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by Luqman Buchori

Optimization of Monoglycerides Production Using KF/CaO-MgO Heterogeneous Catalysis

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Abstract

The production of monoglyceride or monoacylglycerol (MAG) from triglycerides and glycerol has been studied. The purpose of this research was to study the effect of using KF/CaO-MgO catalyst on MAG production with batch reactor. The effect of temperature, reaction time, and amount of catalyst was investigated using the response surface methods (RSM). The temperature was varied at 200-220 ºC, the reaction time varied at 2-4 hours, and the amount of catalyst varied at 0.1-0.3 % w/w. Data was processing using the STATISTICA 12 program. The results of monoglyceride optimization showed that the optimum conditions were X_1 = 0.19 % (w/w), X_2 = 208.37 ºC and X_3 = 3.20 hours. The monoglycerides obtained was 41.58%.

Keywords: *KF/Ca-MgO Catalyst, Monoglyceride, Optimization, Response Surface Method*

1. Introduction

Cooking oil is made from vegetable oils that has been purified and used in the food industry as well as for daily needs. Most of the fat in food (including cooking oil) has formed of triglycerides, which is broken down, triglycerides will turn into one glycerol molecule and three free fatty acid molecules. The more triglycerides that break down will cause more free fatty acids to be produced [1]. Monoacylglycerol (MAG)/monoglyceride is a chemical oleo compound that is widely used in the food, pharmaceutical, cosmetics, detergent [2] [3], oil well drilling [4], textiles [5], packaging [6], plastic processing [7], and construction material [8]. Triglycerides are widely converted to monoglycerides and diglycerides, because these two product are very widely used in food processing.

Monoglycerides can be prepared .by glycolysis reactions between fat and fatty acid methyl esters of palm oil. The glycolysis reactions can be carried out by biocatalyst (enzymatic glycolysis / enzymatic reactions), without catalyst (non-catalyst reaction), or by chemical catalyst (chemical glycolysis). The most common method is the catalysis reaction using alkaline catalysts such as NaOH [9], $NaOCH_3$ [10], MgO [11, 12] and CaO [13].

Monoglyceride synthesis using KF/CaO-MgO catalyst has been studied [14], but optimization studies of operating conditions have not been carried out. This reserach aims to study MAG production from cooking oil and glycerol using KF/CaO-MgO catalyst in batch reactor and investigate the effect of temperature, reaction time, and amount of catalyst. Optimization was carried out using the RSM method with STATISTICA 12.0. The optimum composition will affect the process of getting good quality of monoglycerides.

2. Material and Methods

2.1. Materials

The chemicals of KF powder, magnesium acetate, ethanol, calcium nitrate ($Ca(NO_3)_2$), acetic acid were obtained from Merck (Germany). Cooking oil as a source of triglycerides was purchased from the local supermarket, glycerol was obtained from Malang and aquadest from the MeR-C laboratory (Membrane Research Center).

2.2. Methods

Monoglycerides are formed through several steps. Molar ratio of cooking oil (triglycerides) with glycerol is 1:3. The catalyst is dissolved in glycerol at a temperature at 90 °C and then stirred until homogeneous. The cooking oil is pored into a glass vessel and heated to 150 °C while stirring. The mixture of glycerol and catalyst is put into a glass vessel and stirred until homogeneous. The temperature is maintained at 150 °C. After all the reactants (cooking oil, glycerol, and catalyst) are completely mixed, the temperature is raised according to the variable of design factor. Products were analyzed by GCMS.

The design model in this experiment is a centralized composite design (CCD) using a response surface method (RSM). This design is widely used for second-order models [15]. The experimental design used was the lowest value, strong and high for each factor which included catalyst percentage, temperature and reaction time. The experimental design can be showed in Table 1.

Table 1. Experimental design for each variable

Factors	unit	Level		
		1	0	+1
Catalyst (X_1)	%	0.1	0.2	0.3
Temperature (X_2)	^{0}C	200	210	220
Time (X_3)	hours	2	3	4

The optimization method uses RSM by creating a model and analyzing the y response which is influenced by the x variable. The relationship between the y response and the x independent variable is:

$$Y = f(X_1, X_2, \dots, X_k) + \varepsilon \quad (1)$$

$i = 1, 2, 3, .k$

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum\sum_{i<j} \beta_{ij} X_i X_j + \varepsilon \quad (2)$$

Where y, the response observed; β_0, regression parameters; x_i, the main linear variable; $x_i x_j$, linear two variables; x_i^2, the square of the main variable. The desired response is the monoglyceride yield.

