

OPTIMIZATION OF MICROWAVE-ASSISTED EXTRACTION (MAE) OF CINNAMON (*CINNAMOMUM BURMANNII*) OLEORESIN USING RESPONSE SURFACE METHODOLOGY

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Abstract: Cinnamon (*Cinnamomum burmanii*) oleoresin is produced from the extraction of the cinnamon plant, mainly its bark. Microwave-Assisted Extraction (MAE) can produce this oleoresin with many advantages i.e. shorter time, lower energy, higher extraction rate and minimum potential of side product.

The research was conducted for the optimization of cinnamon oleoresin extraction using MAE. Response Surface Methodology (RSM) was used for the analysis with Central Composite Design (CCD) for designing the experiment. The three investigated variables were: time (10 - 30 min), solvent volume (100 - 300 mL) and solvent concentration (80 - 90 %). Ethanol was used as solvent, while the yield of oleoresin was the response. From the analysis, it was shown that an extraction time of 23.36 minutes with an ethanol volume of 258.2 mL and an ethanol concentration of 85 % will give a yield of 20.57 %.

Keywords: *central composite design, significant coefficient, yield response*

INTRODUCTION

Cinnamon (*Cinnamomum burmanii*) is one of herb which is used as food flavor and aroma, food preservative, aromatherapy and nowadays is also developed for its antibacterial [1] and antioxidant activities [2]. The use of cinnamon is usually in the form of essential oil that is gained from its bark and leaves. Another product which is also advantageous is cinnamon oleoresin. Oleoresin is a concentrated product that contains the volatile and non-volatile compounds and has complete flavor profile of the spices. Cinnamon oleoresin is mostly used for spice, condiment and flavor [3]. It can be produced from the extraction of the cinnamon bark. Compared with the essential oil, oleoresin contains natural antioxidants which make the product more stable. Oleoresin was also reported as a product that is easily transported, more economic, easily controlled, has a better distribution and has good value if comparing with its spice powder [3, 4].

Oleoresin can be obtained using maceration, Soxhlet and percolation extraction. These methods are usually conducted in long time extraction process and high temperature that refer to the high energy consumption [5]. Using maceration and Soxhlet methods, cinnamon oleoresin was gained after 4 and 5 hours extraction time, respectively [6, 7]. The use of high temperature and longtime extraction can also potentially damage the oleoresin product.

Microwave-Assisted Extraction (MAE) is another alternative for oleoresin extraction. This method needs shorter time and lower energy; also have higher extraction rate and minimum potential of side products [5, 8, 9]. Microwave will be absorbed directly by molecules using ionic conduction and dipole rotation. The ionic conduction is caused by electrophoretic migration that will rise the temperature of solution [10]. Solvent is chosen based on the solubility of component in solvent, solvent dielectric constant and also dissipation factor [9, 11]. The MAE process is successfully used for extraction of essential oil from sandalwood [10], phenolic antioxidant from coriander [12] and *Curcuma longa* oleoresin [13]. Among many solvent, ethanol is the mostly used solvent for oleoresin extraction. The advantages of using ethanol as solvent are its moderate polarity and its nature as green solvent for both human beings and environment [12]. Extraction of cinnamon oleoresin using MAE is influenced by several factors, i.e. time of extraction, solvent and sample ratio and also solvent concentration. Those factors will affect the yield of oleoresin. The effect of factors can be individual or interactive, then it is important to study those effects in order to get the optimum condition for cinnamon oleoresin extraction using MAE.

Response Surface Methodology (RSM) is considered as an efficient approach to evaluate the experimental factors. It is a statistical technique that is often used for complex research and is also commonly used in food processing research [14]. Both individual and interaction effect of variables also can be analyzed using this method [15]. It will also reduce the number of experiments and can get the optimum condition for the extracting process [10]. There were several research correlated with optimization of cinnamon oleoresin extraction, such as optimization of maceration extraction using RSM [6, 16, 17] and optimization of ultrasonic extraction using RSM with 2 variables [18]. However there is still no report about optimization of microwave-assisted extraction of cinnamon oleoresin. Therefore, the objectives of this research were to

investigate the effect of factors affecting the extraction and to optimize the microwave-assisted extraction process of cinnamon oleoresin using RSM.

MATERIALS AND METHODS

Materials

Cinnamon bark as raw material was gotten from local market in Semarang. The bark was washed using distilled water and dried at 40 °C using a LabTech oven (Model LDO-080N, Daihan LabTech Co, Korea) for 24 hours. Bark is then mashed and sieved to get 80 mesh powders. The water content of the sample was analyzed using OHAUS moisture balance (Type MB 23, OHAUS Corp, USA) until below 10 % and kept in sealed container. Ethanol (analysis grade, Merck, Indonesia) was used as solvent for the extraction process.

