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Full Paper

GLYCEROLYSIS REACTION USING KF/CAO-MGO CATALYST: OPTIMIZATION AND REACTION KINETIC

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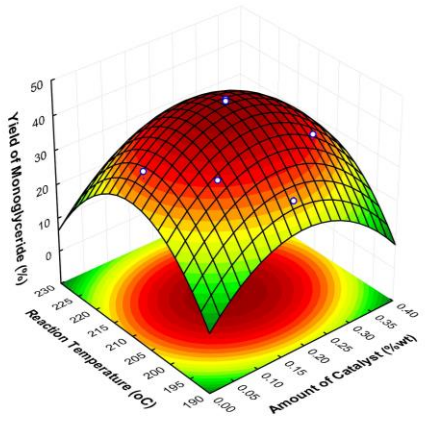

$$TG + GLY \underset{k_2}{\overset{k_1}{\rightleftharpoons}} MAG + DAG$$

Abstract

Monoglycerides can be produced through a glycerolysis reaction using a heterogeneous catalyst. The purpose of this study is to analyze the optimum conditions of the production of monoglycerides from glycerol and cooking oil using KF/CaO-MgO base catalysts and to find the reaction kinetics of the monoglyceride glycerolysis reaction. The Response Surface Method (RSM) was used to find favorable condition by varying the amount of catalyst (X_1) between 0.1, 0.2, and 0.3% (w/w), temperature (X_2) between 210, 220, and 230°C, and reaction time (X_3) from 2, 3, to 4 hours. Gas Chromatography – Mass Spectometry (GC-MS) analysis was used to determine monoglycerides, while catalysts were characterized by XRD (X-Ray Diffraction). The results showed that temperature had the most dominant influence compared to the amount of catalyst and reaction time. The most favorable conditions were obtained at X_1 = 0.19% (w/w), X_2 = 208.37°C and X_3 = 3.20 hours with monoglyceride yield of 41.58%. The constants for the reaction kinetics of the monoglyceride formation, k_1 and k_2 were 1.04189 and 0.88965 hour^{-1}, respectively.

Keywords: glycerolysis, monoglyceride, kinetics, KF/CaO-MgO catalyst, RSM optimization

1.0 INTRODUCTION

Glycerolysis is the reaction between glycerol and oil or fat to produce mono and di-acyl glycerol (MAG and DAG). Monoacylglycerol (MAG)/ monoglycerides (MG) are widely used as surfactants and emulsifiers in food, cosmetics, and pharmaceutical products [1]. In the food industry, the consumption of this surfactant group reaches 75% of the total emulsifying production. The use of monoglycerides in the food industry including used in bakery products, margarine, dairy products, and confectionary [2]. Additionally, it can be used as synthetic constituents and plasticizers [3, 4].

The glycerolysis reaction can be carried out with or without a catalyst. Reaction without catalyst will run slowly. Therefore, the catalyst is needed for the glycerolysis reaction to proceed quickly. In addition to obtaining a relatively short reaction time, the catalyst is also useful for directing OH groups to MAG formation. The glycerolysis reaction for the preparation of monoglycerides can be carried out by two methods, namely chemical synthesis (using acid, basic, or metal oxide catalysts) and enzymatic synthesis (using lipase catalysts) [5]. Compared to chemical synthesis, enzymatic synthesis has several advantages including mild reaction conditions, higher yields, and lower energy consumption [6].

However, the disadvantages of enzymatic synthesis include that the process is complex and time-consuming, more expensive, and the enzymes are difficult to separate from the product [2, 5]. Chemical synthesis has the main advantage of being a short reaction period [7]. Base catalysts are more widely used than acid catalysts because the reaction time is faster, non-corrosive, and high yields [8]. The most commonly used reaction is often under alkaline conditions and the frequently used base catalysts include NaOH [9], $NaOCH_3$ [10], CaO [11] and MgO [3]. However, the use of pure base catalysts especially metal oxides has lower catalyst activity compared to mixed metal oxide [12].

Investigation of impregnated mixed metal oxide catalysts, in particular, the KF/CaO-MgO catalyst in the glycerolysis reaction has not been carried out. Solid metal oxide catalysts impregnated on the supporting material have many advantages such as; increased catalyst surface area, high monoglyceride selectivity, environmentally friendly, easy catalyst separation and inexpensive product purification processes [13]. The potential of this catalyst is very large so that exploration of the use of this catalyst needs to be developed.

The glycerolysis reaction between glycerol and oil is a multiphase reaction. Therefore, the reaction is carried out at a high temperature (250°C). This is intended to increase the solubility of glycerol in the oil. The solubility of glycerol in oil at room temperature is very low at only around 4% [14]. Due to the multiphase properties of the sample, kinetics studies of the glycerolysis reaction of glycerol and triglycerides have not been reported in previous studies. For this reason, the kinetics of the glycerolysis reaction need to be studied.

This study aims to determine the optimum conditions of the glycerolysis reaction process of glycerol and triglycerides and determine the reaction rate constants based on the optimum conditions obtained. Optimization is carried out using the RSM method with statistical software version 12.0 concerning the amount of catalyst (X_1), reaction temperature (X_2) and reaction time (X_3). Reaction kinetic is solved by the fourth-order Runge-Kutta.

2.0 METHODOLOGY

2.1 Materials

In this research, the KF/CaO-MgO catalyst was made using potassium fluoride (KF), magnesium acetate, absolute ethanol (99.9%), calcium nitrate ($Ca(NO_3)_2$), and citric acid from Merck (Germany). Tropical cooking oil used as a source of triglycerides was acquired from supermarkets, while glycerol (85%) was obtained from Merck.

2.2 Preparation of KF/CaO-MgO Catalyst

Preparation of KF/CaO-MgO catalyst consists of 2 steps, which include preparation of CaO-MgO catalyst and continued with impregnation of KF into the CaO-MgO catalyst. In the first step, the preparation of CaO-MgO catalysts was carried out by dissolving the solids of magnesium acetate, calcium nitrate, and citric acid into 95% ethanol solution and stirring until homogeneous (clear colored). The mixed solution was then stirred at a speed of 300 rpm while being heated to form a sol. The heating was continued while stirring until it reaches a temperature of 80°C and a gel was formed. The formed gel was dried in an oven at 110°C overnight. The dry solid was then calcined in a Ney Vulcan box furnace at 550°C for 3 hours. The solid product obtained was a CaO-MgO catalyst.

The second step was the impregnation of the CaO-MgO catalyst with the KF solution. Two percent of KF was dissolved in aquadest. Impregnation was carried out by immersing the CaO-MgO catalyst in a KF solution for 1 hour while stirred and was then dried in a Memmert oven at 140°C for 6 hours. The dried solid catalyst was then calcined at a temperature of 450, 500 and 550°C in the box furnace for 3 hours. The resulted solid catalyst was called KF/CaO-MgO.

2.3 Characterizations of Catalyst and Product

The catalyst was characterized using XRD (X-Ray Diffraction). XRD analysis was carried out in Shimadzu XRD-7000. The XRD patterns were measured under radiation conditions Cu-Kα (k = 1.54 Å) operated at 30 mA and 40 kV. The diffraction pattern was produced in an angle range of 2θ from 10° to 70° with a step size of 0.017 and a step time of 0.5 seconds. The diffractogram/peak obtained was compared with data from the JCPDS library (Joint Committee on Powder Diffraction Standards).

Monoglyceride products were analyzed using Gas Chromatography-Mass Spectrometry (GC-MS) (QP2010S SHIMADZU, DB-1 column). GC-MS was also used to determine the molecular weight of the compound. In GC-MS, sample analysis was carried out at an oven temperature of 50°C (5 minutes). The temperature was raised by 10°C/min to reach 260°C and subsequently held for 33 minutes.

2.4 Glycerolysis Process

The monoglycerides formation was conducted using the molar ratio 1 to 3 for oil (triglyceride) to glycerol. The catalyst (% by weight) was dissolved in glycerol at 90°C in a glass vessel and stirred until the solution was completely homogeneous. Afterward, the triglyceride was placed into a glass vessel and heated to 150°C while stirring. Once the oil reaches the feed temperature, the mixture of glycerol and catalyst was gradually added while stirring. During the mixing process, the temperature was maintained at 150°C. Operating conditions were varied according to the optimization variable. The product was separated from the residue and analyzed using GC-MS. The reaction rate kinetics was determined by varying the reaction time from 1 to 5 hours with a batch system using the results of optimization of the operating conditions.

2.5 Experimental Design

The design model was created and used to determine the effect of response variables with a central composite design (CCD) and response surface method (RSM). This approach is widely used to design the second-order model. Second-order polynomial models were used to verify the effect and interactions of the linear and quadratic of the process variables [15]. By applying a CCD, the effect of each parameter can be evaluated quickly and effectively [16]. The experimental design was used to establish the low, center and high values for the amount of catalyst (% w/w), temperature and reaction time. Table 1 shows the experimental design.

Table 1 Range and level of independent variables for RSM

Variables	Unit	Variable Level		
		Low level (-1)	Center level (0)	High level (+1)
Amount of catalyst (X_1)	%(w/w)	0.1	0.2	0.3
Reaction temperature (X_2)	^{0}C	200	210	220
Reaction time (X_3)	Hours	2	3	4

The experimental design for optimization had 16 runs and the experiments were carried out to obtain optimal monoglyceride results using Expert Software StatSoft (statistics) version 12.0. The results were as shown in Table 2.

The Design-Expert 12.0 software was used to analyze the experimental data and was installed into second-order polynomial equations. The interaction between the dependent and independent variables is achieved through Eq. (2) [17].

$$Y = f\,(X_1, X_2, \ldots, X_k) + \varepsilon \qquad (1)$$

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

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

Where, Y is the observed response, β_0 is a regression parameter, β_i is the linear effect, β_{ii} is the quadratic effect, β_{ij} is the interaction effect, X_i is the main linear variable, X_iX_j are two linear variables, X_i^2 is the square of the main variable, and ε is the random error between predicted and measured values. The desired response is monoglyceride yield. ANOVA was used to test the statistical significance of the square variation average ratio due to regression and mean square error residuals [18]. The correlation coefficient (R^2) was used to express the quality of the fit of the polynomial model. The main indicators include probability values (Prob > F), F-values model (Fisher ratio variation), and adequate precision indicating the adequacy and significance of the model used. Maximization was used to determine the best and optimized local maximums. These individual targets were combined into the function of the overall desire using the software.

Table 2 RSM for three independent variables in the corresponding values and code unit

	Independent variables			Coded variables		
Run	Amount of Catalyst (%w/w)	Temperature (°C)	Reaction Time (Hours)	X_1	X_2	X_3
1	0.10	200.00	2.00	-1.00	-1.00	-1.00
2	0.10	200.00	4.00	-1.00	-1.00	1.00
3	0.10	220.00	2.00	-1.00	1.00	-1.00
4	0.10	220.00	4.00	-1.00	1.00	1.00
5	0.30	200.00	2.00	1.00	-1.00	-1.00
6	0.30	200.00	4.00	1.00	-1.00	1.00
7	0.30	220.00	2.00	1.00	1.00	-1.00
8	0.30	220.00	4.00	1.00	1.00	1.00
9	0.03	210.00	3.00	-1.68	0.00	0.00
10	0.37	210.00	3.00	1.68	0.00	0.00
11	0.20	193.18	3.00	0.00	-1.68	0.00
12	0.20	226.82	3.00	0.00	1.68	0.00
13	0.20	210.00	1.32	0.00	0.00	-1.68
14	0.20	210.00	4.68	0.00	0.00	1.68
15	0.20	210.00	3.00	0.00	0.00	0.00
16	0.20	210.00	3.00	0.00	0.00	0.00

2.6 Kinetic Model

The glycerolysis reaction of monoglycerides is reversible. Excessive use of glycerol is theoretically necessary to shift the equilibrium to the right so that the total monoglyceride obtained increases [19].