The experimental design for optimization was obtained 16 times experiment to obtain optimum monoglyceride yield. The design for this experiment uses the Design Expert Software (Statistics) method version 12.0 which can be seen in Table 2.

3. Results and Discussion

3.1 The effect of glicerolysis process to yield monoglyceride.

The overall process of glycerolysis was given in Table 2.

Table 2. GCMS analysis results for yield of monoglyceride.

Run	Factors			Monoglycerides	
	X_1	X_2	X_3	Actual	Predicted
	-1	0	+1		
1	0,10	200,00	2,00	27,58	28,12
2	0,10	200,00	4,00	37,07	37,60
3	0,10	220,00	2,00	31,72	33,58
4	0,10	220,00	4,00	30,61	29,98
5	0,30	200,00	2,00	30,19	29,48
6	0,30	200,00	4,00	38,19	34,99
7	0,30	220,00	2,00	36,24	34,37
8	0,30	220,00	4,00	28,68	26,80
9	0,03	210,00	3,00	36,55	34,54
10	0,37	210,00	3,00	29,10	33,01
11	0,20	193,18	3,00	30,16	31,21
12	0,20	226,82	3,00	28,07	28,92
13	0,20	210,00	1,32	33,15	32,61
14	0,20	210,00	4,68	31,77	34,21
15	0,20	210,00	3,00	36,89	41,45
16	0,20	210,00	3,00	46,33	41,45

X_1, catalyst (%wt); X_2, temperature (^{0}C); X_3, time (hours);

3.2 Optimization of monoglyceride by regression analysis

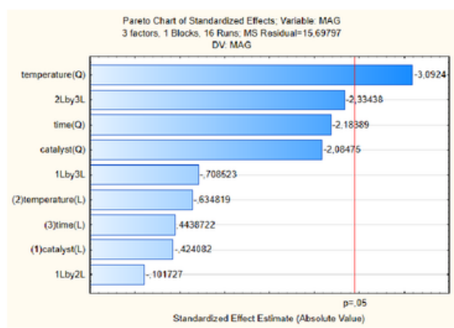
The results of anova variable analysis for monoglyceride conversion results is depicted in Table 3.

Table 3. Significant regression coefficient for monoglyceride

Factors	Regression Coeff.	F-value	p-value
X_0	41,4475		
X_1	-0,4547	0,1798	0,6863
X_{11}	-2,7138	4,3462	0,0823
X_2	-0,6806	0,4030	0,5490
X_{22}	-4,0255	9,5630	0,0213
X_3	0,4759	0,1970	0,6727
X_{33}	-2,8428	4,7694	0,0717
X_{12}	-0,1425	0,0103	0,9223
X_{13}	-0,9925	0,5020	0,5052
X_{23}	-3,2700	5,4493	0,0583
Erorr	94,1878		
R^2	0,7459		

The results of analysis of variance for monoglycerides production showed R^2 value of 74.58 %. The three variables (catalyst procentage, temperature, reaction time) have an effect > 70 % of the models. All p-value of data on monoglycerides production have a degrees of significance $\alpha = 5$ % indicating that the variables have a significant impact on the model.

$$Y = 41{,}44755 - 0{,}45467\,x_1 - 2{,}71378\,x_1^2 - 0{,}68061\,x_2 - 4{,}02546\,x_2^2 + 0{,}47589\,x_3 - 2{,}84282\,x_3^2 - 0{,}14250\,x_1x_2 - 0{,}99250\,x_1x_3 - 3{,}27000\,x_2x_3 \quad (3)$$



Q: Quadratic, L: Linear

Figure 1. Pareto chart of effect of variables for monoglycerides conversion.

Figure 1 (Pareto chart) shows there are variables that affect the number of products. Among the three variables, temperature has a very significant effect on the product yield. Other variables such as reaction time and catalyst percentage give a significant effect but not large, so the optimum conditions for obtaining monoglyceride results should be sought.

