Optimization of Essential Oil Extraction from Dried Clove Leaves (*Syzygium aromaticum*) using Solvent-Free Microwave Extraction by Face-Centered Central Composite Design

Yurie Nurmitasari¹ and Mahfud Mahfud¹*

¹Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Surabaya, 60111 Indonesia

*Corresponding author: mahfud@chem-eng.its.ac.id

Abstract. Clove (*Syzygium aromaticum*) leaves are agricultural waste of clove plants which can still be valorised by extracting their essential oil. The aim of this research is to perform the extraction process of clove essential oil using Solvent free microwave extraction by studying the effects of extraction parameters, such as microwave power, feed to distiller ratio and extraction time and finding optimal conditions with the response surface methodology using FCCD design. The operating parameters of this experiments are microwave power (300 - 600 W), feed to distiller ratio (0.06 - 0.14 g/mL), and extraction time (20 - 60 minutes). The existence of analysis of variance values (ANOVA) which indicates an important factor that determines the results of the study. From the analysis results obtained 4 parameters that have a significant effect (p-value <0.05), these parameters are microwave power (A), F/D ratio (B), Extraction Time (C) and the effect of extraction time squared (C2). The results showed that the optimum conditions were at microwave power 542.04 W, F/D ratio 0.07 g / mL, extraction time 44.5 minutes. From this optimum condition, the maximum prediction result is 4.45%. It can be neglected that these results indicate the suitability of the model used in the extraction of dry clove leaf essential oil (R² = 0.8906). Chemical analysis was also carried out using GC-MS. The results showed that the largest component was Eugenol 95.68%. While the physical properties, specific gravity 1.62 and solubility 1: 2. The results of the value analysis are in accordance with the range of quality standards SNI 06-2387-2006.

Key words – Optimization; Extraction; Clove Leaves; *Syzygium aromaticum*; SFME.

1. Introduction

Plants used by the essential oil industry are mostly native Indonesian plants. Essential Oil has many values, for personal use (domestic) or trading. Oil-producing plants are grown in Indonesia (approximately 45 types), there are about 15 types of plants as export commodities. One of them is spice plant, Clove (*Syzygium aromaticum*). It is an original plant from the Maluku Islands (Ternate and Tidore). Clove is potential as a producer of essential oils mostly extracted from the clove plant parts such as leaves, flowers, and stems. Clove leaves have not been used much by farmers, compared with flowers and cloves that are widely used for cigarette and food industry, clove leaves have an oil content of 1-4% and can be essential oil of high economical value. The content of compounds contained in clove oil such as (Eugenol, Caryophyllene, furfural, vanillin, tannin, Sitosterol, etc.). Eugenol is a major component compound of clove and colourless essential oil, has a distinctive spicy flavour and odour because it is mostly used for the fragrance and flavour industry [1].
Essential oils have many benefits, such as food flavourings, medicines and non-traditional medicines for many years [2]. And beneficial in pharmaceutical areas such as anti-cancer, antimicrobial, insecticidal and anti-parasitic properties [3]. The most common used essential oil extraction method from clove leaves is hydro-distillation (HD) using Clevenger and Soxhlet equipment, however this process requires a long extraction time. Thus, with the development of the current technology, the extraction is based on the renewable technology, namely microwave hydro distillation, ultrasound extraction, subcritical water, and supercritical fluid extraction. But it has some disadvantages such as a lot of solvent volume, high heat temperature, the presence of toxic solvents, and expensive equipment used. While research with microwave extraction, proves that microwave-based extraction technology is capable of being applied to different process systems that are more customizable with lower energy consumption and better environmental impingement [4].

Solvent-free microwave extraction (SFME) is one of the widely used extraction processes and this method is more efficient and better quality to produce essential oils [5] [6]. Equipment of SFME is a combination of microwave heating and dry distillation, in an atmospheric pressure and has a lot of advantages such as effective heating, fast energy transfer, time-saving and low operating costs [7,8]. Therefore, we use SFME method to extract essential oils from dried clove leaves. But in this process it still needs optimization to estimate the variables used during the extraction. And optimized by Response Surface Methodology (RSM), with Face-centred Central Composite Design (FCCD) is an effective application to correlate the individual effects and interactions between variables. The FCCD was chosen for this study, because this design suitable for researching quadratic response surfaces and development of a polynomial model. Advantages of FCCD was that it can estimate second-order and three-order, to detect correlations between the factors and to locate response optimal. Disadvantages of FCCD as compared to a three-level factorial design and inability to estimate certain interactive terms[9]. Therefore, the aim of this research is to perform the extraction process of clove essential oil using Solvent free microwave extraction by studying the effects of extraction parameters, such as microwave power, feed to distiller ratio and extraction time and finding optimal conditions with the response surface methodology using FCCD design.