The reaction rate kinetics are used to estimate a constant rate for all possible reactions. This approach requires a thorough understanding of the steps in a sequential reaction. The formation of the monoglyceride equation is shown in equations (3) to (6).

$$\text{TG} + \text{GLY} \underset{\text{Catalyst}}{\overset{\text{KF/CaO-MgO}}{\rightleftharpoons}} \text{MAG} + \text{DAG} \qquad (3)$$

$$\text{aA} + \text{bB} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{cC} + \text{dD} \qquad (4)$$

Being an equation

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A C_B - k_2 C_C C_D \qquad (5)$$

$$\frac{dX_A}{dt} = k_1 C_{A_0}^2 (1 - X_A)(\theta_B - \theta_A) - k_1 C_A^2 X_A^2 \qquad (6)$$

Equation (6) is solved by the fourth-order Runge-Kutta, which is used in solving problems related to numerical calculations. It is an important tool for solving differential equations with initial conditions.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Catalyst

X-Ray Diffraction (XRD) pattern of the before and after impregnation with varied calcinations temperature of KF/CaO-MgO catalysts were illustrated in Figure 1.

The XRD pattern on the catalyst before being impregnated is illustrated in Figure 1(a). While the XRD pattern of the catalyst after being impregnated with calcination temperature variations is shown in Figure 1(b, c, d). In Figure 1(a), the XRD diffractogram shows the peaks of the CaO (37.36°, 74.65°, 78.70°) and MgO (42.91°, 62.15°) components. After the catalyst was calcined at 450°C, a peak of $Ca(OH)_2$ component appeared at 18.19°, 29.39°, 50.77° and 58.74°. This shows that the calcination temperature is still low. When the calcination temperature is increased to 500 and 550°C, new peaks form as $CaKF_3$ and $MgKF_3$ crystals. $CaKF_3$ and $MgKF_3$ are active sites formed due to the addition of KF as support. The presence of $CaKF_3$ and $MgKF_3$ crystals will produce high catalyst activity so that they are able to produce higher monoglyceride yields [20].

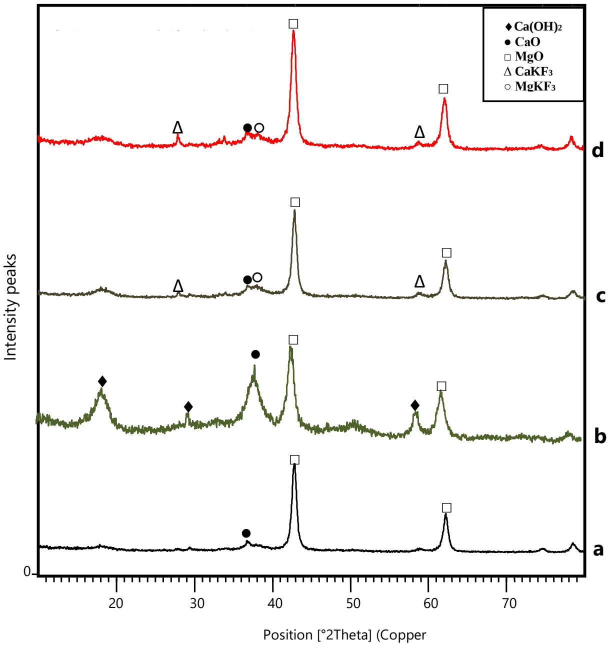

Figure 1 XRD pattern of the KF/CaO-MgO catalysts : (a) CaO-MgO catalyst; (b) KF/CaO-MgO catalyst (450°C); (c) KF/CaO-MgO catalyst (500°C); (d) KF/CaO-MgO catalyst (550°C)

3.2 Model Fitting

According to the experimental design, 16 experimental runs were carried out according to the optimization variables, including the amount of catalysts, temperature, and reaction time as shown in Table 2. The data from the experimental results were fitted to the polynomial equation to quantify the curvature effects [18]. The second-order fitting polynomial equation of coded factors was expressed as shown in Eq. (7).

$$\begin{aligned} Y = {} & -2750.60 + 299.09X_1 - 434.98X_1^2 + 25.08X_2 \\ & - 0.06X_2^2 + 98.58X_3 - 4.57X_3^2 - 0.14X_1X_2 \\ & - 9.92X_1X_3 - 0.33X_2X_3 \end{aligned} \qquad (7)$$

The complete 16 sets of the experimental design matrix and response based on experimental and predicted values on the yield of monoglycerides proposed by CCD are tabulated in Table 3 [16]. Table 3 also shows the raw and absolute residual values, as well as the percentage of error responses for all batches. By comparing experimental and predicted values, the model is verified. Figure 2 shows the results of a comparison between experimental and predictive values. Figure 2 proves that the percentage obtained from the efficiency of monoglyceride yield varies between 27.58 to 46.33% and the predicted value of the model matches the experimental results satisfactorily.

Table 3 Experimental and predictions values of monoglyceride yield using RSM

Run	Yield of monoglycerides		Raw residuals	Error (%)	Absolute residuals
	Experimental	Predicted			
1	27.580	28.042	-0.46	-1.67	0.46
2	37.070	37.513	-0.44	-1.19	0.44
3	31.720	33.504	-1.79	-5.64	1.79
4	30.610	29.903	0.71	2.32	0.71
5	30.190	29.381	0.81	2.68	0.81
6	38.190	34.892	3.30	8.64	3.30
7	36.240	34.284	1.95	5.38	1.95
8	28.680	26.711	1.97	6.87	1.97
9	36.550	34.664	1.89	5.17	1.89
10	29.100	33.090	-3.99	-13.71	3.99
11	30.160	31,332	-1.17	-3.88	1.17
12	28.070	29.037	-0.97	-3.46	0.97
13	33.150	32.737	0.41	1.24	0.41
14	31.770	34.337	-2.57	-8.09	2.57
15	46.890	46.449	0.44	0.94	0.44
16	46.330	46.448	-0.12	-0.26	0.12

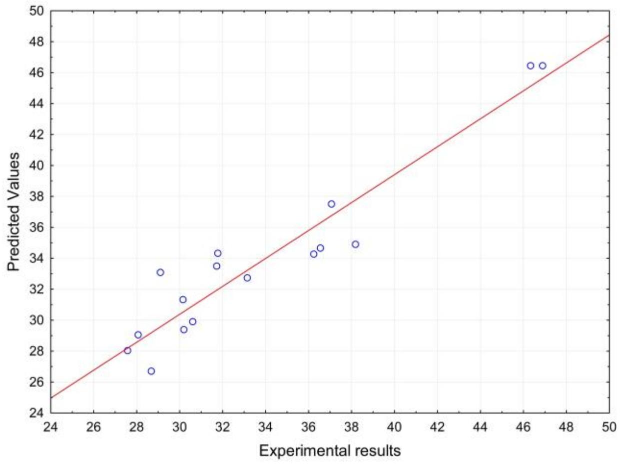

Figure 2 Predicted and experimental values for monoglyceride yield

3.3 Statistical

Analysis of variance (ANOVA) using Design-Expert 12.0 software was used to appropriately assess the polynomial model (Eq. (7)) taking into account the interactions [21]. Fisher F-test, where F-value is the ratio between the squares of the regression and the average error, was used to determine the statistical significance of the factor to the response. Table 4 shows the results of ANOVA for the monoglyceride percentage.

The results of the analysis of variance on monoglyceride production showed an R^2 of 90.28%. The R^2 value indicates that 90.28% of the data in the CCD can be explained by the response surface model. The effect of variables on the response value can be expressed by the model which can then predict the maximum response value in subsequent optimization experiments. The three optimization variables (amount of catalyst, temperature, and reaction time) have an effect > 90% from the model.

Table 4 ANOVA for the percentage of monoglycerides

Factors	Regression Coeff.	DF	F-value	p-value
X_0	-2750.60			
X_1	299.09	1	0.1798	0.3469
X_{11}	-434.98	1	4.3462	0.0038
X_2	25.08	1	0.4030	0.0009
X_{22}	-0.06	1	9.5630	0.0010
X_3	98.58	1	0.1970	0.0049
X_{33}	-4.57	1	4.7694	0.0033
X_{12}	-0.14	1	0.0103	0.8957
X_{13}	-9.92	1	0.5020	0.3778
X_{23}	-0.33	1	5.4493	0.0201
Erorr	8.6933	6		
R^2	0.9028			

Based on the ANOVA, the calculated F-value of the model was obtained at 60.45. The F-value of this model is greater than the tabulated F-value of 3.49. The F-value shows a statistically significant regression at a significance level of 5% [22]. This shows that the Fisher variance ratio calculated at this level is large enough to justify the very high degree of adequacy of the quadratic model and also to exhibit that the combination of treatments is very significant [23]. All p-values of monoglyceride production data produce a degree of significance $\alpha < 5\%$, except X_1, X_{12}, and X_{13}, indicating that the variable has a significant impact on the model.

3.4 Optimization Analysis

The optimum condition of the synthesis of monoglycerides is predicted using the optimization function. The empirical model derived from the RSM method can be used accurately to describe the relationship between the factors and response in the conversion of monoglycerides [19].

The optimum condition of the synthesis of monoglycerides is predicted using the optimization function. Figures 3 and 4 show 3D and 2D graphs of the response surface and contour plots of the effect of the amount of catalyst on the reaction temperature. Figures 3 and 4 display that the relationship between the amount of catalyst (% wt) and temperature in a monoglyceride product has a maximum stationary area. This is because the determination of the range of data selection codes (points -1, 0, 1) needs to be carefully considered to attain the optimal point [24]. The optimal conditions derived from software statistics are shown in Table 5.

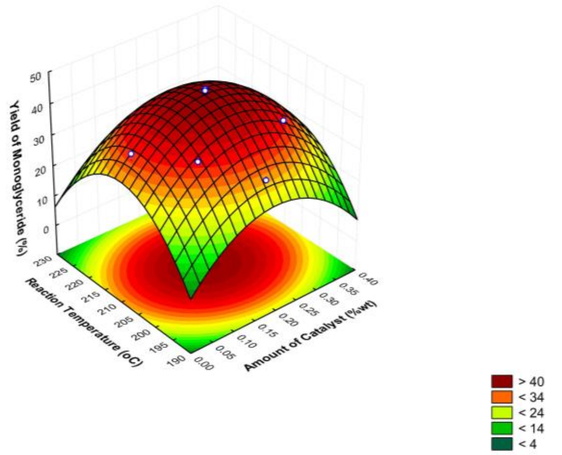

Figure 3 3D surface plots showing the interaction between amounts of catalyst (X_1) with reaction temperature (X_2) at reaction time (X_3) 3 hours for monoglycerides production

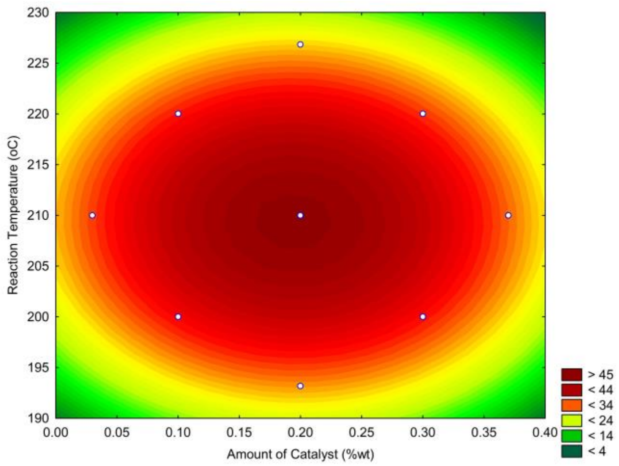

Figure 4 2D contour plot showing the interaction between the amounts of catalyst (X_1) with reaction temperature (X_2) at reaction time (X_3) 3 hours for monoglyceride production

Table 5 Optimal values of parameters

Parameters	Optimum value
Yield of Monoglyceride (%)	41.58
Amount of Catalyst (% w/w)	0.19
Reaction Temperature (°C)	208.37
Reaction Time (hours)	3.20

3.5 Kinetics

Figure 5 indicates the effect of monoglyceride concentration on reaction time.