3.3 Response surface plot

The optimum condition of monoglycerides can be seen from the responses were represented in Figures 2-7 in three dimensions (3D) or as contour plots that can help visualize the surface shape of the response. The contour is the constant response curve drawn in xi, xj and keeping all the other variables fixed. Each contour corresponds to a certain height of surface response. From the surface contours, bias is seen where the optimum position or condition is reached, which in 3D or eclipse lies at the top and on the contour lines on the smallest part inside the contour surface [16].

a. Temperature vs catalyst

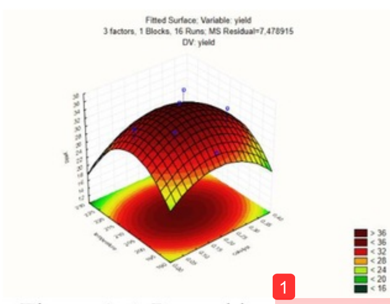


Figure 2. 3-D graphics response surface plot showing the effect of reaction catalyst versus temperature on the yield monoglycerides at fixed time 3 hours.

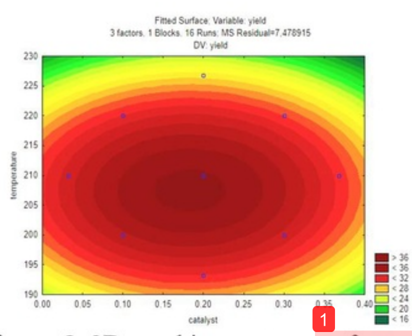


Figure 3. 2D graphics contour surface plot showing the effect of reaction catalyst versus temperature on the yield monoglycerides at fixed time 3 hours.

Surface optimization and contour graphs (Figures 2 and 3) shows the effect of temperature and catalyst on glycerolysis reaction. The lowest temperature conditions at 193 °C and the highest at 226 °C. However, when we repeat of the number of percentages of the same catalyst that is 0.2 %, which appears at the lowest temperature, it produces a monoglyceride yield of 30.16 %. This is because the glycerolysis reaction has not reached its optimum condition. The optimum conditions achieved at a temperature of 210 °C with a 0.2 % catalyst can produce monoglyceride of 36.89 %. However, at too high a temperature of 226 °C there was a decrease in yield, the results obtained were 26.24 %. This fact shows glycerolysis carried out at a temperature of 220 °C using an alkaline catalyst will produce a dark-colored product and a different flavors so that have an impact on the results obtained [17].

b. Reaction time vs catalyst

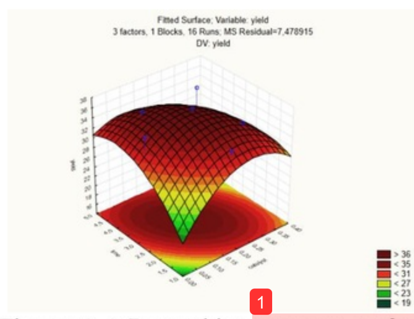


Figure 4. 3-D graphics response surface plot showing the effect of reaction time versus catalyst on the yield monoglycerides at fixed temperature 210 ^{0}C.

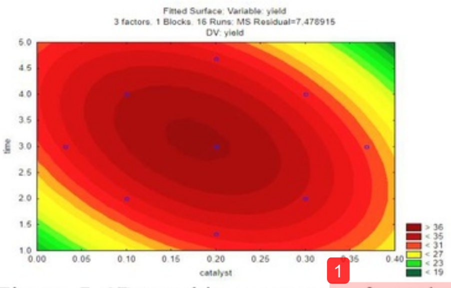


Figure 5. 2D graphics contour surface plot showing the effect of reaction time versus catalyst on the yield monoglycerides at fixed temperature 210 ^{0}C.

