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SYNTHESIS OF PALMITOYL-ETHANOLAMIDE FROM PALMITIC ACID AND MONOETHANOLAMINE: ANALYSIS OF VARIANCE AND SURFACTANT CHARACTERISTICS

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ABSTRACT

Analysis of variance and characteristics of surfactant palmitoyl-ethanolamide was observed in this study. Palm oil fraction, palmitic acid (PA), is reacted with monoethanolamine (MEA) to produce palmitoyl-ethanolamide using $ZrCl_4$ catalyst and a mixed solvent of isopropanol-hexane. The observed effect of substrate mole ratio (1/6.6-1/13.4 PA/MEA), catalyst concentration (1.6-8.4 w/w PA) and solvent ratio (0.32/1-3.7/1 v/w PA) to the conversion of palmitic acid was arrange by Central Composite Design (CCD) and performed using Response Surface Methodology (RSM). In the analysis of variance, observed the assumptions of normality, homoscedasticity, and independence to ensure the significance of the regression model that is compiled. The results of analysis of variance indicate that the required assumptions have been met and the regression model made is appropriate and usable. The characteristic test of surfactant palmitoyl-ethanolamide showed that the value of HLB palmitoyl-ethanolamide was 12.857 with the decrease of the surface tension of 32.61 dyne/cm.

Keywords: palmitoyl ethanolamide, ethanolamine, surfactant, response surface methodology, analysis of variance.

INTRODUCTION

Amides are typically organic compounds with high surface activity. Generally, the amide compound has a high melting point with good stability and has low solubility in various solvents [1]. The application of fatty acid amides as surfactants depends on the polarity between the two interface groups. When a liquid and solid phase is used, it is usually applied as a wetting agent, while in liquid-liquid phase it is usually used as a foam stabilizer and emulsifier [2].

The surfactant of fatty acid amides is obtained from the reaction of fatty acids with alkanolamines such as monoethanolamine. This reaction produces amides and releases water. Fatty acid amides are a rapidly expanding group of nonionic surfactants. Some examples of amide surfactants are shown in Figure-1.

Palmitic acid is the most common saturated fatty acid found in animals and plants. Palmitic acid is the main component of oil from palm trees, which is the first fatty acid produced in the process of lipogenesis in the form of carboxylic acids with long and unbranched tails [3]. So that palmitic acid is an abundant raw material that can be used in various fields of oleo chemical industry.

The search for a new and efficient chemical processes leads to the development of using Lewis acids as promoters, especially transition metal salts. Lewis acid catalysts must have characteristics such as abundant availability, high efficiency, and stability, low toxicity and allow for recycling. Zirconium is a group of IV transition metals that have abundant availability in the earth's crust, have low toxicity and are not considered toxic, so have been used as Lewis acid catalysts in many important organic transformations including carbon-carbon bonds and chemical de-protection [4].

Response surface methodology (RSM) is a set of mathematical and statistical techniques to analyze the effect of some independent variables on the response variable with the ultimate goal to optimize the response [5]. By constructing a mathematical model, the researcher can know the value of the independent variables that cause the response variable value to be optimal [6].

To examine the significance of the mathematical model obtained, it is necessary to analyze the variance and test the model verification. The model verification test, is performed by checking the residual suitability with the required assumptions. The usual assumptions taken in the analysis of variance (ANOVA) are the assumption of normality, the assumption of homoscedasticity and the assumption of independence [7].

Therefore, the purpose of the study is to analyze of variance and verification test of a mathematical model, which states the relationship between substrate mole ratio, catalyst concentration and solvent ratio to the conversion of palmitic acid. The study continued by observing the surfactant characteristics generated which included determination of Hydrophilic-Lipophilic Balance (HLB) value and the decrease of surface tension, and structure test using FT-IR.

MATERIALS AND METHODS

Materials

The materials used in palmitic acid ($C_{16}H_{32}O_2$), monoethanolamine (C_2H_7NO), zirconium (IV) chloride ($ZrCl_4$) catalyst, and mixed solvent hexane (C_6H_{14}) isopropyl alcohol (C_3H_8O) are obtained from E Merck, Darmstadt Germany. Figure-2 shows the synthesis of fatty

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alkanolamide from fatty acids with alkanolamine. This reaction produces a by-product of water.

