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A TWO-STEP CATALYTIC PRODUCTION OF COCO FATTY ACID AMIDE FROM COCONUT OIL USING A METAL CATALYST

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ABSTRACT

Coconut oil was used as a feedstock potential for alkanolamide production. For that, a two-step process was implemented in this research. Firstly, the triglycerides in coconut oil were transesterified with methanol to be fatty acid methyl esters (FAME), and in the second, FAME was amidized with monoethanolamine (MEA) using metal catalyst $ZrCl_4$ to coco fatty acid amide. Response Surface Methodology and 5-level-3-factor Central Composite Design were adopted to evaluate the effects of synthesis variables, including reaction time (1.3-4.7 h), substrate molar ratio (1.3/1-4.7/1 MEA/FAME), and the solvent ratio (2.3/1-5.7/1 v/wFAME) on the percentage of fatty acid conversion. Based on analysis of variance, the optimum condition for maximum fatty acid conversion (86.22%) was obtained at reaction time 3 h, substrate molar ratio 3/1 (MEA/FAME) and solvent ratio 4/1 (v/wFAME). The suitable range of the effective process parameters was achieved for the desirable the FAME conversion were at a catalyst concentration of 6% (w/wFAME), the temperature of 90^oC and stirring speed of 350 rpm.

Keywords: coco amide, coconut oil, central composite design, zirconium (IV) chloride.

INTRODUCTION

Alkanolamide is a surfactant that can be synthesized from vegetable oils whose use has been growing lately. A large amount of the content in medicines contains this amide functional group [1, 2]. Alkanolamide is a non-ionic surfactant obtained from the reaction between primary and secondary alkanolamines and triglycerides or fatty acids [3, 4, 5]. The application of non-ionic surfactants is generally used in the food, health, textile, plastic, glass, paper and fiber industries. Non-ionic surfactants, in general, have a better ability compared to other surfactants [6, 7, 8, 9].

The most common reaction to produce amides is by reacting primary or secondary alkanolamine with fatty acids, methyl esters, or triglycerides such as coconut oil. Coconut oil is obtained from dry coconut kernels with low water content (6-8%). Coconut oil is rich in medium chain fatty acids and is easy to digest [2, 8]. The main fatty acids (FA) found in coconut oil are lauric acid (12:0), myristate (14:0) and palmitate (16:0), each representing 46%, 17% and 9% FA [10].

Coco fatty acid amide is monoethanolamide from coconut oil fatty acid which is reacted with monoethanolamine. Another name for coco fatty acid amide is cocamide mea, coco-n-(2-hydroxyethyl), coco-monoethanolamide, coconut fatty acid monoethanolamide, and cocoyl monoethanolamine. Coco fatty acid amide functions as a surfactant for thickener, foam stabilizer and as a cosmetic formulation [2].

The first stage of the synthesis of coco fatty acid amide is the transesterification process of coconut oil into fatty acid methyl ester using methanol and alkaline catalyst, sodium hydroxide [11, 12]. The oxidation process of fatty acid methyl ester coconut oil with monoethanolamine is the second stage of the synthesis of coco fatty acid amide. Monoethanolamine is an alkanolamine group that has both amine and alcohol groups, so this group of amines can experience various kinds of reactions that are commonly used for amines and alcohol [2, 8]. Therefore, monoethanolamine can be used for the synthesis of coco fatty acid amide surfactants.

The metal catalyst zirconium (IV) chloride is one of the effective metal catalysts for use in the oxidation of carboxylic acids with primary and secondary amines [3, 8]. Zirconium (IV) chloride can work well in a variety of solvents, can be recycled and the most important thing is to have the ability to coordinate strongly so that it will produce good reaction gains. Zirconium (IV) chloride has also been used as a Lewis acid catalyst in many important organic transformations including carbon-carbon bonds and chemical deprotection protection [13].

On the basis of the theory described, it is necessary to do research on the manufacture of nonionic coco fatty acid amide surfactants from coconut oil and monoethanolamine through an amidation reaction using a zirconium (IV) chloride ($ZrCl_4$) catalyst and to obtain important information about the effect of reaction time, substrate molar ratio and the ratio of solvent to surfactant produced.