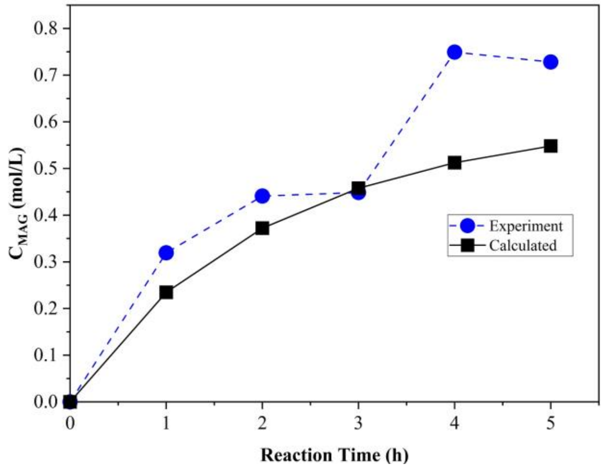

Figure 5 The relationship between MAG (monoacylglycerol/monoglyceride) concentration from experimental results and calculations on reaction times

Figure 5 shows the difference between the concentrations of monoglycerides obtained from experimental results and the one predicted. Monoglycerides produced from experimental are not stable, while the predicted results are more consistent and tend to increase. Additionally, the results of the experimental monoglycerides decreased at the 5th hour reaction time. This is because once the production of monoglycerides is optimum, it is influenced by the side reactions and forms diglycerol-acid (DAG) [25].

Computational results using the fourth-order Runge-Kutta method indicate the reaction rate constants $k_1 > k_2$ and $k_2 > 0$ with values k_1 and k_2 were 1.04189 and 0.88965 hour^{-1}, respectively. Figure 6 shows the conversion results obtained by calculating the reaction rate. The coefficient of determination (R^2) is 0.936, obtained based on the relationship between reaction time and conversion.

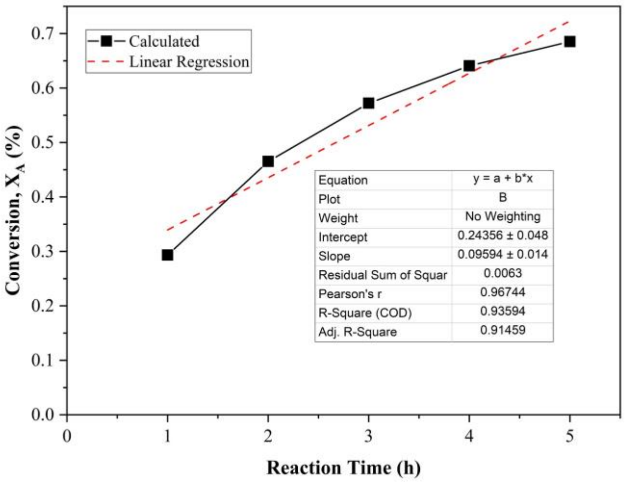

Figure 6 The conversion value of XA (%) to the reaction time (hour) in monoglyceride production

4.0 CONCLUSION

The results obtained from the optimization using the RSM method shows the temperature effect has the most dominant influence with a p-value of 0,0009 and R^2 0.9028. The amount of catalyst and reaction time also has an influence but not too dominant. Besides, optimization of monoglycerides indicates that the optimum condition is reached at X_1 (amount of catalyst) = 0.19% (w/w), X_2 (reaction temperature) = 208.37°C and X_3 (reaction time) = 3.20 hours with a monoglyceride content of 41.58%. Monoglyceride conversion from the experimental results and calculations using the fourth-order Runge-Kutta method results tend to decrease after 5 hours of operating conditions. Reaction rate constants show $k_1>k_2$ and $k_2>0$ with k_1 and k_2 values of 1.04189 and 0.88965 $hour^{-1}$, respectively. The determinant value (R^2) obtained was 0.936.

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References

[1] Wang, F. C. and Marangoni, A. G. 2016. Advances in the Application of Food Emulsifier a-Gel Phases: Saturated Monoglycerides, Polyglycerol Fatty Acid Esters, and their Derivatives. *Journal of Colloid and Interface Science*. 483: 394–403.
DOI : https://doi.org/10.1016/j.jcis.2016.08.012

[2] Naik, M. K., Naik, S. N., and Mohanty, S. 2014. Enzymatic Glycerolysis for Conversion of Sunflower Oil to Food Based Emulsifiers. *Catalysis Today*. 237: 145–149.
DOI : https://doi.org/10.1016/j.cattod.2013.11.005

[3] Ferretti, C. A., Fuente, S., Ferullo, R., Castellani, N., Apesteguía, C. R., and Di Cosimo, J. I. 2012. Monoglyceride Synthesis by Glycerolysis of Methyl Oleate on MgO: Catalytic and DFT Study of the Active Site. *Applied Catalysis A: General*. 413–414: 322–331.
DOI : https://doi.org/10.1016/j.apcata.2011.11.025

[4] Belelli, P. G., Ferretti, C. A., Apesteguía, C. R., Ferullo, R. M., and Di Cosimo, J. I. 2015. Glycerolysis of Methyl Oleate on MgO: Experimental and Theoretical Study of the Reaction Selectivity. *Journal of Catalysis*. 323: 132–144.
DOI : https://doi.org/10.1016/j.jcat.2015.01.001

[5] Miao, S. and Lin, D. 2019. Monoglycerides: Categories, Structures, Properties, Preparations, and Applications in the Food Industry. *Encyclopedia of Food Chemistry*. 155–163.
DOI : https://doi.org/10.1016/b978-0-08-100596-5.21595-3

[6] Freitas, L., Paula, A. V., dos Santos, J. C., Zanin, G. M., and de Castro, H. F. 2010. Enzymatic Synthesis of Monoglycerides by Esterification Reaction Using Penicillium camembertii Lipase Immobilized on Epoxy SiO2-PVA Composite. *Journal of Molecular Catalysis B: Enzymatic*. 65(1–4): 87–90.
DOI : https://doi.org/10.1016/j.molcatb.2009.12.009

[7] Siri-nguan, N. and Ngamcharussrivichai, C. 2016. Alkoxide-intercalated Mg–Al Layered Double Hydroxides as Selective Catalysts for the Synthesis of Monoglycerides. *Reaction Kinetics, Mechanisms and Catalysis*. 119(1): 273–289.
DOI : https://doi.org/10.1007/s11144-016-1018-5

[8] Buchori, L., Istadi, I., and Purwanto, P. 2016. Advanced Chemical Reactor Technologies for Biodiesel Production from Vegetable Oils - A Review. *Bulletin of Chemical Reaction Engineering & Catalysis*. 11(3): 406–430.
DOI : https://doi.org/10.9767/bcrec.11.3.490.406-430

[9] Kore, P. P., Kachare, S. D., Kshirsagar, S. S., and Oswal, R. J. 2012. Base Catalyzed Glycerolysis of Ethyl Acetate. *Organic Chemistry Current Research*. 1(4): 108–111.
DOI : http://dx.doi.org/10.4172/2161-0401.1000108

[10] Satriana, Arpi, N., Lubis, Y. M., Adisalamun, Supardan, M. D., and Mustapha, W. A. W. 2016. Diacylglycerol-enriched Oil Production Using Chemical Glycerolysis. *Europian Journal of Lipid Science and Technology*. 118(12): 1880–1890.
DOI : https://doi.org/10.1002/ejlt.201500489

[11] Schulz, G. A. S., da Silveira, K. C., Libardi, D. B., Peralba, M. do. C. R., and Samios D. 2011. Synthesis and Characterization of Mono-acylglycerols through the Glycerolysis of Methyl Esters Obtained from Linseed Oil. *Europian Journal of Lipid Science and Technology*. 113(12): 1533–1540.
DOI : https://doi.org/10.1002/ejlt.201100079

[12] Taufiq-Yap, Y. H., Lee, H. V., Hussein, M. Z., and Yunus, R. 2011. Calcium-based Mixed Oxide Catalysts for Methanolysis of Jatropha Curcas Oil to Biodiesel. *Biomass and Bioenergy*. 35(2): 827–834.
DOI : https://doi.org/10.1016/j.biombioe.2010.11.011

[13] Hoo, P. and Abdullah, A. Z. 2016. Monolaurin Yield Optimization in Selective Esterification of Glycerol with Lauric Acid over Post Impregnated HPW/SBA-15 Catalyst. *Korean Journal of Chemical Engineering*. 33(4): 1200–1210.
DOI : https://doi.org/10.1007/s11814-015-0246-0

[14] Temelli, F., King, J. W., and List, G. R. 1996. Conversion of Oils to Monoglycerides by Glycerolysis in Supercritical Carbon Dioxide Media. *Journal of the American Oil Chemists' Society*. 73(6): 699–706.
DOI : https://doi.org/10.1007/BF02517943

[15] Anggoro, D. D., Oktavianty, H., Kurniawan, B. P., and Daud, R. 2019. Optimization of Glycerol Monolaurate (GML) Synthesis from Glycerol and Lauric Acid Using Dealuminated Zeolite Y Catalyst. *Jurnal Teknologi*. 81(4): 133–141.
DOI : https://doi.org/10.11113/jt.v81.13511

[16] Yang, F., Xiang, W., Sun, X., Wu, H., Li, T., and Long, L. 2014. A Novel Lipid Extraction Method from Wet Microalga Picochlorum sp. at Room Temperature. *Marine Drugs*. 12(3): 1258–1270.

DOI : https://doi.org/10.3390/md12031258

[17] Yetilmezsoy, K., Demirel, S., and Vanderbei, R. J. 2009. Response Surface Modeling of Pb(II) Removal from Aqueous Solution by Pistacia vera L.: Box-Behnken Experimental Design. *Journal of Hazardous Materials*. 171(1–3): 551–562.
DOI : https://doi.org/10.1016/j.jhazmat.2009.06.035

[18] Sangeetha, V., Sivakumar, V., Sudha, A., and Devi, K. P. 2014. Optimization of Process Parameters for COD Removal by Coagulation Treatment Using Box–Behnken Design. *International Journal of Engineering and Technology*. 6(2): 1053-1058.

[19] Sonntag, N. O. V. 1983. Glycerolysis of Fats and Methyl Esters-Status, Review and Critique. *Journal of the American Oil Chemists' Society*. 60(7): 1245–1249.
DOI : https://doi.org/10.1007/BF02634442

[20] Xuan, J., Zheng, X., and Hu, H. 2012. Active Sites of Supported KF Catalysts for Transesterification. *Catalysis Communications*. 28: 124–127.
DOI : https://doi.org/10.1016/j.catcom.2012.08.032

[21] Fregolente, L. V., Batistella, C. B., Filho, R. M., and Maciel, M. R. W. 2005. Response Surface Methodology Applied to Optimization of Distilled Monoglycerides Production. *Journal of the American Oil Chemists' Society*. 82(9): 673–678.
DOI: https://doi.org/10.1007/s11746-005-1127-9

[22] Istadi, 1. and Amin, N. A. S. 2006. Optimization of Process Parameters and Catalyst Compositions in Carbon Dioxide Oxidative Coupling of Methane over CaO–MnO/CeO_2 Catalyst Using Response Surface Methodology. *Fuel Processing Technology*. 87: 449 – 459.
DOI: https://doi.org/10.1016/j.fuproc.2005.11.004

[23] Mustafa, M. N., Shafie, S., Wahid, M. H., and Sulaiman, Y. 2019. Optimization of Power Conversion Efficiency of Polyvinyl-Alcohol/Titanium Dioxide Compact Layer Using Response Surface Methodology/Central Composite Design. *Solar Energy* 183: 689–696.
DOI: https://doi.org/10.1016/j.solener.2019.03.074

[24] Montgomery, D. C. 2001. *Design and Analysis of Experiments*. Fifth Eds. United States of America: John Wiley & Sons, Inc.

