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One-Pot Conversion and Separation of Methyl Eugenol by Vacuum Fractionation

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Abstract. The conversion and direct separation of methyl eugenol (ME) in one-pot fractionation vacuum is presented. Mixtures containing eugenol (Eu), sodium hydroxide (NaOH) and dimethyl sulphate (DMS) as methylation agent were reacted in pot of fractionation vacuum. After finished methylation, the mixture direct separation in same pot of fractionation vacuum. The parameter process is observed ratio Eu to DMS, time reaction and temperatures. The best results is obtained 1:3 of the ratio Eu to DMS, 6 hour of time reaction and 100oC of temperatures. Concentration methyl eugenol after separation gave 98.06%. The one-pot fractionation is good conversion directly separation to obtain ME from Eu of clove oil with high concentration and efficient process.

Keywords; Methyl eugenol, eugenol, one pot, fractionation, clove oil.

1. Introduction

Clove oil is one bigger production in Indonesia. Eugenol from clove oil is one major compound with a variety of reactive functional groups, there are allyl, hydroxyl and methoxy. The presence of these functional groups brings eugenol possible to undertake the transformation into various derivative compounds with diverse activities, through reactions such as substitution, addition, hydration, isomerization, oxidation, and also methylation. Methyl eugenol (ME) is one derivatives from eugenol and methylation reaction with presence catalyst to obtain ME and also have functions for sex pheromone component in the male fruit fly (*Bactrocera dorsalis*) [1-6]. In other side, Insect traps and lure products to attract certain fruit flies such as the Oriental fruit fly on affected food crops. Methyl eugenol is also used as a flavoring added to ice cream, cookies, pies, puddings, candy, cola soft drinks, chewing and bubble gum, etc. For example, clove oil contains approximately 15% ME, and clove oil and its derivatives are affirmed as GRAS (generally recognized as safe) by the Food and Drug Administration as a food additive [6].

ME is an environmentally friendly way the control of attractants. It can be chemicals known as semio chemicals. These compounds can be affect the behavior of insects, such as finding food, laying eggs, sexual intercourse and more. One of the semiochemicals is kairomones, which it can stimulated the sensory of insects by methyl eugenol [7]. The properties of ME are fragrant aroma, light yellow or colorless and will become dark if long exposed to air (oxidation). The methylation reaction is carried



out by reacting eugenol with a basic NaOH solution which will produce sodium eugenolate, then reacted by adding DMS (dimethyl sulphate), upon addition of DMS, the sodium will be exchange with methyl group to form methyl eugenol. After the methyl eugenol occurred, the mixture of methyl eugenol is required separation and washing process to remove the impurities. However, the use of both these process should be long time and need another reagent to obtain ME. Therefore, this research will be released two process (separation and washing) and also the reaction will be put in one pot with directly separated by fractionation vacuum. This technique is new for methylation process with shorten and simple process. Various previous researcher have been conducted methylation of eugenol with presence bentonite as catalyst by reflux process at 300oC and 25.71% yield [4]. Improvement the methylation of eugenol by mechanical stirring have occurred 53% yield of ME and 47% yield of benzyleugenol [2]. Synthesis of methyl eugenol from crude clove leaf oil by reflux process obtained 99.14% of ME [8]. The separation from mixture by fractionation distillation have been enhanced the major compound with under vacuum [9]. However, there are several references about methylation process from eugenol in one pot and directly separation by fractionation vacuum.

The process of separation using fractionation vacuum has been done to get the major compound of essential oil such as eugenol from clove oil, citronellal from citronella oil etc. [10]. This research will be combined methylation reaction in pot of fractionation and directly separated in same equipment at vacuum condition. The Objective of this research is to obtain the simple reaction of methyl eugenol include separation in the one pot vacuum fractionation. The ratio eugenol to DMS, reaction time and temperatures are parameter for this research. Separation methyl eugenol make to fix based on the previous research.

2. Experimental

2.1. Material and equipment

Eugenol (Eu) was obtained from local essential oil company with purity of 99.4% (by gas chromatography), colorless and pungent smell. Dimethyl sulphate (DMS) and sodium hydroxide (NaOH) were supplied from chemical company in Indonesia. The standard methyl eugenol was purchased from e-Merck Indonesia. The main equipment using fractionation vacuum as reactor for methylation and also separation product for final process. The specification of fractionation is 6 liter volume of pot, 2 meter of high column with rash rings packed, equipped with reflux ratio, and also with high vacuum pump until 10-3 mbar. For detailed the equipment is showed in Figure 1.