2. Materials and Methods

2.1. Materials and experimental apparatus

![Schematic experimental apparatus for solvent-free microwave extraction.](image)

Figure 1 shows that a schematic representation for extraction of an essential oil from Dried Clove Leaf (Syzygium aromaticum) using solvent-free microwave extraction [9]. Raw material dried clove
leaves obtained from the area of Malang, East Java. Dried leaves are obtained by a leaves that had a water content of ± 15%. The leaves to be extracted are minced by a size of ± 2 cm. The chemical required for this research referred is 70% ethanol obtained from PT. Brataco Chemicals.

2.2. Solvent-Free Microwave Extraction

Solvent-free microwave extraction was conducted at atmospheric pressure with dry clove leaves (± 2 cm in size) using a commercial microwave (Electrolux EMM-2007X), 20 L volume, 800W maximum power, and 2.45 Ghz wave frequency (Fig. 1). First of all, the raw materials are weighed and immersed in water for 1 hour then separated the water and then introduced in a distiller flask. Then the operating variables were adjusted such as Microwave Power (300, 450, 600 W), extraction time (20, 40, 60 minutes) and the ratio between the mass of dry clove leaves and the volume of distiller (F/D): 0.06, 0, 10 and 0.14 g/mL. N-hexane is used to capture oil in the distilled water mixture that leaves the condenser. After that the oil is purified with the following calculation formula:

\[
\text{Yield} \left(\% \text{ w/w}\right) = \frac{\text{Mass of Extracted cloves oil}}{\text{Mass of dried cloves leaves} \times (1-\text{water content})} \times 100\% \quad (1)
\]

2.3. Chemical Analysis and Physical Properties of Clove Leaves Essential Oil

Oil components derived from the extraction of dried clove leaves, will be analyzed chemically using the Gas Chromatography-Mass spectrometry (GC-MS) with AGILENT 6980N chromatography gas which is connected to the mass of AGILENT 5973 spectrometry. It uses the HP-5 column (column length 30 m, internal diameter of 0.25 μm, and 0.32 mm thickness of the film). Helium is as a carrier gas and most of the components are identified by the mass spectrum. While the physical nature of clove oil, analyzed by testing the density and solubility in alcohol. Density analysis is performed using Pycnometer, while analyzing the solubility using 70% ethanol.

2.4. Response Surface Methodology (RSM)

The extraction of essential oils from dried clove leaves with Solvent-Free Microwave Extraction (SFME) method is optimized using the Surface Methodology (RSM) response. RSM is required for optimization of selected process parameters with Face-Centered Central Composite Design (FCCD), this method was chosen to model, optimize and analyze the interactions and effects of each variable using Design Expert version 11 (State-Ease Inc, Minneapolis, MN, USA) was applied to 20 experiments to optimize the 3 variables studied: Microwave power (A), ratio (F/D) (B) and Extraction Time (C) shown in Table 1. Where the microwave power value ranges between 300W-600W, the F/D ratio ranged from 0.06 g/mL-0.14 g/mL, while the extraction time ranged from 20min-60min.

| Factors             | Unit | Low  | Middle | High |
|---------------------|------|------|--------|------|
| A: Microwave Power  | W    | 300  | 450    | 600  |
| B: F/D Ratio        | g/mL | 0.06 | 0.10   | 0.14 |
| C: Extraction Time  | min  | 20   | 40     | 60   |

To predict the optimal point on the quadratic equation model is presented as Maran Prakash J. And Manikandan S. (2012) [10] with the Eq.2:

\[
Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \sum_{j=2}^{k} \beta_{ij} X_i X_j + \varepsilon \quad (2)
\]

Where Y is the experimental response, X_i and X_j were variables (A; B and C), \(\beta_0\) was a constant, \(\beta_i\); \(\beta_{ij}\) were the coefficients, \(\varepsilon\) was an error factor, while k was the number of variables. Coefficient is determined by multiple linear regression approaches [11].
3. Result and Discussion

