Quality improvement by batch vacuum distillation and physicochemical characterization of clove leaf oil in Central Java, Indonesia

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Abstract. Clove leaf oil is one of the essential oils which have high economic value and produced in considerable amount in Indonesia. As many as 60% of clove oil produced by Indonesia has exported to many countries in the world. Musuk and Ringinlarik Village, Boyolali District, Central Java Province is one of the areas in Indonesia which became the primary supplier of Indonesian clove leaf oil. Although, the quality of the resulting yield is still low because it uses a simple distillation kettle in the form of the iron plate or used the drum. The clove leaf oil produced by steam distillation from the dry whole leaves of the clove tree. The color of the oil is brownish black and dirty with the odor are fresh distilled, spicy, warm, and terpenic. The specific gravity at 25 °C of 1.529, the refractive index at 20 °C of 1.030, and based on GC-MS analysis, eugenol levels only 68% and caryophyllene is too high, i.e., 20%. The quality of clove leaf oil produced does not meet the specifications of international market standards. This work aimed to improve the quality of Indonesian clove leaf oil. The purifications done in this research was used by batch vacuum distillation with mode operation at vacuum -76 cmHg and reflux ratios 5:1. Clove leaf oil produced by using this method has a better physicochemical characterization, i.e., the appearance that is yellow to pale color with the odor is spicy, woody, warm, and terpenic. The specific gravity at 25 °C of 1.533, the refractive index at 20 °C of 1.038, and eugenol and caryophyllene contents has yielded 80.58% and 10%, respectively. By The enhancement quality of clove leaf oil by batch vacuum distillation, these oil is already meet international standards and income of clove leaf oil grower in Musuk and Ringinlarik Village, Boyolali District, Central Java Province, Indonesia could be increased.

1. Introduction

Essential oils (EO) are also known as the etheric oils or oil fly (volatile oil) produced by physical means from a plant. EO can be obtained from the roots, stems, leaves, and flowers of plants. EO have volatile properties at room temperature without decomposition, has a bitter taste (pungent taste), following the smell of aromatic plants, are soluble in organic solvents and insoluble in water [1, 2]. Indonesia is a potential country as a source of EO raw materials. Indonesia produces 40 types of 80...
One of the most useful CLO that obtained by distillation of the dried leaves of the clove tree [7, 8]. CLO has a broad spectrum of medicinal properties, including pain relief, promotion of healing [5], and antimutagenic [12], anti-inflammatory [3], analgesic, anesthetic [16], hepatoprotective [4], and antioxidant [13] effects. Moreover, CLO is used widely for use in medicine, perfume, food flavoring, and the protection of agricultural products and foods [11, 15], due to their antibacterial [6], mosquito repellent [9], antifungal [14], acaricidal [10], and antiviral activities [5].

Although the potential benefits of CLO are considerable in industry, it turns out the quality of CLO from Central Java, Indonesia is still low [1]. The quality of CLO which produced has not been able to meet international market standards. Some things that can be used as a solution to improve the qualitative and quantitative of CLO, among others, is the distillation techniques and equipment used, the treatment of clove leaf, and CLO refining process. Several types of methods can be done to separate or get CLO, among others distillation, extraction and others. CLO is mostly present in the plant in particular glands named trichomes. During steam distillation, as steam flows over the oil-containing glands, the trichomes slowly release their content, because of high temperature, and, finally, become deflated when they release all their CLO content. Regarding distillation techniques are used, by using steam distillation method can be produced CLO yield better than the conventional method using distilled water (hydrodistillation) [17, 18]. Nevertheless, this quality of CLO that produced via steam distillation is still low. Therefore, in order to fulfill quality in the production of CLO, the process to extract valuable component in CLO was improved to maintain the purity of CLO. Crude CLO is purified in batch distillation columns in order to enrich the product in some components while decreasing the number of other components.

