PROCEEDING BOOK I

CHEMMPRO 2014

MINERAL AND MATERIAL PROCESSING

International Seminar on Chemical Engineering
in conjunction with
Seminar Teknik Kimia Soehadi Reksowardojo (STKSR) 2014

"Minerals and Materials Processing Toward Sustainable Development"

Bandung, Indonesia
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PREFACE

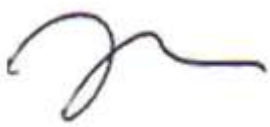
International Seminar on Chemical Engineering in conjuction with Seminar Teknik Kimia Soehadi Reksowardojo (STKSR) was held at East Hall, Institut Teknologi Bandung during 30 – 31 October 2014. This international conference had a theme of "Mineral and Material Processing" which was applicable with the enactment of Law No.4 of 2009 on Mineral and Coal Mining where the ban on the export of unprocessed minerals has been applied since January 2014. Chemical engineers hold a significant role in this area, especially to develop and implement appropriate processing technologies to the mineral resources, which also should considering the sustainable development.

There were five plenary lectures in this two-days conferences, with theme "Sustainable Mineral and Metal Processing" and "The Advancement of Chemical Engineering Technology" along with plenary discussion about "Overcome the Challenges in Indonesia's Mineral and Materials Processing Industry". This proceeding comprises the summary of these outstanding speech and the collected papers that has been presented in the parallel sessions. These papers are divided into several general themes: mineral processing, material processing, material refining and recovery, advance materials, nanotechnology, catalyst, polymers, and others.

The international conference provides an opportunity to publicize research works which done or in ongoing ones in many research institution and showcase their latest advancement and technologies. We have expectation in this occasion is not only a good place to exchange and discuss the progress of their research in chemical engineering that applicable to material and mineral processing, but also a venue to collect and to disseminate the most updated technologies and the researches of regional issue and public interest in order to contribute to the community and to draw support from the industrial and the governmental sectors.

We would like to grateful to all participants and sponsors who has contributed to the conference, to the organizing committee for their commitment in their busy days so that the conference is possible to be held and conducted successfully.

Thank you,



Dr. Dendy Adityawarman
Conference Chairman

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International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

Optimization in Eugenol Production from Clove Oil with Saponification – Neutralization Process by using Response Surface Methods

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Abstract: The objective of this research was to obtain optimum condition in eugenol production from clove oil with response surface methods. Clove oil was founded from essential oil cluster in Batang district Central Java. The eugenol was produced with saponification and neutralization process. Eugenol was obtained with vacuum distillation. Eugenol concentration was analyzed with gas chromatography. In this research, the variable was studied are temperature and ratio of sodium hydroxide to clove oil and yield of eugenol as response variable. So the results was obtain in minimum condition with yield of eugenol 39.17% at X_1 = -0,0109 and X_2 = 0.3095 with determinant coefficient 0.764.

Keywords: *eugenol, clove oil, saponification –neutralization process, yield of eugenol, and surface response methods (SRM)*

1. Introduction

Batang Regency, Central Java, is one of the producers of clove oil in Indonesia with production 250 tons in 2011[1]. Clove oil is kind of essential oil that can be obtained from clove plant (*Eugenia caryophyllata Thunb*), in some part like leaves, flower, and stem. The quality of cloves oil analysed by amount of phenol, especially eugenol[2,3]. The problem in clove oil eugenol contents is under SNI standard. The Small Medium Entrepreneurship (SME) in Batang Regency produce clove oil that eugenol contents is 80% and sometime under 80%[1,4] .

Eugenol or Phenol, 2-methoxy-4-(2-propenyl) is main component of clove oil, colourless, has spicy taste and special odour so it used for fragrance and flavour industry. Eugenol can use as antiseptic, eugenol used for pharmacy industry. β-*Caryophyllene* is impurities that cause decrease clove oil quality[4]. According to USP (United States Pharmacopeia) standard, eugenol product must have purity more than 98 %. Clove oil with purity under 70% priced Rp 120.000,00/ kg[5]. So eugenol with purity 98 % priced 500.000/kg. Because of that, further

step must be done to obtain clove oil with eugenol purity more than 98% in order to clove oil has higher economic value.