Microwave-assisted extraction of oleoresin

A domestic microwave oven from SHARP Model R-230R(S) (made in Thailand) was modified for extraction process. Microwave was equipped with a 1000 mL flask inside while the condenser was placed outside the microwave (Figure 1). Ten (10) g of sample was placed in the flask and ethanol was added. The time, ethanol volume and concentration of ethanol used were based on the experimental design. The sample was then extracted using Microwave Assisted Extraction (MAE) at an irradiation power of 30 % max (maximum power of 399 W). After extraction process, solution was filtered. Filtrate was evaporated using rotary vacuum evaporator to get the oleoresin. The oleoresin yield was then analyzed.

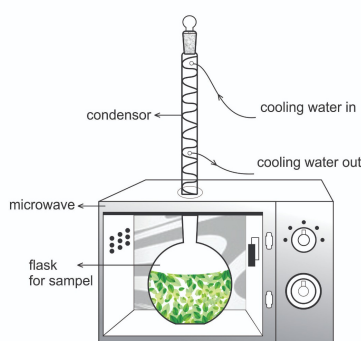


Figure 1. Schematic apparatus of microwave-assisted extractor

Analysis of oleoresin

Yield of cinnamon oleoresin was calculated by comparing the mass of oleoresin gained and the mass of sample used (Equation 1).

$$\text{Yield (\%)} = \frac{\text{mass of oleoresin (g)}}{\text{mass of sample (g)}} \times 100 \% \quad (1)$$

Experimental design

Experimental design use Central Composite Design 3 factors with three independent variables. The variables are time, ethanol volume and ethanol concentration. The range and levels of variables were given in Table 1.

Table 1. Range and levels of independent variables

Variable	Range and levels				
	Star point (- α /1.682)	Low level (-1)	Center level (0)	High level (+1)	Star point (+ α /1.682)
Time [min]	3.18	10	20	30	36.82
Ethanol volume [mL]	31.8	100	200	300	368.2
Ethanol concentration [% b/v]	76.6	80	85	90	93.4

Using this design, there will be 16 experiments conducted. The analyses were carried out by means of Statistica 8.0. Mathematical model will follow Equation (2).

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad (2)$$

This model will show the relationship between independent and dependent variables to the yield gained. The coefficient of determination R^2 was used to express the quality of fit of the equation. Statistical significance was determined by the F-test. The significance of the interaction effects were checked from the p value (probability value). The smaller was the value of p, the more significant was the corresponding coefficient. The p-value < 0.05 is regarded as a significant coefficient, while more than 0.05 is insignificant.

RESULTS AND DISCUSSIONS

The experimental design and its result were shown in Table 2.

Table 2. Experimental response

No.	Time [min]	Ethanol volume [mL]	Ethanol conc. [%]	Yield [%]
1	10	100	80	9.1
2	10	100	90	8.8
3	10	300	80	15.8
4	10	300	90	11.2
5	30	100	80	4.0
6	30	100	90	13.7
7	30	300	80	18.1
8	30	300	90	16.5
9	3.18	200	85	13.8
10	36.82	200	85	16.0
11	20	31.82	85	2.4
12	20	368.18	85	19.0
13	20	200	76.59	18.8
14	20	200	93.41	21.8
15	20	200	85	23.1
16	20	200	85	14.9

Each response was evaluated under process conditions of variable time (X_1), ethanol volume (X_2) and ethanol concentration (X_3), while the response was oleoresin yield (Y). From the yield resulted in Table 2, it was shown that microwave assisted the extraction process and reduced the extraction time. The higher yield in shorter time was happened because of heat and mass gradients which work on the same direction. In microwave extraction, both heat and mass were transferred from the inside to the outside of materials [19]. The extraction process itself happens in three different steps. The first step is equilibrium phase where solubilization and partition occurred, makes the substrate remove from the outer surface of particle. The second step is transition phase to diffusion where convection and diffusion occurred, and the last step is diffusion of the solute to the solvent because solute can break away from its matrix. The last step is oftenly regarding as the limiting process [20].

From the heating side, two mechanisms of energy transfer happens simultaneously in microwave, they are ionic conduction and dipole rotation. Ionic conduction happen when electromagnetic field is applied, cause the electrophoretic migration of ion. While dipole rotation is rearrangement of dipole with the applied field [19].