Figures 4 and 5 shows the effect of the catalyst on the glycerolysis reaction time. The addition of a catalyst can reduce the activation energy of the glycerolysis reaction and accelerate the reaction [18]. The addition of a catalyst was carried out between 0.03 % to 0.37 % and at the same time, which is 3 hours. The addition of a catalyst amount of 0.03% produce monoglyceride yield about 35.00 %. However, excess catalysts can reduce conversion and decrease the ability of triglyceride to dissolve glycerol [12]. The monoglyceride yield obtained was 27.03 %. Addition of excess catalyst can cause a side reaction which is a saponification reaction to oil which causes a decreased monoglyceride content [19]. The optimum percentage of catalyst for this reaction is 0.2 %.

c. Reaction time vs temperature

The optimum reaction time is affected by temperature, amount of catalyst, type of solvent and other operating conditions. Figures 6 and 7 show the optimization and contour of the surface from the effect of reaction time and operating temperature. Increased reaction time and operating temperature can increase the yield of monoglyceride. At the same temperatures (210 °C), the optimum reaction time obtained is 3 hours. This is in accordance with the research conducted by Fanny and Prakoso [20] that the optimum time conditions for producing high monoglycerides yield is 3 hours. At the lowest reaction time of 1 hour 32 minutes, the monoglyceride yield of 33.15 % was obtained and the highest reaction time, at 4 hours 68 minutes, obtained monoglyceride yield of 30.81 %. The highest time conditions get lower results. This is due to the glycerolysis reaction is a reversible reaction so that if the reaction time is too long it will form another groups, di and triglycerides [21].

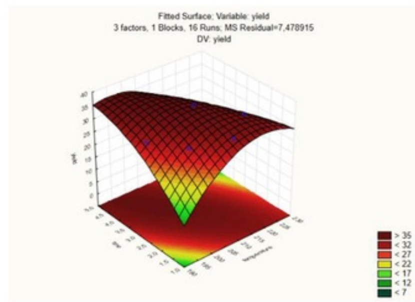


Figure 6. 3-D graphics response surface plot showing the effect of reaction time versus temperature on the yield monoglycerides at fixed catalyst 0,2 %wt.

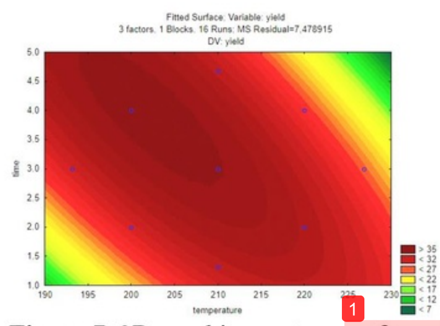


Figure 7. 2D graphics contour surface plot showing the effect of reaction time versus temperature on the yield monoglycerides at fixed catalyst 0,2 %wt.

3.4 Optimization condition

The optimum condition of the synthesis of monoglycerides was predicted using the optimization function of the statistic software version 12. The empirical model derived from RSM can be used accurately to describe the relationship between the factors and response in the conversion of monoglycerides. The relationship between the amount of the catalyst and temperature operating on the yield of monoglycerides has a maximum stationary area. This is due to determining the range of data selection code (point -1, 0, +1) must be considered to get the optimum point. Optimization of monoglycerides shows that the optimum conditions are X_1 = 0.19% (w/w), X_2 = 208.37 °C and X_3 = 3.20 hours with levels of monoglycerides obtained 41.58 %.

4. Conclusion

Optimization of monoglyceride reaction using KF/CaO-MgO catalyst was solved by software statistic version 12.0. There are three variables that are optimized i.e. the amount of catalyst, operating temperature and reaction time. The Pareto graph shows that the operating temperature gives the most significant effect compared to the other two variables. Optimization of monoglycerides showed that the optimum conditions were X_1 = 0.19 % (w/w), X_2 = 208.37 °C and X_3 = 3.20 hours with monoglycerides levels obtained 41.58 %.

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References

[1] G. R. Takeoka, G. H. Full, and L. T. Dao, (1997). "Effect of Heating on the Characteristics and Chemical Composition of Selected Frying Oils and Fats," *J. Agric. Food Chem.*, vol. 45, no. 8, pp. 3244–3249.

[2] U. T. Bornscheuer, "Lipase-catalyzed syntheses of monoacylglycerols," *Enzyme Microb. Technol.*, vol. 17, no. 7, pp. 578–586, 1995.

[3] D. S. Negi, T. Kimmel, G. Wozny, and R. Schomäcker, (2007). "Glycerolysis of fatty acid methyl esters: 2. Simulation and experiments in continuous reactors," JAOCS, J. Am. Oil Chem. Soc., vol. 84, no. 1, pp. 91–96.