The main problems faced by the SME in Batang District are low product quality due to availability of eugenol and darkness of colour[5]. The solution of this problem has been attempted by several researches by using chelating agent. The chelating agents that used for increasing eugenol contents in clove oil as citric acid and sodium EDTA[1,4,6-8]. Commonly, this process can be increase eugenol contents from 78% to 80%. In the other process that use for eugenol purification as saponification and distillation, fractionation. Anny (2002), Sukarsono and workers (2003) used saponification and distillation. Sodium hydroxide react with clove oil and neutralized by adding sulphuric acid or hydrochloride acid. The product then separated with decantation and distillation process. Eugenol contents on product has eugenol purity 82,6 % (minimum)[9-10]. Widayat and workers (2013, 2014) done experiments and simulation about clove oil purification. They use fractional distillation process at vacuum pressure. The product has purity of eugenol from 93 % up to 97 %[11-12]. This process has not been applied yet for eugenol with low purity that produced by small industry in Batang Regency. Therefore, the objective of this research is doing optimization of eugenol purification from clove oil using neutralization process and fractional distillation with Response Surface Methodology (RSM).

2. Methodology

Materials and Equipments

Materials that used in this study were obtained from clove oil essential oils Cluster Batang District. The clove oil has eugenol contents 80%[1,4]. Sodium hydroxide and hydrochloride acid have technical specification that found in chemical shop in Semarang. Aquadest or distilled water obtained from Laboratory in the Department of Chemical Engineering. The equipment used saponification process like presented in Figure 1. A beaker glass 500 ml used as reactor and magnetic stirrer used for heating and stirring. Figure 2 is a equipment that used for distillation. The distillation was operated in vacuum pressure that obtained with vacuum pump. Distillation column used packing system.

Research Design

The experimental design used is Response Surface Methodology (RSM) as described in Table 1 with two variables: operation temperature and the ratio of clove oil to sodium hydroxide (NaOH). Experiment process were performed on a laboratory scale and batch processes. The operating conditions used are as follows;

a. Fixed Variables
- ✓ Clove oil volume (ml) : 150
- ✓ Materials : clove oil
- ✓ Operational time : 45 minute

b. Experimental variables:
- Temperature : (-1) : (40) and (+1) (60) ^{o}C
- Ratio NaOH/Clove oil (v/v) : (-1) (2,5) and (+1) (3,5)

Figure 1 Saponification and Neutralization equipments

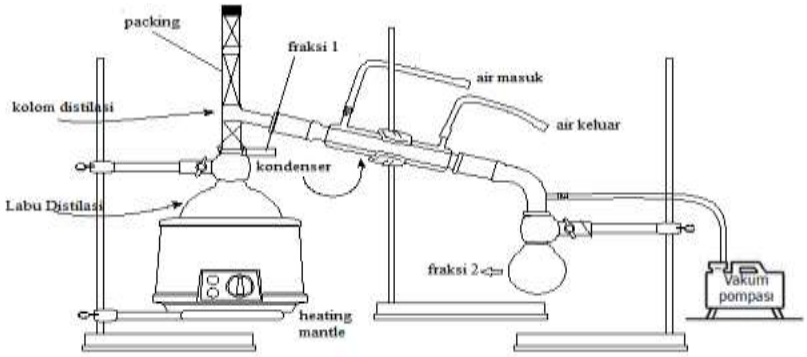


Figure 2 Vacuum Distillation equipment

Procedure

The experiments start with oil density measurement, so by determination of specific volume which desired, will be known the requirement of clove leaf oil weight. For each experiment clove oil has been purified first using citric acid[4]. 150 ml of clove oil and put in a flask and NaOH was added with ratios of variables. Saponification reaction time is 45 minutes, and then performed decantation for 1 day. Solids or soaps which formed is then neutralized with hydrochloride acid and reacted for 5 minutes. Decantation process is then

performed for 15 minutes. Then the eugenol product is distilled (Figure 2) for 1.5 hours. The final product is collected in a sample. The final product was measured and the volume and refractive index. The products were also analyzed by gas chromatography concentration.

