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SYNTHESIS OF N-ACYL ARGININE SURFACTANTS FROM TETRADECANOL AND ARGININE USING TERT-AMYL ALCOHOL

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ABSTRACT

The surfactant N-acyl arginine can affect the surface properties of a material and can be synthesized from tetradecanol and arginine. The main problem in the synthesis of the surfactant N-acyl arginine is knowing the effect of reaction time, catalyst, solvent, and substrate to produce the best tetradecanol conversion. The amidation process is carried out by reacting tetradecanol and arginine in a ratio of 1/1.32 - 1/4.68 ($mol_{tetradecanol}/mol_{arginine}$) with the addition of tert-amyl alcohol and sodium methoxide catalyst with 1.64-8.36% ($w/w_{substrate}$). The purification process is carried out by adding 10% citric acid, and then it is filtered with filter paper and heated at 90 ° C to evaporate the remaining solvent. The product will be analyzed by determining the acid number to obtain the percent conversion of tetradecanol to N-acyl arginine. The optimum conversion percentage obtained was 91.6% at a catalyst concentration of 7 % ($w/w_{substrate}$), a solvent ratio of 1/3 ($mL/mL_{tetradecanol}$), and a substrate ratio of 1/4 ($mol_{tetradecanol}/mol_{arginine}$), at a temperature of 65 ° C and a time of 4 hours.

Keywords: N-acyl arginine, arginine, tetradecanol, solvent, catalyst.

INTRODUCTION

Surfactants are substances added to liquids to increase their dispersion properties by lowering the surface tension of the liquid. The surfactants' ability to lower voltage because surfactants have an amphipathic structure with a molecular structure consisting of hydrophilic and hydrophobic groups [1]. Almost half of the surfactants produced are for the washing and cleaning sector. Surfactants are also used in cosmetics, dissolving, dispersing, wetting, emulsification, and foaming [2].

Commercial surfactants are used as the essential ingredients of soap making. Most of these commercial surfactants are synthetically synthesized from petroleum derivatives and are mainly used in washing applications that can cause significant environmental problems in long-term use [3,4].

Amino acid-based surfactants belong to surfactants with high biodegradability, low toxicity, and excellent surface-active properties. Amino acid-based surfactants have excellent emulsifying properties, producing a delicate foam, light for the skin and eyes [5]. N-fatty acyl amino acid surfactant is one of the options used in the production of food, pharmaceutical, and cosmetic processes. It can be made by chemical methods using renewable raw materials, including amino acids and vegetables [6].

Arginine is a necessary amino acid and is classified as a conditionally essential amino acid. One of the main functions of arginine is to play a role in the synthesis process. Arginine is also involved in several roles in the body, such as ammonia detoxification formed during amino acid nitrogen catabolism through the formation of urea [7]. Arginine-based surfactants are promising alternatives to other antimicrobial surfactants with high intrinsic toxicity. Arginine-based surfactants were initially used as preservatives in the medical and cosmetic fields. The antimicrobial activity of arginine-based surfactants is directly related to the cationic charge of the proton guanidine group of amino acids [8, 9].

Amino acid-based surfactants have several different structural features, as shown by the chemical formula derived from N-acyl arginine. The unique properties shown by this type of compound are due to the strong hydrogen bond of the amide bond located between the hydrophilic (amino acid residue) and the hydrophobic part of this molecule [10].

Surfactants can be synthesized from basic oleochemicals, both fatty alcohol, fatty acid, and methyl esters. Tetradecanol is a fatty alcohol that has a formula of $C_{14}H_{30}O$, has a molecular weight of 214.39 g/mol, boiling point 289 ^{o}C, and freezing point 37-40 ^{o}C. Fatty alcohol comes from vegetable oils such as palm oil and coconut oil, which serve as raw materials for various household products and surfactants. Fatty alcohol is used as a raw material in making surfactants because it has the advantage of being resistant to the environment's pH, so it is easy to use in lotions and creams [11].