In the last few years, batch distillation has received increasing attention because of its simplicity of operation, flexibility and lower capital cost rather than continuous distillation. Batch distillation is a single column that can separate many different components from a multi-component feed of multiple cuts with different product specification from the binary feed. The use of batch distillation is becoming increasingly crucial for the separation and purification of high-value chemicals in many chemicals, food and pharmaceutical processes [19, 21-23]. Moreover, the advantages of using batch distillation when the amount of the light component in the feed charge is small and the products are to be recovered at high purity [19, 20]. Then, another interesting method of distillation is vacuum distillation. Vacuum distillation is a technique applied to the distillation of liquid mixtures at temperatures below their usual boiling points. The vacuum distillation method has found widespread use in multiple industries because of its benefits, namely, the prevention of material thermal decomposition, reduction in energy usage, recovery of waste heat, and mitigation of safety hazards [19]. Therefore, this study aimed to investigate a quality improvement by batch vacuum distillation and physicochemical characterization of CLO. By The enhancement quality of CLO, these oil is...
already meet international standards and income of CLO grower in Musuk and Ringinlarik Village, Boyolali District, Central Java Province, Indonesia could be increased.

2. Methods
2.1. Material
The crude CLO from CLO grower in Musuk and Ringinlarik Village, Boyolali District, Central Java Province, Indonesia was used in this study. The crudes CLO grower were collected by the steam distillation method. The leaves of clove (*Eugenia aromatica* or *caryophyllata* or *Syzygium aromaticum*) plant 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 8 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 weightier density than water will be visible at the down of the separatory funnel. Wait for the water and oil separated entirely and formed two layers and oil was collected. Solid of Na₂SO₄ was used to adsorb the residual of water that fused with the oil.

2.2. Vacuum batch distillation
The vacuum batch distillation was built in stainless steel 316 L (SUS 316 L). A batch of the mixture to be distilled is boiled in a closed vessel. Cooling condenses the vapors, and the distillate is collected. The capacity reactor of 25 kg consists of reflux column, mixer, condenser, and tank product. All part connected to a vacuum pump (Figure. 1).

To understand the behavior of CLO purification performance for the operation process of batch vacuum distillation, experiments will be conducted during a period of this research. Raw materials for the experiments are crude CLO. From the crude, it is purified by using batch vacuum distillation with single short of vessel column. Crude CLO is in the liquid phase and black. It is obtained from steam distillation process from CLO grower in Musuk and Ringinlarik Village, Boyolali District, Central Java Province, Indonesia. The steam distillation process is not conducted due to beyond the scope of this research. Before starting the experiment, crude CLO is filtered to avoid muck at the vessel after heating. The yields of CLO purified was calculated using the formula:

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\% \text{Yield} = \frac{\text{Weight of Crude CLO (g)}}{\text{Weight of CLO purified (g)}} \times 100\%
\]
2.3. Physical Constants
The specific gravity and refractive index of crude CLO were measured from CLO grower in Musuk, and Ringinlarik Village, Boyolali District, Central Java Province, Indonesia, and CLO produced from the purification process by using batch vacuum distillation reactor. The specific gravity measured at 25 °C and refractive index measured at 20 °C.

2.4. GC/MS Analysis
Crude CLO and CLO composition were obtained using gas chromatography-mass spectrometry (GC–MS). GC-MS analyses were 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. Results and discussion
In this study, the crude CLO from CLO grower in Musuk and Ringinlarik Village, Boyolali District, Central Java Province, Indonesia that produced from the leaves of clove (Eugenia aromatica or caryophyllata or Syzygium aromaticum) plant 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 weightier density than water and could be separated using proper method and instruments. Then, crude CLO from this grower is purified by using batch vacuum distillation.

3.1. Product yields of clove leaf oil purified
The CLO was obtained from CLO grower by using steam distillation methods are brown to black color and has freshly distilled in odor. The mass yields of clove leaf oil purified from crude CLO varied from 88.28–86.82% and shown in Table 1. CLO purified are colorless to yellow color and has spicy in odor. The purifications in this research were used by batch vacuum distillation with mode operation at vacuum -76 cmHg and reflux ratios 5:1.

| Parameter       | Clove Leaf Oil Purified |
|-----------------|-------------------------|
|                 | I  | II | III | IV | V  |
| Crude CLO Weight (kg) | 20.00 | 20.10 | 20.10 | 20.00 | 20.05 |
| CLO Purified (Kg)    | 17.60 | 17.45 | 17.60 | 17.55 | 17.70 |
| Yield (%)            | 88.00 | 86.82 | 87.56 | 87.75 | 88.28 |

3.2. Physical properties of clove leaf oil
Physicochemical analysis of CLO to ensure the quality of CLO such as appearance, color, odor, specific gravity, refractive index, and solubility will directly affect the quality of a CLO. The characteristics of this essential oil can help to identify the quality of essential oils from the beginning.