Methods

The Palmitic acid, a mixture of hexane-isopropyl alcohol, monoethanolamine, and zirconium (IV) chloride catalyst are reacted at 55 ^{o}C for 3 hours with a 250 rpm stirring rate. The mixture is then separated from the catalyst by filtration and the solvent is evaporated. Determined the acid numbers [8], saponification number [9], surface tension analysis and Hydrophilic-Lipophilic Balance (HLB) value for all samples. Determination of HLB value of a surfactant is useful to know the usefulness of the surfactant produced. The determination of the HLB value of a non-ionic surfactant can be determined using the following equation [10].

$$HLB=20(1-S/A) \quad (1)$$

where S is Saponification number and A is an acidnumber.

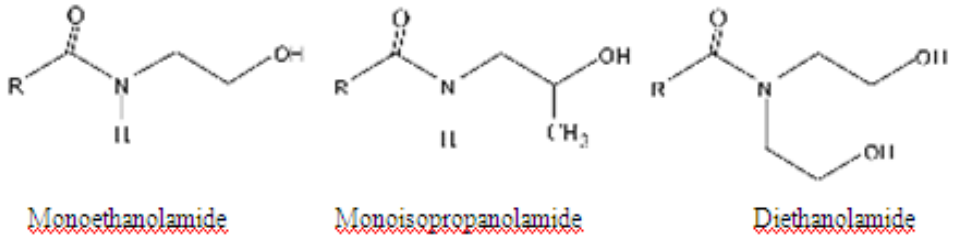

Figure-1. Some examples of Amide surfactants.

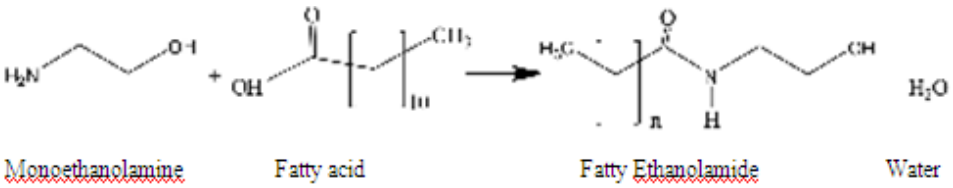

Figure-2. The synthesis of fatty Alkanolamide fom fatty acids with Alkanolamine.

Research data obtained, then analyzed by using RSM and MINITAB 17® (free trial) software. Central Composite Design (CCD) is used as a form of experimental design because it is considered to provide a systematic design to obtain interactions between variables [11]. From this design will be obtained the interaction of three variables, the substrate mole ratio (X_1), the catalyst concentration (X_2) and the solvent ratio (X_3).

RESULTS AND DISCUSSIONS

The successful synthesis of palmitoyl-ethanolamine was measured from the acquisition of the percent value of converted palmitic acid. The percent value of conversion of palmitic acid is obtained from the difference between the acid value at the beginning and the end of the reaction. The percent conversion oh the data was analyzed using RSM. RSM aims to create models and measure the strength of relationships and the influence of response variables and predictor variables [7, 12]. The response variable in this synthesis is the percent value of conversion of palmitic acid and the predictor variable is the substrate mole ratio, the catalyst concentration, and the solvent ratio.

Analysis of variance

The form of relationship between these variables can be determined by regression analysis [13]. The equations obtained were then tested with ANOVA that aimed to test the acceptability of the regression model from a statistical perspective in the form of a diversity analysis [14]. Table-1 shows the results of variance analysis of the regression model for the synthesis of palmitoyl-ethanolamide.

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Table-1. The results of variance analysis of the regression model.

Source	DF	Adj SS	Adj MS	F-VALUE	P-value
Regression	9	1081.62	120.180	20.77	0.000
Linear	3	844.46	281.488	48.65	0.000
Substrate mole ratio (X1)	1	0.06	0.058	0.01	0.923
Catalyst Concentration (X2)	1	44.48	44.482	7.69	0.020
Solvent ratio (X3)	1	799.92	799.923	138.24	0.000
Square	3	228.40	76.135	13.16	0.001
X1*X1	1	0.30	0.305	0.05	0.823
X2.X2	1	54.1	54.007	9.33	0.012
X3.X3	1	190.42	190.424	32.91	0.000
2-Way Interaction	3	8.75	2.917	0.50	0.688
X1.X2	1	0.01	0.009	0.00	0.969
X1.X3	1	5.67	5.670	0.98	0.346
X2.X3	1	3.07	3.072	0.53	0.483
Total	19	1139.48			