Table 1 Variable Central Composite Design for Experiment

Run	Block	X_1	X_2	Y
1	1	-1	-1	Y_1
2	1	-1	+1	Y_2
3	1	+1	-1	Y_3
4	1	+1	+1	Y_4
5	1	0	0	Y_5
6	2	0	-1,424	Y_6
7	2	0	+1,424	Y_7
8	2	-1,424	0	Y_8
9	2	+1,424	0	Y_9
10	2	0	0	Y_{10}

Where:
X_1 = Coding for variable ratio oil to NaOH
X_2 = Coding for temperature variable
Y = Yield

Data Analysis

The responses in this research are density, viscosity and eugenol concentration. The eugenol concentration was analyzed by gas chromatography that did in Malang Polytechnic Laboratory. The liquid product was analysed by using gas chromatography (HP 5890, with HP 608 column) with FID detector. The operating condition used helium as gas carries with flow rate of 20 ml/minute, temperature of 100-200^{o}C with temperature gradient 5^o/minute and initial time 5 minute. Detector temperature is 275^{o}C. The product was analysed with internal standard methods.

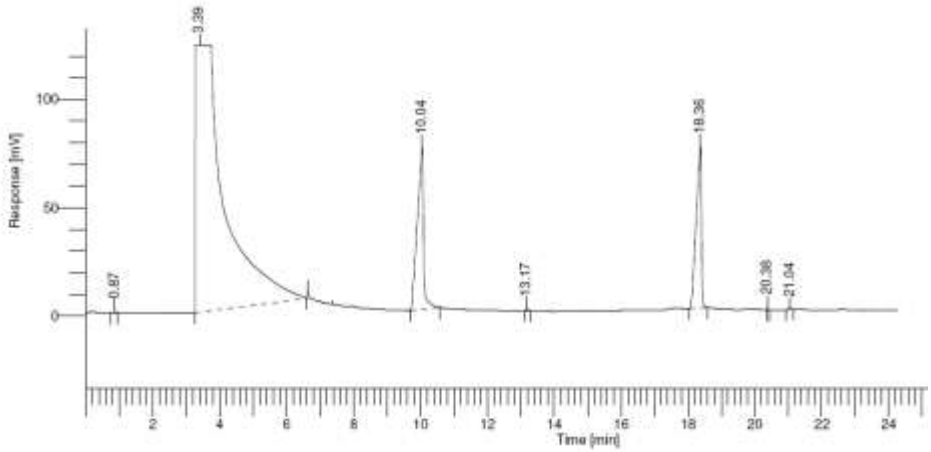
6 µL eugenol standard solutions was added with internal standard (benzyl alcohol) 6 µL and 1 ml of solvent. The solution injected on GC equipment and did triple runs. The response detector was calculated with sample area divided internal standard area. This parameter was averaged and used for eugenol concentration calculation. Eugenol concentration was used for calculation of yield of eugenol with equation 1. The data were processed using Statistica software.

$$\text{Yield (\%)} = \frac{\text{weight of eugenol}}{\text{weight of clove oil}} x100 \quad (1)$$

