Improvement of Clove Oil Quality by Using Adsorption-distillation Process

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Research Article

Improvement of Clove Oil Quality by Using Adsorption-distillation Process

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Abstract: The objective of this research was to improve the quality of clove oil by using adsorption-distillation process. Clove oil is one of essential oil products extracted from clove plants and currently considered as the most main product of Essential Oils Cluster in Batang Regency, Central Java. The main problem of essential oil production is low product quality due to high level of Eugenol and dark color of oil which does not met the National Standard. Therefore, process improvement was required to increase product quality as well as yield of product. The results showed that equipment material contributes significantly to the colors due to the availability of Fe ions. The addition of citric acid of 0.6-10% could improve the colors. The stirring process was proved as important variables to yield of products, while optimum time and temperature were optimum at 60 min and 50°C, respectively.

Keywords: Adsorption, eugenol, oil, stirred tank, the percentage of Fe bound

INTRODUCTION

Batang District is one of the largest regions of clove oil productions in Central Java Indonesia. The number of oil refineries in this area is more than 30 units which owned by a Small Medium Entrepreneurship (SME). This SME produces clove oil, clove stem oil and patchouli oil which reaches 20% of production growth (Profil Kluster Minyak Atsiri Kabupaten Batang Propinsi Jawa Tengah, 2011).

Clove oil is an essential oil extracted from clove plants (*Eugenia caryophyllata* thunb), especially from its flowers, stems and leaves. The quality of clove oil is normally indicated by its eugenol and carryophyllene contents (Badan Standarisasi Nasional, 2006). The content of eugenol in oil is mainly affected by quality of raw materials and oil refining methods. The highest eugenol level is shown by oil extracted from flowers and stem of clove plants (Table 1).

Eugenol is an alkyl bond ($C_{10}H_{12}O_2$) or 2-methoxy-4- (2-propenyl) phenol and it is a member of the alkyl benzene. Eugenol is very reactive to the strong base such as NaOH and KOH. Apparently, eugenol is liquid form with colourless or slightly yellowish and it is soluble in alcohol, chloroform and ether and slightly soluble in water, smelling clove oil, burning taste and heat in the skin. The boiling point of eugenol is 256°C and flash point of 104°C while the vapor pressure of 10 mmHg at 123°C. The chemical structure of eugenol is shown in Fig. 1 and it has density of 1.064 to 1.068 g/mL, a molecular weight of 164.20 g/mol and a refractive index of 1.541 at 20°C.

Table 1: Eugenol content in clove oil (Guenther, 1987)

Sources	Content (%)
Flower	90-95
Stem	83-95
Leaf	82-87

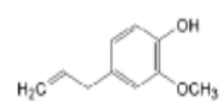

Fig. 1: Chemical structure of eugenol

The eugenol is mostly utilized in the perfume industries, flavor concentrates and in the pharmaceutical industry-as an antiseptic and anesthetic drug. It is also used to produce isoeugenol as a raw material in the manufacture of vanillin. Oyedemi *et al*. (2009) studied the use of eugenol for the metabolic activity of bacteria types *Listeria monocytogenes*, *Streptococcus pyogenes*, *Escherichia coli* and *Proteus vulgaris*. Cheng *et al*. (2008) utilize this compound and sinamaldehid as an anti-fungal for the type of fungus and *Laetiporus sulphureus*, which is considerable as inhibitory activity. Shelly *et al*. (2010) used methyl eugenol (eugenol derivative) to increase fertility of insects and the results were quite promising. Sadeghian *et al*. (2008) have conducted a synthesis of eugenol derivatives and tested to inhibit the activity of the enzyme 15-lipogenase. This enzyme was involved in many diseases such as asthma and lung cancer. The results showed that the compound could inhibit the performance of the enzyme 15-lipogenase. Furthermore, Chami *et al*. (2004) also have tested

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eugenol as anti fungus *Candida albicans*. Vidhya and Devaraj (2011) experienced eugenol for inducing lung cancer, which showed inhibitory phenomena in lung cancer.

