OPTIMIZING PROCESS CONDITION FOR AMIDIFICATION OF STEARIC ACID AND UREA USING RESPONSE SURFACE METHODOLOGY

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ABSTRACT

Stearic acid (SA) and urea (U) are very potential for use in stearamide production through the amidification process. Using metal catalyst zirconium tetrachloride and 2-propanol with n-hexane as a mixed solvent, parameters such as substrate molar ratio, catalyst concentration, and solvent ratio have been varied to maximize the yield of stearamide. Response Surface Methodology (RSM) is supported by Central Composite Design (CCD) was applied to determine the optimum parameter value that produces the maximum conversion of stearic acid. Results showed that the regression model can be used and shows a very strong relationship between parameters which is characterized by the value of R^2 (0.9207) was high and the p-value of the interaction of variance was <0.05 . According to this model, increasing of the substrate molar ratio and catalyst concentration leads to increasing the conversion of stearic acid, and the highest yield of stearamide concentration was obtained at substrate molar ratio of 8/1 (U/SA), catalyst concentration of 4% (w/wSA) and the solvent ratio of 1/1 (v/wSA). The highest conversion of stearic acid was found to be 90%.

Keywords: Stearamide, Zirconium Tetrachloride, Amidification, Response Surface Methodology.

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INTRODUCTION

Surfactants The amide chain formation is one of the most important catalytic reactions in various fields of chemistry that are environmentally friendly.¹ Many studies have been conducted to develop amide formation methods from various raw materials.²⁻³ Amide formation mostly uses methods that involve the reaction of amines with carbonyl compounds, and the method used is very similar to the manufacture of esters.⁴

The amide compounds have various uses, such as sulfoamide which can treat various kinds of infectious diseases, and N-steroyl glutamide which is used as a surfactant and antimicrobial.⁵ Likewise, for amides in the form of a fatty acid amide, these compounds are widely used as lubricants in the manufacture of resins, like emulsifiers, detergent, surfactants, and cosmetic ingredients.⁶⁻⁹

One of the fatty acid amides that can be obtained from vegetable oils or derivatives is stearamide. Stearamide is one of the fatty acid amides that produced on a large scale for use in the production of rubber materials and the production of waterproof fabrics, by reacting with formaldehyde, pyridine and hydrochloric acid.¹⁰⁻¹¹

Stearamide can be obtained from the oxidation of stearic acid and urea. Stearic acid can be obtained in large quantities from vegetable oil derivatives and is a long-chain saturated fatty acid so that it is more stable than unsaturated fatty acids.¹² The use of urea is also very interesting to develop because urea is one of the ingredients that can react well in organic solvents. Also, compared to using ammonia, the use of urea can minimize the use of high temperature and high pressure on fatty amide synthesis.¹ The potential use of stearamide is no doubt. It is, therefore, necessary to compile a reliable method for the synthesis, analysis and optimizing of the acquisition of stearamide. RSM is one method that can be used

to optimize acquisition.¹⁴⁻¹⁵ In RSM, the observation data obtained is used to predict an appropriate empirical model that can be used to determine the effect of interactions between variables and analyze optimum conditions that can produce the maximum response.¹⁶⁻¹⁷

This research uses zirconium tetrachloride ($ZrCl_4$) as a catalyst and 2-propanol with n-hexane as a mixed solvent. The metal catalyst $ZrCl_4$ was chosen because it is more economical and has high efficiency even after several times of use.¹⁸⁻²⁰ The mixed solvent of 2-propanol with n-hexane is chosen by considering the solubility of raw materials and products against solvents. The resulting amide products and urea were found to be more soluble in a polar alcohol solvent, while pure fatty acids were less soluble in a polar solvent but more soluble in non-polar solvents such as n-hexane. Thus, the mixtures of alcohol and n-hexane are recommended to be the best solvents because these mixtures can dissolve all the necessary components and produce the maximum products.^{8,21}

To analyze the process, three significant variables, substrate molar ratio, catalyst concentration, and solvent ratio, with one dependent variable (stearic acid conversion) were studied. Heretofore, no research has been done to compare the above three factors together to verify the extent of their influence on the amidification process. Thus in this study, the interaction among the variables as well as their direct impacts on the process are discussed.

EXPERIMENTAL

Materials

Stearic acid ($C_{18}H_{32}O_2$), Urea (CH_4N_2O), zirconium (IV) chloride ($ZrCl_4$), n-hexane (C_6H_{14}) and 2-propanol (C_3H_8O) were purchased from E Merck. All common chemicals and solvents were purchased from commercial sources and used as received.