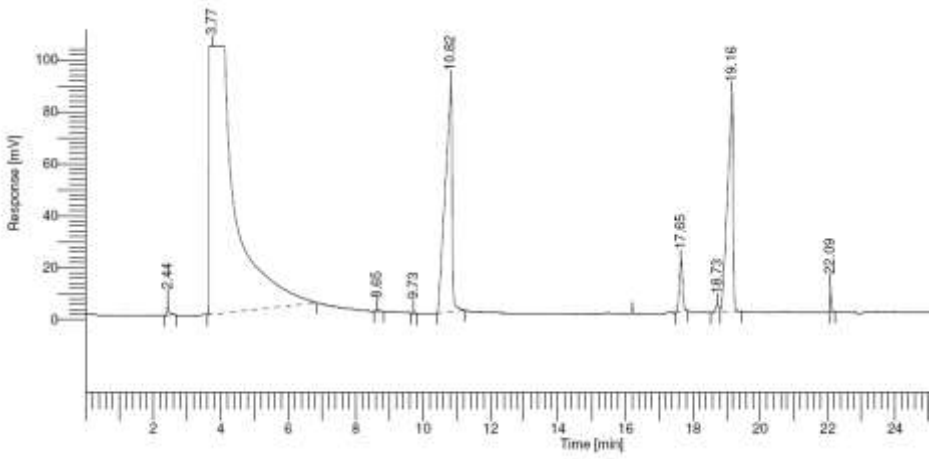
3. Result and Discussion

Chromatography Analysis

The results of qualitative and quantitative analysis for eugenol and benzyl alcohol were presented in Fig. 3. Fig. 3 shows chromatogram for methanol as solvent, benzyl alcohol and eugenol with retention time of 3.39; 10.04 and 18.36 minute, respectively. The eugenol contents in product varied 75.10 – 96.00%. If compared with Widayat (2013, 2014) that eugenol produced with fractionation process, this products have eugenol contents less than product from fraction process. The eugenol contents in eugenol product that produce with fractionation distillation process is 76.5-98.93%[12,13]. Figure 3.a. is a chromatogram for eugenol and internal standard and figure 3.b. for product sample. The both chromatogram in figure 3 don't different. Retention time in sample product just shift, but all components shift too.



a. Eugenol and internal standards



b. Sample with internal standard

Figure 3. Chromatogram of eugenol

Response Surface Methods Analysis

The results of statistic analysis include mathematical model, t test, analysis of variance, paretto analysis and validation of mathematical model. Polynomial equations to mathematical model the surface response methods follow:

$$Y = X_o + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 \quad (2)$$

Where:
Y = predicted response
β_1, β_2 = linear coefficient for 1, 2 variable
β_{11}, β_{22} = squared term coefficient for 1,2 variable
β_{12} = interactions variable coefficient
X_1:, X_2 = non dimensional number of independent variables

The results of analysis regression for equation 2 like presented in equation 3.

$$Y = 34.4639 - 0.5886\ X_1 + 19.6363\ X_1^2 - 5.6989\ X_2 + 9.2652\ X_2^2 + 3.2853\ X_1 X_2 \quad (3)$$

In 3 equations, shown that the value of each of the linear variables X_1 and X_2 is negative and quadratic and interaction variables are positive. The negative value can be explained that if ratio oil to NaOH (X_1) and temperature (X_2) increase can cause reduce yield of eugenol (for X_1 and X_2>0). However, the interaction between the variables of temperature and the addition of NaOH or X_1X_2, and quadratic variable of X_1 and X_2 are positive which means that increase the value can increase yield of eugenol. If the reduction of eugenol yield any increase in single variable compared with quadratic variable, showed that the increase in

yield caused by the quadratic variable is greater than a single variable. Increasing quadratic variable is 33.36 times larger than the single variable (X_1) and 1.63 times for X_2 variable. This is showed that single variable (X_1) not yet effect in yield of eugenol.

In Table 2 contains the coefficients, their standard errors, test statistic (t), p-values and 95% confidence interval for each predictor variable. For this table shown 3 equations is a multivariate regression.

Table 2. Regression analysis result

Parameters	Regression	Std.Err.	t(3)	p	-95.%	+95.%
Mean/Interc.	34.4639	11.0747	3.1119	0.0528	-0.7808	69.7085
Blocking	-5.5849	4.9528	-1.1276	0.3415	-21.3468	10.1770
$\mathbf{X_1}$	-0.5886	5.5374	-0.1063	0.9221	-18.2109	17.0337
$\mathbf{X_1^2}$	19.6363	7.3252	2.6806	0.0750	-3.6759	42.9485
$\mathbf{X_2}$	-5.6989	5.5374	-1.0292	0.3791	-23.3212	11.9235
$\mathbf{X_2^2}$	9.2652	7.3252	1.2648	0.2952	-14.0470	32.5773
$\mathbf{X_1X_2}$	3.2853	7.8310	0.4195	0.7031	-21.6365	28.2070