The main problem faced by the SME in Batang District are low product quality due to availability of eugenol and darkness of colour (Profil Kluster Minyak Atsiri Kabupaten Batang Propinsi Jawa Tengah, 2011). The solution of this problem has been attempted by several researches by using bleaching agent. This method showed an extraction of eugenol content from 80 to 82% (Silviana and Dan Errysa, 2006). In other hand, citric acid and Na_3EDTA were also used to improve quality of clove oil (Marwati *et al*., 2005; Silviana, 2007; Ma'mun, 2008). However, the levels of eugenol were still lower than required by the EOA (Essential Oil Association) of USA (1975). Therefore, the objective of this research was to study process improvement to produce high product quality by using adsorption-distillation process. Adsorption process showed an interesting technology to overcome the problem of dark colour of oil as normally found by conventional process (Silviana and Dan Errysa, 2006; Silviana, 2007; Ma'mun, 2008; Marwati *et al*., 2005). The distillation was integrated to solve the eugenol content.

MATERIALS AND METHODS

Materials: The clove oil used in this research was obtained from clove oil cluster at Batang District, Central Java. The raw material was analyzed under Indonesian Standard method for its colour and odour, refractive index, density, viscosity, solubility in ethanol and eugenol total. Moreover, raw materials were also analyzed by gas chromatography. Citric acid was utilized for the colour quality improvement. The purification of eugenol has been performed by using NaOH and HCl and done in Laboratory of Process Engineering, Department of Chemical Engineering, Diponegoro University. The equipment used was a laboratory scale and pilot plant scale which was the result of the design and production-scale trials.

Experimental design: The experiment was carried out at in a laboratory scale under batch processes (Fig. 2). The clove oil volume was set at 200 mL under atmospheric pressure (1 atm), while the citric acid was varied between 3-6% and operation temperature of 40-60°C. The Design of Experiment was used response surface methodology (Box *et al*., 1978). The response surface methodology was used to formulate the number of experiment which was tabulated in Table 2.

Experimental procedure: The adsorption experiment was performed by using citric acid and heating was applied between 50-70°C in an Erlenmeyer equipped with a stirrer for 1 h. The effluent of this heating process is then purified by using citric acid in a vacuum pump strainer.

Fig. 2: Experimental set up with batch process

Table 2: Experimental design

Run	Citric acid %	Temperature °C	Respond
1	3.00	40.0	Y_1
2	3.00	60.0	Y_2
3	6.00	40.0	Y_3
4	6.00	60.0	Y_4
5	4.50	50.0	Y_5
6	2.38	50.0	Y_6
7	6.62	50.0	Y_7
8	4.50	35.9	Y_8
9	4.50	64.1	Y_9
10	4.50	50.0	Y_{10}

Table 3: Raw material analysis and comparison to standard

Parameter	Analysis	SNI 06-2387-2006
Colour	Dark brown	Yellowish
Density 20°/20°C	1.030	1.025-1.049
Refractive index ($^nD_{20}$)	1.530	1.528-1.535
Solubility in ethanol	1:2 clearness	1:2 clearness
Eugenol total	73%	Min. 78%
Caryophyllene content	20%	Maximum 17%

The amount of iron bound calculated by the following equation:

$$\text{Weight Fe} = \frac{\text{MW Fe}}{\text{MW Fe-citrate}} x \text{ Weight Fe-citrate} \quad (1)$$

$$\text{\% Fe bound} = \frac{\text{Mole Fe}}{\text{Mole citric-acid}} x 100\% \quad (2)$$

The responses were density, viscosity, total eugenol, heavy Fe citrate. The data was further processed by using Statistical 6.

RESULTS AND DISCUSSION

Raw material analysis: Clove oil can be obtained from clove plants such as leaves, stems/handle and flower (Guenther, 1987). Clove oil is an essential oil produced from the clusters obtained from the stems and leaves. The results of the analysis as compared to the standard are presented in Table 3. The result showed that clove oil does not meet the standards especially for levels of eugenol and color. Therefore, the next step is to improve the quality of clove oil by using adsorption-distillation method.

