Eugenol Production from Clove Oil in Pilot Plant Scale for Small and Medium Enterprises (SME)

Ali Nurdin[1]
[1]*Pusat Teknologi Sumberdaya Energi dan Industri Kimia, Badan Pengkajian dan Penerapan Teknologi, Puspiptek Serpong, Indonesia*

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Abstract: Clove oil was the largest essential oil commodity in Indonesia and production at Small and Medium Enterprises (SME) was still below the standard quality due to low eugenol levels (70-80%). The eugenol level can be increased by isolation which generally can be carried out by saponification and neutralization methods. This method was the most widely used, inexpensive, and easy to scale-up from the laboratory scale to the pilot plant scale. In this research, the production of eugenol from clove oil has been carried out in a pilot plant scale with stages of saponification reaction using sodium hydroxide and neutralization using sulfuric acid followed by vacuum distillation. All stages of this process produce eugenol with a yield of 50.25%, and an increase in eugenol levels from 75% to 98%. The eugenol production technology that has been carried out was expected to provide a solution for the small clove oil industry to improve its quality.

1 INTRODUCTION

Indonesia is one of the major Asian producers of clove besides India, Malaysia and Sri Lanka (Kamatou, et al., 2012). Clove oil production in Indonesia reached 2500 MT – 3000 MT (Dewan Atsiri Indonesia, 2017). Most of the clove oil is produced in some small industries (Industri Kecil dan Menengah/IKM). There are several types of clove oil, namely clove bud oil, clove stem oil, and clove leaf oil (Anonim, 2013), but the most is clove leaf oil.

Clove oil consists of a mixture of a different compounds, with the main compound being eugenol, eugenyl acetate, and caryophyllene. The quality of clove oil is determined by eugenol. Eugenol is a phenolic compound, which is weakly acidic, slightly soluble in water and soluble in organic solvents (Kamatou, et al., 2012). Eugenol has many roles both in flavor, fragrance, and pharmacology. Standar Nasional Indonesia (SNI) requires minimum eugenol content in clove oil is 78% (v/v) (Badan Standardisasi Nasional, 2006). Clove leaf oil from the distillation of farmers (small industries) generally has not been able to fulfill this requirement, and this is still become the problem for small clove oil industries (Widayat and Hardiyanto, 2016). The eugenol content in clove leaf oil is influenced by various factors such as soil type, distillation time, type of plant, and equipment of distillation. Therefore further processes are needed to improve eugenol content (Sastrohamidjojo and Fariyatun, 2016)

There are some methods can be used on the isolation of eugenol in order to increase eugenol contents. The most common method for eugenol isolation is saponification-distillation. Several methods have been modified to get more efficient as compared to the traditional method, like microwave-assisted extraction (Kapadiya, et al., 2018), supercritical carbon dioxide extraction (Cassiana et al., 2019), ultra-sound assisted extraction (Khalil et al., 2017), and polymeric membrane technology (Kusworo, 2018)

The eugenol isolation method that can be applied to small industries (IKM) by considering the availability of equipment, a simple production method and energy-efficient is the saponification-distillation method. In this research, eugenol isolation from clove leaf oil using saponification-distillation method was studied in the pilot plant scale. Clove leaf oil was saponified with sodium hydroxide and neutralized with sulfuric acid followed by separation using distillation. The result obtained from this research would be beneficial for the IKM applicability to give simple method on eugenol production.

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2 MATERIALS AND METHODS

2.1 Materials

The clove leaf oil (CLO) from small industry in Jawa Timur, sodium hydroxide (NaOH) technical grade, and sulfuric acid (H_2SO_4) technical grade.

The equipment for isolation eugenol in the pilot plant scale was described in Figure 1. Chemical composition was determined by Gas Chromatography-Mass Spectrometer (GCMS) Agilent 6890.

2.2 Methods

2.2.1 Clove Leaf Oil Characterization

The characterization was carried out on clove leaf oil includes specific gravity, refractive index, solubility in alcohol and chemical component using GCMS.