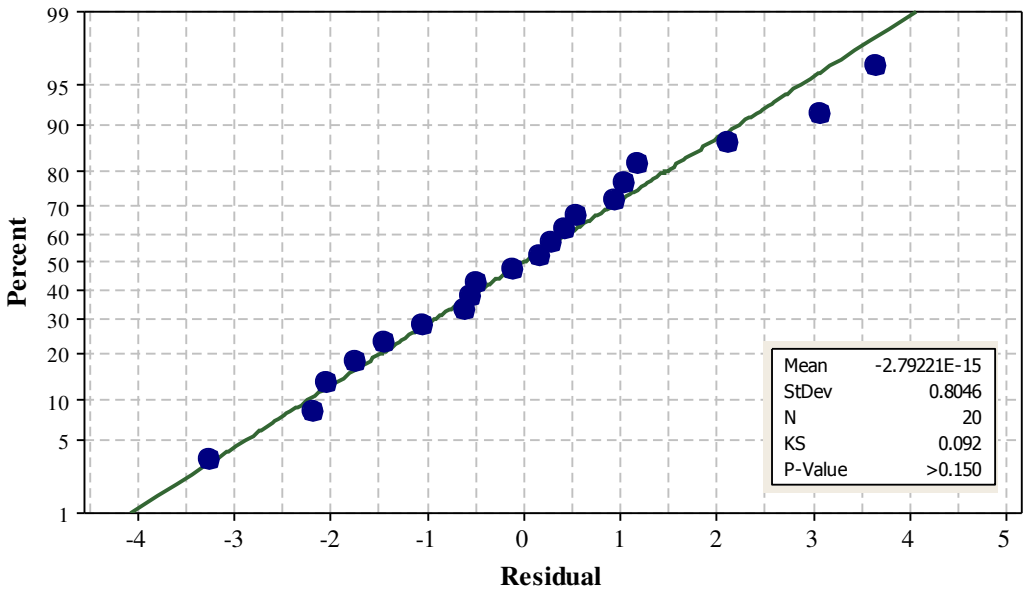

Figure-3. The plot of normality for the distribution of residual data.

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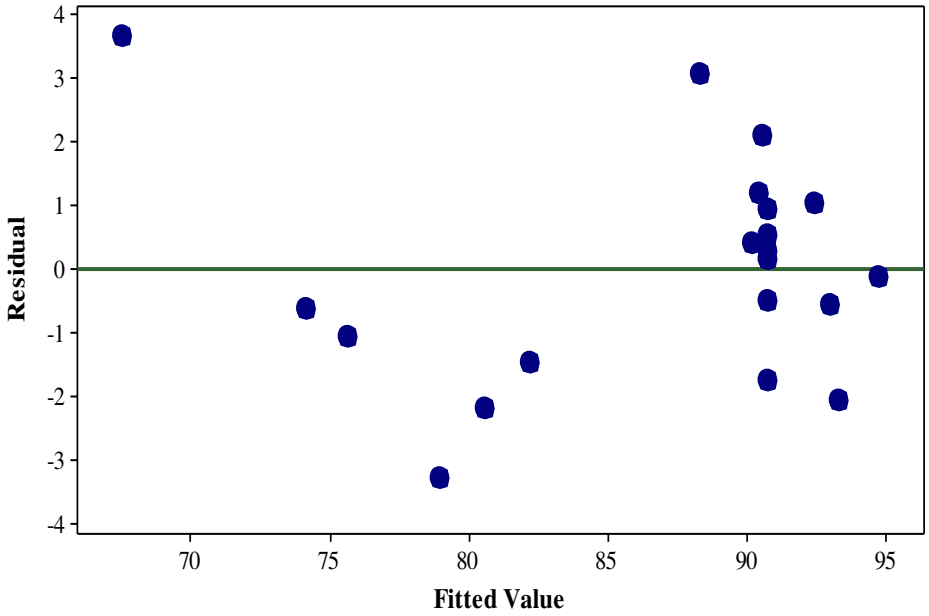

Figure-4. The residual plot with fitted value in the synthesis of Palmitoyl-Ethanolamide.

From ANOVA table will get the value of F. F value is calculated from comparison of MS (mean square) regression with MS residual. Test F is done, by comparing the value of $F_{arithmetic}$ with the F_{table}. If $F_{arithmetic}$ is greater than F_{table} ($F_{count} > F_{table}$), then there is a significant relationship between variables [15]. From Table-1, the value of $F_{arithmetic}$ is obtained by 11.70 and the F_{table} value is 3.24. Value $F_{count} = 11.70 > F_{table} = 3.24$, so it can be concluded that there is a significant relationship or regression model accepted.

The result of analysis of variance also shows that the linear model (P = 0.000), quadratic model (P= 0.001) and nonlinear model which include interaction between factors (P= 0.688) is significant because P value of the linear model and quadratic model that include interaction between factor less than α used. This means that linearly and quadratically, the independent variables contribute significantly to the model formed for use in the synthesis of palmitoyl-ethanolamide. Nonlinearly, however, which involves interaction between factors, the independent variables do not contribute significantly to the model formed.