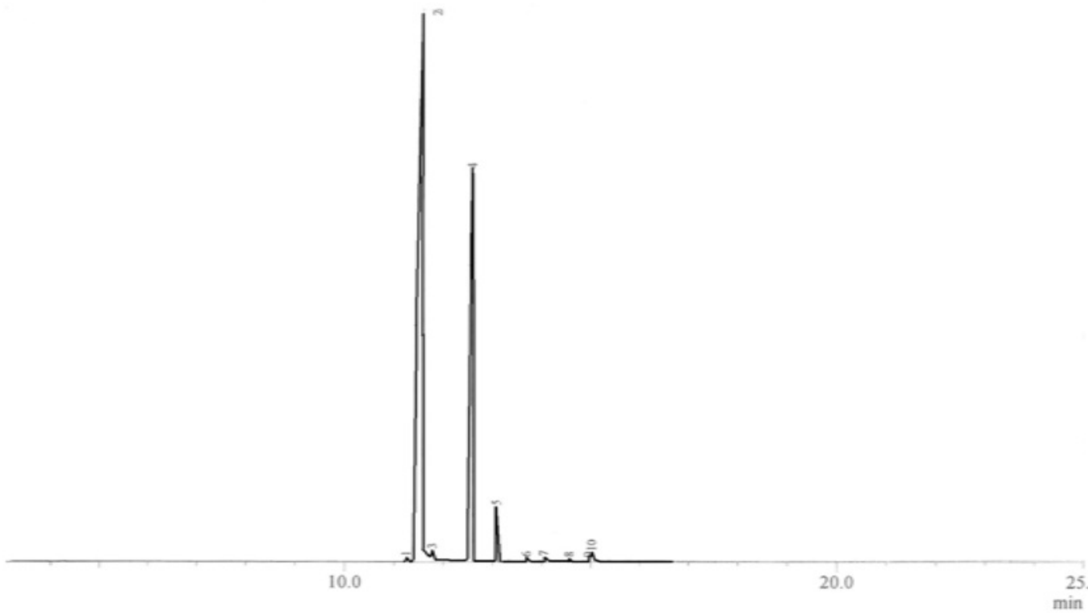

Fig. 3: GCMS analysis of clove oil

Table 4: The eugenol and impurity in the clove oil

R-time	Komponen	Komposisi (%)
11.243	Alpha cubebene	0.17
11.548	Eugenol	73.10
11.775	Alpha copaene	0.55
12.565	Trans-caryophyllene	22.40
13.080	Alpha humulene	2.64

The analysis of clove oil was performed by using Gas Chromatography and Mass Spectrometry (GCMS) (Fig. 3). The GCMS result shows 5 pieces of the chromatogram peak with the retention time of 11 to 13 min. The complete results of analysis are presented in Table 4 including Euogenol content. The impurity components in clove oil is dominated by trans-caryophyllene and alpha humulene. Clove oil contains two major components, namely eugenol (70-80%) and trans-caryophyllene (15-20%) as well as some of small quantities components such as β-carryophylene, α-cubebene, α-copaene, humulene, γ-cadien and 1, 3, 5-trien cadina.

Clove oil improvement: The previous research had shown the use of bleaching earth method to reduce colour and eugenol content (Silviana and Dan Errysa, 2006). The results suggested that the clay can be used to reduce the colour of clove oil. Other researches have also been done by Marwati *et al*. (2005), Silviana (2007) and Ma'mun (2008) in which citric acid was used as a chelating agent to reduce colour of oil. Since citric acid showed more efficient in reducing dark colour, therefore this method was subjected as our further experiment. To compare the adsorption, zeolite was also used. The treatment of natural zeolite was

(a) (b)

Fig. 4: Purification of clove oil by using citric acid (a) and combination citric acid-zeolite (b)

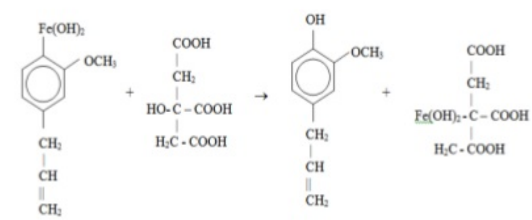

Fig. 5: The mechanism of Fe bounded to citric acid

Table 5: Effect of citric acid and temperature to Fe bounded

Run	Citric acid (%)	Temp°C	Fe bounded (%)
1	3.00	40.0	81.3400
2	3.00	60.0	97.8570
3	6.00	40.0	80.1300
4	6.00	60.0	82.8080
5	4.50	50.0	72.6320
6	2.38	50.0	82.7330
7	6.62	50.0	79.5767
8	4.50	35.9	73.0380
9	4.50	64.1	73.6830
10	4.50	50.0	80.8820

Table 6: Correlation analysis of Eq. (3)