MATERIALS AND METHODS

Materials

The coconut oil used as commercial oil that is Braco®. Monoethanolamine ($CH_2(OH)CH_2NH_2$), zirconium (IV) chloride ($ZrCl_4$), n-hexane, sodium hydroxide (NaOH), potassium hydroxide (KOH), methanol (CH3OH¬) and all analysis material are obtained from E Merck, Darmstadt Germany.

Methods

Homogenous base catalyzes transesterification

A 100 g of filtered coconut oil was washed in a three-necked round-bottom flask equipped with a reflux condenser and a temperature controller and a stopper. The

flask was immersed in a constant temperature bath while the stirring rate was fixed at 300 rpm to avoid mass transfer limitations through the process. A solution of sodium hydroxide (1% v/wOil) in methanol was prepared at the ratio of methanol to coconut oil of 6/1. The mixture is stirred for one hour at 60°C. After the reaction is complete the mixture is separated in the separating funnel, then the bottom layer is separated. The top layer is washed with hot water. Then, the methyl esters can be analyzed.

Heterogeneous $ZrCl_4$ catalyzed amidification

FAME and a different molar ratio of MEA were added to 2.3/1-5.6/1 (v/wFAME) n-hexane, followed by the 5% (w/wFAME) of zirconium (IV) chloride. Amidification reaction was carried out with MEA to FAME molar ratio of 1.3/1-4.7/1 (MEA/FAME) and reaction times of 1.3-4.7 h. The effect of reaction time, substrate molar ratio and solvent ratio were studied at temperatures 70°C. $ZrCl_4$ catalyst was added to the solution with a concentration of 5% by weight of the total solution. The solution is stirred with a stirring speed of 200 rpm. The catalyst was then filtered off and the solvent and ethanol are evaporated.

Experimental design

RSM with CCD is used to observe the effect of interaction of three research variables on reaction time, substrate molar ratio and solvent ratio to response, namely percent conversion of FAME [12, 14]. After the number of run selection using the Minitab 17 trial version software, the number of runs to be performed and the level used of each independent variable is obtained. CCD with 3 factors and 5 levels consists of factorial points $n_f = 2^3$ plus 6 center points and 6 axial points, so the total observation is 20, with the value $\alpha = (n_f)^{1/4} = (8)^{1/4} = 1.682$ [15, 16, 17].

Table-1 shows the independent factors (X_i), levels and experimental designs in terms of coded and uncoded and Table-2 states the actual experiments to be carried out and developed from the model and percent conversion of FAME obtained. The regression model prediction and analysis of variance (ANOVA) were conducted using Minitab software.

Table-1. Levels and Experimental Designs.

Variables	Levels				
	-1.682	**-1**	**0**	**1**	**1.682**
Reaction time (X_1, h)	1.318	2	3	4	4.682
Substrate molar ratio (X_2, MEA/FAME)	1.318	2	3	4	4.682
Solvent ratio (X_3,v/wFAME)	2.318	3	4	5	5.682

Table-2. The Actual Experiments.

No.	Reaction time (X_1)	Substrate molar ratio (X_2)	Solvent ratio (X_3)	Conversion (Y, %)
1	-1	-1	-1	73.53
2	1	-1	-1	82.35
3	-1	1	-1	82.35
4	1	1	-1	82.35
5	-1	-1	1	79.41
6	1	-1	1	85.29
7	-1	1	1	82.35
8	1	1	1	76.47
9	-1.682	0	0	76.47
10	1.682	0	0	79.41
11	0	-1.682	0	76.47
12	0	1.682	0	82.35
13	0	0	-1.682	79.41
14	0	0	1.682	82.35
15	0	0	0	85.29
16	0	0	0	85.29
17	0	0	0	85.29
18	0	0	0	85.29
19	0	0	0	88.24
20	0	0	0	88.24

RESULTS AND DISCUSSIONS

Transesterification of coconut oil

The initial experiment was performed to obtain fatty acid methyl ester (FAME) from coconut oil and methanol using sodium hydroxide catalyst. The catalyst used has a significant effect on the reaction, especially in increasing the reaction rate. Sodium hydroxide is the base catalyst chosen so that the transesterification reaction can take place at a more moderate temperature.