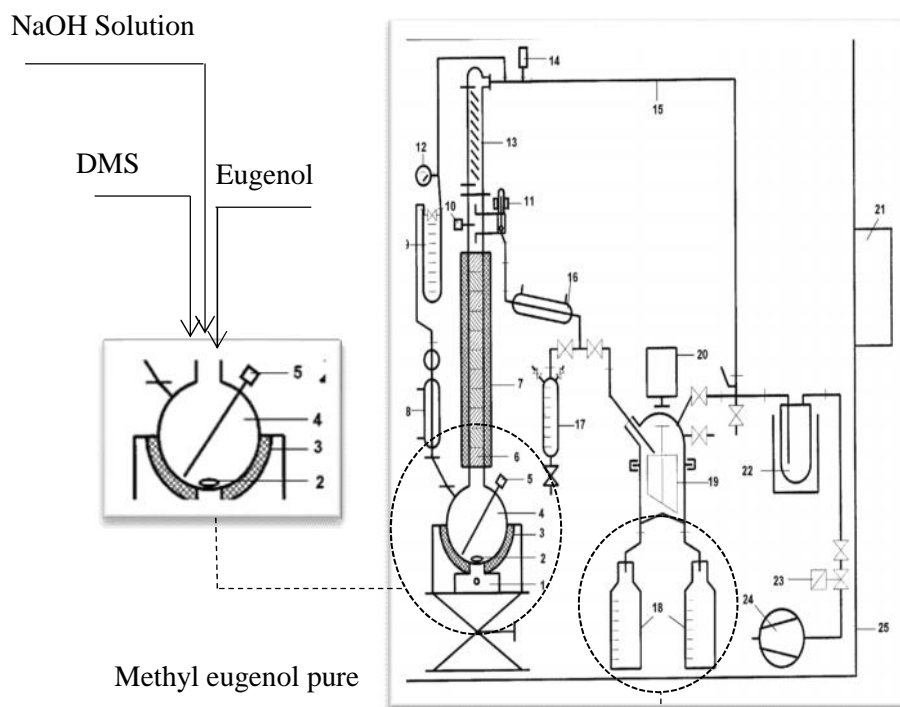


Figure 1. Scheme of pot fractionation vacuum

2.2. Material and equipment

Eugenol was added 500 g to a 6 liter pot fractionation vacuum which was equipped magnetic stirring and thermocouple. By the stoichiometry of reaction ME (ratio Eu:DMS to 1:1-1:3), the powder of NaOH first dissolved completely in water and then mixture of 1,474 g NaOH solution dropped to pot fractionation vacuum. After finished that, added 464.73 g of DMS with slowly dropped by tunnel flask and heated 110°C (90-110°C) during 8 hours (sampling each hour). The reaction completely finished after added 500 mL water to the mixture and mixed during 30 minutes. Separated the mixture of methyl eugenol by fractionation vacuum based on condition of clove oil in the previous work at our research group. The fixed condition of fractionation vacuum maintained at vacuum of 1-2 mbar, flask temperature of 130 – 150°C, time separation of 4 – 5 hours and also the product will be divided three fraction (fore fraction, main fraction and impurities fraction).

2.3. Analysis

Product eugenol and methyl eugenol were analyzed by gas chromatography and refractive index. The sampling product each hour in the process was controlled by curve calibration refractive index between purity methyl eugenol. These mixtures were diluted to obtain solutions, known concentrations in the range of 0.2 – 2 ml, and used to calibration curves of methyl eugenol and eugenol. In relation to curve calibration by Microsoft excel and linear regression is the best describe the linear relationship between concentration of methyl eugenol (y) and refractive index sample (x). The formula is following equation (1) with

$$r^2 = 0.9711$$

$$y = 37.262x - 55.89 \quad (1)$$

The gas chromatography condition is following Agilent type 15977A Series equipped with column DB 1 (30 m x 250 μ m x 0.25 μ m), carrier gas helium 40 ml/min, temperature injector 250°C, and temperature increase after 10°C/min, initial temperature 70°C, and volume sample is 1 μ l. The refractive index using digital refractometer Atago series 5000 alpha