2.2.2 Determination of Sodium Hydroxide Concentration Excess for Saponification

This experiment was done in laboratory scale, to observe the effect of sodium hydroxide excess on the saponification process. CLO was mixed with NaOH in varying excess concentrations (3%, 5%, and 10%). The mixture was stirred with a magnetic stirrer for 30 minutes and then allowed to stand 24 hours, there will be two layers, the top layer is an organic layer and the bottom layer contains sodium eugenolate layer. The separation was observed to determine NaOH concentration optimum.

2.3.3 Eugenol Isolation in the Pilot Plant Scale

Eugenol isolation was being carried out in three-stages. The first stage was saponification using NaOH, followed by neutralizing with sulfuric acid 98% and vacuum distillation. This experiment was done in a pilot plant scale using equipment was described in Figure 1. CLO was mixed with NaOH (the concentration NaOH was obtained from the previous experiment) for 30 minutes and decanted for 12 hours.

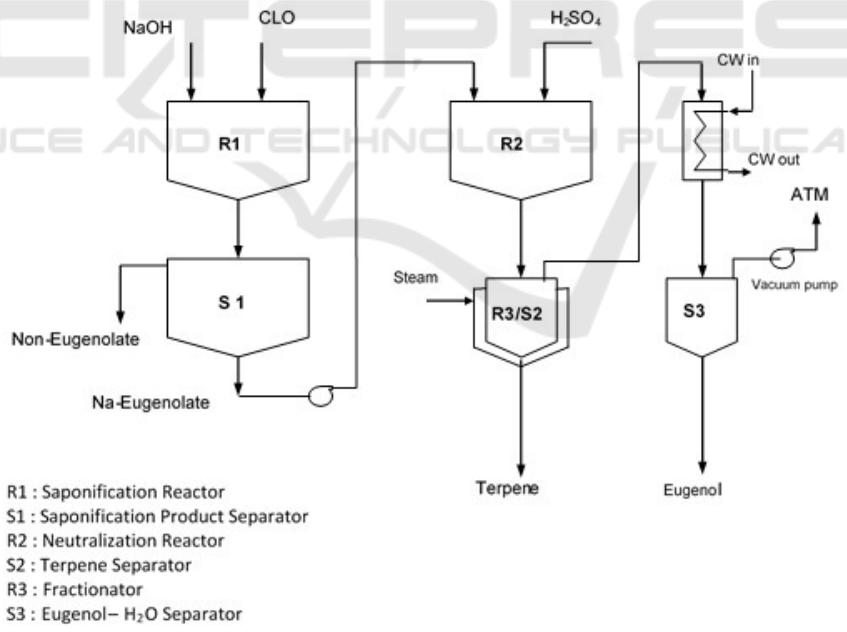

Figure 1: Scheme of eugenol production equipment

Na-eugenolate was neutralized with H_2SO_4 98% until pH 5-7 and continued with decantation. The eugenol product was distilled in atmospheric on 120°C to separate water and other component in crude eugenol and continued with vacuum distillation on 140°C-150°C. The results were analyzed by GCMS.

3 RESULTS AND DISCUSSION

3.1 Characterization of Clove Leaf Oil

The results of clove leaf oil characterization of which includes physical and chemical properties can be seen in Table 1. The characteristics of clove leaf oil in general, include relative density, refractive index, and miscibility in ethanol appropriated with the requirements in SNI 06-2387-2006 Clove leaf oil.

Table 1: Clove oil characterization

Specification	Unit	Result	Requirements in SNI 06-2387-2006
Relative density at 20°C	-	1.024	1.025 – .,049
Refractive index ($^nD_{20}$)	-	1.53	1.528 – 1.535
Miscibility in ethanol 70%, 20°C	-	1:2 clear	1 : 2 clear

Figure 2 shows the analysis of clove leaf oil using GCMS. The chromatogram has 5 peaks on retention time 23.007 min to 31.147 min, with two major components are eugenol (75.22%) and beta-caryophyllene (15.40%), and the others small quantities components such as alpha humulene, delta cadinene and caryophyllene oxide (Table 2).

