	0.880	0.880	0.881

3.2 Chemical Composition of Java Citronella Oil

The combination of gas chromatography and mass spectrometry (GC-MS) allows rapid identification of essential oil components, provided that these compounds are already known and their mass spectra available in a library. According to the data of GC-MS analysis, we investigated essential oil in *Cymbopogon winterianus* grasses consist mostly of terpenoid compounds. The chemical composition of java citronella oil shown in Table 3. The main component of Java citronella oil are citronellal, citronellol, and geraniol has yielded 21,59%; 7,43%; and 34,27%, respectively. The Chromatogram of java citronella oil shown in Figure 3.

Table 3. Chemical Compositions of Java Citronella Oil (*Cymbopogon winterianus*)

Composition	RT	Percent (%)
β-myrcene	4.274	0.10
α-pinene	5.007	6.739
β-cis-ocimene	5.216	1.903
Linalool	6.311	1.07
Neo-allo-ocimene	7.321	0.18
β-citronellal	7.991	21.59
(-)-L-isopulegol	8.272	0.36
Capraldehyde	10.011	0.26
β-citronellol	11.421	7.43
cis-3,7-Dimethyl-2,6-octadienal	11.518	0.44
cis-geraniol	12.852	34.27
α-citral	12.944	0.61
Geranyl formate	14.403	0.10
Citronellyl acetate	16.418	1.63
Nerylacetate	16.699	0.04
Geranyl acetate	17.395	4.89
(-)-*β*-elemene	18.103	0.72
β-caryophyllene	18.978	0.88
α-bergamotene	19.545	0.72
α-humulene	19.978	0.13
(E)-β-farnesene	20.064	0.13
Methyl iso-eugenol	20.577	3.00
(-)-germacrene D	20.766	1.18
α-farnesene	21.155	2.90
α-muurolene	21.317	0.16
α-amorphene	21.668	0.27
δ-cadinene	21.917	0.75
Elemol	22.452	1.07
Geranyl butyrate	22.673	1.24

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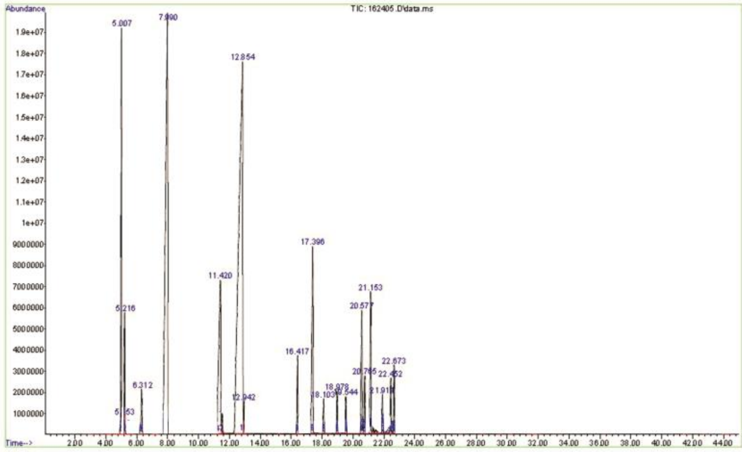
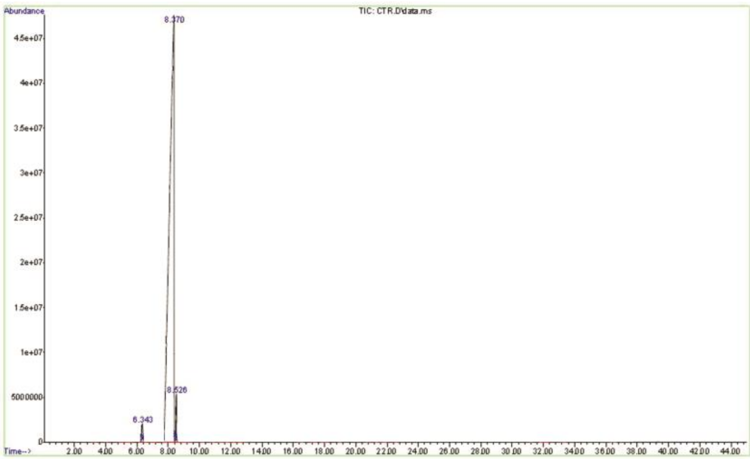