[25] Feuge, R. O. and Bailey, A. E. 1946. Modification of Vegetable Oils: VI. The Practical Preparation of Mono- and Diglycerides. *Oil & Soap*. 23(8): 259-264.
DOI: https://doi.org/10.1007/BF02696133

02. Editor Decision (Revision Required) (12 Juli 2020)

E-mail
@che.undip.ac.id

Luqman Buchori <luqman.buchori@che.undip.ac.id>

[JT] Editor Decision (RR) #14585

2 messages

Professor Dr. Rosli Md Illias <r-rosli@utm.my> Sun, Jul 12, 2020 at 8:31 AM
To: Luqman Buchori <luqman.buchori@che.undip.ac.id>
Cc: Mohammad Djaeni <moh.djaeni@live.undip.ac.id>, Ratnawati Ratnawati <ratnawati.hartono@gmail.com>, Diah Susetyo Retnowati <diahsusetyo@gmail.com>, Hadiyanto Hadiyanto <hady.hadiyanto@gmail.com>, Didi Dwi Anggoro <dididwianggoro@lecturer.undip.ac.id>, journal_utm@utm.my

Dear Luqman Buchori:

We have reached a decision regarding your submission to Jurnal Teknologi, "Glycerolisis Reaction Using KF/CaO-MgO Catalyst: Optimization and Reaction Kinetic".

Our decision is: REVISION REQUIRED
----

2. Reviewers have now commented on your paper. You will see that they are advising you to revise your manuscript. If you are prepared to undertake the work required, I would be pleased to consider your article for publication.

3. For your guidance, reviewers' comments are attached.

4. Please be advised all articles that have been chosen to be published in Jurnal Teknologi will be charged MYR 530.00.
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a) Revised Manuscript.
b) List of CORRECTIONS DONE.
and
c) Filled document "JT Invoice Request and Payment Instructions NORMAL ISSUE" to enable us prepare a formal invoice for payment purpose.

We look forward for your favourable reply. Thank you.

Yours sincerely;

Professor Dr. Rosli Md Illias
Universiti Teknologi Malaysia
r-rosli@utm.my

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Luqman Buchori <luqman.buchori@che.undip.ac.id> Mon, Jul 13, 2020 at 7:42 AM
To: "Professor Dr. Rosli Md Illias" <r-rosli@utm.my>

Dear Editor,

Thanks for your information.
I will revise my article according to the advice of the reviewer and will follow the procedure for publishing articles in accordance with the procedures of the Journal of Technology.

Thank you for your support.

Warm regards

Luqman Buchori
[Quoted text hidden]
--
Dr. Luqman Buchori, ST, MT
Department of Chemical Engineering, Faculty of Engineering
Diponegoro University, Indonesia

03. Review Form Response (Reviewer Comment) (12 Juli 2020)

Review Form Response

Review Form 1

Article Title

GLYCEROLYSIS REACTION USING KF/CAO-MGO CA

Series

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Referee's comments

Comments:

1. English need to be improved. The manuscript must be proof read and a the area which was corrected/improved must be clearly shown. A letter/certificate from a qualified proof reader must be shown as a proof.

2. Which catalyst is being used for the reaction? It is not being mentioned in the manuscript. There are 3 version of catalysts - those three are calcined at 450, 500 or 550?

3. Having only XRD as the only characterization seems not to be sufficient for a manuscript that is synthesizing catalyst. It is recommended to have at least another characterization that is Nitrogen Adsroption BET. The authors also mentioned about the importance of surface area in the second page, left column that is : "....Solid metal oxide catalysts impregnated on the supporting material have many advantages such as; increased catalyst surface area...". This clearly shows that the author knows the importance of having surface area information for a new catalyst.

4. Please be clear and specific which optimization software is being used. First appearance, this is being mentioned = "statistical software version 12.0" - no software name. Second appearance, this is being mentioned = "Expert Software StatSoft (statistics) version 12.0". Third appearance, this is being mentioned = "Design-Expert 12.0 software". The fourth appearance, this is being mentioned = "Design-Expert 12.0 software".

Hence, from the observation, I thought and assume you are using Design Expert software. So, please be consistent in mentioning this.

However, upon reading further, all the graphics showed that you are using Statistica software and not Design Expert. Please be clear and accurate and honest which one is being used.

5. I suggest to include the pareto chart to be included in the factor analysis because it will clearly show which is the most significant factor.

6. It's best to discuss and analyze and relate all the findings obtained. This manuscript lacks the inter-relate discussion between for example characterization result and optimization. Between optimization and reaction kinetics etc.

7. Why analysis is being made by GCMS? GCMS is meant for identification of compounds and you can only make qualitative analysis. Kindly explained how the results are being derived from GCMS.

Thanks.

A. Evaluations

Please evaluate the paper according to the following criteria:

1. The topic is important and relevant for publication *

● Yes
○ No

Comment

Yes

2. The work presented in the manuscript is original *

● Yes
○ No

Comment

It is original

3. The manuscript uses sufficient references *

● Yes
○ No

Comment

Agreed

4. The manuscript uses appropriate language and styles *

● Yes
○ No

Comment

It can be considered average. Still there are the need to proof read.

5. The title of the manuscript is appropriate *

● Yes
○ No

Comment

Appropriate

6. The order of presentation is satisfactory *

● Yes
○ No

Comment

Yes it is fine.

7. The abstract adequately summarizes the content of the manuscript *

● Yes
○ No

Comment

OK

8. The introduction is adequately developed *

○ Yes
● No

Comment

I was hoping it to be longer and much detail

9. The problem described in the manuscript is clearly stated *

○ Yes
● No

Comment

Not really

10. The adopted methodology described in the manuscript is sound *

● Yes
○ No

Comment

Yes

11. The findings of this manuscript are correctly interpreted *

● Yes
○ No

Comment

Yes, but for me it is not sufficient. Needs to be longer and more detail, more analytical.

12. The manuscript is free from obvious errors *

○ Yes
● No

Comment

The software used for optimization is not consistent throughout the manuscript.

13. The quality of figures and illustrations is acceptable for publications *

● Yes
○ No

Comment

OK.

14. The manuscript does not dwell on any sensitive issues *

● Yes
○ No

Comment

Yes

B. Suggestions to the author(s)

What can the author(s) do to improve the quality of this paper?

*

1. Proof read.
2. Add BET analysis.
3. Mentioned the correct statistical software employed.
4. Add pareto chart.
5. Link analysis from all results and findings together.

C. Recommendations to the editors

The manuscript should be:

*

○ Published as it is
● Published with changes as recommended
○ Returned to the writer to be completely reworked and rewritten
○ Rejected

Close

* Denotes required field

04. Revised Manuscript Submission + List of Corrections Done (21 Juli 2020)

E-mail
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Luqman Buchori <luqman.buchori@che.undip.ac.id>

Revised Manuscript and JT Invoice Request and Payment Instructions NORMAL ISSUE

2 messages

Luqman Buchori <luqman.buchori@che.undip.ac.id> Tue, Jul 21, 2020 at 11:37 PM
To: Editor-in-Chief <journal_utm@utm.my>, qpenerbit@utm.my
Cc: "Professor Dr. Rosli Md Illias" <r-rosli@utm.my>
Bcc: Didi Dwi Anggoro <anggorophd@gmail.com>, Luqman Buchori <luqman.buchori@gmail.com>

Dear Editor,

I have revised my manuscript according to the comments of the reviewer. I wish to send my revised manuscript through the system, but the system in the Jurnal Teknologi cannot be accessed. For this reason, I send my revised manuscript via this email.

In this email, I have attached:
1. Revised manuscript
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I hope the revision of this manuscript can be well received.

Thank you for your help and support.

Warm regards,
--
Dr. Luqman Buchori, ST, MT
Department of Chemical Engineering, Faculty of Engineering
Diponegoro University, Indonesia

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Journal UTM <journal_utm@utm.my> Wed, Jul 22, 2020 at 7:25 AM
To: Luqman Buchori <luqman.buchori@che.undip.ac.id>
Cc: "UTM eJournal Tech. Support Penerbit UTM Press" <qpenerbit@utm.my>, "Professor Dr. Rosli Md Illias" <r-rosli@utm.my>

Dear Author Sir / Madam,

Received. We will forward them to the Chief Editor/SectioN Editor for his final decision.

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REVISION NOTE BASED ON REVIEWER COMMENTS

Journal Name: JURNAL TEKNOLOGI

Manuscript ID: 14585

Title: "Glycerolysis Reaction Using KF/CaO-MgO Catalyst: Optimization and Reaction Kinetic"

Author(s): Luqman Buchori, Mohammad Djaeni, R. Ratnawati, Diah Susetyo Retnowati, H. Hadiyanto, Didi Dwi Anggoro.

Thank you very much for the valuable Reviewers' Comments. We have answered the question and revised the manuscript according to Reviewers Comments.

Reviewer:

No.	Comment from Reviewer	Answer/Revision Note	Location of Revision in Revised Manuscript
1.	English need to be improved. The manuscript must be proof read and a the area which was corrected/improved must be clearly shown. A letter/certificate from a qualified proof reader must be shown as a proof.	Thank you for Reviewer suggestion. The article has been proof read by a qualified proof reader (Enago). We have attached the proof of article which is proof read and proof reader certificate. To show tracked changes, please click the vertical line at the left of the manuscript.	-
2.	Which catalyst is being used for the reaction? It is not being mentioned in the manuscript. There are 3 version of catalysts - those three are calcined at 450, 500 or 550^{o}C?	Thank you for Reviewer comments. The glycerolysis process uses 1 catalyst, which is a catalyst that has been calcined at 550^{o}C. We have added this statement in the article.	Page 2, section 2.4, right column, paragraph 1, line 3. Page 5, left column, paragraph 2.
3.	Having only XRD as the only characterization seems not to be sufficient for a manuscript that is synthesizing catalyst. It is recommended to have at least another characterization that is Nitrogen Adsorption BET. The authors also mentioned about the importance of surface area in	Thank you for Reviewer recommendation. We have added another catalyst characterization namely Nitrogen Adsorption BET in the article (Section 2.3). Discussion of the BET results has also been added in the article (Section 3.1).	Abstract, line 10-11. Page 2, right column, section 2.3, paragraph 1, line 2-4.

	the second page, left column that is : "....Solid metal oxide catalysts impregnated on the supporting material have many advantages such as; increased catalyst surface area...". This clearly shows that the author knows the importance of having surface area information for a new catalyst.		Page 2, right column, section 2.3, paragraph 2. Page 4, right column, paragraph 2-3.
4.	Please be clear and specific which optimization software is being used. First appearance, this is being mentioned = "statistical software version 12.0" - no software name. Second appearance, this is being mentioned = "Expert Software StatSoft (statistics) version 12.0". Third appearance, this is being mentioned = "Design-Expert 12.0 software". The fourth appearance, this is being mentioned = "Design-Expert 12.0 software". Hence, from the observation, I thought and assume you are using Design Expert software. So, please be consistent in mentioning this. However, upon reading further, all the graphics showed that you are using Statistica software and not Design Expert. Please be clear and accurate and honest which one is being used.	Thank you for Reviewer comments. In this study, we use Statistica software version 12. We have used the phrase "Statistica software version 12" in this article. I apologize for this inconsistency.	Page 2, left column, paragraph 4, line 6. Page 3, right column, paragraph 1, line 1. Page 5, right column, section 3.3, paragraph 1, line 1.
5.	I suggest to include the pareto chart to be included in the factor analysis because it will clearly show which is the most significant factor.	Thank you for Reviewer suggestion. We have added the pareto chart.	Page 6, left column, paragraph 3.
6.	It's best to discuss and analyze and relate all the findings obtained. This manuscript lacks the inter-relate discussion between for example characterization result and optimization. Between	Thank you for Reviewer comments. In this study, catalyst characterization was carried out to determine changes in the character of the catalyst to the addition of metals and calcination temperature. The best results from catalyst characterization are used for the glycerolysis process. In this	Pages 5, left column, paragraph 2, line 1-3. Page 7, left column,

	optimization and reaction kinetics etc.	study, the catalyst used was the KF/CaO-MgO catalyst which was calcined at 550^{o}C. We have included this statement in the article. Meanwhile, optimization is used to determine the optimum conditions of the glycerolysis process which includes reaction temperature, reaction time and the amount of catalyst. The optimum conditions obtained are used to find the reaction kinetics.	section 3.5, paragraph 1, line 1-2.
7.	Why analysis is being made by GCMS? GCMS is meant for identification of compounds and you can only make qualitative analysis. Kindly explained how the results are being derived from GCMS.	Thank you for Reviewer comments. From GCMS analysis, we get %composition of all components in the product. Yield of monoglyceride (MAG) is calculated by the following formula: $Yield_{MAG}(\%) = \frac{weight\ of\ product\ (g)}{weight\ of\ cooking\ oil\ (g)} x\%composition_{MAG}$ We have added this formula in the article.	Page 3, left column, paragraph 1, line 6.