Amidification of fatty acid methyl ester (FAME)

A statistical approach aims to better understand the relationship between variables to response (percent conversion FAME). On the base of this concept, a large-scale process can be optimized with a small time and less labor requirements [2].

The relationship of interactions between variables and their responses can be better understood by designing a series of surface and contour plots [12]. In general, the three contours of the exhibit similar behavior plot where the predicted conversion will increase with increasing reaction time, molar ratio and solvent ratio substrate.

Table-3. The Results of Regression Coefficients.

Term	Coefficient	P
Constant (Y)	86.2243	0.000
Reaction time (X_1)	1.6950	0.048
Substrate molar ratio (X_2)	1.5798	0.062
Solvent ratio (X_3)	0.9709	0.226
(X_1)*(X_1)	-7.4268	0.000
(X_2)*(X_2)	-5.9568	0.001
(X_3)*(X_3)	-4.4868	0.005
(X_1)*(X_2)	-7.2761	0.001
(X_1)*(X_3)	-3.1183	0.089
(X_2)*(X_3)	-5.1972	0.011
R-Sq = total squared = 91.34%		
R-Sq(adj) = squares due to treatment = 83.54%		

The model obtained from Table-3 that describes the relationship of the three variables to FAME conversion is as follows:

$$Y_{FAME} = 86.2243 + 1.695\ X_1 + 1.5798\ X_2 + 0.9709\ X_3 - 7.4268\ X_1^2 - 5.9568\ X_2^2 - 4.4868\ X_3^2 - 7.2761\ X_1X_2 - 3.1183\ X_1X_3 - 5.1972\ X_2X_3 \quad (1)$$

where X_1, X_2, X_3 are the substrate ratio, solvent ratio, and reaction time respectively.

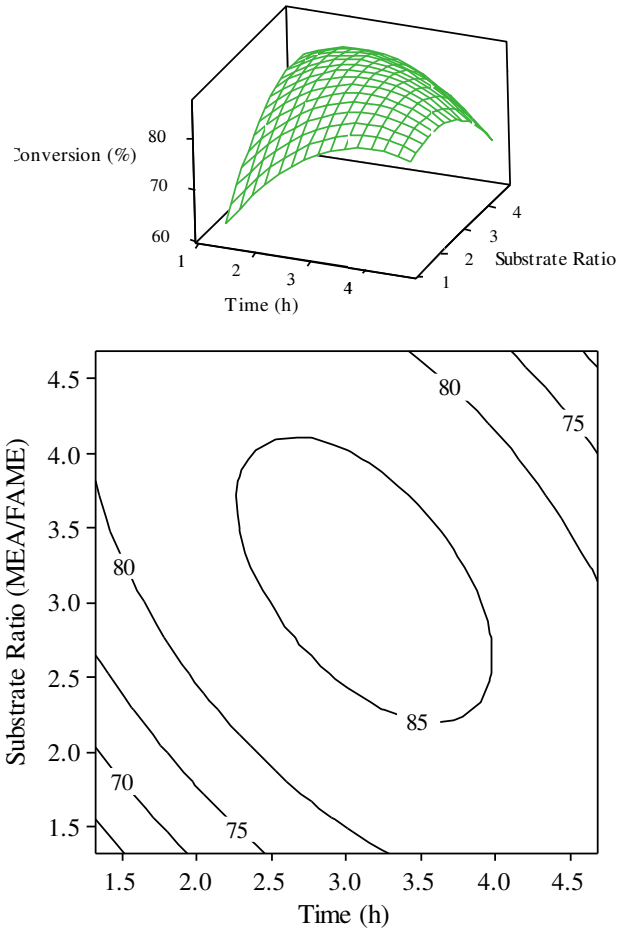

Figure-1. The influence of varying substrate molar ratio and reaction time.

The model adequacy was checked and it was found to be adequate, the goodness of fit of the model was expressed by the coefficient of determination R^2, which was calculated to be 0.9134, indicating that 91.34% of the variability in the response could be explained by the model.