The process of making surfactants has been done using NaOH catalyst, calcium oxide. In this case, the manufacture of surfactants with sodium methoxide catalyst can also be used. Sodium methoxide is a catalyst that can be obtained by dissolving NaOH with methanol. Sodium methoxide can react smoothly under low-temperature conditions as well as atmospheric pressure. Sodium methoxide catalyst is an active catalyst used in producing surfactants [12, 13, 14].

Tert-amyl alcohol has a relatively high hydrophilicity. In general, the catalytic activity of enzymes in hydrophilic solvents is relatively low. However, the tolerant properties of organic solvents in surfactant

production may indicate high activity in hydrophilic solvents. Especially tert-amyl alcohol, high catalytic performance activity was found in the manufacture of Carlsberg surfactant-subtilisin, which is comparable to hydrophobic organic solvents such as octane [15].

The response surface method (RSM) is a useful experimental strategy if several factors influence the response. The purpose of the experiment is to find the optimal response. This method makes it easy for us to determine the suitable conditions for the amidation reaction and obtain the maximum conversion of fatty acids and alkanolamides. When there is more than one response, it is essential to find the optimal compromise that does not optimize only one response. RSM is useful in three different techniques or methods: (i) statistical experimental design, (ii) regression modeling techniques, and (iii) optimization methods. Response Surface Methodology is most commonly used in industry, biology and clinical sciences, social sciences, food sciences, and physics and engineering sciences [16,17].

MATERIALS AND METHODS

The ingredients used are arginine ($C_6H_{14}N_4O_2$), tetradecanol ($C_{14}H_{30}O$), sodium methoxide (CH_3ONa), tert-amyl alcohol, citric acid, and acetone obtained from E. Merck.

Research plan, according to Central Composite Design with three variables and five levels. The design in Table 1 is used as a combination of independent variables and levels developed using Central Composite Design. At each run, start by heating tert-amyl alcohol and tetradecanol in a three-necked pumpkin. Further added arginine with a variation of 1/1.32-1/4.68 ($mol_{tetradecanol}$/ $mol_{arginine}$). Sodium methoxide catalyst with a weight ratio of 1.64-8.36% ($w/w_{substrate}$), was put in a beaker glass and put into a three-necked pumpkin after dissolving tetradecanol. It was heated with a heating temperature variation of 65 ^oC for 3 hours.

The mixture is separated from the catalyst using a filter, and the solvent is evaporated. The mixture was added to 10% citric acid in 5 mL to precipitate its catalyst, and the formed sediment was separated by filtration. The product mixed with the solvent is separated by evaporating the solvent at a temperature of 90 ^oC. Products that contain excess arginine are then washed with acetone twice the volume of the product mixture, which will dissolve arginine. The product will be obtained as a bottom layer, while excess arginine will dissolve with acetone as the top product. Acetone is excessively evaporated, the volume obtained is measured, and the percentage of conversions is calculated. Further analysis is performed to predict the regression model, as well as and test the resulting model verification. The optimization results of the conversion of tetradecanol is given in Table-2.

RESULTS AND DISCUSSIONS

Effect of Reaction Time

Determining the best temperature and reaction time needs to be done where the result of this determination will be used as a fixed variable at the next stage.

Table-1. Variables and levels developed using central composite design.

Variable	Code Levels of Variables				
	-1.682	**-1**	**0**	**1**	**1.682**
Catalyst ($w/w_{substrate}$)	1.64	3	5	7	8.36
Solvent ($mL/mL_{tetradecanol}$)	0.32/1	1/1	1/2	1/3	1/3.68
Substrate ($mol_{tetradecanol}/mol_{arginine}$)	1/1.32	1/2	1/3	1/4	1/4.68

Table-2. The optimization results of the conversion of tetradecanol.