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Teknologi

Full Paper

GLYCEROLYSIS ~~REACTION~~ USING KF/CAO-MGO CATALYST: OPTIMIS~~Z~~ATION AND REACTION ~~KINETIC~~KINETICS

Luqman Buchori*, Mohammad Djaeni, R. Ratnawati, Diah Susetyo Retnowati, H. Hadiyanto, Didi Dwi Anggoro

Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Jl. Prof. Soedarto, SH Tembalang, Semarang, 50275, Indonesia

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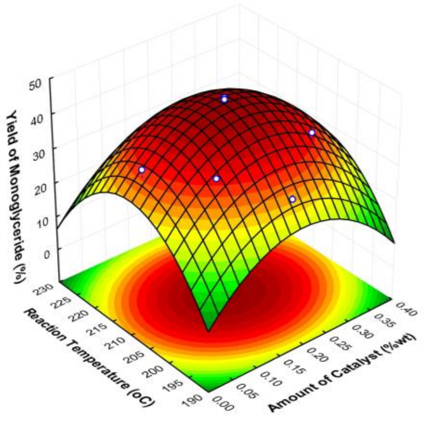
Graphical abstract



$$TG + GLY \underset{k_2}{\overset{k_1}{\rightleftharpoons}} MAG + DAG$$

Abstract

Monoglycerides can be produced through ~~a~~ glycerolysis ~~reaction~~ using a heterogeneous catalyst. The purpose of this study is to analys~~z~~e the optimum conditions ~~of~~for the production of monoglycerides from glycerol and cooking oil using KF/CaO-MgO base catalysts and to ~~find~~investigate the ~~reaction~~ kinetics of the monoglyceride glycerolysis reaction. The ~~Response Surface Method~~response surface method (RSM) was used to ~~find~~determine the favourable~~rable~~ ~~condition~~conditions by varying the amount of catalyst (X_1) between 0.1, 0.2~~,~~ and 0.3% (w/w~~),~~); the reaction temperature (X_2) between 210, 220~~,~~ and ~~230 °C,~~230°C and reaction time (X_3) ~~from~~between 2, 3~~,~~ ~~to~~and 4 hours. Gas ~~Chromatography – Mass Spectometry~~chromatography-mass spectrometry (GC-MS) ~~analysis~~ was used to determine the monoglycerides, while catalysts were characteris~~z~~ed by X-ray diffraction (XRD ~~(X-Ray Diffraction~~) and ~~BET (~~the Brunauer-Emmett-Teller~~)~~ method~~.~~ (BET). The results showed that ~~reaction~~, among the three factors examined, temperature ~~had~~shows the most ~~dominant influence compared to the amount of catalyst and~~control over this glycerolysis reaction ~~time~~. The most favourable~~rable~~ conditions ~~were obtained at~~are X_1 = 0.19% (w/w), X_2 = 208.~~37 °C~~37°C and X_3 = 3.20 hours ~~with~~, which provide a monoglyceride yield of 41.58%. The constants for the reaction kinetics of the monoglyceride formation, k_1 and k_2 ~~were~~are 1.04189 and 0.88965 hour^{-1}, respectively.

Keywords: glycerolysis, monoglyceride, kinetics, KF/CaO-MgO catalyst, RSM ~~optimization~~optimisation

1.0 -INTRODUCTION

Glycerolysis is the reaction of glycerol ~~and~~with triglycerides (fats/oils) to form mono-acyl glycerol (MAG) and di-acyl glycerol (DAG). Monoacylglycerol (MAG)/monoglycerides (MG) are widely used as surfactants and emulsifiers in food, cosmetics~~,~~ and pharmaceutical products [1]. In the food industry, the consumption of ~~this surfactant group~~MAG/MG reaches 75% of the total emulsifying production. ~~The use of~~Specifically, monoglycerides ~~in the food industry including~~are used ~~in~~for the productions of bakery products, margarine, dairy products~~,~~ and confectionary [2]. Additionally, ~~it~~they can be used as synthetic constituents and plasticisers~~zers~~ [3, 4].

~~The glycerolysis reaction~~ Glycerolysis can be carried out with or without a catalyst. ~~Reaction without~~ The catalyst ~~will run slowly. Therefore,~~simply accelerates the ~~catalyst is needed for the glycerolysis~~

~~reaction to proceed quickly. In addition to obtaining a relatively short reaction time, the catalyst is also useful for~~ reaction by directing OH groups to MAG formation. The ~~glycerolysis~~ reaction ~~for the preparation of monoglycerides~~ can be carried out ~~by~~ with either of two methods~~, namely~~: chemical synthesis (using acid, basic, or metal oxide catalysts~~) and~~), or enzymatic synthesis (using lipase catalysts) [5]. Compared to chemical synthesis, enzymatic synthesis has several advantages including mild reaction conditions, higher yields~~,~~ and lower energy consumption [6]. However, ~~the disadvantages of~~ enzymatic synthesis ~~include that the process~~ is more complex, ~~and~~ time-consuming, ~~more~~ expensive~~,~~ and the enzymes are difficult to separate from the product [2, 5]. ~~Chemical~~In contrast, chemical synthesis has ~~the main advantage of being~~ a short reaction period [7]. Base catalysts are more widely used than acid catalysts because the reaction time is faster, the reaction is non-corrosive~~,~~ and ~~high~~it produces higher yields [8]. ~~The most commonly used~~Most often, the reaction ~~is often~~proceeds under alkaline conditions and the most frequently used base catalysts include NaOH [9], $NaOCH_3$ [10], CaO [11~~]~~] and MgO [3]. However, ~~the use of~~ pure base catalysts, especially metal oxides ~~has~~, have lower catalyst ~~activity~~activities compared to mixed metal ~~oxide~~oxides [12].

~~Investigation~~The use of impregnated mixed metal oxide catalysts, ~~in particular, the~~ KF/CaO-MgO catalyst in particular, in the glycerolysis reaction has not been ~~carried out. Solid metal oxide catalysts impregnated on~~investigated yet. Impregnating the supporting material ~~have~~with a solid metal oxide catalyst has many advantages such as ~~as;~~ increased catalyst surface area, high monoglyceride selectivity, environmentally friendly, easy catalyst separation and inexpensive product~~-~~ purification processes [13]. ~~The potential of~~Since this catalyst shows great potential, it is ~~very large so that exploration of the~~important to explore its use ~~of this catalyst needs to be developed~~in glycerolysis.

The glycerolysis reaction between glycerol and oil is a multiphase reaction. ~~Therefore, the reaction~~It is carried out at ~~a~~ high temperature (~~250°C). This is intended~~ 250°C) in order to increase the solubility of glycerol in the oil~~. The solubility of glycerol in oil~~ , which is only around 4% at room temperature ~~is very low at only around 4%~~ [14]. Due to the multiphase properties of the sample, ~~kinetics~~ studies of the kinetics of the glycerolysis reaction ~~of~~between glycerol and triglycerides have not been ~~reported in previous studies. For this reason, the kinetics of the glycerolysis reaction need to be studied.~~carried out.

~~This~~The present study aims to determine the optimum conditions and the corresponding reaction rate constants of the glycerolysis reaction ~~process of~~between glycerol and triglycerides ~~and determine the reaction rate constants based on the optimum conditions obtained.~~. ~~Optimization~~Optimisation is carried out using the ~~RSM~~response surface method (RSM) with the Statistical software version 12.0 concerning the amount of catalyst (X_1), reaction temperature (X_2~~)~~) and reaction time (X_3). ~~Reaction kinetic~~ The reaction kinetics is solved ~~by~~using the fourth-order Runge-Kutta.

2.0 -METHODOLOGY

2.1 -Materials

In this research, the KF/CaO-MgO catalyst was made using potassium fluoride (KF), magnesium acetate, absolute ethanol (99.9%), calcium nitrate ($Ca(NO_3)_2$)~~,~~ and citric acid from Merck (Germany). Tropical cooking oil ~~used as~~that is a source of triglycerides was acquired from ~~supermarkets, while~~a supermarket and glycerol (85%) was obtained from Merck.

2.2 -Preparation of KF/CaO-MgO Catalyst

~~Preparation of~~The KF/CaO-MgO catalyst ~~consists of 2~~was prepared in two steps~~, which include preparation of CaO-MgO catalyst and continued with impregnation of KF into~~. First, we prepared the CaO-MgO catalyst~~.~~, which was then impregnated with KF. In the first step, the preparation of CaO-MgO catalysts was carried out by dissolving ~~the solids of~~ magnesium acetate, calcium nitrate~~,~~ and citric acid into a 95% ethanol solution and stirring until the solution became homogeneous (clear coloured~~red~~). The mixed solution was then stirred at a speed of 300 rpm while being heated to form a sol. ~~The heating~~Heating was continued while stirring ~~until it reaches a temperature of 80°C~~up to 80°C and a gel was formed. The formed gel was dried in an oven at ~~110°C~~110°C overnight. The dry solid was then calcined in a Ney Vulcan box furnace at ~~550°C~~550°C for 3 hours. The obtained solid product ~~obtained~~ was a CaO-MgO catalyst.

The second step was the impregnation of the CaO-MgO catalyst with the KF solution. Two percent of KF was dissolved in aquadest. Impregnation was carried out by immersing the CaO-MgO catalyst in ~~a~~the KF solution for ~~1~~one hour while ~~stirred and was then dried~~stirring, followed by drying in an oven (Memmert) at ~~140°C~~140°C for 6 hours. The dried solid catalyst was then calcined at ~~a temperature of~~ 450, 500 and ~~550°C~~550°C in ~~the~~a box furnace for 3 hours. The resulted solid catalyst was called KF/CaO-MgO.

2.3 ~~Characterizations~~Characterisation of Catalyst and Product

The catalyst was characteris~~z~~ed ~~using~~ through X-ray diffraction (XRD ~~(X-Ray Diffraction~~) and the Brunauer-Emmett-Teller (BET) surface ~~—~~ area~~area~~ method (ChemBET PULSAR Quantachrome). XRD analysis was carried out ~~in~~using a Shimadzu XRD-7000. The XRD patterns were measured under Cu-Kα radiation conditions ~~Cu-Kα~~ (k = 1.54 Å) ~~operated~~ at 30 mA and 40 kV. The diffraction pattern was produced in an angle range of 2θ from ~~10°~~10° to ~~70°~~70° with a step size of 0.017 and a step time of 0.5 seconds. The diffractogram/peak obtained was compared with data from the JCPDS library (Joint Committee on Powder Diffraction Standards).

The surface area of the catalyst was measured using ~~Nitrogen~~nitrogen adsorption at 77.15 K. ~~A total of~~ 0.2 grams of the sample ~~was~~were degassed with nitrogen gas under vacuum ~~pressure~~ for 1 hour at ~~200°C~~200°C before the absorption measurements.

~~Monoglyceride~~The monoglyceride products were analys~~z~~ed using ~~Gas Chromatography-Mass Spectrometry~~gas chromatography-mass spectrometry (GC-MS) (QP2010S SHIMADZU, DB-1 column). GC-MS was also used to determine the molecular weight of the compound. In GC-MS, the sample ~~analysis~~ was ~~carried out~~analysed at an oven temperature of ~~50°C~~50°C (5 minutes). The temperature was raised by ~~10°C~~10°C/min up to ~~reach 260°C~~260°C and subsequently held there for 33 minutes.