The influence of varying substrate molar ratio and reaction time on the conversion of FAME at a constant solvent ratio is shown in Figure-1. In the synthesis of cocoamide DEA from DEA and FAME, it was shown that amide conversion increased from a ratio of diethanolamine and FAME 2/1 to 4/1. In this study, the effect of the substrate molar ratio to the conversion of FAME tends to increase significantly from the substrate mole ratio of 2.5/1 to 3.5/1. The best molar ratio is obtained at a ratio of 3/1. Furthermore, excess amines shift the reaction equilibrium to the product side [18, 19].

The substrate molar ratio is one of the important factors affecting the ethanolamide yield and a high molar ratio is usually used to obtain high monoethanolamide yields where the amount of results obtained is influenced by the amount of amine [19, 20]. With the increase in the substrate ratio, the results of monoethanolamide also increase. But a further increase in the substrate ratio resulted in a decrease in monoethanolamide yield due to

the effect of dilution of ethanolamine [18]. If excess amine substrate is used, the amine will be confirmed as an amine ester which will reduce the conversion of amines to amides. Yield amine esters can be reduced by using high amine concentrations in the reaction mixture. However, under this condition the excess amine which is not easily dissolved will inhibit the mass transfer of the system, thereby reducing yield.

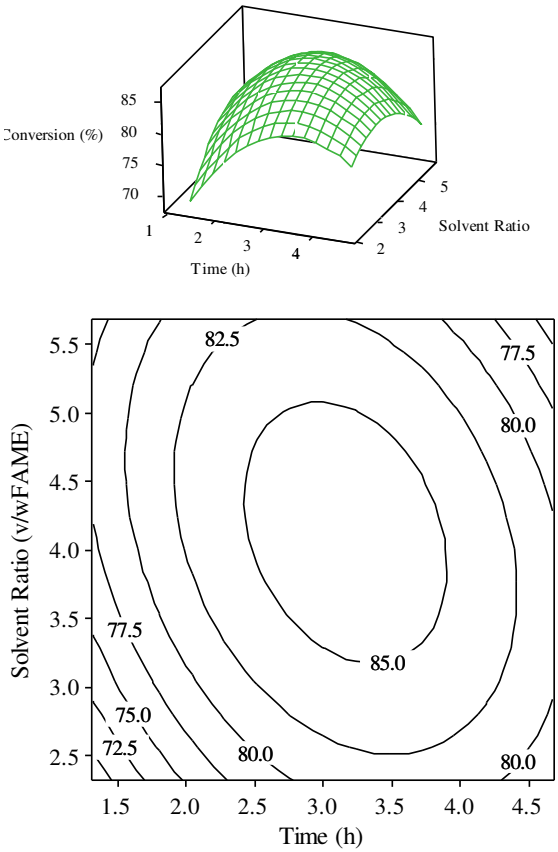

Figure-2. The effect of reaction time and solvent ratio.

The time profile is a good indicator to determine the performance of the amidation reaction. Figure-2 represents the effect of reaction time and also the ratio of solvent to the synthesis of cocoamide at 60°C, 5% catalyst and 300 rpm stirring speed. As the time exceeded 1 h, the conversion was only slightly increased, and in the 2.5 to 4 hour period, the maximum conversion will be obtained. From this study, the highest percent conversion results when the reaction time is 3 hours. Based on Figure-2, there was a decrease in percent conversion when the reaction time was extended to 5 hours. This is due to the occurrence of side reactions such as saponification [20]. Whereas based on research conducted by Wang, *et al.* (2016), the increase in reaction time did not give a significant result of amide recovery [7].

Then in this study n-hexane solvents will be used. The use of this solvent was chosen based on the solubility of the raw material and product to the solvent where it is known that fatty acids are less soluble in polar solvents but more soluble in non-polar solvents such as hexane. A profile similar to the previous image is found in Figure-3, namely the interaction profile between the solvent ratio and the molar ratio of the substrate to the conversion of FAME.