3. Results and Discussion

3.1. Effect of ratio dimethyl sulfate on concentration methyl eugenol

The initial step of the methylation reaction is the reaction of eugenol with a sodium hydroxide (NaOH) following Williamson's reaction. Eugenol has hydrogen bonded to an oxygen atom which is attacked by a NaOH, and formed sodium eugenolate salts. After that, the reaction of sodium eugenolate salt with methylation agent dimethyl sulphate to occurred methyl eugenol and methyl sulphate as side reaction [7]. The effect of reaction time and ratio dimethyl sulphate on the methyl eugenol concentration has been illustrated in Figure 2. The reaction time is found to be one of important operating conditions. It was found that the concentration of methyl eugenol was increased with increasing the reaction time in the amount of DMS. The ratio eugenol to DMS (1:1, 1:2 and 1:3) gave the similar trend. When reaction time is increase, the high concentration of methyl eugenol is enhanced significantly about 98.29% with ratio eugenol to DMS (1:3) compared to ratio eugenol to DMS (1:1 and 1:2). The concentration of methyl eugenol is 71.84% to 86.75% with ratio eugenol to DMS (1:1) and 1 – 8 hours of reaction time. The similar results with ratio eugenol to DMS (1:2) is found the 52.09% to 91.22% of concentration methyl eugenol. It indicated that chemical reaction may be the controlling step instead of mass transfer. Although same trend with other various, ratio eugenol to DMS (1:3) is best condition with high concentration methyl eugenol. It showed that the curve mention is increased and steady at 6 – 8 hours of reaction time. The flask of fractionation has duty as reactor methylation and also separation to be methyl eugenol with high purity. With one pot reaction is minimize the error experiment and maintained the condition parameter. According Riyanto et al (2016), the influence of DMS is very reactive which one methyl group is transferred more quickly than the second. Methyl transfer is typically assumed to occur via an SN2 reaction [8]. Compared to other methylation agents, dimethyl sulphate is preferred by the industry because of its low cost and high reactivity [11].

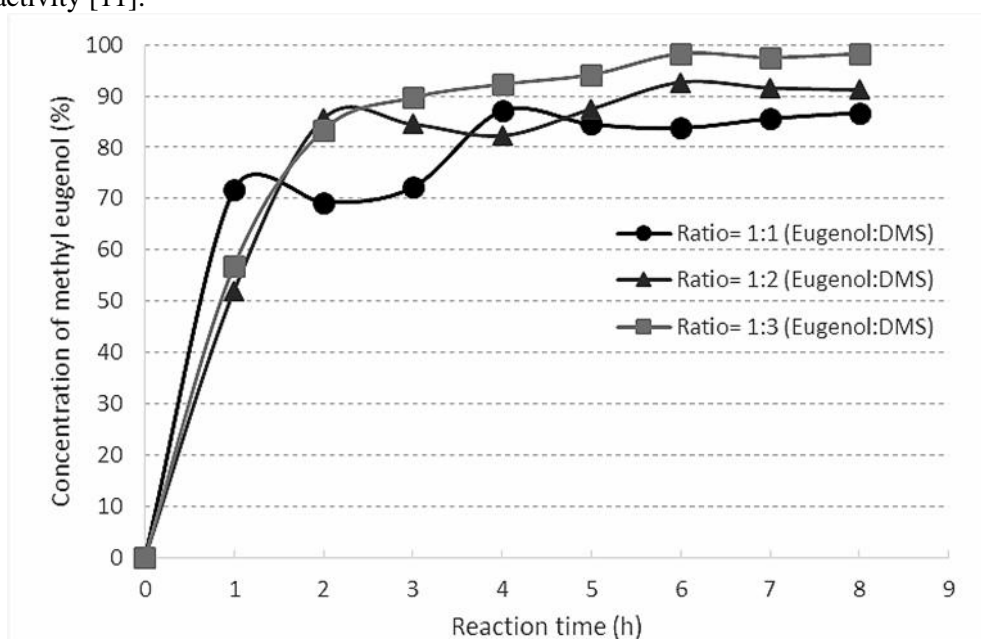


Figure 2. The effect of reaction time and ratio eugenol to dimethyl sulphate (DMS) on the concentration of methyl eugenol at 100°C

3.2. Effect of temperature on concentration methyl eugenol

The methyl eugenol is obtained colorless to pale yellow clear liquid with sweet fresh warm spicy odor. Temperature reaction is important parameter for conversion of methylation reaction.