2.4 -Glycerolysis ~~Process~~

The formation of monoglycerides ~~formation~~ was ~~conducted~~achieved using ~~the molar ratio 1 to 3 for~~ oil (triglyceride~~)~~)-to~~-~~-glycerol~~.~~ molar ratio of 1 to 3. The catalyst, which ~~has~~had been calcined at ~~550°C~~550°C (% by weight~~)~~), was dissolved in glycerol at ~~90°C~~90°C in a glass vessel and stirred until the solution was completely homogeneous. Afterward, the triglyceride was placed ~~into~~in a glass vessel and heated to ~~150°C~~150°C while stirring. Once the oil ~~reaches~~reached the feed temperature, the mixture of glycerol and catalyst was gradually added while stirring. During the mixing process, the temperature was maintained ~~at 150°C. Operating~~stable at 150°C. The operating conditions were varied according to the ~~optimization~~optimisation variable. The product was separated from the residue and analys~~z~~ed using GC-MS. ~~Yield of~~The monoglyceride (MAG) ~~is~~yield was calculated ~~by~~using Eq. (1).

$$Yield_{MAG}(\%) = \frac{weight\ of\ product\ (g)}{weight\ of\ cooking\ oil\ (g)}\, x\%composition_{MAG} \quad (1)$$

The reaction rate kinetics was determined by varying the reaction time from 1 to 5 hours with a batch system ~~using~~based on the ~~results of~~operating conditions' ~~optimization~~optimisation ~~of the operating conditions~~results.

2.5 -Experimental Design

~~The design model was created and used~~ In order to determine the effect of the response variables ~~with a~~on the glycerolysis reaction, we designed the experiment based on the principles of central composite design (CCD) and using the RSM~~response surface method (RSM)~~. This approach is widely used to design ~~the~~ second-order ~~model~~models. Second-order polynomial models were used to verify the effect and interactions of the linear and quadratic of the process variables [15]. By applying a CCD, the effect of each parameter can be evaluated quickly and effectively [16]. The experimental design was used to establish the low, centre~~er~~ and high values ~~for~~of the ~~amount of~~ catalyst amount (% w/w), the reaction temperature and the reaction time. Table 1 shows the experimental design.

The experimental design for ~~optimization~~optimisation had 16 runs and the experiments were carried out to obtain the optimal monoglyceride results~~. The results were as shown in~~ (Table 2~~.~~).

Table 1 Range and level of independent variables for RSM

Variables	Unit	Variable Level		
		Low level ~~(-~~ (−1)	**Centre~~er~~ level (0)**	**High level (+1)**
~~Amount of catalyst~~Catalyst amount (X_1)	%(w/w)	0.1	0.2	0.3
Reaction temperature (X_2)	^{0}C	200	210	220
Reaction time (X_3)	Hours	2	3	4

The Statistical software version 12.0 was used to analys~~z~~e the experimental data and was installed into the second-order polynomial equations. The interaction between the dependent and independent variables ~~is~~was achieved through Eq. (3) [17].

$$Y = f\,(X_1, X_2, \ldots, X_k) + \varepsilon \quad (2)$$

i = 1, 2, 3,-.k

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i X_i + \sum_{i=1}^{k}\beta_{ii} X_i^2 + \sum\sum_{i<j}\beta_{ij} X_i X_j + \varepsilon \quad (3)$$

~~Where,~~where Y is the observed response, β_0 is a regression parameter, β_i is the linear effect, β_{ii} is the quadratic effect, β_{ij} is the interaction effect, X_i is the main linear variable, X_iX_j are two linear variables, X_i^2 is the square of the main variable~~,~~ and ε is the random error between the predicted and the measured values.

Table 2 RSM for three independent variables in the corresponding values and code unit

Run	Independent variables			Coded variables		
	~~Amount of~~ Catalyst Amount (%w/w)	**Reaction Temperature (~~º~~°C)**	**Reaction Time (Hours)**	**X_1**	**X_2**	**X_3**

1	0.10	200.00	2.00	~~-~~−1.00	~~-~~−1.00	~~-~~−1.00
2	0.10	200.00	4.00	~~-~~−1.00	~~-~~−1.00	1.00
3	0.10	220.00	2.00	~~-~~−1.00	1.00	~~-~~−1.00
4	0.10	220.00	4.00	~~-~~−1.00	1.00	1.00
5	0.30	200.00	2.00	1.00	~~-~~−1.00	~~-~~−1.00
6	0.30	200.00	4.00	1.00	~~-~~−1.00	1.00
7	0.30	220.00	2.00	1.00	1.00	~~-~~−1.00
8	0.30	220.00	4.00	1.00	1.00	1.00
9	0.03	210.00	3.00	~~-~~−1.68	0.00	0.00
10	0.37	210.00	3.00	1.68	0.00	0.00
11	0.20	193.18	3.00	0.00	~~-~~−1.68	0.00
12	0.20	226.82	3.00	0.00	1.68	0.00
13	0.20	210.00	1.32	0.00	0.00	~~-~~−1.68
14	0.20	210.00	4.68	0.00	0.00	1.68
15	0.20	210.00	3.00	0.00	0.00	0.00
16	0.20	210.00	3.00	0.00	0.00	0.00

The desired response ~~is~~was the monoglyceride yield. The statistical significance of the average ratio of the square variation due to regression and the mean square error residuals was tested with ANOVA [18]. The correlation coefficient (R^2) was used to state the quality of the conformity of the polynomial model. The main indicators ~~include~~included the probability values (Prob > F), the F-values model (Fisher ratio variation)~~,~~ and the adequate precision indicating the adequacy and significance of the model used. Maximis~~z~~ation was used to determine the best and optimis~~z~~ed local maximums. These individual targets were combined into the function of the overall desire using the software.

2.6 Kinetic Model

The glycerolysis reaction of monoglycerides is reversible. Excessive use of glycerol is theoretically necessary to shift the equilibrium to the right so that the total monoglyceride obtained increases [19].

The reaction~~–~~ rate~~rate~~ kinetics ~~are~~were used to estimate a constant rate for all possible reactions. This approach requires a thorough understanding of the steps in a sequential reaction. The formation of the monoglyceride equation is shown in ~~equations~~Eqs. (4) to (7).

$$\mathrm{TG + GLY} \underset{\text{Catalyst}}{\overset{\text{KF/CaO-MgO}}{\rightleftarrows}} \mathrm{MAG + DAG} \tag{4}$$

$$aA + bB \underset{k_2}{\overset{k_1}{\rightleftarrows}} cC + dD \tag{5}$$

Being an equation

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A C_B - k_2 C_C C_D \tag{6}$$

$$\frac{dX_A}{dt} = k_1 C_{A_0}^2 (1 - X_A)(\theta_B - \theta_A) - k_1 C_A^2 X_A^2 \tag{7}$$

Equation (7) ~~is~~was solved by the fourth-order Runge-Kutta, which is used in solving problems related to numerical calculations. It is an important tool for solving differential equations with initial conditions.

3.0 RESULTS AND DISCUSSION

3.1 Characteris~~z~~ation of the catalyst~~Catalyst~~

~~X-Ray Diffraction (XRD) pattern~~The XRD patterns of the catalyst before and after impregnation ~~with~~at varied calcinations ~~temperature of KF/CaO-MgO catalysts were illustrated~~temperatures are shown in Figure 1.

The XRD pattern on the CaO-MgO catalyst before being impregnated with KF is ~~illustrated~~presented in Figure 1(a). ~~While the~~The XRD pattern of the catalyst after being impregnated with KF at the different calcination ~~temperature variations~~temperatures is shown in Figure 1(b, c, d). In Figure 1(a), the XRD diffractrogram shows the peaks of the CaO (37.~~36°,~~36°, 74.~~65°,~~65° and 78.~~70°)~~70°) and MgO (42.~~91°,~~91° and 62.~~15°)~~15°) components. After the catalyst was calcined at ~~450°C, a peak of~~ 450°C, peaks corresponding to the $Ca(OH)_2$ component appeared at 18.~~19°,~~19°, 29.~~39°,~~39°, 50.~~77°~~77° and 58.~~74°.~~74°. This shows that the calcination temperature of 450°C is ~~still~~ low. When the calcination temperature is increased to 500 and ~~550°C,~~ 550°C, $CaKF_3$ and $MgKF_3$ crystals form, which appear in the XRD patterns as new peaks ~~form as $CaKF_3$ and $MgKF_3$ crystals.~~. $CaKF_3$ and $MgKF_3$ are active sites formed due to the addition of KF as support. The presence of ~~$CaKF_3$ and $MgKF_3$~~these crystals ~~will produce high~~increases the catalyst activity ~~so that they are able to produce~~and produces higher monoglyceride yields [20].

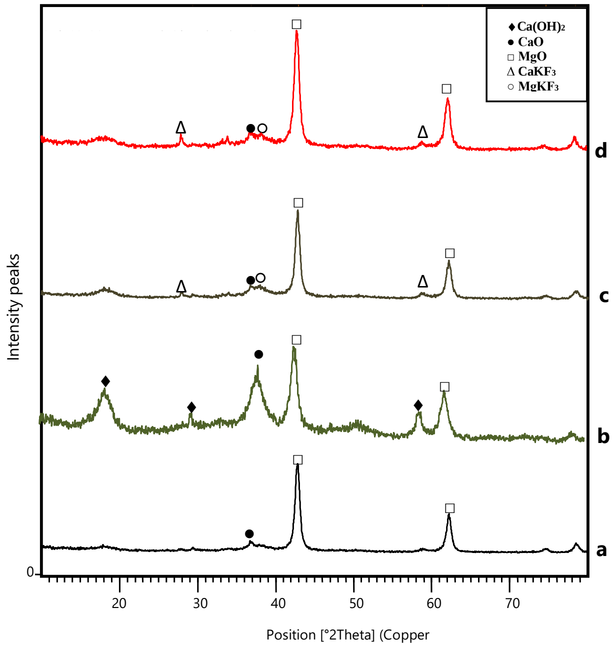


Figure 1 XRD pattern of the KF/CaO-MgO catalysts: (a) CaO-MgO catalyst; (b) KF/CaO-MgO catalyst (~~450°C~~450°C); (c) KF/CaO-MgO catalyst (~~500°C~~500°C); (d) KF/CaO-MgO catalyst (~~550°C~~550°C)

The results of the surface ~~-~~ area~~area~~ characteris~~z~~ation are presented in Table 3.

Table 3 The surface area of the catalyst ~~in~~under various treatments

Catalyst	Surface Area (m²/g)
CaO-MgO	112,250
KF/CaO-MgO (~~450°C~~450°C)	132,456
KF/CaO-MgO (~~500°C~~500°C)	119,706
KF/CaO-MgO (~~550°C~~550°C)	110,924

Table 3 shows the increase in the catalyst surface area after impregnation with KF. However, the surface area of the catalyst decreases with increasing calcination temperature. This ~~fact~~ may be caused by ~~the~~ aggregation of the catalyst as a result of the formation of the new active catalyst sites ($CaKF_3$ and $MgKF_3$) that ~~occur~~occurs at high calcination temperatures. However, the formation of $CaKF_3$ and $MgKF_3$ ~~will~~ increase the catalyst activity. ~~From Figure 1, it can be seen that~~Indeed, the increase in the calcination temperature ~~at~~to 500 and ~~550°C~~550°C forms new crystals (Figure 1), namely $CaKF_3$ (28.~~28°~~28° and 59.~~32°)~~32°) and $MgKF_3$ (38.~~58°). Addition of~~58°). KF addition to heterogeneous catalysts and high calcination temperatures ~~will~~ produce new crystals (such as $CaKF_3$ and $MgKF_3$) as active sites that can produce higher yields due to the high catalytic activity [20].

Based on the characteris~~z~~ation of this catalyst, the catalyst used for the glycerolysis process is KF/CaO-MgO, which is calcined at ~~550°C~~550°C.