Run no.	Catalyst (X_1)	Solvent (X_2)	Solvent (X_3)	Tetradecanol Conversion (Y, %)
1	-1	-1	-1	87.5
2	1	-1	-1	87.5
3	-1	1	-1	79.1
4	1	1	-1	83.3
5	-1	-1	1	66.6
6	1	-1	1	66.6
7	-1	1	1	83.3
8	1	1	1	91.6
9	-1.682	0	0	79.1
10	1.682	0	0	83.3
11	0	-1.682	0	75.0
12	0	1.682	0	83.3
13	0	0	-1.682	87.5
14	0	0	1.682	75.0
15	0	0	0	75.0
16	0	0	0	75.0
17	0	0	0	70.8
18	0	0	0	75.0
19	0	0	0	75.0
20	0	0	0	75.0

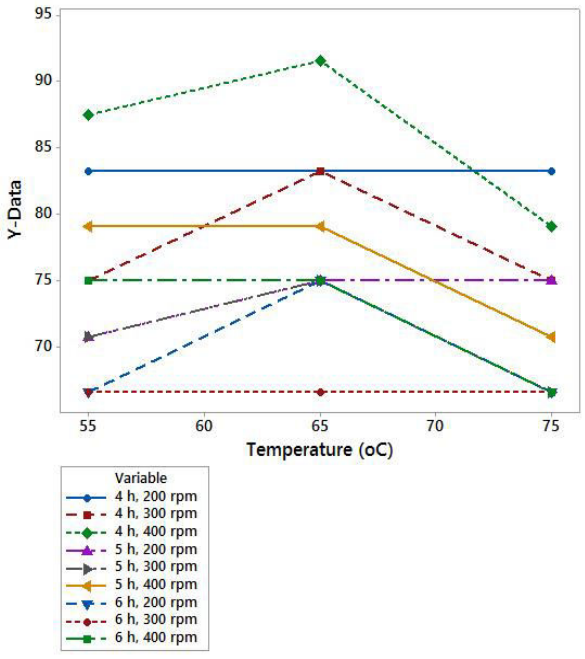

Figure-1. The reaction temperature determination.

Observations were made by reacting tetradecanol and arginine at 1/1 ratio, with tert-amyl alcohol solvent at 1/1 ratio, and sodium methoxide catalyst at 5% concentration. The reaction temperature is chosen at 55 - 75°C, at a reaction time of 4 to 6 hours and a stirring speed of 200-400 rpm.

The results of the reaction temperature determination are shown in Figure-1. It can be seen that there are three conditions where the increase in temperature does not increase the conversion, namely in the condition of 4 hours 200 rpm, 5 hours 200 rpm, and 6 hours 300 rpm. So, it seems that the 200 rpm motor rotation has not affected tetradecanol conversion. It is also generally found that by increasing the reaction temperature to 75°C, the reaction conversion will be reduced compared to the 65°C temperature. This is due to the temperature around 75°C. The solvent used is almost completely evaporated, so it is not optimal for use.

It was concluded that the highest conversion was obtained when the reaction temperature was 65 °C, with a stirring rotation of 400 rpm and the sampling time at 4 hours. Based on the results of the data obtained, the best temperature and reaction time to be used in the

optimization research is a temperature of 65 ^{o}C and a reaction time of 4 hours with a conversion of 91%.

Model Prediction

Catalyst concentrations, solvent ratios and substrate ratios, were variables selected to obtain the N-acyl arginine surfactant in this study. Where is the substrate itself in this case as a reactant with the base of tetradecanol and the arginine amino acid, with the catalyst sodium methoxide, and tert-amyl alcohol as solvents in this reaction.

Where the catalyst weight of CH_3NaO (%) is denoted by X_1, the solvent is the ratio denoted by X_2, and the substrate is the ratio of tetradecanol to arginine, denoted by X_3. The optimization results with the CCD method are given in Table-1.