Model verification test

To check the residual suitability with the required assumptions, a model verification test is performed. Normality assumptions, homoscedasticity assumptions, and independence assumptions are common assumptions taken on model verification tests.

The assumption of normality can be known in various ways, one of which is the Kolmogorov-Smirnov test. The normality interpretation using Kolmogorov Smirnov (KS) test is done using significance value (α) = 0.05. Based on statistical data of Kolmogorov Smirnov [7] for α = 0.05 and observation count of 20 observations obtained 0.294 (two-way test). This value will be used as a guide in the conclusion based on normality test of research data. The Kolmogorov statistical value obtained from the observation that is KS = 0.092, less than the Kolmogorov statistical value in the table. It is found that $KS < KS^{1-\alpha}$ it can be concluded that the residual linear regression model made has followed the normal distribution. Furthermore, the plot of normality in Figure-3 shows that the distribution of residual data is in a straight line environment. It appears that the distribution tends to form a straight line, so it can be said that the normality assumption not to be violated. The residual average is very small because it is close to 0. Therefore, the conclusion of the residual normality test result is the residual normality assumption, on a regression model has been met by the regression model and the regression model made is appropriate and can be used.

Homoscedasticity test aims to determine the homogeneity of variance. The residual plot with fitted value in the synthesis of palmitoyl-ethanolamide is shown in Figure-4. It appears that the data distribution tends to be random and does not form a particular pattern, hence it can be concluded that the homogeneity assumption of variance (homoscedasticity) has been met.

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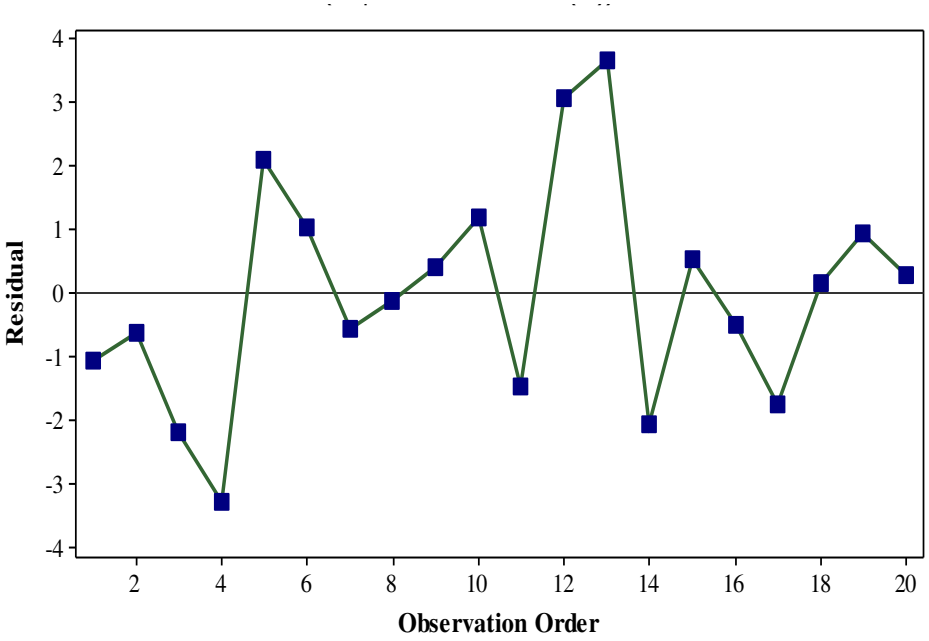

Figure-5. The plot of residuals with the model order on the synthesis of Palmitoyl-Ethanolamide.

The assumption of independence aims to determine whether between independent variables are related or correlated. Therefore, the data in Figure-5 is used to check residuals with the model order on the synthesis of palmitoyl-ethanolamide. From the plot in Figure-5, it is seen that the distribution of residual data versus sequence (order) tends to be random and not patterned, so it can be said that the assumption of independence has been met.

Characteristic analysis of Palmitoyl-ethanolamide

The acid number represents the amount of free fatty acids present in the product. High acid numbers will affect the polarity and foam thereby decreasing the quality of the final product [14]. From the research results obtained the acid number of the best product is 11.781.

The saponification numbers represent the ability of potassium hydroxide (KOH) to convert 1 gram of fat into soap. The result of measurement of saponification number of palmitoyl-ethanolamide surfactant is 4.207. The data of saponification number of palmitoyl-ethanolamide along with its acid number can be used to determine the HLB value of the surfactant produced.