3.2 ~~-~~Model Fitting

According to the experimental design, 16 experimental runs were carried out according to the ~~optimization~~optimisation variables~~, including~~ (the catalyst amount~~ of catalysts,~~, the reaction temperature~~,~~ and the reaction time), as shown in Table 2. The ~~data from the~~ experimental ~~results~~data were fitted to the polynomial equation to quantify the curvature effects [18]. The second-order fitting polynomial equation of the coded factors was expressed as shown in Eq. (8).

$$Y = -2750.60 + 299.09X_1 - 434.98X_1^2 + 25.08X_2 - 0.06X_2^2 + 98.58X_3 - 4.57X_3^2 - 0.14X_1X_2 - 9.92X_1X_3 - 0.33X_2X_3 \qquad (8)$$

The complete 16 sets of the experimental design matrix and ~~response based on~~the experimental and predicted values ~~on~~of the yield of monoglycerides proposed by CCD are tabulated in Table 4 [16]. Table 4 also shows the raw and absolute residual values, as well as the percentage of error responses for all batches. The model is verified by comparing the experimental ~~and~~with the predictive values~~.~~ ~~Figure~~ (Figure 2~~ shows the results of a comparison between experimental and predictive values. Figure 2 proves that the percentage~~). Indeed, the obtained ~~from the efficiency of~~ monoglyceride yield varies between 27.58 to 46.33% and the values predicted ~~value of~~by the model ~~matches~~match the experimental results satisfactorily.

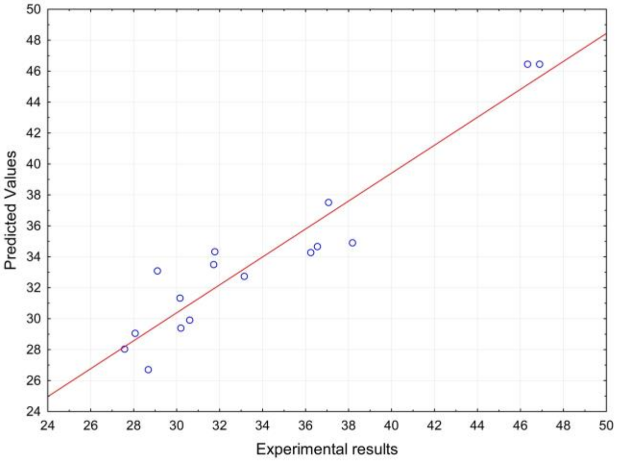


Figure 2 Predicted and experimental values for monoglyceride yield

3.3 ~~-~~Statistical analysis results

ANOVA~~nalysis of variance (ANOVA)~~ using Statistical software version 12.0 was used to appropriately assess the polynomial model (Eq. (8)) taking into account the interactions [21]. Fisher F-test, where F-value is the ratio between the squares of the regression and the average error, was used to determine the statistical significance of the factor to the response. The ANOVA results for the percentage of monoglycerides are presented in Table 5.

The results of the analysis of variance on monoglyceride production ~~showed~~gave an R^2 of 90.28%. ~~The R^2 value~~This indicates that 90.28% of the data in the CCD can be explained by the response surface model. The effect of the variables on the response value can be expressed by the model which can then predict the maximum response value in subsequent ~~optimization~~optimisation experiments. The model results that the three ~~optimization~~optimisation variables (~~amount of~~ catalyst amount, reaction temperature~~,~~ and reaction time) have an effect ~~>~~greater than 90~~% from the model.~~%.

Table 4 Experimental and ~~predictions values of~~predicted monoglyceride yield using RSM

Run	Yield of monoglycerides		Raw residuals	Error (%)	Absolute residuals
	Experimental	Predicted			
1	27.580	28.042	~~-~~−0.46	~~-~~−1.67	0.46
2	37.070	37.513	~~-~~−0.44	~~-~~−1.19	0.44
3	31.720	33.504	~~-~~−1.79	~~-~~−5.64	1.79
4	30.610	29.903	0.71	2.32	0.71
5	30.190	29.381	0.81	2.68	0.81
6	38.190	34.892	3.30	8.64	3.30
7	36.240	34.284	1.95	5.38	1.95
8	28.680	26.711	1.97	6.87	1.97
9	36.550	34.664	1.89	5.17	1.89
10	29.100	33.090	~~-~~−3.99	~~-~~−13.71	3.99
11	30.160	31,332	~~-~~−1.17	~~-~~−3.88	1.17
12	28.070	29.037	~~-~~−0.97	~~-~~−3.46	0.97
13	33.150	32.737	0.41	1.24	0.41
14	31.770	34.337	~~-~~−2.57	~~-~~−8.09	2.57
15	46.890	46.449	0.44	0.94	0.44
16	46.330	46.448	~~-~~−0.12	~~-~~−0.26	0.12

Table 5 ANOVA for the percentage of monoglycerides

Factors	Regression Coeff.	DF	F-value	p-value
X_0	~~-~~−2750.60			
X_1	299.09	1	0.1798	0.3469
X_{11}	~~-~~−434.98	1	4.3462	0.0038
X_2	25.08	1	0.4030	0.0009
X_{22}	~~-~~−0.06	1	9.5630	0.0010
X_3	98.58	1	0.1970	0.0049
X_{33}	~~-~~−4.57	1	4.7694	0.0033
X_{12}	~~-~~−0.14	1	0.0103	0.8957
X_{13}	~~-~~−9.92	1	0.5020	0.3778
X_{23}	~~-~~−0.33	1	5.4493	0.0201
Erorr	8.6933	6		
R^2	0.9028			

Based on the ANOVA, the ~~calculated~~ F-value ~~of~~obtained by the model ~~was obtained at~~ is 60.45~~.~~ ~~The F-value of this model~~, which is greater than the tabulated F-value of 3.49. ~~The~~This F-value shows a statistically significant regression at a significance level of 5% [22]. ~~This shows that~~Therefore, the Fisher variance ratio calculated at this level is large enough to justify the very high degree of adequacy of the quadratic model and also to exhibit that the combination of treatments is very significant [23]. All p-values of monoglyceride production data produce a degree of significance $\alpha < 5\%$, except X_1, X_{12}~~,~~ and X_{13}, indicating that the variable has a significant impact on the model.

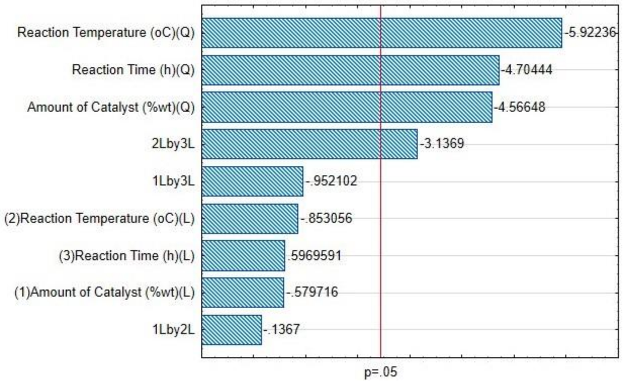


Figure 3 Pareto chart for variables that have a significant effect on the glycerolysis process

The ~~variable~~variables that ~~has~~have the most significant effect ~~is~~are presented in Figure 3 (Pareto chart). ~~Figure 3 shows that the reaction temperature~~Temperature has the most significant effect compared to the other variables.

3.4 ~~Optimization~~Optimisation Analysis

The optimum ~~condition of~~conditions for the synthesis of monoglycerides ~~is~~are predicted using the ~~optimization~~optimisation function. The empirical model derived from the RSM method can be used ~~accurately~~ to describe accurately the relationship between the factors and the response in the conversion of monoglycerides [19].

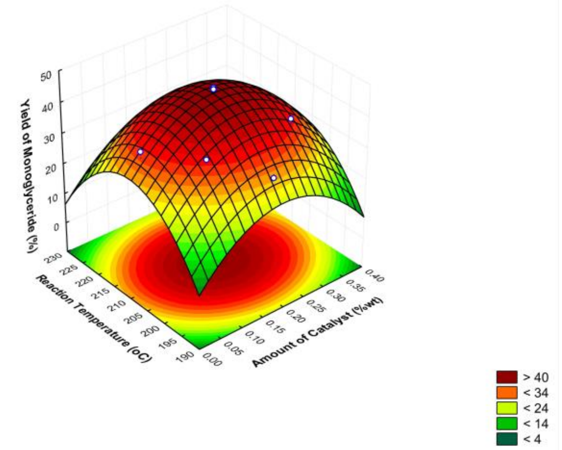


Figure 4 3D surface plots showing the interaction between amounts of catalyst (X$_1$) with reaction temperature (X$_2$) at a reaction time (X$_3$) of 3 hours for monoglycerides production

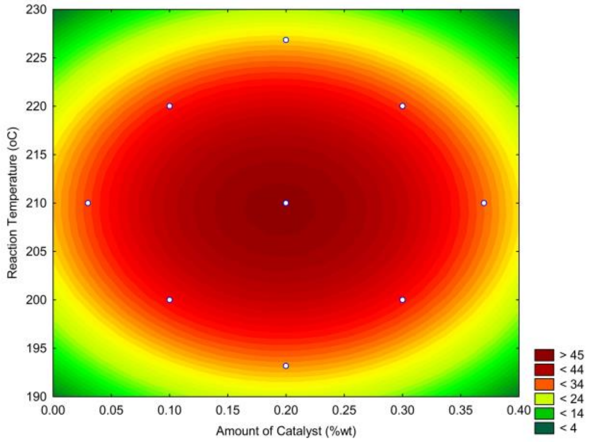


Figure 5 2D contour plot showing the interaction between the amounts of catalyst (X$_1$) with reaction temperature (X$_2$) at a reaction time (X$_3$) of 3 hours for monoglyceride production

~~The optimum condition of the synthesis of monoglycerides is predicted using the optimization function.~~ Figures 4 and 5 show 3D and 2D graphs of the response surface and contour plots of the effect ~~of~~that the ~~amount of~~ catalyst amount has on the reaction temperature. ~~Figures 4 and 5 display that the~~ The relationship between the ~~amount of~~ catalyst amount (% wt) and the reaction temperature in a monoglyceride product has a maximum stationary area. This is because ~~the determination of~~it is necessary to carefully determine the range of data selection codes (points ~~-~~−1, 0, 1) ~~needs to be carefully considered~~in order to attain the optimal point [24]. The optimal conditions derived from ~~statistica~~the Statistical software are shown in Table 6.

Table 6 Optimal values of parameters

Parameters	**Optimum value**
Yield of Monoglyceride (%)	41.58
Amount of Catalyst (% w/w)	0.19
Reaction Temperature (~~o~~°C)	208.37
Reaction Time (hours)	3.20

3.5 Kinetics

The ~~optimization~~optimisation results obtained are used to determine the reaction kinetics. Figure 6 indicates the effect of the reaction time on the obtained monoglyceride ~~concentrations~~concentration.

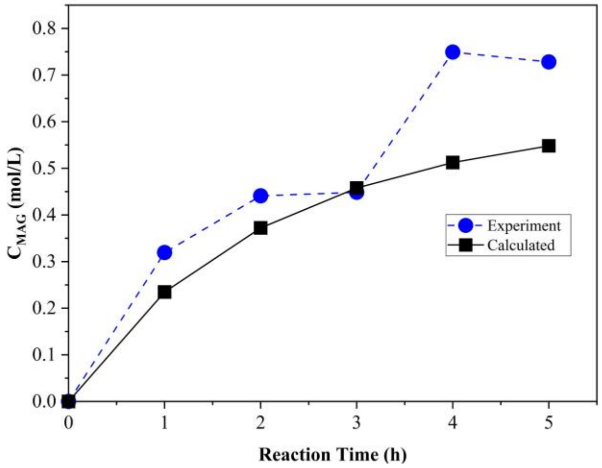


Figure 6 The relationship between the reaction time ~~to~~ and the obtained MAG (monoacylglycerol/monoglyceride) concentration ~~of~~based on the experimental ~~and calculation~~ results and the model calculations.