Amidification of Urea with Stearic Acid

A total of 1 mol of stearic acid (SA) was determined the initial acid value.²² Furthermore, stearic acid and a mixture of 2-propanol and n-hexane (1/1, v/v) were added to the three-neck flask. Variation of the solvent ratio was carried out from 0.318 to 3.682 (v/ wSA). After homogeneous, urea (U) with a variation of the substrate mole ratio of 2.636 to 9.36 (mole U/SA) is added to the three-neck flask. Followed by the addition of zirconium tetrachloride at 1.318 to 4.682 (w/wSA). The mixture was heated at 65°C, for 3 hours and stirred at a speed of 250 rpm.

The product was washed with 5 ml citric acid 10% to be purified. The catalyst will settle and be separated by filtration. The filtrate was separated in a rotary evaporator at 90°C to separate the product and solvent. Then using acetone the product is washed, to remove the remaining urea. Urea will dissolve with acetone as the top product and stearamide will be obtained as a lower layer. Furthermore, the value of stearic acid is converted from the following formula.³

$$\text{Conversion(\%)} = \frac{\text{Initial Acid Value} - \text{Acid Value}}{\text{Initial Acid Value}} \cdot 100\% \quad (1)$$

Response Surface Methodology

Response Surface Methodology (RSM) is used to state the process of output as a surface and contour plots and to predict the model that describes the relationship between some influencing parameters to the response, and in this case, is the stearic acid conversion.^{4,8,23} The main benefit of using RSM is that a series of design experiments can achieve optimal response. In this case, a second-degree polynomial model is used in RSM as follows:

$$Y = \beta_1 + \beta_2 X_1 + \beta_3 X_2 + \beta_4 X_3 + \beta_5 X_1 X_2 + \beta_6 X_2 X_3 + \beta_7 X_1 X_3 + \beta_8 X_1^2 + \beta_9 X_2^2 + \beta_{10} X_3^2 \quad (2)$$

Where, Y = stearic acid conversion (%); β_1 = intercept (constant); β_2 - β_4 = linear coefficient; β_5 - β_7 = cross product coefficient; β_8 - β_{10} = quadratic coefficient; X_1 = substrate molar ratio (U/SA); X_2 = catalyst concentration (w/wSA) and X_3 = solvent ratio (v/wSA).

The experimental design used was the Central Composite Design (CCD). Furthermore, the independent variables were varied according to the design in Table-1. The optimal reaction variables that will produce the maximum percent conversion of stearic acid are statistically analyzed through Minitab version 17 software (trial version).

Table-1: Variables and Levels Developed For Stearic Acid Synthesis

Variable	Variable with Level Code				
	-1.682	-1	0	1	1.682
Substrate molar ratio (U/SA)	2.636/1	4/1	6/1	8/1	9.364/1
Catalyst concentration (w/wSA)	1.318/1	2/1	3/1	4/1	4.682/1
Solvent ratio (v/wSA)	0.318/1	1/1	2/1	3/1	3.682/1

RESULTS AND DISCUSSION

The procedure of RSM consists of the following steps of experiments, development of an approximate model, optimization of the approximate model, and representation of direct and interactive effects of the process parameters.^{17,23-24}

The results of stearamide synthesis in the percent conversion of stearic acid are shown in Table-2. The percent conversion of stearic acid was obtained from the difference between the acid number at the beginning and the end of the reaction.

Table-2: The Results of Stearamide Synthesis

No.	Substrate Molar Ratio (X ₁)		Catalyst Concentration (X ₂)		Solvent Ratio (X ₃)		Conversion (%)
	Code	Actual	Code	Actual	Code	Actual	
1	-1	4/1	-1	2/1	-1	1/1	85.17
2	1	8/1	-1	2/1	-1	1/1	88.78
3	-1	4/1	1	4/1	-1	1/1	83.81
4	1	8/1	1	4/1	-1	1/1	90.66
5	-1	4/1	-1	2/1	1	3/1	81.23
6	1	8/1	-1	2/1	1	3/1	82.77
7	-1	4/1	1	4/1	1	3/1	80.11
8	1	8/1	1	4/1	1	3/1	89.62
9	-1.682	2.636/1	0	3/1	0	2/1	85.08
10	1.682	9.364/1	0	3/1	0	2/1	89.88
11	0	6/1	-1.682	1.318/1	0	2/1	81.71
12	0	6/1	1.682	4.682/1	0	2/1	83.56
13	0	6/1	0	3/1	-1.682	0.318/1	82.38
14	0	6/1	0	3/1	1.682	3.682/1	80.47
15	0	6/1	0	3/1	0	2/1	80.30
16	0	6/1	0	3/1	0	2/1	80.72
17	0	6/1	0	3/1	0	2/1	80.23
18	0	6/1	0	3/1	0	2/1	80.08
19	0	6/1	0	3/1	0	2/1	80.88
20	0	6/1	0	3/1	0	2/1	80.88

