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GLYCEROLYSIS USING KF/CaO-MgO CATALYST: OPTIMISATION AND REACTION 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

*Corresponding author
luqman.buchori@che.undip.ac.id

Graphical abstract

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

Abstract

Monoglycerides can be produced through glycerolysis using a heterogeneous catalyst. The purpose of this study is to analyse the optimum conditions for the production of monoglycerides from glycerol and cooking oil using KF/CaO-MgO base catalysts and to investigate the kinetics of the monoglyceride glycerolysis reaction. The response surface method (RSM) was used to determine the favourable conditions by varying the catalyst amount (X_1) between 0.1, 0.2 and 0.3% (w/w); the reaction temperature (X_2) between 210, 220 and 230°C and reaction time (X_3) between 2, 3 and 4 hours. Gas chromatography-mass spectrometry (GC-MS) was used to determine the monoglycerides, while catalysts were characterised by X-ray diffraction (XRD) and the Brunauer-Emmett-Teller method (BET). The results showed that, among the three factors examined, temperature shows the most control over this glycerolysis reaction. The most favourable conditions are $X_1 = 0.19\%$ (w/w), $X_2 = 208.37°C$ and $X_3 = 3.20$ hours, which provide a monoglyceride yield of 41.58%. The constants for the reaction kinetics of the monoglyceride formation, k_1 and k_2 are 1.04189 and 0.88965 hour^{-1}, respectively.

Keywords: Glycerolysis, monoglyceride, kinetics, KF/CaO-MgO catalyst, RSM optimisation

1.0 INTRODUCTION

Glycerolysis is the reaction of glycerol 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 MAG/MG reaches 75% of the total emulsifying production. Specifically, monoglycerides are used for the productions of bakery products, margarine, dairy products and confectionary [2]. Additionally, they can be used as synthetic constituents and plasticisers [3, 4].
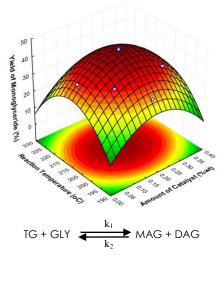
Glycerolysis can be carried out with or without a catalyst. The catalyst simply accelerates the reaction by directing OH groups to MAG formation. The reaction can be carried out with either of two methods: chemical synthesis (using acid, basic, or metal oxide catalysts), or enzymatic synthesis (using lipase catalysts) [5]. Compared to chemical synthesis, enzymatic synthesis has several advantages including mild reaction conditions, higher yields and lower energy consumption [6]. However, enzymatic synthesis is more complex, time-consuming, expensive and the enzymes are difficult to separate from the product [2, 5]. In contrast, chemical synthesis has 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 it produces higher yields [8]. Most often, the reaction proceeds under alkaline conditions and the most frequently used base catalysts include $NaOH$ [9], $NaOCH_3$ [10], CaO [11] and MgO [3]. However, pure base catalysts, especially metal oxides, have lower catalyst activities compared to mixed metal oxides [12].

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

The glycerolysis reaction between glycerol and oil is a multiphase reaction. It is carried out at high temperature (250°C) in order to increase the solubility of glycerol in the oil, which is only around 4% at room temperature [14]. Due to the multiphase properties of the sample, studies of the kinetics of the glycerolysis reaction between glycerol and triglycerides have not been carried out.

The present study aims to determine the optimum conditions and the corresponding reaction rate constants of the glycerolysis reaction between glycerol and triglycerides. Optimisation is carried out using the response surface method (RSM) with the Statistica software version 12.0 concerning the catalyst amount (X_1), reaction temperature (X_2) and reaction time (X_3). The reaction kinetics is solved 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 that is a source of triglycerides was acquired from a supermarket and glycerol (85%) was obtained from Merck.

2.2 Preparation of KF/CaO-MgO Catalyst

The KF/CaO-MgO catalyst was prepared in two steps. 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 magnesium acetate, calcium nitrate and citric acid into a 95% ethanol solution and stirring until the solution became homogeneous (clear coloured). The mixed solution was then stirred

at a speed of 300 rpm while being heated to form a sol. Heating was continued while stirring up to 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 obtained solid product 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 the KF solution for one hour while stirring, followed by drying in an oven (Memmert) at 140°C for 6 hours. The dried solid catalyst was then calcined at 450, 500 and 550°C in a box furnace for 3 hours. The resulted solid catalyst was called KF/CaO-MgO.

2.3 Characterisation of Catalyst and Product

The catalyst was characterised through X-ray diffraction (XRD) and the Brunauer-Emmett-Teller (BET) surface area method (ChemBET PULSAR Quantachrome). XRD analysis was carried out using a Shimadzu XRD-7000. The XRD patterns were measured under Cu-Kα radiation conditions (k = 1.54 Å) 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).

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

The monoglyceride products were analysed 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, the sample was analysed at an oven temperature of 50°C (5 minutes). The temperature was raised by 10°C/min up to 260°C and subsequently held there for 33 minutes.

