

Reactive Extraction Process in Isolation of Eugenol of Clove Essential Oil (*Syzygium aromaticum*) Based on Temperature and Time Process

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Abstract: The purpose of this study was to obtain optimum conditions for a reactive extraction process in isolation of eugenol from clove essential oil associated with temperature and time process. Research stage begins by inserting a 100 ml clove essential oil and 0.8 N NaOH solution at a ratio of 1:1.1 to the reactor. Turn on the hot plate and set the appropriate reaction temperature variables of the study (30, 40 and 50°C) and set the stirrer speed of 100 rpm. After a reaction time achieved according to the study variables (15, 30, 45, 60 and 75 minutes) the reaction product was then separated. The bottom layer was Na-eugenolat (aqueous layer) and the top layer was organic layer. Na-eugenolat (aqueous layer) was then added 5 N HCl to obtain a pH of 4. Before placing distillation flask, Na-eugenolat that has been mixed with HCl silenced while for NaCl precipitate formed, then the newly inserted distillation flask which had been fitted condenser and thermometer. The mixture was then heated with a hot plate at a temperature of 195°C and vacuum pressure of 6.10^{-2} kPa for 30 minutes. Distillate was eugenol and the residue was NaCl residual reaction products. Eugenol distillate which was then measured its volume and analyzed eugenol concentration by GC. The optimum process conditions obtained in the reactive extraction temperature of 40°C, reaction time of 30 minutes at a concentration of eugenol of 51.07% and yield of 97.10%.

Keywords: reactive extraction, vacuum distillation, clove essential oil, eugenol, yield.

1. Introduction

Essential oil of cloves (*Syzygium aromaticum*) is one of Indonesia's many essential oil demand in the world market from year to year increase. Clove essential oil was produced from the leaves, flowers and stems plant cloves with the extraction process. Potential autumn leaf clovers as raw materials essential oil of approximately 2,368,043 tons/year of 455 393 ha of land area with a yield of 1-4%¹. Based on data from Agricultural Research and Development (2007) exports of Indonesian clove essential oil provides 60% of the world clove oil. Clove oil prices in the world market is US \$ 4.75/kg and the price of eugenol US \$ 7.80/kg. From these data there is a considerable price difference between clove oil and eugenol. Although Indonesia is the largest clove oil exporter in the world, but the fulfillment of eugenol Indonesia still have to import from other countries².

Eugenol is the main component in the essential oil of clove. Clove essential oil (*Syzygium aromaticum* L. Myrtaceae) were isolated by hidrodestilasi process, from the analysis of GC-MS has the composition of eugenol (88.58%), β -caryophyllene (1.39%), 2-heptanone (0.93%), ethyl hexanoate (0.66%), humulene

(0.27%), α -humulene (0.19%), calacorene (0.11%) and calamenene (0.10%)³. Essential oil of clove leaf (*Syzigium caryophyllatum* (L.) Alston) from Bangladesh were isolated by hidrodestilasi process, from the analysis of GC-MS has the composition of eugenol (74.3%), eucalyptol (5.8%), caryophyllene (3.85%) and α -cadinol (2.43%)⁴.

Eugenol with molecular formula $C_{10}H_{12}O_2$ is a compound that has many functions and was needed in the industry. Eugenol serves as an analgesic, anti-inflammatory, antimicrobial, antiviral, antifungal, antiseptic, antispasmodic, antiemetic, a stimulant and a local anesthetic that was widely used in the pharmaceutical world^{5,6}. Eugenol microemulsion with a concentration of 0.6% is able to fight the bacteria *Salmonella Typhi* and *Listeria monocytogenus* compared with clove essential oil at the same concentration⁷. Eugenol microemulsion with a concentration of 61.7% as a more powerful antioxidant than clove essential oil microemulsion⁷. Eugenol which was reacted with a cyclic sulfonic acid ester klorosulfat produce that could inhibit *Escherichia coli* and *Staphylococcus aureus*⁸. Eugenol can be synthesized into 3-(3,4-dimetoksifenil)-propanal as the raw material synthesis of derivatives of antibiotic C-9154⁹. Synthetic vanilla can be made of eugenol, and about 95% of world demand for vanilla flavor filled with synthetic vanilla^{10,11,12}. Vanilla acetate can also be used as a substitute for natural vanilla because of the similarity in nature, and used as food additives¹³.