There are several variables that could affect the microwave extraction process. Among those variables, time, ethanol volume and ethanol concentration were selected in this research for the optimization. Solvent selection was the most important factor in MAE process [19]. This point was including solvent selection, solvent composition and also solvent to solid ratio. Solvent used in MAE process was selected based on its dielectric constant and also its interaction and penetration to the sample. Moreover, the solvent selection in MAE process can't directly apply from the result of conventional method, since the capacity of solvent to absorb microwave energy must also be considered. It was reported that ethanol is one of good microwave-absorbing solvent [9]. Another research also had been conducted using combination solvent, such as methanol-water and ethanol-water with different composition. The addition of small amount of water to the solvent showed better heating process and also better mass transfer rates. The changes of yield toward water addition could be attributed by the change of solvent polarity when the concentration was changed. Regarding with ethanol as solvent, it is reported that ethanol with 70 - 90 % (v/v) was the best proportion for optimization [21]. Solvent volume was correlated with solvent to solid ratio. This factor was also important, since solvent had to immerse the whole sample for whole irradiation proces. Some studies reported the optimum ratio of solvent to solute ration was between 10:1 to 20:1, although in some cases, optimum condition could be higher or lower. Low solvent to solid ratio could make the material was overheated and it would decrease the yield, but too high solvent to solid ratio could make the waste of heating that will decrease the efficiency [10]. Another important factor in MAE process was time. MAE process could be conducted from few minutes to around half-hour for assuring that there will be no thermal degradation of components [9, 19]. Longer extraction time could increase the yield, but the increase would be lower when longer time was applied.

Mathematic model for predicting the cinnamon oleoresin yield was shown in Equation 3.

$$Y = 19.28 + 1.62X_1 + 7.89X_2 + 1.21X_3 - 4.26X_1^2 - 7.23X_2^2 - 0.44X_3^2 + 1.95X_1X_2 + 3.25X_1X_3 - 3.90X_2X_3 \quad (3)$$

The coefficient of determination R^2 was 84.9 %, which means that the model is influenced only in a proportion of 84.9 % by the variables (time, ethanol volume and ethanol concentration) and around 15.1 % was influenced by another factor that can't be explained. The determination of significant factor that affect the extraction process can be done by checking the p value (Table 3). From Table 3 we can conclude that ethanol volume (X_2), both linier and quadratic were significant factors.

Table 3. ANOVA results

Factor	SS	df	MS	F	p-value
X_1	6.9099	1	9.0218	0.6991	0.435
X_2	212.8693	1	212.8693	16.4953	0.006
X_3	4.9782	1	4.9782	0.3858	0.557
X_1X_2	7.6050	1	7.6050	0.5893	0.472
X_1X_3	21.1250	1	21.1250	1.6369	0.248
X_2X_3	30.4200	1	30.4200	2.3573	0.175
X_1X_1	42.0722	1	42.0722	3.2602	0.121
X_2X_2	121.1316	1	121.1316	9.3865	0.022
X_3X_3	0.4560	1	0.4560	0.0353	0.86
Error	77.4289	6	12.9048		

Figure 2 showed the contour plot of time and ethanol volume on fixed ethanol concentration 85 %.

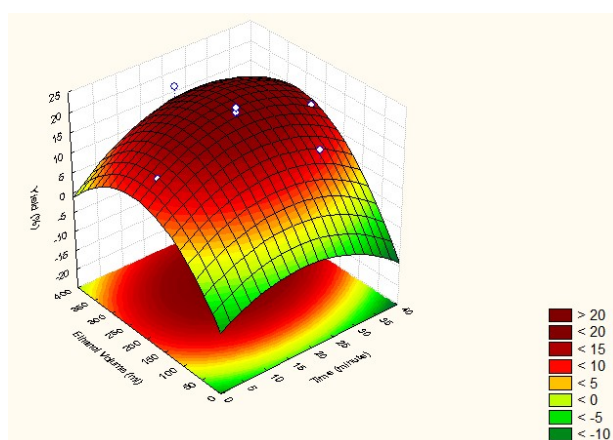


Figure 2. Contour plot of yield between time and solvent volume on fixed solvent concentration 85 %

From Figure 2 we could see that at fixed extraction time, the increase of ethanol volume will increase oleoresin yield. Ethanol volume that will give highest yield area was on range 200 - 300 mL. Under 200 mL or above 300 mL of ethanol volume, yield will be predicted under 15 %, even under 100 mL ethanol, yield was predicted below 10 %. The ethanol volume was correlated with the solvent per solute ratio. This ratio was one of important factor in extraction process, because solvent must dissolve whole samples to ensure that diffusion process will occur from sample to solvent when the irradiation process takes place [9]. This ratio also refers to the density of solution. Low ethanol volume will increase the density of solution, and it could make the hole that will reduce the yield [10]. The importance of solvent volume was also indicated in the

experiment result (Table 2) where the minimum solvent volume (31.8 mL) gave the lowest yield (2.4 %). But too high volume of solvent may not give better yield also, because there will be worse distribution of sample and worse irradiation exposure [9]. From Figure 2 we can also conclude that time will increase the yield slightly only. The recommended extraction time to get high yield in this experiment was around 15 - 30 minutes. If the extraction time was too short, the diffusion process of the solute to the solvent will be limited. The diffusion process usually occurs slowly, hence short contact time will reduce the yield. While using excess extraction time, it can cause the degradation of the oleoresin [10].