Variance of mathematical model was analyzed and the results presented in Table 3. Table 3 can be used to determine whether the independent variables simultaneously significant effect on the dependent variable. The degree of confidence that is used is 0.05[13-14]. The parameters have F value more than p for all parameters except X_1 quadratic variable and interaction variable. X_1 quadratic variable has F value = 0.0113 p=0.9221 and and interaction variable X_1 and X_2 parameter has F=0.1759 and p= 0.2953. The results of variance analysis support the t-test in Table 2 for X_1 and X_2 variable (single variable). It also shows that the mathematical model already in optimum condition (maximum / minimum) no stripes ascend and mathematical model can use in optimization.

Table 3 Analysis of variance(ANOVA)

Parameter	SS	df	MS	F	p
Blocks	311.911	1	311.911	1.2716	0.3415
$\mathbf{X_1}$	2.771	1	2.771	0.0113	0.9221
$\mathbf{X_1^2}$	1762.671	1	1762.671	7.1858	0.0750
$\mathbf{X_2}$	259.816	1	259.816	1.0592	0.3791
$\mathbf{X_2^2}$	392.427	1	392.427	1.5998	0.2953
$\mathbf{X_1X_2}$	43.172	1	43.172	0.1759	0.7031
Error	735.896	3	245.299		
Total SS	3120.280	9			

Pareto diagram can assist in efforts on the most important on process[13-14]. Pareto diagram in this study are presented in Figure 4. Figure 4 show that a linear variable X_2 has the smallest value. So this variable can be neglected or not effect in this process. The all variable have histogram don't cross the line p = 0.05. Pareto chart show quadratic variable of X_2^2 has a histogram near with line p = 0.05. This was shown a quadratic variable X_2^2 has the most effect in eugenol yield. This condition can be increase for obtain optimum condition.

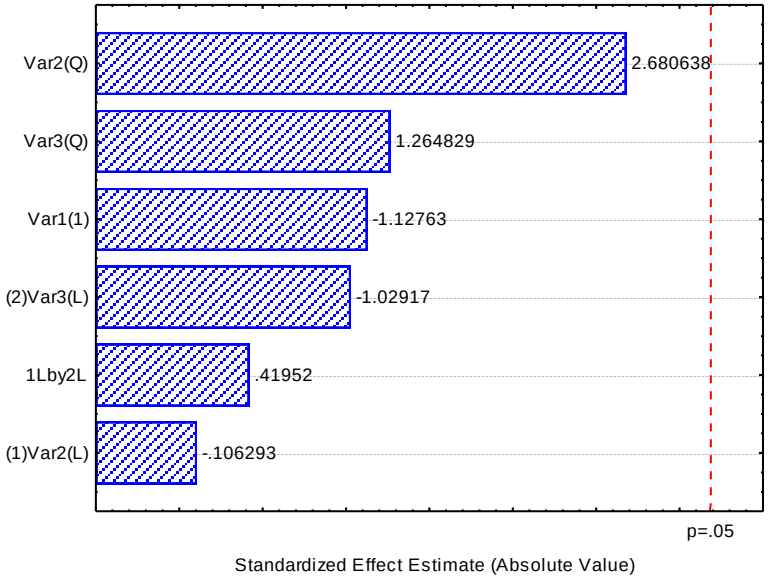


Figure 4 Parreto Diagram

The optimum conditions can be seen in Figure 5. Figure 5 is a surface response graph that consists of x and y axis as independent variable (X_1 and X_2) and z-axis as dependent variable or yield of eugenol (Y). In surface contours figuring in colour areas, so it can be seen profile graph. Figure 4 has the form a minimum point. This is shown the type of optimization process is already minimized.