To determine the usefulness of the surfactant, it is usually determined by its HLB value. The value of HLB surfactant product obtained was 12.857. The value of this HLB indicates that the surfactant palmitoyl- ethanolamide can be used as a detergent mixture. The surfactant is water-soluble and is used to make an oil-in-water emulsion [16].

Water has a surface tension of 72.8 dyne/cm at a temperature of 20°C [17]. The addition of surfactant in a solution will cause the drop in surface tension of a solution. At a certain concentration, the surface tension will be constant and will not change even if the surfactant concentration is increased. Critical Micelle Concentration (CMC) is the dissolution of surfactant molecules in a water or polar solvent above a certain concentration [18]. The decrease of the surface tension can be calculated by looking at the difference in surface tension before and after the addition of purified palmitoyl-ethanolamide. From the results of the analysis that has been done on the best-converted product, the decrease of surface tension is 32.61 dyne/cm or 45.30%.

Identification of Palmitoyl-ethanolamide with FT-IR spectroscopy

Figure-6 shows the results of the FT-IR spectrum on the ratio of the substrate to 12:1 (MEA/PA), the catalyst concentration of 7% (w/w PA), and the solvent ratio to 3:1 (v/w PA). From the FT-IR spectrum test results, the vibrations for the C-N bond for the amide are at wave numbers 1250-1020 cm^{-1}. The absorption peak at the wave number 627.37 cm^{-1} indicates the presence of an N-H group, wherein this wave number indicates the sample contains an amide group. While the absorption at wavenumber 3307.30 cm^{-1} indicates the presence of OH group [19]. The OH group is present in monoethanolamine compounds. The absorption peaks 2925.18 cm^{-1} indicate the presence of C-H and wave 1023.19 cm^{-1} groups indicating the presence of C-O for alcohols.

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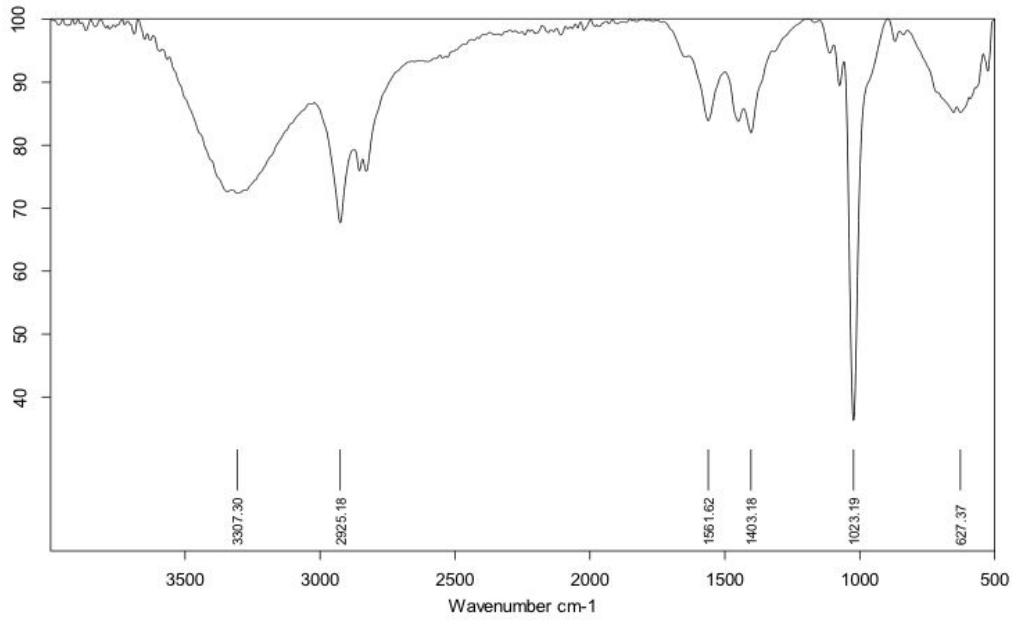

Figure-6. The FT-IR spectrum analyzes on the synthesis of Palmitoyl-Ethanolamide.

CONCLUSIONS

Based on the discussion of the fatty alkanolamide surfactant, it is found that in the analysis of variance performed, from the three assumptions, which are normality assumption, homoscedasticity, and independence, all of which show that the required assumption has been fulfilled and the regression model is significant. The characteristic test of surfactant palmitoyl-ethanolamide showed that the value of HLB palmitoyl-ethanolamide was 12.857 with the decrease of the surface tension of 32.61 dyne/cm. Identification with FT-IR Spectroscopy also showed that the surfactant obtained was in the alkanolamide group.

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