Figure 6 shows the difference between the experimental and modelled monoglyceride concentrations ~~obtained from the results of experimental and calculated. Monoglycerides produced from experimental are~~. In the experiment, the monoglyceride concentration is not stable, ~~while~~whereas the calculated ~~results are~~concentration using the model is more consistent and ~~tend~~tends to increase. Additionally, in the ~~results of the experimental~~experiment, monoglycerides ~~decreased at the 5th hour~~decrease after five hours reaction time. This is because once the production of monoglycerides is optimum, it is influenced by the side reactions and forms diglycerol-acid (DAG) [25].

~~Computational~~The computational results using the fourth-order Runge-Kutta method indicate that the reaction rate constants k_1 ~~>~~ > k_2 and k_2 ~~>~~ > 0, with ~~values~~ k_1 ~~and k_2 were~~= 1.04189 hour^{-1} and k_2 = 0.88965 hour^{-1}~~, respectively~~. Figure 7 shows the conversion results obtained by calculating the reaction rate. The coefficient of determination (R^2) is 0.936, obtained based on the relationship between the reaction time and the conversion.

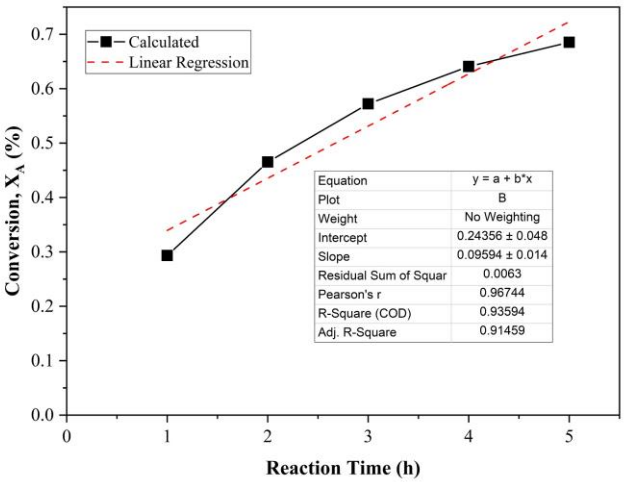


Figure 7 The conversion value of X_A (%) to the reaction time (hour) in monoglyceride production

4.0 CONCLUSION

The results obtained from the ~~optimization~~optimisation using the RSM method ~~shows the~~show that temperature ~~effect~~ has the most dominant influence with a p-value of 0,0009 and R^2 0.9028. The ~~amount of~~ catalyst amount and the reaction time ~~also has an~~have lesser, yet significant, influence~~ but not too dominant.~~. Besides, ~~optimization of monoglycerides indicates that~~ the optimum ~~condition is reached at~~reaction conditions are X_1 (~~amount of~~ catalyst amount) = 0.19% (w/w), X_2 (reaction temperature) = 208.~~37°C~~37°C and X_3 (reaction time) = 3.20 hours with a monoglyceride content of 41.58%. ~~Monoglyceride conversion from~~Based on the experimental results and calculations using the fourth-order Runge-Kutta method~~ results tend~~, monoglyceride conversion tends to decrease after ~~5~~five hours of ~~operating conditions. Reaction~~reaction time. The reaction rate constants ~~show~~are k_1 ~~>~~ > k_2 and k_2 ~~>~~ > 0 ~~with~~ k_1 ~~and k_2 values of~~= 1.04189 hour^{-1} and k_2 = 0.88965 hour^{-1}~~, respectively.~~. The obtained determinant value (R^2) ~~obtained was~~is 0.936.

Acknowledgement

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References

[1] Wang, F. C. and Marangoni, A. G. 2016. Advances in the Application of Food Emulsifier a-Gel Phases: Saturated Monoglycerides, Polyglycerol Fatty Acid Esters, and their Derivatives. *Journal of Colloid and Interface Science*. 483: 394–403.
DOI : http://dx.doi.org/10.1016/j.jcis.2016.08.012

[2] Naik, M. K., Naik, S. N., and Mohanty, S. 2014. Enzymatic Glycerolysis for Conversion of Sunflower Oil to Food Based Emulsifiers. *Catalysis Today*. 237: 145–149.
DOI : http://dx.doi.org/10.1016/j.cattod.2013.11.005

[3] Ferretti, C. A., Fuente, S., Ferullo, R., Castellani, N., Apesteguía, C. R., and Di Cosimo, J. I. 2012. Monoglyceride Synthesis by Glycerolysis of Methyl Oleate on MgO: Catalytic and DFT Study of the Active Site. *Applied Catalysis A: General*. 413–414: 322–331.
DOI : http://dx.doi.org/10.1016/j.apcata.2011.11.025

[4] Belelli, P. G., Ferretti, C. A., Apesteguía, C. R., Ferullo, R. M., and Di Cosimo, J. I. 2015. Glycerolysis of Methyl Oleate on MgO: Experimental and Theoretical Study of the Reaction Selectivity. *Journal of Catalysis*. 323: 132–144.
DOI : http://dx.doi.org/10.1016/j.jcat.2015.01.001

[5] Miao, S. and Lin, D. 2019. Monoglycerides: Categories, Structures, Properties, Preparations, and Applications in the Food Industry. *Encyclopedia of Food Chemistry*. 155–163.
DOI : http://dx.doi.org/10.1016/b978-0-08-100596-5.21595-3

[6] Freitas, L., Paula, A. V., dos Santos, J. C., Zanin, G. M., and de Castro, H. F. 2010. Enzymatic Synthesis of Monoglycerides by Esterification Reaction Using Penicillium camembertii Lipase Immobilized on Epoxy SiO2-PVA Composite. *Journal of Molecular Catalysis B: Enzymatic*. 65(1–4): 87–90.
DOI : http://dx.doi.org/10.1016/j.molcatb.2009.12.009

[7] Siri-nguan, N. and Ngamcharussrivichai, C. 2016. Alkoxide-intercalated Mg–Al Layered Double Hydroxides as Selective Catalysts for the Synthesis of Monoglycerides. *Reaction Kinetics, Mechanisms and Catalysis*. 119(1): 273–289.
DOI : http://dx.doi.org/10.1007/s11144-016-1018-5

[8] Buchori, L., Istadi, I., and Purwanto, P. 2016. Advanced Chemical Reactor Technologies for Biodiesel Production from Vegetable Oils - A Review. *Bulletin of Chemical Reaction Engineering & Catalysis*. 11(3): 406–430.
DOI : http://dx.doi.org/10.9767/bcrec.11.3.490.406-430

[9] Kore, P. P., Kachare, S. D., Kshirsagar, S. S., and Oswal, R. J. 2012. Base Catalyzed Glycerolysis of Ethyl Acetate. *Organic Chemistry Current Research*. 1(4): 108–111.
DOI : http://dx.doi.org/10.4172/2161-0401.1000108

[10] Satriana, Arpi, N., Lubis, Y. M., Adisalamun, Supardan, M. D., and Mustapha, W. A. W. 2016. Diacylglycerol-enriched Oil Production Using Chemical Glycerolysis. *Europian Journal of Lipid Science and Technology*. 118(12): 1880–1890.
DOI : http://dx.doi.org/10.1002/ejlt.201500489

[11] Schulz, G. A. S., da Silveira, K. C., Libardi, D. B., Peralba, M. do. C. R., and Samios D. 2011. Synthesis and Characterization of Mono-acylglycerols through the Glycerolysis of Methyl Esters Obtained from Linseed Oil. *Europian Journal of Lipid Science and Technology*. 113(12): 1533–1540.
DOI : http://dx.doi.org/10.1002/ejlt.201100079

[12] Taufiq-Yap, Y. H., Lee, H. V., Hussein, M. Z., and Yunus, R. 2011. Calcium-based Mixed Oxide Catalysts for

Methanolysis of Jatropha Curcas Oil to Biodiesel. *Biomass and Bioenergy*. 35(2): 827–834.
DOI : http://dx.doi.org/10.1016/j.biombioe.2010.11.011

[13] Hoo, P. and Abdullah, A. Z. 2016. Monolaurin Yield Optimization in Selective Esterification of Glycerol with Lauric Acid over Post Impregnated HPW/SBA-15 Catalyst. *Korean Journal of Chemical Engineering*. 33(4): 1200–1210.
DOI : http://dx.doi.org/10.1007/s11814-015-0246-0

[14] Temelli, F., King, J. W., and List, G. R. 1996. Conversion of Oils to Monoglycerides by Glycerolysis in Supercritical Carbon Dioxide Media. *Journal of the American Oil Chemists' Society*. 73(6): 699–706.
DOI : http://dx.doi.org/10.1007/BF02517943

[15] Anggoro, D. D., Oktavianty, H., Kurniawan, B. P., and Daud, R. 2019. Optimization of Glycerol Monolaurate (GML) Synthesis from Glycerol and Lauric Acid Using Dealuminated Zeolite Y Catalyst. *Jurnal Teknologi*. 81(4): 133–141.
DOI : http://dx.doi.org/10.11113/jt.v81.13511

[16] Yang, F., Xiang, W., Sun, X., Wu, H., Li, T., and Long, L. 2014. A Novel Lipid Extraction Method from Wet Microalga Picochlorum sp. at Room Temperature. *Marine Drugs*. 12(3): 1258–1270.
DOI : http://dx.doi.org/10.3390/md12031258

[17] Yetilmezsoy, K., Demirel, S., and Vanderbei, R. J. 2009. Response Surface Modeling of Pb(II) Removal from Aqueous Solution by Pistacia vera L.: Box-Behnken Experimental Design. *Journal of Hazardous Materials*. 171(1–3): 551–562.
DOI : http://dx.doi.org/10.1016/j.jhazmat.2009.06.035

[18] Sangeetha, V., Sivakumar, V., Sudha, A., and Devi, K. P. 2014. Optimization of Process Parameters for COD Removal by Coagulation Treatment Using Box–Behnken Design. *International Journal of Engineering and Technology*. 6(2): 1053-1058.

[19] Sonntag, N. O. V. 1983. Glycerolysis of Fats and Methyl Esters-Status, Review and Critique. *Journal of the American Oil Chemists' Society*. 60(7): 1245–1249.
DOI : http://dx.doi.org/10.1007/BF02634442

[20] Hussain, K., Ismail, F., and Senu, N. 2016. Solving Directly Special Fourth-order Ordinary Differential Equations Using Runge–Kutta Type Method. *Journal of Computational and Applied Mathematics*. 306: 179–199.
DOI : http://dx.doi.org/10.1016/j.cam.2016.04.002

[21] Xuan, J., Zheng, X., and Hu, H. 2012. Active Sites of Supported KF Catalysts for Transesterification. *Catalysis Communications*. 28: 124–127.
DOI : http://dx.doi.org/10.1016/j.catcom.2012.08.032

[22] Fregolente, L. V., Batistella, C. B., Filho, R. M., and Maciel, M. R. W. 2005. Response Surface Methodology Applied to Optimization of Distilled Monoglycerides Production. *Journal of the American Oil Chemists' Society*. 82(9): 673–678.
DOI : http://dx.doi.org/10.1007/s11746-005-1127-9

[23] Istadi, 1. and Amin, N. A. S. 2006. Optimization of Process Parameters and Catalyst Compositions in Carbon Dioxide Oxidative Coupling of Methane over CaO–MnO/CeO_2 Catalyst Using Response Surface Methodology. *Fuel Processing Technology*. 87: 449 – 459.
DOI : http://dx.doi.org/10.1016/j.fuproc.2005.11.004

[24] Mustafa, M. N., Shafie, S., Wahid, M. H., and Sulaiman, Y. 2019. Optimization of Power Conversion Efficiency of Polyvinyl-Alcohol/Titanium Dioxide Compact Layer Using Response Surface Methodology/Central Composite Design. *Solar Energy* 183: 689–696.
DOI : http://dx.doi.org/10.1016/j.solener.2019.03.074

[25] Montgomery, D. C. 2001. *statis and Analysis of Experiments*. Fifth Eds. United States of America: John Wiley & Sons, Inc.

[26] Feuge, R. O. and Bailey, A. E. 1946. Modification of Vegetable Oils: VI. The Practical Preparation of Mono- and Diglycerides. *Oil & Soap*. 23(8): 259-264.
DOI : http://dx.doi.org/10.1007/BF02696133

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