CLO was obtained from CLO grower has black to black purplish. This CLO has a specific gravity of 1.529, refractive index 1.030, and eugenol content is only 68%. The quality of oil produced does not meet the specifications of international market standards. Therefore, CLO needs to be processed again to achieve international standards by using batch vacuum distillation. CLO produced by using the reactor has a better appearance that is yellow, pale color, specific gravity 1.533, refractive index 1.038, and eugenol 80.58%. CLO is already meet international standards. The physical properties of crude CLO and CLO purified compare with CLO in standard worldwide 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. The solubility of crude CLO, CLO purified, and CLO in standard international shown in Table 3.
### Table 2. The Physical Properties of Clove Leaf Oil

| Parameter                        | Crude CLO                  | CLO Purified              | International Standard |
|----------------------------------|----------------------------|---------------------------|------------------------|
| Appearance                       | Oily liquid                | Oily liquid               | Oily liquid            |
| Color                            | Black – Black purplish     | Pale Yellow               | Colorless – Yellow     |
| Odor                             | Spicy, woody, warm,       | Spicy, woody, warm,       | Spicy, woody, warm,    |
|                                 | terpenic                   | terpenic                  | terpenic               |
| Refractive Index at 20 ºC        | 1.030                      | 1.038                     | 1.032 – 1.042          |
| Specific Gravity at 25 ºC        | 1.528                      | 1.533                     | 1.530 – 1.535          |
| Eugenol                          | 68%                        | 80.58%                    | Min. 80%               |
| Caryophyllene                    | 20%                        | 10%                       | Maks. 17%              |
| Humulene                         | 2%                         | 2%                        | Maks. 3%               |

### Table 3. The Solubility of Clove Leaf Oil

| Solvent       | Volume Ratio (Oil : Solvent) | Crude CLO  | CLO Purified | International Standard |
|---------------|-----------------------------|------------|--------------|------------------------|
| Water         | 1 : 1                       | Immiscible | Cloudly      |                        |
|               | 1 : 5                       |            |              |                        |
| Ethanol       | 1 : 1                       | Miscible   |              |                        |
| Ethanol 70%   | 1 : 2                       | Miscible   |              |                        |
| Chloroform    | 1 : 1                       | Miscible   |              |                        |
| Ether         | 1 : 1                       | Miscible   |              |                        |
| Petroleum Ether | 1 : 1                     | Miscible   |              |                        |
| Vegetable Oil | 1 : 1                       | Miscible   |              |                        |
| Glycerol      | 1 : 1                       | Miscible   |              |                        |
| Propylene Glycol | 1 : 1                    | Miscible   |              |                        |

3.3. Chemical composition of clove leaf oil

The combination of gas chromatography and mass spectrometry (GC-MS) allows rapid identification of essential oil, 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 crude CLO, and CLO Purified consist mostly of eugenol, caryophyllene, and humulene. The chemical composition of crude CLO and CLO Purified shown in Table 4 and Their the chromatogram shown in Figure 2.

![Figure 2. Chromatogram of (a) Crude CLO (b) Purified CLO](image-url)
4. Conclusion
Crude CLO oil from CLO grower in Musuk and Ringinlarik Village, Boyolali District, Central Java Province, Indonesia mainly consist of 68% eugenol, 20% caryophyllene, and 2% humulene. The quality of CLO products is still far below the international market standard that is black, refractive index, and specific gravity does not enter the standard, and the content of eugenol about 68% is still below the minimum that is at least 80%. By Batch vacuum distillation under reduced pressure with mode operation at vacuum -76 cmHg and reflux ratios 5:1 yielded eugenol with a purity of 80.58%, caryophyllene with purity of 10%, and humulene with a purity of 2%. Purification by using batch vacuum distillation succeeded to improve the quality of CLO produced by CLO grower that produces CLO with yellow color until colorless, refractive index, and specific gravity have entered standard and also eugenol content 80.58% also entered in the international standard that is at least 80%.

Acknowledgment
This research was funded by The Ministry of Research, Technology and Higher Education Republic of Indonesia.

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