The model prediction is made by looking at the regression value (R^2) of the model. Where this value R^2 will be displayed in the form of a percent to make it easier to see the magnitude of the influence of independent variables on the measured parameters [4]. Another thing to note is the p-value of the model, where the p-value is not more than the value of α [16]. The results of the N-Acyl arginine regression coefficient results are given in Table 3. In addition to the p-value obtained by using the Minitab program, there is also an equation model that is useful to show the relationship of reaction variables and their interaction to the conversion percentage, where the modeling can be used to find the model conversion value [17]. The model of the equation obtained is as follows.

Conversion = 74.307 + 1.433 Catalyst + 3.153 Solvent
- 3.685 Substrate + 2.392 Catalyst*Catalyst
+ 1.667 Solvent*Solvent
+ 2.410 Substrate*Substrate
+ 1.562 Catalyst*Solvent
+ 0.512 Catalyst*Substrate
+ 6.788 Solvent*Substrate (1)

There are negative and positive signs in the above equation, where the positive sign shows a significant influence on the conversion compared to other experimental variables. In contrast, the negative sign in the equation shows the inverse relative relationship with the positive sign on the conversion [18]. The value of the coefficient of determination (R^2) of the analysis results of 97.68% indicates that the independent variable in the experiment affects the dependent variable (% conversion) of 97.68%.

Residual Plot for Conversion

The residual plot for the conversion test is carried out so that the equation model made does not deviate much. So that through this verification test, it can be checked the conformity between the assumptions required and the residuals. Four residual plots have been taken, namely normal probability plot, residual versus fitted value, residual versus histogram plot, and residual versus order [16].

The results of the residual plot for conversion are shown in Figure-2. The first test residual plot is a normal probability plot. This assumption is known using the Kolmogorov Smirnov (KS) test using a significance value (α) = 0.05. From the statistical table for the number of observations 20, the KS test value is 0.294. Kolmogorov's statistical value from observations is smaller than the value of 0.294. The distribution tends to form a straight line so that the assumption of normality can be said not to be violated.

The plot of residuals versus fixed values is used to see the homogeneity of variance. It can be seen that the assumption of homogeneity of variance has also been fulfilled because the data distribution does not form a specific pattern and tends to be random. The residual versus order model is also conducted to determine the relationship and correlation between independent variables. As with the residual versus fit plot, it is found that the residual versus order model plot has also been fulfilled because the resulting residual versus order data also tends to be random and patternless. The prediction of regression coefficient on coded coefficients is given in Table-3. From the four residual for conversion plots in Figure-2, it can be concluded that the regression model made is appropriate and can be used.

Table-3. The prediction of regression coefficient on coded coefficients.

Term	Effect	Coef	SE Coef	T-Value	P-Value	VIF
Constant (Y)		74.307	0.603	123..30	0.000	
Catalyst	4.818	2.409	0.672	3.58	0.005	1.00
Solvent	10.605	5.303	0.672	7.89	0.000	1.00
Substrate	-12.394	-6.197	0.672	-9.22	0.000	1.00
Catalyst*Catalyst	13.53	6.77	1.10	6.15	0.000	1.02
Solvent*Solvent	9.43	4.72	1.10	4.28	0.002	1.02
Substrate*Substrate	13.63	6.82	1.10	6.19	0.000	1.02
Catalyst*Solvent	8.84	4.42	1.48	2.99	0.014	1.00
Catalyst*Substrate	2.90	1.45	1.48	0.98	0.350	1.00
Solvent*Substrate	38.40	19.20	1.48	12.99	0.000	1.00