Vanilla acetate can be made from the oxidation reaction of isoeugenol acetate with $KMnO_4$ with microwave heating¹⁴. A mixture of cloves eugenol from 1.25 to 2.5% with a hydrophobic starch solution can be used as a food packaging¹⁵. Compound eugenol contained in the commercial formulation has a level of stability which varies depending on the concentration. Eugenol with a concentration of 95.26% stable for 24 hours and 100.99% concentration is stable for 20 days¹⁶. Clove bud oil emulsion (CBO) in alkaline solution with the addition of whey protein emulsifier, gum arabic, lecithin or a mixture of all of them is stable for 7 days of storage¹⁷.

Studies on the extraction of essential oil of cloves has been done. Prianto et al.¹⁸ get a yield of 8.6% on a steam distillation process of clove (*Syzigium aromaticum*) for 8 hours with the physical properties of essential oils that meet SNI 06-4267-1996. In the supercritical CO_2 extraction to get the yield 19.6% and 58.77% eugenol concentration at a pressure of 10 MPa, 50°C for 2 hours¹⁹. Extraction of essential oils clove buds by steam distillation process for 8-10 hours at a yield of 10.1%, hidrodestilasi for 4-6 hours at a yield of 11.5% and soxhlet extraction for 6 hours at a yield of 41.85%¹⁹. On the extraction of essential oil of cloves with *Eugenia caryophyllata* hidrodestilasi method for 150 minutes get a yield of 5.06%, method microwave assisted extraction (MAE) for 10-30 minutes at a yield of 7.42% and microwave steam distillation method (MSD) for 10-30 minutes at a yield of 16.25%²⁰.

Research on the isolation of eugenol from clove oil also has been done. Hidayati²¹ gaining 99.45% eugenol drawn from the oil extraction time of 30 minutes and the volume ratio of oil to the solvent hexane = 1:2. In the isolation of eugenol from clove oil yield of 70.6% gain in the reaction time of 3 hours, stirring speed of 100 rpm, the standing long 19 hours and the ratio of water phase: n-hexane for washing is 1:1, 1:1/2: 1:1/2²². Lutfi et al.²³ get a eugenol content of 90.20% of the initial level of 70% at a concentration of 0.8 N NaOH, the temperature distillation of 195°C, vacuum pressure of 6.10^{-2} kPa and distillation time of 30 minutes. In the purification eugenol from clove oil, get a yield of 81.3% and eugenol concentration increased from 79.10% to 95.10% by using 1.8 N HNO_3 ²⁴.

In the study of isolation eugenol from clove oil, there is no data on the reaction temperature used and reaction time used is relatively long. The aim of this study was to obtained optimum process conditions such as temperature and reaction time, and was expected to optimize the isolation of eugenol from clove oil and produce higher yields.

2. Experimental

2.1 Materials and tools

The main research material that clove essential oil purchased from CV. Panadia. Reagents used in the study include HCl (Sigma-Aldrich, 37%), potassium hydrogen ptalat (Sigma-Aldrich, 99%) and NaOH pellets (Riedel-de Haen, 99%). The reaction was performed on a laboratory scale using a three-neck round bottom

flask fitted condenser, thermometer and hot plate magnetic stirrer. The reaction temperature was maintained in accordance study variables using water bath and atmospheric pressure. The separation of the reaction products was done by separating funnel. Then proceed purification of the reaction products using a set of distillation apparatus equipped with a vacuum pump.

2.2 Preparation

Clove essential oil that has prepared with analyzed eugenol concentration by GC. Creating 0.8 N NaOH solution, then standardized with potassium hydrogen ptalat. Assembling the reactor as a reaction consisting of a three-neck flask and condenser and to strengthen its position with the buffer and the stand. Then put the reactor on a magnetic stirrer hot plate. Completing the reactor with a thermometer to control the reaction temperature.

2.3 Reactive Extraction

Incorporating 100 ml clove essential oil and 0.8 N NaOH solution which has been standardized by a ratio of 1:1.1 to the reactor²³. Turn on the hot plate and set the temperature at the reaction temperature rotation corresponding research variable (30, 40 and 50°C) and set the lap button magnetic stirrer at a speed of 100 rpm²². Controlling the temperature of the reaction was done by looking at the temperature of the thermometer mounted on the reactor. After a reaction time achieved according to the study variables (15, 30, 45, 60 and 75 minutes) the reaction product was then inserted separating funnel and allowed to stand for 24 hours to form two layers. The bottom layer was Na-eugenolat (aqueous layer) and the top layer was organic layer. Separating the two layers and measuring the volume of the aqueous layer.