Parameter	Effect	S.E.	t (3)	p	-95% conf limit	+95% conf limit
Mean	76.75690	5.298191	14.48738	0.000713	59.8957	93.61811
Blocking	-4.97118	4.738846	-1.04903	0.371223	-20.0523	10.10995
X_1	-5.18111	5.298191	-0.97790	0.400242	-22.0423	11.68010
X_1^2	8.53580	7.008848	1.21786	0.310325	-13.7695	30.84109
X_2	5.02651	5.298191	0.94872	0.412754	-11.8347	21.88772
X_2^2	0.74192	7.008848	0.10586	0.922378	-21.5634	23.04721
X_1X_2	-6.91984	7.492774	-0.92353	0.423844	-30.7652	16.92551

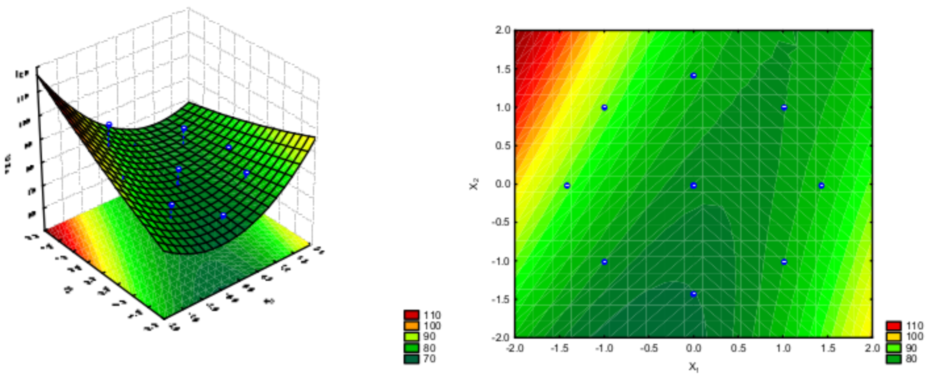

Fig. 6: Contour response of Eq. (3)

done through chemical and physical treatments by addition of hydrochloric acid and calcinations. In other hand, the experiment by using citric acid was done by addition of 0.6% citric acid without heating. The heating efficiency was subjected as main consideration. The experimental results are documented and presented in Fig. 3.

Figure 4 show that the addition of citric acid at a concentration of 0.6 and 10% has the ability to improve the colour quality of clove oil. More citric acid used, the clove oil is brighter because of Fe bound to citric acid. However, the citric acid in clove oil is not preferred and therefore must be reduced. The use of 2% zeolite improves this quality (Fig. 4b), however there was a smell problem ranging from typical odor of cloves to smell fragrant vanilla.

Process improvement: In this phase, the experiment was carried out on the basis of 200 g of oil of cloves with a magnetic stirrer stirring system at a speed of 200 rpm. During experiment, it was observed that heavy precipitation was formed. Heavy iron deposition is assumed as citrate, which was then used to calculate the bounded iron. The reaction of Metal binding (Fe) in eugenol with adsorbent citric acid can be described by Fig. 5 as follows.

The variation of citric acid concentration and temperature to Fe bounded is shown in Table 5.

Respond data in Table 6 is then processed by using Statistica 6 for mathematical modeling, model validation, analysis of variation, the response surface graphs. The output of this optimization is non-linear equation of Fe bounded correlated to citric acid and temperature Eq. (3). N From the correlation analysis shows that coefficient of variable temperature (X^2) is positive meaning that increasing temperature will also increase the Fe bounded in citric acid. Vice versa, coefficient of X1 is negative that mean increasing citric acid will reduce the Fe bound in the solution:

$$Y = 76.7569 - 5.1811X_1 + 5.0265X_2 + 8.5358\ X^2{}_1 + 0.7419\ X^2{}_2 - 6.9198\ X_1X_2 \quad (3)$$

The completed correlation analysis is tabulated in Table 6.

Equation (3) has been used to illustrate the surface response. Figure 6 indicate that under range of proposed variable, the optimum condition is still not discovered. Further experiment is needed to evaluate optimal point of this purification process.

CONCLUSION

Clove oil material did not comply with the standard SNI 06 2387 2006, especially from the color and eugenol total. Addition of citric acid up to 10% could reduce the dark colour while the stirring process and temperature of 50ºC will significantly improve the quality of clove oil.

The temperature gives a positive effect to the quality, while the amount of citric acid gives a negative impact to the quality of clove oil.

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