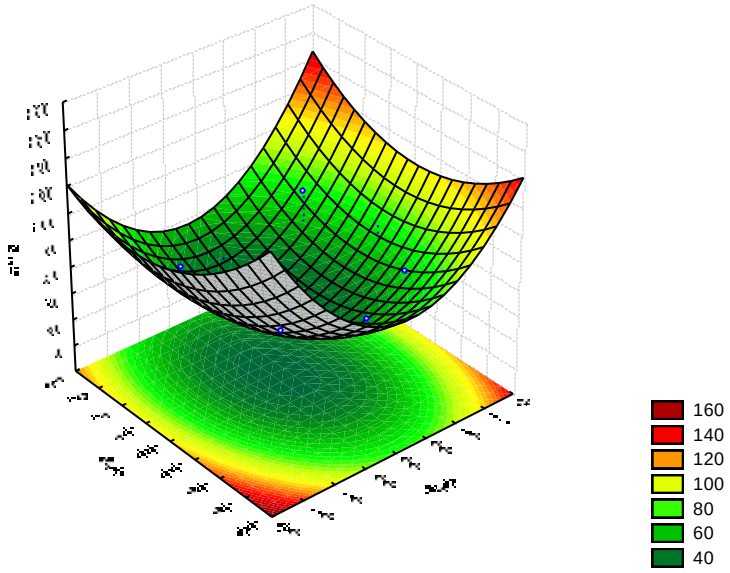


Figure 5 Countour Graphics of optimization results material ratio and temperature

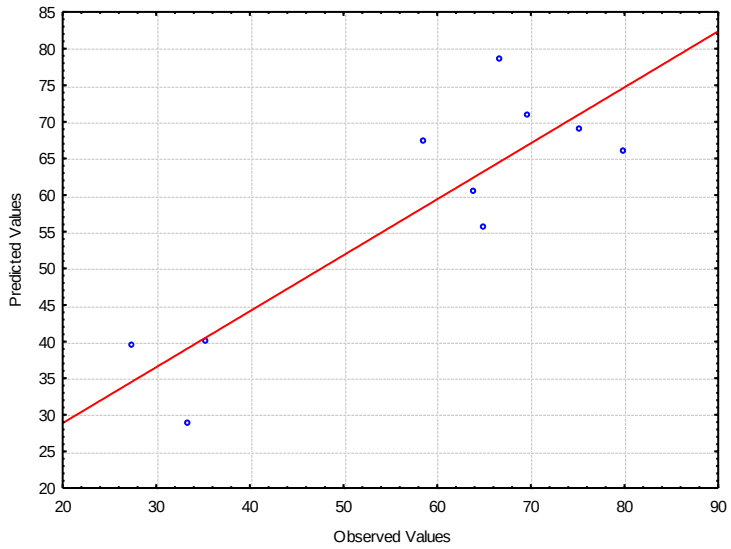


Figure 6 Model validation with experimental data

Mathematical model in equations 3 was validated with experiments data. The result of this analysis presented in Figure 6. Mathematical model is less valid because the experimental data coincide with the results of the calculation very little. The coefficient determination obtain R^2=0.764. This value is more than 0.7, so mathematical model can be used in optimization process can be follow to obtain optimum condition.

In table 4, the critical value of dimensionless numbers for each variable. Critical dimensionless value obtained for X_1 (ratio clove oil to sodium hydroxide) is -0.0109 and X_2 (temperature) 0.3095. X_1 and X_2 critical value is substituted to equation 6 to obtained yield of eugenol. Yield of eugenol in minimum condition is 39.17%.

Table 4 Critical value results / optimization

Solution: minimum			
	Observed	**Critical**	**Observed**
X_1	-1.4142	-0.0109	1.4142
X_2	-1.4142	0.3095	1.4142

4. Conclusion

The Surface Response Method (SRM) employed for optimization and analysis of production and purification of eugenol from clove oil by using neutralization and fractionation distillation from process. In minimum condition of increasing surface was obtained yield of eugenol 39.17% at X_1 -0.0109 and X_2 0.3095. The mathematical coefficient determination model is 0.7642.

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MINERAL AND MATERIAL PROCESSING

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International Seminar on Chemical Enginnering
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"Minerals and Materials Processing Toward Sustainable Development"
30-31 October, 2014 at East Hall, Institut Teknologi Bandung, Indonesia

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