2.4 Vacuum Distillation

Na-eugenolat (aqueous layer) was then added 5 N HCl to obtain pH 4²¹. Before placing Na-eugenolat distillation flask that has been mixed with HCl silenced while for NaCl precipitate formed, then the newly inserted distillation flask which had been fitted behind the cooler and thermometer. The mixture was then heated with a hot plate at a temperature of 195°C and vacuum pressure of 6.10^{-2} kPa for 30 minutes²³. Distillate was eugenol and the residue was residual NaCl reaction products.

2.5 Analysis

Eugenol distillate which was then measured and analyzed of volume concentration of eugenol using gas chromatography (GC).

3. Results and Discussion

The raw material was the essential oil of cloves eugenol its concentration was analyzed by GC and found concentrations of 25.261%. Yield of eugenol was calculated using the following equation:

$$\text{Yield (\%)} = \frac{[\text{Volume of distillate} \times \text{concentration of eugenol}]_{\text{end}}}{[\text{Volume of oil} \times \text{concentration of eugenol}]_{\text{initial}}} \times 100$$

3.1 Effect of Temperature and Reaction Time to Volume Aqueous Layer (Na-eugenolat)

The bottom layer with the separation of the aqueous layer separating funnel which was Na-eugenolat reaction products between eugenol and NaOH. The aqueous layer volume measurements performed for each variable temperature and reaction time. From Table 1 it can be seen that the temperature and reaction time influence on the volume of aqueous layer obtained. The higher the temperature and reaction time, the greater the volume of aqueous layer to obtain optimum conditions.

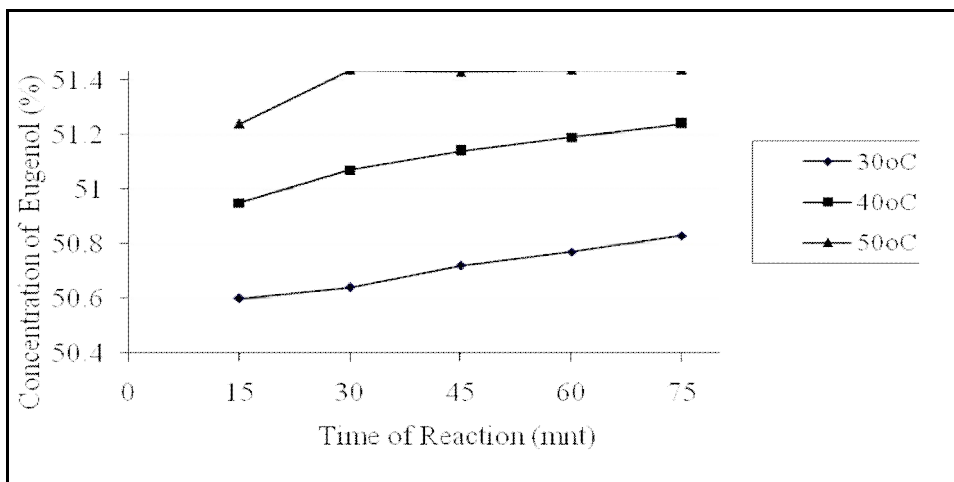
Table 1. Volume aqueous layer (Na-eugenolat) at various temperatures and reaction time

Temperature (°C)	Time of Reaction (mnt)	Volume <i>aqueous layer</i> (mL)
30	15	86
	30	87
	45	89
	60	90
	75	91
40	15	96
	30	97
	45	91
	60	89
	75	89
50	15	88
	30	93
	45	96
	60	89
	75	87

The best conditions of each of the different variables- At 30°C temperature variables, the best conditions obtained in a reaction time of 75 minutes with a volume of 91 mL of aqueous layer. In the variable temperature of 50°C, the best conditions obtained on reaction time 45 minutes with a volume of 96 mL of aqueous layer. The variable 40°C, the best conditions obtained in a reaction time of 30 minutes with a volume of 97 mL of aqueous layer and this results in an optimum condition. Theoretically it was known that the higher the reaction temperature the greater the reaction speed, which means the formation of more and more products, but this condition was limited to the optimum condition is reached. NaOH function in this process there are two, namely as a solvent in the extraction process that removes eugenol from kariofilin phase to the aqueous phase. Subsequently NaOH serves as a reactant that will react with eugenol.