The purpose of the research is to determine the optimal variable value used (microwave power, F/D ratio and extraction time) by means of Response Surface Methodology (RSM) which provides the identification of the optimal conditions needed to achieve maximum results. FCCD is applied with Design Expert version 11 on the ground of 20 experiments aiming to obtain the optimum yield of Clove Leaves Oil, can be seen in Table 2. ANOVA (analysis of variance) was used to show the important criteria in certifying modeling and identifying important factors that affect yield results with p-value = 0.05.

| No. | Microwave power (W) | F/D ratio (g/mL) | Extraction time (min) | Experimental Yield (%) | Predicted Yield (%) | Residual |
|-----|---------------------|------------------|-----------------------|------------------------|---------------------|----------|
| 1   | 300                 | 0.1              | 40                    | 2.077391               | 2.733838            | -0.65645 |
| 2   | 300                 | 0.14             | 20                    | 0.705431               | 0.271725            | 0.433706 |
| 3   | 300                 | 0.14             | 60                    | 2.613556               | 2.598704            | 0.014852 |
| 4   | 300                 | 0.06             | 60                    | 4.136866               | 3.679008            | 0.457678 |
| 5   | 300                 | 0.06             | 20                    | 1.920454               | 2.170242            | -0.24979 |
| 6   | 450                 | 0.1              | 40                    | 3.570511               | 3.212727            | 0.357784 |
| 7   | 450                 | 0.1              | 40                    | 3.570511               | 3.212727            | 0.357784 |
| 8   | 450                 | 0.1              | 60                    | 2.753999               | 3.231476            | -0.47748 |
| 9   | 450                 | 0.14             | 40                    | 2.466845               | 2.896377            | -0.42953 |
| 10  | 450                 | 0.1              | 40                    | 3.558496               | 3.212727            | 0.345769 |
| 11  | 450                 | 0.1              | 20                    | 1.523736               | 1.423987            | 0.099748 |
| 12  | 450                 | 0.1              | 40                    | 2.990913               | 3.212727            | -0.22181 |
| 13  | 450                 | 0.1              | 40                    | 3.038172               | 3.212727            | -0.17456 |
| 14  | 450                 | 0.1              | 40                    | 3.523417               | 3.212727            | 0.31069  |
| 15  | 450                 | 0.06             | 40                    | 4.243038               | 4.191234            | 0.051804 |
| 16  | 600                 | 0.06             | 20                    | 3.545835               | 3.466254            | 0.07958  |
| 17  | 600                 | 0.14             | 20                    | 1.593598               | 1.956844            | -0.36325 |
| 18  | 600                 | 0.14             | 60                    | 4.407277               | 4.063057            | 0.344221 |
| 19  | 600                 | 0.1              | 40                    | 4.392739               | 4.11402             | 0.278719 |
| 20  | 600                 | 0.06             | 60                    | 4.414979               | 4.754253            | -0.33927 |

ANOVA analysis can be seen in Table 3, which shows that the F-value of the model was 9.95 and p-value 0.0006 which means that the model is significant. And in this study, the factors that influence the identification results with the p-value < 0.05 which have a big impact on yield, were on the parameters of microwave power (A), F/D ratio (B) and extraction time (C). As for the interaction between variables has a p-value >0.05, it can be interpreted that the interaction between variables does not have a significant effect. Therefore, this model can be used to design space maneuvers.

The response curve, illustrated by 2D and 3D contour, was used to identify the correlation between variables and estimate the maximum value of each variable that will show the optimal value. The response curve is shown in Fig. 2, with the explanation (a) Interaction between Microwave power and F/D ratio in respect to the yield at a constant extraction time; (b) Interaction between Microwave power and extraction time in respect to the yield at a constant F/D ratio; (c) The interaction between the F/D ratio and extraction time in respect to the yield at a constant Microwave power.

Fig. 2(a) Indicates that the yield increases when the microwave power is high. This is because the higher the power, the faster the temperature achievement. Microwave power on SFME as a driving force due to the breakdown of cell membrane structure of plants and causing diffused oil and presence of dissolution [12]. Fig.2(b) Increasing extraction time with microwave power will increase the extraction yield of essential oils.
Table 3. ANOVA of operating conditions