Figure 3 described the interaction of time and ethanol concentration for the fixed ethanol volume 200 mL. It can be seen that ethanol concentration will affect the yield. At fixed extraction time, the decrease of ethanol concentration will decrease the oleoresin yield. Ethanol concentration between 85 - 93 % will give high yield on around 20 - 30 minutes extraction time. Both high ethanol concentration on short extraction time and low ethanol concentration of high extraction time will decrease the yield, even less than 12 %.

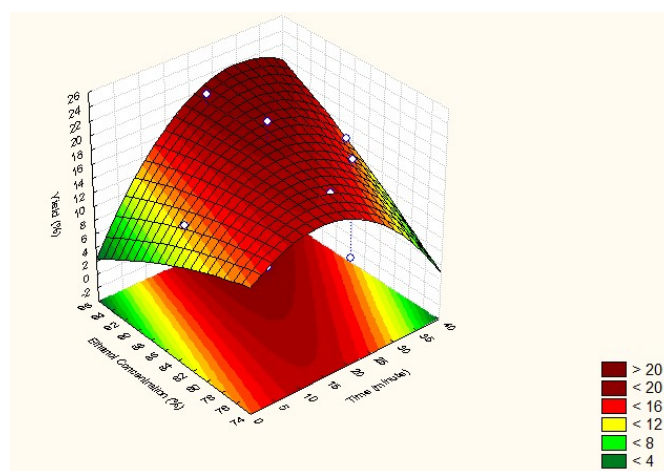


Figure 3. Contour plot of yield between time and ethanol concentration on fixed solvent volume 200 mL

Figure 4 showed the relationship of ethanol volume and ethanol concentration at fixed time 20 minutes. It was seen that the yield was not influenced much by ethanol concentration when ethanol volume was 200 - 300 mL. But if ethanol volume was lower than 200 mL or higher than 300 mL, then the ethanol concentration will affect the yield much. Ethanol concentration will change the solvent polarity and this will affect the yield. On the range of ethanol volume 200 - 300 mL, ethanol concentration needed for high yield was on the range 75 - 89 %. Higher ethanol concentration on this ethanol volume range will decrease the yield, although it was not significant. The dissolution of component extracted will be hampered when high ethanol concentration was used, hence lowering the extraction rate [21]. Moreover, it was revealed that the yield of component extracted could be slowly decrease when the concentration of ethanol used was higher than 80 %, even the minimum yield was resulted when 100 % (v/v) ethanol used [21]. This result was also corresponded with the p-value analysis where ethanol volume was the significant variable on extraction process.

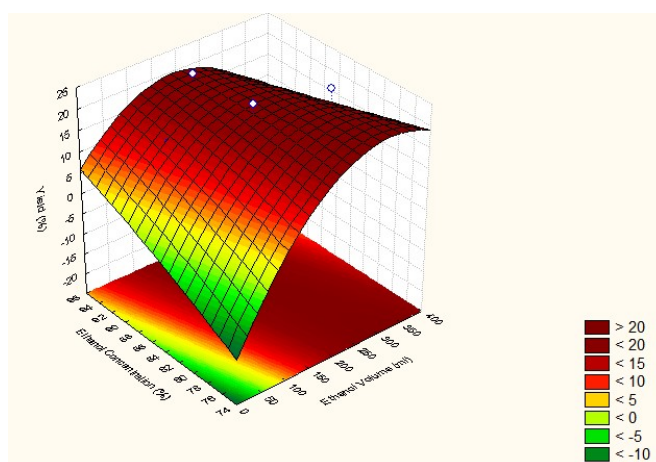


Figure 4. Contour plot of yield between ethanol concentration vs ethanol volume on fixed time of extraction 20 min

The optimal variables for this process were 23.36 min extraction time, ethanol volume of 258.2 mL and ethanol concentration of 85 % that will give 20.57 % yield. This result was lower than ultrasound extraction conducted for 72 min with 27.61 % yield [18], but higher than ultrasound extraction conducted with 66 minute that will gave oleoresin yield 17.96 % [4]. Both these ultrasound extractions were using ethanol 96 % as the solvent. The yield resulted from this research was almost the same with the one registered in the maceration process (21.05 %) conducted for 4.2 hr using methanol [16]. From this comparison, it was shown that microwave assisted extraction was one of saving time extraction method, especially compared with conventional extraction process.

CONCLUSIONS

RSM can be used to optimize the extraction of cinnamon oleoresin using MAE. From the analysis, it was shown that the extraction time 23.36 min, ethanol volume 258.2 mL and ethanol concentration 85 % will give yield 20.57 %. Among three variables investigated, solvent volume is regarded as significant variable that affects the extraction process.

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