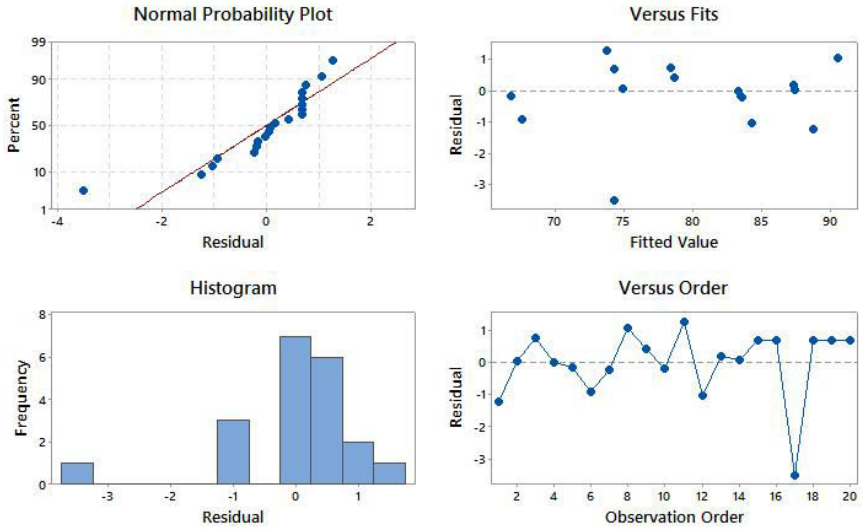

Figure-2. The four residual plots for conversion.

Effect of Catalyst and Solvent

The effect of the interaction between the catalyst concentration and the solvent ratio on the conversion of tetradecanol to surfactant N-acyl arginine can be seen from Table 2, where it is found that the single variable catalyst and the solvent has a significant effect on product formation, which is indicated by the value obtained by the p-value of both < α or 0.05. Catalyst squares and solvent squares also have a significant effect. The interaction between catalyst and solvent also gives a p-value of 0.014, which means it is also significant in the formation of the surfactant N-acyl arginine.

Based on the regression equation, it is also found that the solvent has a more significant factor than the catalyst and substrate, namely 3.153, and the interaction between the catalyst and the solvent has a moderate positive effect, namely 1.562, compared to the interaction of the catalyst with the substrate and the solvent with the substrate

So that in line with the above analysis, Figure-3 shows the response surface of the interaction between the catalyst and the solvent. It can be seen that as the amount of catalyst used increases, the resulting conversion tends to fluctuate. On the substrate as a hold value at point 0, and the solvent at -1, the increase in the amount of catalyst initially decreases the conversion. After the amount of catalyst is 0, the conversion will increase at a constant amount of solvent. For maximum use of solvent, increasing the amount of catalyst will increase the conversion significantly, although at first, it decreases the conversion slightly. From this surface plot, it can also be concluded that, in general, the interaction of the two will increase the conversion, and the best conversion is obtained at the maximum use of catalyst and solvent [11].

In the substrate as a hold value with a maximum value of 1.682, a surface plot is obtained, as shown in Figure 4. When the catalyst concentration is kept constant -1, an increase in the solvent ratio will increase the linear conversion, and the same pattern is also found with maximum catalyst use. The conversion of tetradecanol to surfactant will increase linearly with maximum catalyst usage [3].

The best conversion is found in the use of catalysts and maximum solvent. Conversely, if the solvent is kept constant, the use of catalysts, both minimum and maximum, will only slightly affect the changes in the fatty alcohol conversion. From this surface plot, it can be concluded that in observing the optimum conversion, the solvent gives a more significant effect than the catalyst on the substrate ratio, which is kept constant.

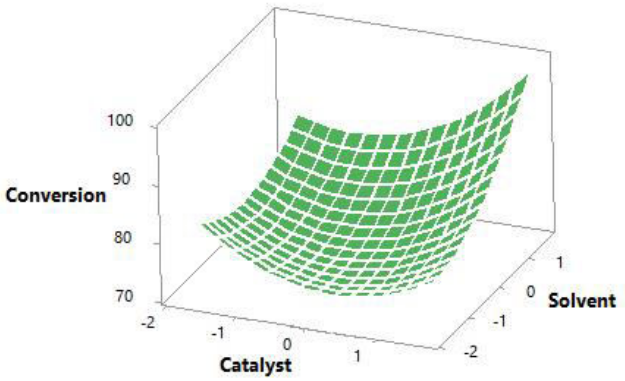

Figure-3. The response surface of the interaction between the catalyst and the solvent at substrate hold value of 1.