Model Prediction

The purpose of developing a regression model is to find out the relationship between the percent conversion of stearic acid (Y) with substrate molar ratio (X₁), catalyst concentration (X₂) and the solvent ratio (X₃), and also to optimize the response of stearic acid conversion. In Table 3, the results of predictions of regression coefficients are listed to compile a response surface model of stearamide synthesis. The confidence level used in this study is 95%, so the level of significance (α) allowed is 1-0.95= 0.05.¹⁵⁻¹⁶ The significance level shows the allowed error, where if the value of α = 0.05, it means that the results of the study have a true chance of 95% and the maximum of error tolerance of 5%.

Based on Table-3, the equation model that can show the relationship of reaction variables and their interaction with the percent conversion of stearic acid (Y) is obtained as follows:

$$Y = 80.4619 + 3.2243X_1 + 0.7341X_2 - 2.6233X_3 + 7.9468X_1X_2 + 3.1018X_1X_3 + 221.8918X_2^2 + 5.1654X_1X_2 + 1.4107X_1X_3 + 3.0441X_2X_3 \quad (3)$$

Where, X_1 , X_2 , X_3 are the substrate molar ratio, catalyst concentration, and solvent ratio respectively. The R-square value (R^2) can also be seen from the results of variance analysis. R^2 value from the analysis result of 92.37% shows that the independent variable in the experiment affects the dependent variable (% conversion) by 92.07%.

Table-3: The Predictions of the Regression Coefficients

Term	Coef	P
Constant (Y)	80.4619	0.000
Substrate Molar Ratio (X_1)	3.2243	0.001
Catalyst Concentration (X_2)	0.7341	0.003
Solvent Ratio (X_3)	-2.6233	0.000
$(X_1)*(X_1)$	7.9469	0.000
$(X_2)*(X_2)$	3.1018	0.017
$(X_3)*(X_3)$	1.8918	0.114
$(X_1)*(X_2)$	5.1654	0.005
$(X_1)*(X_3)$	1.4107	0.358
$(X_2)*(X_3)$	3.0441	0.064
R-Sq = total squared = 92.07%		
R-Sq(adj) = squares due to treatment = 89.94%		

From the Minitab output, the p-value for the substrate molar ratio, catalyst concentration, and solvent ratio are 0.000, 0.097 and 0.006 respectively. The p-value of the substrate molar ratio and solvent ratio is smaller than α (5%), and the p-value of the catalyst concentration is greater than α . Based on the p-value it can be seen that the substrate molar ratio and solvent ratio are the statistically significant factor because the p-value is smaller than 5%.

Analysis of Variance (ANOVA)

ANOVA is used to examine the significance of the regression model obtained.^{8,14} The results of the variance analysis in Table-5 showed that the linear model ($p = 0.000$), quadratic model ($p = 0.000$) and nonlinear models were significant. The comparison of the model conversion to the actual conversion is given in Table-4 and Fig.-1. In general, it can be concluded that the comparison of the actual conversion to the model conversion shows no significant deviation in the actual conversion produced. The data obtained also states that if the difference between the predictive data and the actual data is small, then it shows that the resulting equation is getting better. Vice versa, if the deviation of predictive data with actual data is getting farther away, this indicates that the resulting equation is not so good.

The standard deviation generated from the model is 1.3515. This shows that the equation model produced by the statistical method is acceptable because the resulting deviation is a little with a small error of 0.3022.

Table-4: The Value of the Model Conversion to the Actual Conversion

Observation Order	Experimental Results	Simulation Results	$(X_1 - X_2)$	$(X_1 - X_2)^2$
1	85.17	85.41	-0.23	0.06
2	88.78	86.79	1.99	3.96
3	83.81	82.67	1.14	1.30
4	90.66	89.62	1.05	1.09
5	81.23	81.32	-0.09	0.01
6	82.77	83.05	-0.28	0.08
7	80.11	81.24	-1.13	1.27
8	89.62	88.52	1.10	1.20
9	85.08	84.57	0.51	0.26
10	89.88	91.86	-1.98	3.92
11	81.71	82.22	-0.51	0.26
12	83.56	84.52	-0.96	0.93
13	82.38	84.34	-1.96	3.83
14	80.47	79.98	0.49	0.24