| Source         | Sum of Squares | df | Mean Square | F-value | P-value |
|----------------|----------------|----|-------------|---------|---------|
| Model          | 19.78          | 9  | 2.20        | 9.95    | 0.0006  |
| A-Microwave power | 4.76         | 1  | 4.76        | 21.56   | 0.0009  |
| B-F/D ratio    | 4.19           | 1  | 4.19        | 18.98   | 0.0014  |
| C-Extraction time | 8.17          | 1  | 8.17        | 36.98   | 0.0001  |
| AB             | 0.0757         | 1  | 0.0757      | 0.3428  | 0.5712  |
| AC             | 0.0244         | 1  | 0.0244      | 0.1103  | 0.7466  |
| BC             | 0.3347         | 1  | 0.3347      | 1.52    | 0.2464  |
| A²             | 0.1227         | 1  | 0.1227      | 0.5554  | 0.4733  |
| B²             | 0.3014         | 1  | 0.3014      | 1.36    | 0.2698  |
| C²             | 2.15           | 1  | 2.15        | 9.75    | 0.0108  |
| Residual       | 2.21           | 10 | 0.2208      |         |         |
| Lack of Fit    | 1.86           | 5  | 0.3722      | 5.35    | 0.0447  |
| Cor Total      | 21.99          | 19 |             |         |         |

Fig. 2(c), shows that Interactions F/D ratio also affects the extraction of Clove oil can be extracted well (density factor of low). While the increase in the F/D ratio, the yield was decreased (increased density in the distiller, and caused difficulties to extract). So, the difficulty of steam penetrates raw materials to propagate clove oil molecules from the ingredients. This density relates to the inter-material space in the Distiller, and can lead to the formation of steam lines that can reduce the yield and quality of clove oil.

![Fig 2(a)](image1.png)  ![Fig 2(b)](image2.png)  ![Fig 2(c)](image3.png)

Fig 2. Response surfaces 2D and 3D contour plots showing effect of (a) the microwave power and the F/D ratio on the yield at a constant extraction time (44.494 min), (b) the microwave power and the extraction time on the yield at a constant F/D ratio (0.07042 g/mL), (c) the F/D ratio and the extraction time on the yield at a constant microwave power (542.037 W)
In addition, after the extraction process getting optimal results, the equation below was used to predict the yield of clove leaves oil and also Eq.3 was used, so a contour plot is obtained. And from this research result, the yield value is \( R^2 = 0.8096 \) which shows the suitability of the model used in the extraction of dried clove leaves.

\[
\text{Yield} = 2.805 - 0.047 A - 75.094 B + 0.205 C + 206.924 B^2 - 0.0022 C^2 \quad (3)
\]

In this study, chemical and physical properties were analyzed to determine the quality of clove leaves oil obtained using Solvent-Free Microwave Extraction (SFME) method. The test results were then compared with the quality standard of clove leaves oil about the purity of the essential oil, with the method in this study the results have a clear oil appearance.

**Table 4.** A comparison of Clove Leave Oil component groups determined by GC-MS analysis

| No | Component           | % Composition |
|----|---------------------|---------------|
| 1  | Alpha-Cucubene      | 0.09          |
| 2  | Eugenol             | 95.68         |
| 3  | Delta-Cadinene      | 0.33          |
| 4  | Carphyllene oxide   | 2.99          |
| 5  | Santolina triene    | 0.88          |

Chemical analysis with GC-MS was expected to be extracted according to SNI 06-2387-2006. The results of the analysis showed that the content of the Eugenol component was 95.68%, this was due to the reduction in thermal and hydrolytic effects [13], as shown in Table 4, the GC-MS analysis results from a sample of clove leaves oil extraction with Microwave Power of 600 W, F/D ratio of 0.1 g/mL and extraction time of 40 min. Eugenol is major compound characteristic of clove leaves essential oil. When analyzing the chemical composition of clove leaves essential oil, Cassiana et al [14] found a content of 29.84% eugenol by supercritical CO\(_2\) and 5.67% eugenol using soxhlet method. Comparing with research using other methods, the results of the highest Eugenol components were using the SFME method. The principle of this method is the water in the plant cell is stimulated to rotate under microwave radiation, so it can quickly change the arrangement of cells in the plant due to increased pressure in the plant cells. This will result in rupture of the cell and the discharge of the desired material[15]. As for the results of physical properties analysis can be seen in Table 5, shows the specific gravity of clove leaf oil has a value between the range of SNI values. In the solubility test, the results show that the solubility obtained is appropriate to SNI standards.