[4] D. L. Breeden and R. L. Meyer, (2011). "Ester-Containing Downhole Drilling Lubricating Composition And Processes Therefor And Therewith," *USOO6884762B2*, vol. 2, no. 12, pp. 12–15.

[5] J. R. Martin, W. F. S. Neillie, G. A. Turner, and D. Wraige, (1989). "Fabric Conditioning Composition This," no. c, pp. 1–4.

[6] H. G. Franke and D. R. Bittner, (1996). "Compositons For Reslent Bodegradable Packaging Material Products," no. 5,512,090. United States Patent.

[7] Shizuo Narisawa, Y. Taira, Y. Yoshii, and T. Kondou, (1984). "Cement Composition," no. 19, pp. 1–6, 1984.

[8] M. Rosen and L. K. Hall, (1982). "Glyceryl Monostearate Plastic Lubricants," no. 4,363,891. United States Patent.

[9] P. P. Kore, S. D. Kachare, S. S. Kshirsagar, and R. J. Oswal, (2012). "Base Catalyzed Glycerolysis of Ethyl Acetate," *Org. Chem. Curr. Res.*, vol. 01, no. 04, pp. 108–111.

[10] H. Sihotang and M. Ginting, (2006). "Making Monogliserida Through Palm Oil Cultural Glycerolysis Using Catalyst," Journal of Chemical Science. vol. 10, no. 2, pp. 51–57.

[11] E. F. Purwaningtyas, M. Kasmiyatun, M. F. S. Mulyaningsih, and I. W. Negeri, (2015). "Optimization of Glycerolysis Temperature Process for the Synthesis of Monoglyceride-Diglyceride Surfactants Derived from oil of Silkworm Pupae,". ISSN 1693-4393, pp. 1–7.

[12] D. D. Anggoro and F. S. Budi, (2008). "Glycerolysis Process Of Palm Oil Oil To Mono And Diacetyl Glycerol With N-Butanol Solutions And Mgo Catalyst," *Reaktor*, vol. 12, no. 1, pp. 22–28.

[13] M. Nainggolan, R. D. Purba, and M. Y. Ritonga, "The Temperature of Glycerolysis Reaction in the Making of

Mono and Diacylglycerol (Dag) Using a Eggshell Ash Catalyst" vol. 3, no. 4, pp. 44–50, 2014.

[14] D. Anggoro and H. Oktavianty, (2018) "Optimization of Basicity of KF / Ca-MgO Catalyst by Impregnation Method," submitted in The 3 International Conference on Chemical and Material Enginering *(ICCME).* Department of Chemical Engineering, Diponegoro University.

[15] F. Yang, W. Xiang, X. Sun, H. Wu, T. Li, and L. Long, (2014). "A novel lipid extraction method from wet microalga Picochlorum sp. at room temperature," *Mar. Drugs*, vol. 12, no. 3, pp. 1258–1270.

[16] A Cornell, (1991). "Designs , Models , and the Analysis of Mixture," vol. 86, no. 415, pp. 56–57.

[17] H. Noureddini, D. W. Harkey, and M. R. Gutsman, (2004). "A Continuous Process for the Glycerolysis of Soybean Oil," JAOCS, J. Am. Oil Chem. Soc., vol. 81, no. 2, pp. 203–207.

[18] A. K. Coker, (2001). "Modeling of Chemical Kinetics and Reactor Design," *Model. Chem. Kinet. React. Des.*, pp. xvii–xxx.

[19] F. D. Gunstone and F. B. Padley,(1998). "Lipid Technologies and Applications. Book Reviews," *Lit. Linguist. Comput.*, vol. 13, no. 4, pp. 228–229.

[20] W. A. Fanny and T. Prakoso, (2012). "Development of Calcium Oxide Catalysts for Biodiesel Synthesis," *J. Tek. Kim. Indones.*, vol. 11, no. 2, pp. 66–73.

[21] H. Hermansyah and dan F. A. P. , Tania Surya Utami, (2011). "The Mathematical Model Of The Reaction Of Diacylglycerol Synthesis Using Biocatalyst Through The Esterification Mechanism" vol. 15, no. 1, pp. 28–32.

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