2.4 Glycerolysis

The formation of monoglycerides was achieved using oil (triglyceride)-to-glycerol molar ratio of 1 to 3. The catalyst, which had been calcined at 550°C (% 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 in a glass vessel and heated to 150°C while stirring. Once the oil reached the feed temperature, the mixture of glycerol and catalyst was gradually added while stirring. During the mixing process, the temperature was maintained stable at 150°C. The operating conditions were varied according to the optimisation variable. The product was separated from the residue and analysed using GC-MS. The

monoglyceride (MAG) yield was calculated using Equation (1).

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

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

2.5 Experimental Design

In order to determine the effect of the response variables on the glycerolysis reaction, we designed the experiment based on the principles of central composite design (CCD) and using the RSM. This approach is widely used to design second-order 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 and high values of the catalyst amount (% w/w), the reaction temperature and the reaction time. Table 1 shows the experimental design.

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

Table 1 Range and level of independent variables for RSM

| Variables | Unit | Variable Level | | |
		Low level (−1)	Centre level (0)	High level (+1)
Catalyst amount (X_1)	%(w/w)	0.1	0.2	0.3
Reaction temperature (X_2)	^0C	200	210	220
Reaction time (X_3)	Hours	2	3	4

The Statistica software version 12.0 was used to analyse the experimental data and was installed into the second-order polynomial equations. The interaction between the dependent and independent variables was achieved through Equation (3) [17].

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

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

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

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 | | |
	Catalyst Amount (%w/w)	Reaction 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

The desired response 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 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. Maximisation was used to determine the best and optimised local maximums. In order to do this maximisation, these indicators were combined into the function 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 kinetics 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 (4) to (7).

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

$$aA + bB \underset{k_2}{\overset{k_1}{\rightleftarrows}} cC + dD \qquad (5)$$

Being an equation

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

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

Equation (7) 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 [20].

3.0 RESULTS AND DISCUSSION

3.1 Characterisation of the Catalyst

The XRD patterns of the catalyst before and after impregnation at varied calcinations temperatures are shown in Figure 1.

The XRD pattern on the CaO-MgO catalyst before being impregnated with KF is presented in Figure 1(a). The XRD pattern of the catalyst after being impregnated with KF at the different calcination temperatures 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° and 78.70°) and MgO (42.91° and 62.15°) components. After the catalyst was calcined at 450°C, peaks corresponding to the Ca(OH)$_2$ component appeared at 18.19°, 29.39°, 50.77° and

58.74°. This shows that the calcination temperature of 450°C is low. When the calcination temperature is increased to 500 and 550°C, CaKF$_3$ and MgKF$_3$ crystals form, which appear in the XRD patterns as new peaks. CaKF$_3$ and MgKF$_3$ are active sites formed due to the addition of KF as support. The presence of these crystals increases the catalyst activity and produces higher monoglyceride yields [21].
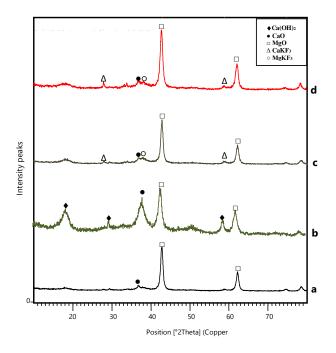

Figure 1 XRD pattern of the KF/CaO-MgO catalysts: (a) CaO-MgO catalyst; (b) KF/CaO-MgO catalyst (450°C); (c) KF/CaO-MgO catalyst (500°C); (d) KF/CaO-MgO catalyst (550°C)

The results of the surface area characterisation are presented in Table 3.

Table 3 The surface area of the catalyst under various treatments

Catalyst	Surface Area (m²/g)
CaO-MgO	112,250
KF/CaO-MgO (450°C)	132,456
KF/CaO-MgO (500°C)	119,706
KF/CaO-MgO (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 may be caused by aggregation of the catalyst as a result of the formation of the new active catalyst sites (CaKF$_3$ and MgKF$_3$) that occurs at high calcination temperatures. However, the formation of CaKF$_3$ and MgKF$_3$ increase the catalyst activity. Indeed, the increase in the calcination temperature to 500 and 550°C forms new crystals (Figure 1), namely CaKF$_3$

(28.28° and 59.32°) and MgKF$_3$ (38.58°). KF addition to heterogeneous catalysts and high calcination temperatures produce new crystals (such as CaKF$_3$ and MgKF$_3$) as active sites that can produce higher yields due to the high catalytic activity [21].
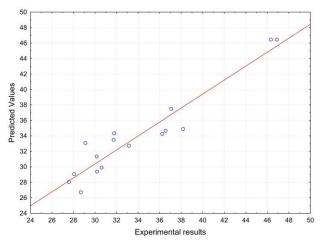
Based on the characterisation of this catalyst, the catalyst used for the glycerolysis process is KF/CaO-MgO, which is calcined at 550°C.
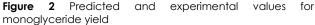
3.2   Model Fitting

According to the experimental design, 16 experimental runs were carried out according to the optimisation variables (the catalyst amount, the reaction temperature and the reaction time), as shown in Table 2. The experimental 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 Equation (8).