**Table 5.** Physical properties of Clove Leaves Oil

| Physical properties | SNI 06-2387-2006 | Extraction Results |
|---------------------|------------------|--------------------|
| Density (20°C)      | 1.025 - 1.049    | 1.048              |
| Solubility in Ethanol 70% (ml/ml) | 1 : 2 | 1 : 2 |

4. **Conclusion**

Extraction of essential oils from dried clove leaf by using Solvent-free microwave extraction (SFME) shows that the yield increase with extraction time dan microwave power. The experimental design proves that optimal results can be obtained on certain variables. Extraction experiment results showed that the optimum conditions at 542,037 W microwave power, F / D ratio 0.07 g / mL, extraction time 44.5 minutes. From this optimal condition, the predicted maximum yield is 4.45%. It can be concluded that these results indicate the suitability of the model used in the extraction of essential oils from dried
clove leaves (R2 = 0.8906). From GC-MS result, as the chemical analysis shows that essential oils contain a high content of Eugenol, which is 95.68%, in appropriate to the essential oil criteria which have a minimum Eugenol content of 78% (SNI 06-2387-2006). The result of physical properties analysis has a specific gravity of oil that is 1.062 g/mL and cloves leaf oil solubility of 1:2, it can be concluded that the extraction of clove oil using SFME method has a value in the range of quality requirements to SNI 06-2387-2006 quality standards.

Acknowledgment
This research was supported financially by the Directorate General of Research and Technology Strengthening Research and Development of Higher Education of the Republic of Indonesia (RISTEKBRIN) under the scheme of a Basic Research fund.

References
[1] Ministry of Trade R I 2011 Indonesian Essential Oils : The Scents of Natural Life vol 1st
[2] Deans S G 1997 Bioactivity of selected plant essential oils against Listeria monocytogenes J. Appl. Microbiol. 82 759–62
[3] Lang G and Buchbauer G 2012 A review on recent research results (2008–2010) on essential oils as antimicrobials and antifungals Flavour Fragr. J. 27 13–39
[4] Bustamante J, van Stempvoort S, García-Gallarreta M, Houghton J A, Briers H K, Budarin V L, Matharu A S and Clark J H 2016 Microwave assisted hydro-distillation of essential oils from wet citrus peel waste J. Clean. Prod. 137
[5] Mahfud M, Putri D K Y, Dewi I E P and Kusuma H S 2017 Extraction of essential oil from cananga (Cananga odorata) using solvent-free microwave extraction: A preliminary study Rasayan J. Chem. 10 86–91
[6] Kusuma H, Putri D, Dewi I and Mahfud M 2016 Solvent-free microwave extraction as the useful tool for extraction of edible essential oils Chem. Chem. Technol. 10 213–8
[7] Lucchesi M E, Smadja J, Bradshaw S, Louw W and Chemat F 2007 Solvent free microwave extraction of Elletaria cardamomum L.: A multivariate study of a new technique for the extraction of essential oil J. Food Eng. 79 1079–86
[8] Kusuma H S and Mahfud M 2016 Preliminary study: Kinetics of oil extraction from basil (Ocimum basilicum) by microwave-assisted hydrodistillation and solvent-free microwave extraction South African J. Chem. Eng. 21 49–53
[9] Fewer, Branchu; S, Forbes ;R, York ;P, Nyqvist ;H S 1999 CCD for Investigating Stability of Liposomes Pharm. Res. 16 702–8
[10] Maran Prakash J and Manikandan S 2012 Response surface modeling and optimization of process parameters for aqueous extraction of pigments from prickly pear (Opuntia ficus-indica) fruit Dye. Pigment. 95 465–72
[11] Mangili I, Lasagni M, Huang K and Isayev A I 2015 Modeling and optimization of ultrasonic devulcanization using the response surface methodology based on central composite face-centered design Chemom. Intell. Lab. Syst. 144 1–10
[12] Hu Z, Cai M and Liang H 2008 Desirability function approach for the optimization of microwave-assisted extraction of saikosaponins from Radix Bupleuri 61 266–75
[13] Ferhat M A, Meklati B Y, Smadja J and Chemat F 2006 An improved microwave Clevenger apparatus for distillation of essential oils from orange peel 1112 121–6
[14] Cassiana P, Andressa K, Palú F, Cardozo-filho L and Antônio E 2019 Evaluation of the effects of temperature and pressure on the extraction of eugenol from clove (Syzygium aromaticum) leaves using supercritical CO2 J. Supercrit. Fluids 143 313–20
[15] Li Y, Fabiano-tixier A S, Vian M A and Chemat F 2013 Solvent-free microwave extraction of bioactive compounds provides a tool for green analytical TRENDS Anal. Chem. 47 1–11