3.2 Effect of Temperature and Time Reactions to concentration of eugenol (%)

Distillate distilled namely the isolated compound eugenol, concentration analyzed by GC. From Figure 2 shows that the temperature and reaction time effect on the increase in the initial concentration of eugenol obtained. The highest increase occurred in all variables reaction temperature with a reaction time of 15 minutes, where the concentration of eugenol increased from 25.261% to ± 51%. After a reaction time of 15 minutes were relatively small increase in the concentration of eugenol and almost evenly on all the variables of temperature and reaction time. The reaction between eugenol and NaOH was a fast reaction reaches equilibrium.

**Figure 1. Effect of temperature and reaction time to the concentration of eugenol (%)**

Eugenol highest concentrations obtained at 50°C with a reaction time of 75 minutes which is 51.444%. An increase of 26.183% of the initial concentration of eugenol 25.261% to 51.444%. This result was better than the results Lutfi et al.²³ get a 20.20% increase in the concentration of eugenol. As well as research results Haryani et al.²⁴ get a 16% increase in the concentration of eugenol.

3.3 Effect of Temperature and Time Reactions to Yield of Eugenol (%)

For the calculation of yield of eugenol measurable results isolation volume. From Figure 2 shows that the temperature and reaction time affect yield eugenol obtained. Visible optimum conditions were different in each study variable. At a reaction temperature of 30°C variable has not been achieved the optimum conditions because the yield eugenol still increase with the highest yield at the reaction time of 75 minutes was 92.56%. At variable reaction temperature reached 40°C optimum conditions on reaction time 40 minutes at a yield of 97.10%. At variable reaction temperature 50°C was reached optimum conditions on reaction time 45 minutes at a yield of 97.73%, the difference was only 0.63% compared to the optimum conditions at 40°C. Yield of eugenol obtained from the results of this study were relatively better when compared to previous studies. Fitri and Kawira²² get 70.6% yield with a reaction time of 3 hours. Research Haryani et al.²⁴ get a yield of eugenol 81.3%. Results of this research differs from research Hidayati²¹ to get 99.45% yield with a reaction time of 30 minutes, whereas in the study did not take into account the yield calculation of the concentration of eugenol obtained.

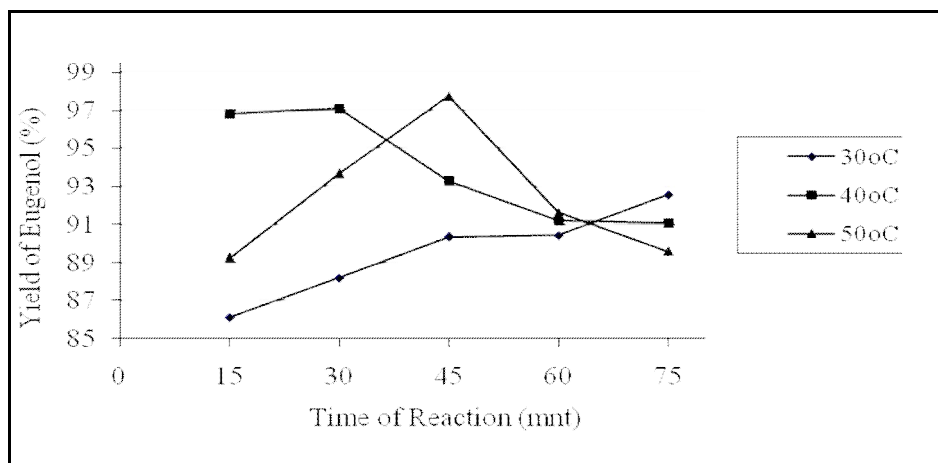


Figure 2. Effect of temperature and reaction time to yield eugenol (%)

4. Conclusions

The optimum conditions of temperature extraction reactive process that was 40°C, reaction time of 30 minutes, 0.8 N NaOH concentration, the volume ratio of oil:NaOH was 1:1.1, stirring speed of 100 rpm, separation using 5 N HCl to pH 4, purification eugenol with vacuum distillation at a temperature of 195°C for 30 minutes with a pressure of 6.10^{-2} kPa. In these conditions the concentration of eugenol obtained 51.07% and yield of eugenol 97.10%.

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