(a)



(b)

Figure 3. (a) Chromatogram of Java Citronella Oil from Steam Distillation of *Cymbopogon winterianus* Grasses and (b) Chromatogram of Citronellal Oil

3.3 Physical Properties of Active Component From Java Citronella Oil

The terpenoids are, by far, the most important group of java citronella oil. They are defined as substances composed of isoprenes (2-methyl butadiene) units such as citronellal, citronellol, and geraniol. Fractional distillation under reduced pressure and continued redistilled are needed to isolate this terpenoids compounds that are active component in java citronella oil. According to this method, we can be isolated the main active component in java citronella oil. They are citronellal, citronellol, geraniol, and also *p*-menthane-3,4 diol. Citronellal is responsible for the characteristic of odor in java citronella oil. It shows an intense citrus-like odor but seems to be less sweet and fruity than citral. Geraniol and citronellol 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 java citronella oil. *p*-menthane-3,8-diol, also known as *para*-menthane-3,8-diol or PMD is a mixture of the cis and trans isomers of *p*-menthane-3,8-diol. This compound is obtained by purification of citronellal through fractional distillation under pressure. PMD is structurally similar to menthol so that the odor like menthol that gave minty and eucalyptus-like aroma. Each of active component has the characteristic of physical properties that shown in Table 4.

Table 4. The Physical Properties of Active Component from Java Citronella Oil (*Cymbopogon winterianus*)

Parameter	Active Component of Java Citronella Oil*				
	C-al	**R-ol**	**C-ol**	**G-ol**	**PMD**
Appearance	Oily Liquid	Oily Liquid	Oily Liquid	Oily Liquid	Oily Liquid Slightly Viscous
Color	Colorless	Light Yellow	Pale Yellow	Pale Yellow	Pale Yellow
Odor	Citrus-like aroma, floral rosy waxy, slightly sweet, green, and aldehyde	Sweet, rosy, floral, waxy, citronellal like with fresh citrus	Herbaceous rose with fruity citrus nuances, floral, and slightly sweet	Sweet rose, floral, fruity and fresh note	Minty, herbaceous, eucalyptus-like aroma
Refractive Index at 20 °C	1.448	1.479	1.462	1.476	1.470
Specific Gravity at 25 °C	0.851	0.905	0.857	0.885	0.965

*Note: * C-al: Citronellal; C-ol: Citronellol; PMD: p-menthane-3,8-diol; R-ol: Rhodinol; G-ol: Geraniol*

3.4 Chemical Composition of Active Component From Java Citronella Oil

The active component of Java citronella oil obtained through fractional distillation method. Redistilled can improve the purity, then distillate collected while the temperature changed. The identification of the active component fraction from java citronella oil was carried out by gas chromatography-mass spectrometry (GC-MS). In the first distillate yielded citronellal with a purity of 95.10%. The chromatogram of citronellal oil shown in Figure 4. The first distillate obtained residue rhodinol product will then be carried back to separation into citronellol and geraniol with the purity of 19.33% and 34.31%, respectively. The purity of citronellol reached 80,65% purity, whereas geraniol reached 76.63% purity. The *p*-menthane-3,8-diol obtained from refining citronellal resulting citronellal and *p*-menthane-3,8-diol reached 75.95% purity.

4 Conclusion

Java citronella oil is rich in citronellal, geraniol, and citronellol with purity of 21,59%; 7,43%; and 34,27%, respectively. Batch vacuum fractional distillation under reduced pressure yielded citronellal with a purity of 75.67%, and the residue rhodinol consist of citronellol and geraniol component with the purity of 19.33% and 34.31%, respectively. Purification of rhodinol yielded citronellol and geraniol with the purity of 80,65% and 76.63%, respectively. Purification resulting citronellal in 95.10% purity and *p*-menthane-3,8-diol reached 75.95% purity.

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