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

The complete 16 sets of the experimental design matrix and the experimental and predicted values 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 with the predictive values (Figure 2). Indeed, the obtained monoglyceride yield varies between 27.58 to 46.33%

and the values predicted by the model match the experimental results satisfactorily.

Figure 2 Predicted and experimental values for monoglyceride yield

3.3   Statistical Analysis Results

ANOVA using Statistica software version 12.0 was used to appropriately assess the polynomial model (Equation (8)) taking into account the interactions [22]. 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.

Table 4 Experimental and 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

The results of the analysis of variance on monoglyceride production gave an R^2 of 90.28%. 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 optimisation experiments. The model results that the three

optimisation variables (catalyst amount, reaction temperature and reaction time) have an effect greater than 90%.

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 F-value obtained by the model is 60.45, which is greater than the tabulated F-value of 3.49. This F-value shows a statistically significant regression at a significance level of 5% [23]. 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 [24]. 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.
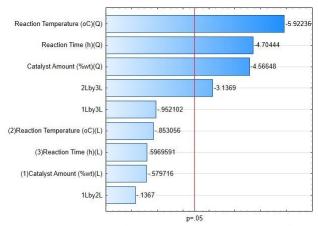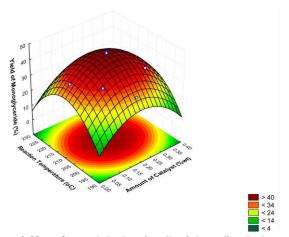

Figure 3 Pareto chart for variables that have a significant effect on the glycerolysis process

The variables that have the most significant effect are presented in Figure 3 (Pareto chart). Temperature

has the most significant effect compared to the other variables.

3.4 Optimisation Analysis

The optimum conditions for the synthesis of monoglycerides are predicted using the optimisation function. The empirical model derived from the RSM method can be used 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 catalyst amount (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 catalyst amount (X_1) with reaction temperature (X_2) at a reaction time (X_3) of 3 hours for monoglyceride production
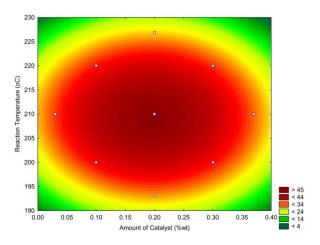
Figures 4 and 5 show 3D and 2D graphs of the response surface and contour plots of the effect that the catalyst amount has on the reaction temperature. The relationship between the catalyst amount (% wt) and the reaction temperature in a monoglyceride product has a maximum stationary area. This is because it is necessary to carefully determine the range of data selection codes (points −1, 0, 1) in order to attain the optimal point [25]. The
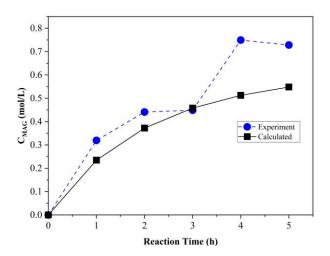
optimal conditions derived from the Statistica software are shown in Table 6.

Table 6 Optimal values of parameters

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

3.5 Kinetics

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

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

Figure 6 shows the difference between the experimental and modelled monoglyceride concentrations. In the experiment, the monoglyceride concentration is not stable, whereas the calculated concentration using the model is more consistent and tends to increase. Additionally, in the experiment, monoglycerides 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 di-acyl glycerol (DAG) [26].

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 $k_1 = 1.04189$ hour^{-1} and $k_2 = 0.88965$ hour^{-1}. 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.
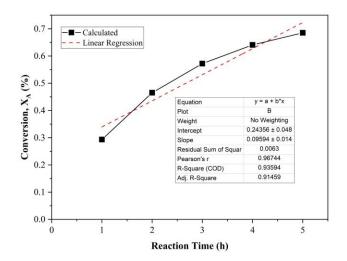

Figure 7 The conversion value of X_A (%) to the reaction time (hour) in monoglyceride production

4.0 CONCLUSION

The results obtained from the optimisation using the RSM method show that temperature has the most dominant influence with a p-value of 0,0009 and R^2 0.9028. The catalyst amount and the reaction time have lesser, yet significant, influence. Besides, the optimum reaction conditions are X_1 (catalyst amount) = 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%. Based on the experimental results and calculations using the fourth-order Runge-Kutta method, monoglyceride conversion tends to decrease after five hours of reaction time. The reaction rate constants are $k_1 > k_2$ and $k_2 > 0$ $k_1 = 1.04189$ hour^{-1} and $k_2 = 0.88965$ hour^{-1}. The obtained determinant value (R^2) is 0.936.

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