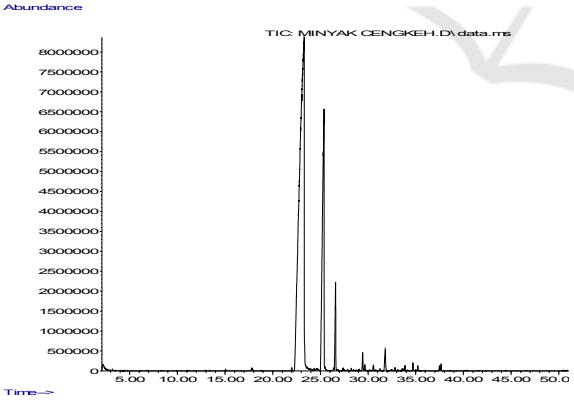

Figure 2: GCMS chromatogram of clove leaf oil

Standard quality for clove leaf oil (SNI 06-2387-2006 Clove leaf oil) requirements minimum eugenol content was 78%. Eugenol contents in clove leaf oil from small industry in Jawa Timur is 75.22%, so it is below standard trade and needs to improve.

Table 2: Chemical compound composition in clove leaf oil

Chemical compound	Abundance (%)
Eugenol	75.22
beta-Caryophyllene	15.40
Alpha-humulene	3.51
Delta-cadinene	1.60
Caryophyllene oxide	3.22

3.2 The Optimization of NaOH Excess on Saponification

Saponification is a reaction in which an ester is mixed with an alkali, such as sodium hydroxide producing a carboxylate salt. Eugenol as an ester reacted with sodium hydroxide to form sodium eugenolate salt:

$$\text{Eug-OH} + \text{NaOH} \longrightarrow \text{Eug-ONa} + H_2O$$

Clove leaf oil which was originally blackish brown when it was added with NaOH became Na-eugenolate (turbid yellow). NaOH excess concentration was added in this experiment are different (3%, 5%, and 10%). 15 minutes after stopped the mixing, the two layers were formed, yellow liquid in the bottom layer (Na-eugenolate) and brown liquid in the top of the layer (organic layer).

The Na-eugenolate forming was not perfect in NaOH excess 3%, the separation between organic layer (terpene) and aqueous layer (Na-eugenolate) have not be seen yet. It indicated that all of eugenol has not converted to Na-eugenolate on NaOH excess 3% so the NaOH concentration must be increased. NaOH excess 5% gave the good separation between terpene and Na-eugenolate, therefore the separation was quick and more obvious with NaOH excess 10%. However, the NaOH excess 5% was selected for the saponification process in this experiment because the eugenol conversion was complete and the NaOH amount was not too excess. Some previous studies used NaOH excess concentration in 3% (Khalil et al., 2017); 5% (Sastrohamidjojo and Fariyatun, 2016); and 2 M (Just et al., 2016) which gave optimum alkali concentration in saponification.

3.3 The Eugenol Isolation in the Pilot Plant Scale

The eugenol isolation in the pilot plant scale can be described in three main steps simultaneous saponification and distillation. Briefly, the steps can be described as follows: saponification using NaOH, neutralization with H2SO4 and separation with decantation. Clove leaf oil as raw material was used about 200 litres (204.8 kg). The saponification

process with NaOH 5% excess needs 39 kg of NaOH (or 40 kg of NaOH flake with purity is 98%).

Saponification process carried out in R1 column (Saponification Reactor). NaOH flake dissolved in 1296 litres of water while stirring to get concentration 3%-wt. After dissolving, clove leaf oil was poured to R1. Saponification reaction in R1 fast. The result of saponification was formed two layers, the upper layer was an organic layer (terpene layer) and the bottom layer was aqueous layer Na-eugenolate layer. Eugenol was reacted with NaOH to form Na-eugenolate which is soluble in water. The other component of clove leaf oil except eugenol such as caryophyllene was not reacted with NaOH and insoluble in water. This mixture was flowed in S1 to separate the layers with decantation. Na-eugenolate was streamed to R2 (neutralization reactor) and the terpene layer was collected. This process results in 52,3 litres of a terpene.