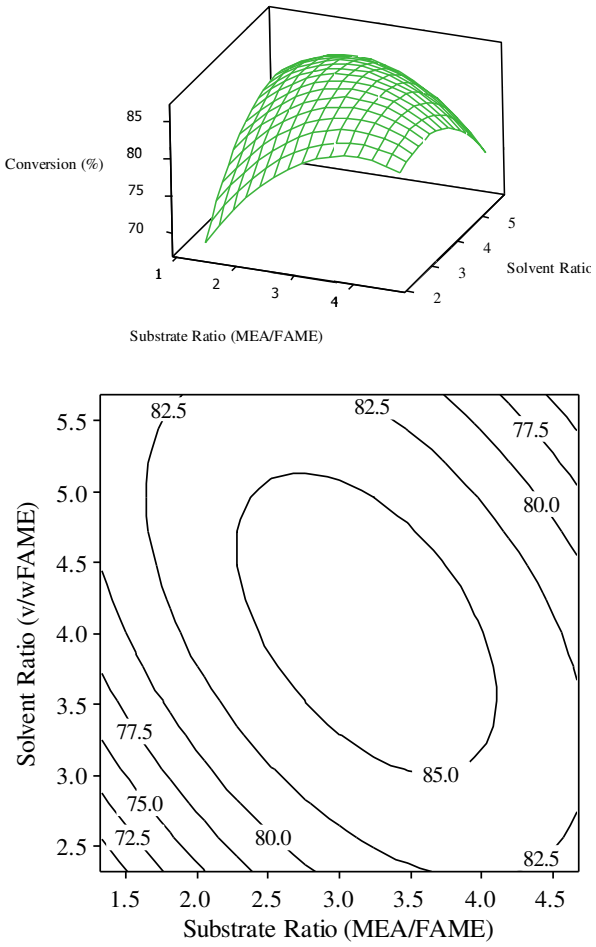

Figure-3. The interaction profile between the solvent ratio and the molar ratio.

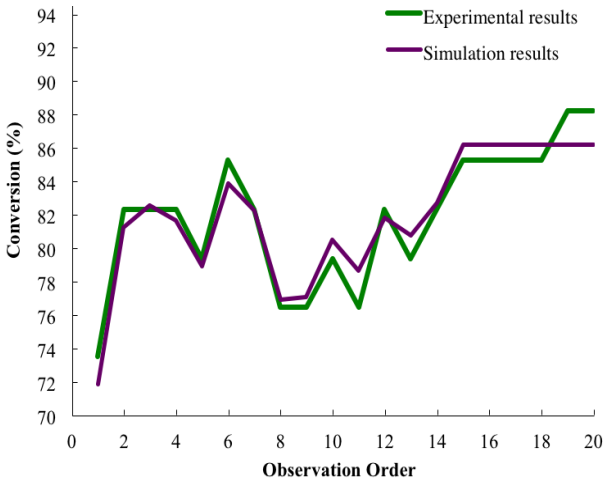

Figure-4. The comparison of the model conversion to the actual conversion.

It can be seen that the increase in the substrate ratio and the solvent ratio both result in FAME conversion. The maximum conversion is obtained at substrate ratio 2.5/1 - 3.5/1 and solvent ratio 3-5. Increasing the value of the two variables will further reduce conversion.

To verify the model that has been prepared, it is necessary to do a comparison between the actual conversion value, and the conversion value obtained from the arranged equation. Figure-4 shows the comparison between the two conversions. It appears that there is no significant deviation between the two values. This chart trend also shows that the difference between actual data and predictive data is small. It can be concluded that the resulting equation is good and appropriate to describe the conversion changes that occur

CONCLUSIONS

Based on the results of the study and discussion on the optimization of coco fatty acid amide synthesis from coconut oil and monoethanolamine, it was found that reaction time was the most important parameter for achieving a higher percentage of conversion of FAME. Based on the analysis of variance, the optimum conditions for coco fatty acid amide synthesis were at the substrate molar ratio 3/1 (MEA/FAME), the reaction time of 3 h, and solvent ratio of 4/1 (v/wFAME), with maximum FAME conversion of 86.22%.

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