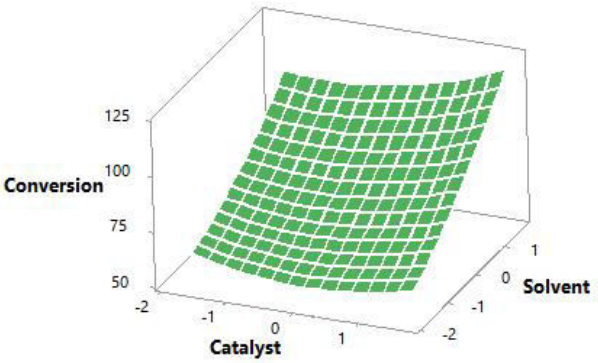

Figure-4. The response surface of the interaction between the catalyst and the solvent at substrate hold value of 1.682.

Effect of Catalyst and Substrate

The catalyst and substrate interactions on the conversion of fatty alcohol to surfactants can be seen in Figure 5 for solvent as hold value at point 0, and in Figure-6 for solvent as holds value at point 1.682. On the surface plot in Figure 5, increasing the catalyst and substrate initially decreases the conversion. The conversion will be a minimum value at the center point of both variables. The increase in the value of the two variables then effectively increased the tetradecanol conversion, and the optimum conversion was obtained at the maximum use of the catalyst and substrate. So, in general, the resulting surface plot forms the smallest crater of the existing surface.

The surface plot in Figure-6 explains that if the solvent as a hold value is a maximum value, 1.682, then the surface plot formed tends to increase linearly. The catalyst appears to have little effect on conversion, while the substrate plays a significant role in increasing conversion. Overall, increasing the values of the two variables, catalyst, and substrate, can increase the fatty alcohol converted, and the optimum value is obtained for the maximum catalyst and substrate [8].

The resulting surface plot is in line with the analysis in Table-2, where single and quadratic variables, both catalyst and substrate, both have a significant effect on surfactant formation. However, the catalyst and substrate interaction did not have a significant effect on a p-value of 0.350. In line with the results of the analysis in Table 2, the regression equation compiled also found that the catalyst has a more significant factor than the substrate. The interaction between the two only has a factor of +0.512 in increasing the conversion of fatty alcohol.

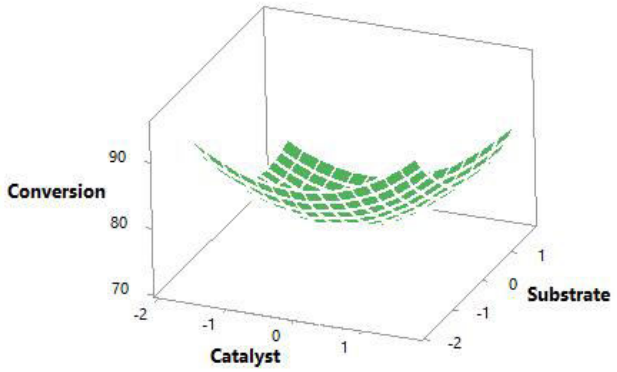

Figure-5. The response surface of the interaction between the catalyst and the substrate at solvent hold value of 1.