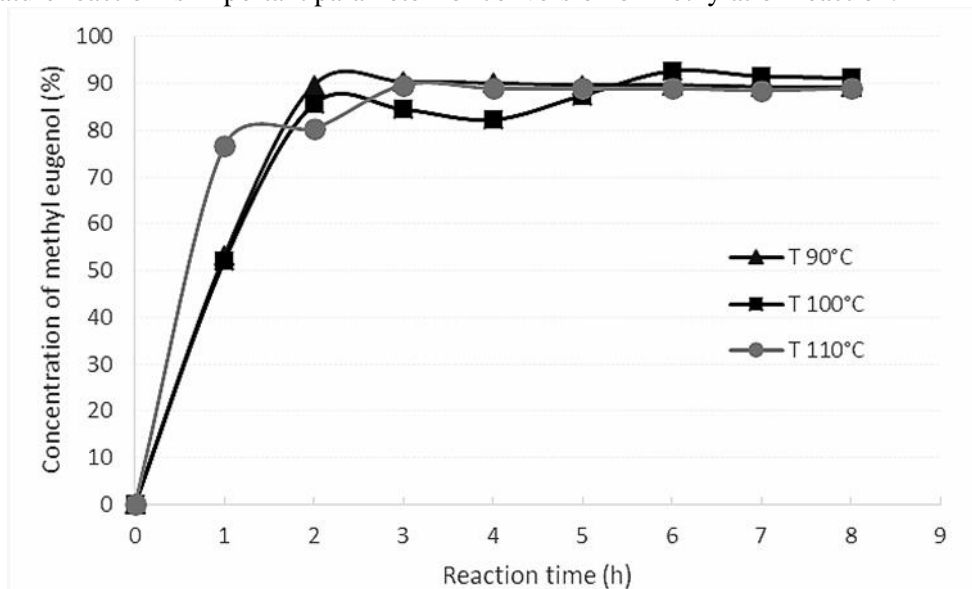


Figure 3. The effect of reaction time and ratio eugenol to dimethyl sulphate (DMS) on the concentration of methyl eugenol at 100°C

Figure 3 describe about influence of time and temperature reaction on concentration methyl eugenol. In this study, various temperature reaction with increase the reaction time have similar trend line. The starting to end process showed that the concentration methyl eugenol always increase with increasing reaction time. Temperature 90oC and 110oC have occurred methyl eugenol about 53.21% to 89.36% and 76.69% to 88.98% at 1 – 8 hours reaction time. Meanwhile, concentration methyl eugenol at condition of temperature 110oC obtained 52.09% to 91.22% during 1 – 8 hours. It showed that the high concentration methyl eugenol is 92.71% at 100oC and 6 hours. The trend line on curve in Figure 2 showed that the rate of reaction is very quickly almost average upper 50% formed methyl eugenol at first time reaction. The curve is suited with Arrhenius law, when reaction temperature is increased, the reaction rate will increase, and thus more eugenol will be converted to sodium-eugenolate and sodium-eugenolate to methyl eugenol [12].

3.3. Chemical composition of methyl eugenol

The GCMS chromatogram of methyl eugenol is showed in Figure 4. Based on the chromatogram peak, it can be seen that the highest peak is methyl eugenol about 98.06% at retention time (tR) of 18.763 min. The lowest peak is eugenol about 0.95% at 22.461 min of retention time (tR) and other peak is impurities. Separation of methyl eugenol from mixture by fractionation vacuum significantly increased purity of methyl eugenol. The process with one pot reactor to occur the methyl eugenol is successfully and high concentration.

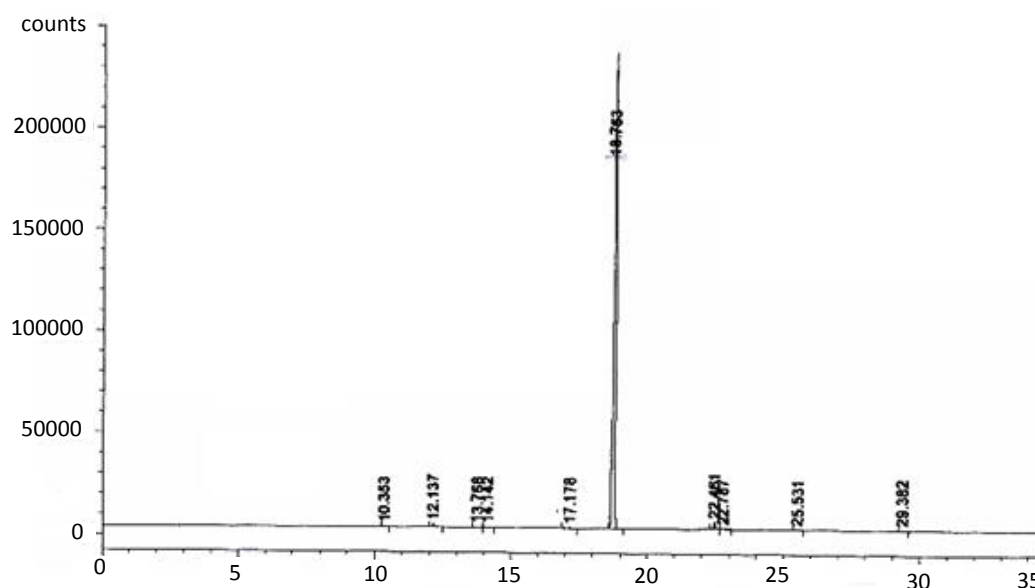


Figure 4. The effect of reaction time and ratio eugenol to dimethyl sulphate (DMS) on the concentration of methyl eugenol at 100°C

4. Conclusion

The one pot vacuum fractionation is successfully achieved for conversion eugenol to methyl eugenol with reaction methylation until separation of impurities and also unreacted chemical. This method gave high yield and simple process to obtain the methyl eugenol with high purity and good appearances.

Acknowledgments

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