Na-eugenolate layer in R2 was added with 49 kg of H_2SO_4 98% to neutralization. The neutralization reaction is:

$$NaO\text{-}Eug + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O + Eug$$

During the addition of acid, the solution was stirred for 30 minutes and the pH was 4,0. The Na-eugenolate was converted to eugenol and Na2SO4 salt was formed. The eugenol was on the bottom layer and Na2SO4 salt was on the upper layer. The eugenol content was 96%. This process results in 157.3 kg of eugenol. The eugenol layer was streamed to R3 (distillation unit) to purification and the salt in R2 was discarded.

The distillation unit (R3) is a distillation reactor with a steam heater, agitator, condenser, storage tank, vacuum pump, and sight glass. The distillation process was carried out using steam distillation. In R3, the process was continued with eugenol purification step using atmospheric distillation and vacuum distillation. The atmospheric distillation intends to separate water and initial fraction that might still be passed of crude eugenol. It has been done at (±120ºC). The heating was carried out until the liquid in the tank are no turbulent when the stirrer is stopped. After the water was separated, the distillation was continued with vacuum distillation on effective pressure 750 mmHg below zero (outside air pressure was 1 atm) and the eugenol distillation temperature was 140ºC-150ºC (in 1 atm, the boiling point of eugenol is 225ºC. because the R3 distillation column only 100 litres, and for safety, carry out was only filled about 90 litres, hence to process 157.3 kg of crude eugenol was carried out with 4 steps. Each step was 90 litres after the residue was only 45 litres the distillate was taken and the residue was added with new eugenol.

Figure 3 and 4 show the chromatogram of eugenol and terpene that were analyzed by GCMS. The GCMS chromatogram in Figure 3 showed the mayor peak in retention time 23.007 which is the eugenol peak with the abundance was 98%. The next peak was beta-caryophyllene. The terpene fraction in Figure 4 showed some peaks with retention time from 22.733 to 31.337. The major component in terpene fraction was beta-caryophyllene and alpha-caryophyllene (Table 4).

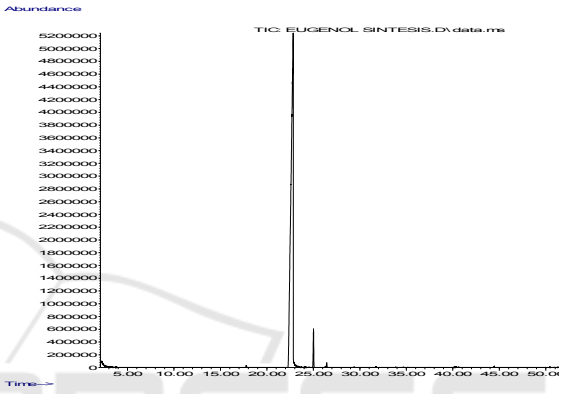

Figure 3: GCMS chromatogram of eugenol

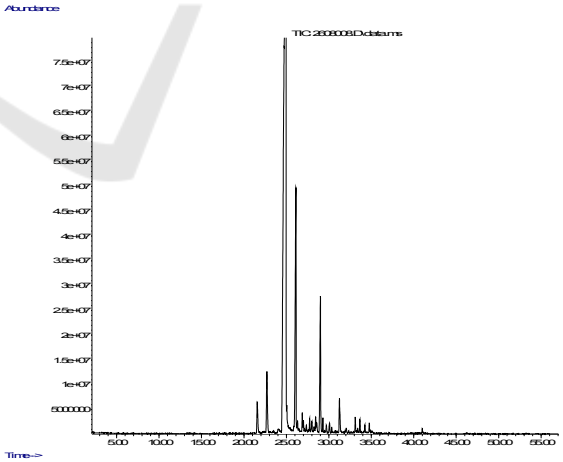

Figure 4: GCMS chromatogram of terpene

Table 3: The summarize of materials and product

CLO (kg)	NaOH (kg)	H_2SO_4 (kg)	Eugenol (kg)	Yield (%)	Terpene (L)
204.8	39	49	102.5	50.25	52.3