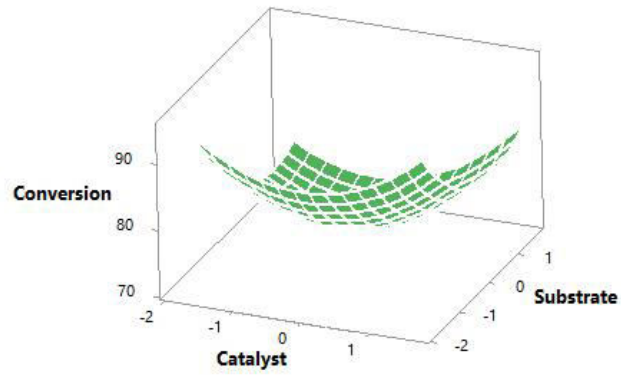

Figure-6. The response surface of the interaction between the catalyst and the substrate at solvent hold value of 1.682.

Effect of Solvent and Substrate

Determination of the optimum tetradecanol conversion is also observed in the interaction of the solvent with the substrate, as shown in the surface plot in Figure-7 and Figure-8. The surface plot in Figure-7 describes the relationship between solvent and substrate with the conversion where it can be seen that the resulting conversion tends to increase exponentially. If the solvent ratio is -1.682, the substrate ratio used, either -1.682 or +1.682, cannot increase the fatty alcohol conversion. An identical trend surface plot is also found in Figure-8, where the catalyst holds the value at 1.682. It was found that at a solvent ratio of 1.682, increasing the substrate would effectively increase the tetradecanol conversion.

This surface behavior is also found from Table-2, where the interaction between the solvent and substrate is very significant in increasing the conversion, namely 0.000. Also, from the resulting regression equation, the solvent and substrate interaction coefficient is positive and significant, namely 6.788.

From the six surface plot images above, it can be concluded that the interaction of the three variables has an effect on the conversion obtained, and the most significant interaction is between the catalyst and the solvent and the solvent with the substrate when the interaction between the catalyst and substrate has an effect on conversion but not significant.

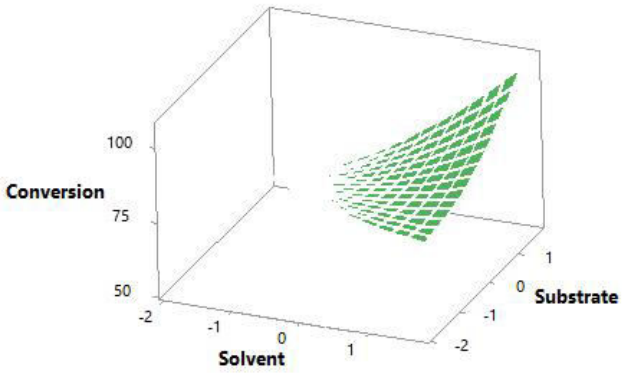

Figure-7. The response surface of the interaction between the solvent and the substrate at catalyst hold value of 1.

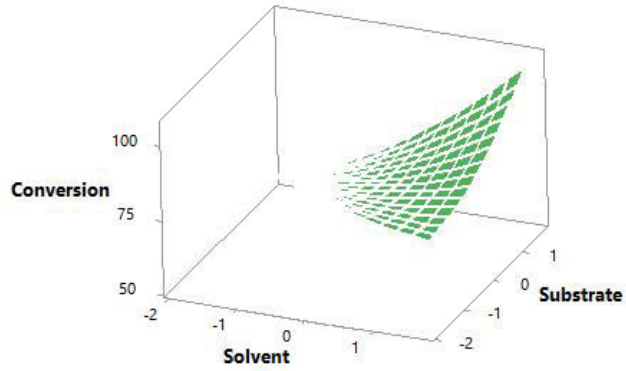

Figure-8. The response surface of the interaction between the solvent and the substrate at catalyst hold value of 1.682.

CONCLUSIONS

The prediction model, which is done, gives an R^2 value of 97.68%. From the six surface plot images above, it can be concluded that the interaction of the three variables has an effect on the conversion obtained, and the most significant interaction is between the catalyst and the solvent and the solvent with the substrate when the interaction between the catalyst and substrate has an effect on conversion but not significant.

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