15	80.30	80.53	-0.23	0.05
16	80.72	80.53	0.19	0.04
17	80.23	80.53	-0.30	0.09
18	80.08	80.53	-0.45	0.20
19	80.88	80.53	0.35	0.13
20	80.88	80.53	0.35	0.13

Fig.-1: The Comparison of the Model Conversion to the Actual Conversion

The Effect of Catalyst and Substrate Molar Ratio

The contour plot of stearamide synthesis is given in Fig.-2. It is shown that the stearic acid conversion will increase as the substrate molar ratio increases. It can be seen that the maximum conversion can be obtained if the substrate molar ratio is at a ratio of 8/1 (U/SA), while the catalyst concentration of 4% (w/wSA). In this condition, we can get the conversion of stearic acid by 90%. This contour plot also shows that the increase in stearic acid conversion is sharper when the substrate molar ratio increases compared to when the catalyst concentration increases.

The addition of urea also showed an increase in produce amide compounds when compared with the addition of other fat substrates. The catalyst zirconium tetrachloride used also provides a positive response because Zr^{4+} has a strong coordinating ability and can work well in various solvents.¹⁹⁻²⁰

Fig.-2: The Contour Plot between Substrate Molar Ratio and Catalyst Concentration

The Effect of Substrate Molar Ratio and Solvent Ratio

The observation of the interaction effect of the substrate molar ratio and solvent ratio on conversion is shown in Fig.-3. It can be seen that stearic acid conversion will increase with increasing solvent ratio and substrate molar ratio to certain limits. So that the greater the solvent ratio used, the greater the substrate that is converted to stearamide. The mixed solvent used also gave a positive effect on the stearamide

formation. The amidification reaction was carried out using 2-propanol with n-hexane as a mixed solvent, where it would produce the best reaction with a yield percentage of 80%.^{7,21} This is because amides are more soluble in polar alcohol solvents while fatty acids are more soluble in non-polar solvents such as n-hexane.^{8,25}

Fig.-3: The Contour Plot between Substrate Molar Ratio and Solvent Ratio

The Effect of Catalyst Concentration and Solvent Ratio

The interaction effect of catalyst concentration and solvent ratio on stearic acid conversion is shown in Fig.-4. The observations show that stearic acid conversion will increase with increasing catalyst concentration and solvent ratio to certain limits. Based on Fig.-4 it can be seen that the optimum conditions obtained when the concentration of ZrCl_4 of 4% (w/wSA) and the solvent ratio of 1/1 (v/wSA) which will result in a conversion of 90.66%. The contour plots show that the increase in stearic acid conversion is sharper when the solvent ratio increases than when the catalyst concentration increases.

Zirconium tetrachloride is a very efficient catalyst for the amidification of primary or secondary carboxylic acids and amines.^{20,25} The best percentage of conversion of 73-90% ever achieved in some types of reactions of carboxylate acid with amine.¹⁸⁻¹⁹ This result is in line with the study conducted where the percent of stearic acid conversion reached 80%.

Fig.-4: The Contour Plot between Catalyst Concentration and Solvent Ratio

Identification of Stearamide With FT-IR Spectroscopy

Figure-5 shows the results of the FT-IR spectrum analysis in the substrate molar ratio of urea with stearic acid 8/1 (U/SA), the catalyst concentration of 4% (w/wSA), and the solvent ratio of 1/1 (v/wSA). It can be seen that the vibration for the C-N bond for the amine is in the wavenumber $1250\text{--}1020\text{ cm}^{-1}$. From the spectrum test, the absorption peak obtained in the wavenumber of 597.73 cm^{-1} indicates the presence of an N-H group. This wavenumber showed the sample contains an amide group. While the absorption at wavenumber 3367.71 cm^{-1} indicates the presence of OH groups. OH, the group is found in

monoethanolamine compounds. The peak of absorption at a wavenumber of 2924.09 cm^{-1} indicates the presence of C-H group and the absorption at 1072.42 cm^{-1} indicates the presence of C-O group for alcoholic compounds.²⁶

Fig.-5: The Results of the FT-IR of Stearamide

CONCLUSION

In this study, stearamide was obtained from the amidification reaction of stearic acid and urea. Optimization of the process can be obtained using RSM. The substrate molar ratio and catalyst concentration significantly affected the acquisition when the solvent ratio had a positive but not significant effect. Analysis using Minitab shows that a model that is expected to be satisfactorily fitted with R^2 of 0.9207. This study shows that amidification of stearic and urea acids using zirconium tetrachloride can be optimally performed to obtain maximum stearamide.

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