Terpene of clove leaf oil as the side product in eugenol isolation has some benefit. Beta-caryophyllene has been commonly used as a fragrance and flavour. In recent years, beta-caryophyllene has attracted to observe because it's biological activities, like antimicrobial and antioxidant (Liu et al., 2013).

Table 4: Chemical compound in terpene

No	Retention time	Compound	Abundance (%)
1	22,733	α-copaene	3,37
2	24,857	β-caryophyllene	63,97
3	26,124	α- caryophyllene	14,28
4	28,972	δ- cadinene	4,27
5	31,337	caryophyllene oxide	4,48

4 CONCLUSIONS

Eugenol isolation from clove leaf oil using a saponification-distillation method in the pilot plant scale was successfully increase the eugenol content from 75% to 98% with the yield was 50.25%. This technology has beneficial in IKM applicability to improve the clove oil quality.

REFERENCES

Anonim, 2013. *The Complete Book on the Spices and Condiments (With cultivation, processing and uses)*.

Badan Standardisasi Nasional, 2006. *Minyak daun cengkih*.

Cassiana, P. *et al.,* 2019. 'Evaluation of the effects of temperature and pressure on the extraction of eugenol from clove (Syzygium aromaticum) leaves using supercritical CO 2', *The Journal of Supercritical Fluids*. Elsevier, 143(July 2018), pp. 313–320. doi: 10.1016/j.supflu.2018.09.009.

Dewan Atsiri Indonesia, 2017. 'Indonesian Essential Oil Output'.

Just, J. *et al.*, 2016 'Extraction of Eugenol from Cloves Using an Unmodi fi ed Household Espresso Machine: An Alternative to Traditional Steam-Distillation', (iii). doi: 10.1021/acs.jchemed.5b00476.

Kamatou, G. P., Vermaak, I. and Viljoen, A. M, 2012. 'Eugenol—From the Remote Maluku Islands to the International Market Place: A Review of a Remarkable and Versatile Molecule', pp. 6953–6981. doi: 10.3390/molecules17066953.

Kapadiya, S. M., Parikh, J. and Desai, M. A., 2018. 'A greener approach towards isolating clove oil from buds of Syzygium aromaticum using microwave radiation', *Industrial Crops & Products*. Elsevier, 112(November 2017), pp. 626–632. doi: 10.1016/j.indcrop.2017.12.060.

Khalil, A. A. *et al.*, 2017 'Essential oil eugenol: sources, extraction techniques and nutraceutical perspectives', *RSC Advances techniques and nutraceutical perspectives*, pp. 32669–32681. doi: 10.1039/c7ra04803c.

Kusworo, T. D., 2018 'Study of Polymeric Membranes Potential for Eugenol Purification from Crude Clove leaf Oil', *Asean Journal of Chemical Engineering*, 18(2), pp. 81–92.

Liu, H. *et al.*, 2013 'Physicochemical characterization and pharmacokinetics evaluation of β-caryophyllene/β-cyclodextrin inclusion complex', *International Journal of Pharmaceutics*. Elsevier B.V., pp. 1–7. doi: 10.1016/j.ijpharm.2013.04.013.

Sastrohamidjojo, H. and Fariyatun, E., 2016. 'Synthesis of Methyl Eugenol from Crude Cloves Leaf Oil Using Acid and Based Chemicals Reactions', 9(10), pp. 105–112. doi: 10.9790/5736-091002105112.

Widayat, Hardiyanto, H. S., 2016. 'Implementasi Proses Adsorbsi Dalam Meningkatkan Kualitas Minyak Cengkeh', in *Simposium Nasional RAPI XV - 2016 FT UMS*, pp. 1–7.