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Application of Box-Behnken Design in Production of Monoglyceride with Esterification of Glycerol and Oleic Acid

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Cite This: *ACS Omega* 2023, 8, 28813−28820

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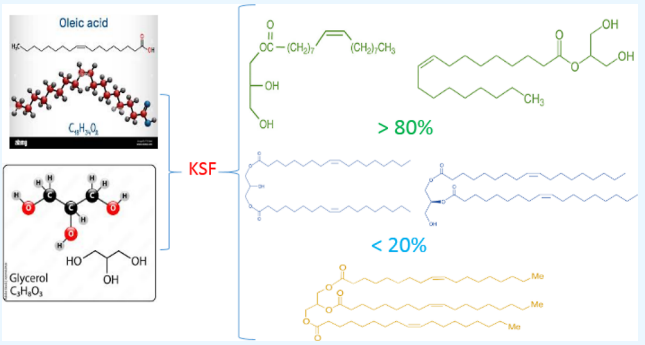
ABSTRACT: Monoglyceride MG has a wide function in the food industry, in particular as a natural emulsifier, pharmaceuticals, cosmetics, antioxidant, and antibacterial. Therefore, the production of polyol ester from esterification of acid (OA) and glycerol was investigated. The process optimization was performed using a Box-Behnken design, examining the effects of temperature, molar ratio, and catalyst amount. For predicting the optimal point, a second-order polynomial model was fitted to correlate the relationship between independent variables and response (% MG). The effects of temperature (100, 150, and 200 °C); catalyst amount (4, 10, and 16% w/w); and glycerol/oleic acid ratio (1:1, 1:2, and 1:3) were investigated and found to deeply affect the reaction outcome. At the optimal reaction conditions: 200 °C, 0.2% w/w KSF, and a glycerol/oleic acid ratio (3:1), more than 71.8% monoglycerides with selectivity of 80% were obtained. Confirmation experiments were performed to demonstrate the effectiveness of this approach, and the characterization of monoglycerides was performed using high-performance liquid chromatography (HPLC).



1. INTRODUCTION

The synthesis of valuable glycerol esters by esterification of glycerol with fatty acids is nowadays one of the important applications of glycerol.[1] The short fatty acid monoesters of glycerol are a very important class of chemicals having wide applications in a variety of areas in the food, pharmaceutical, and cosmetic industries.[2,3] Also, the monoesters of glycerol with long fatty acids are of interest as biosurfactants.[1]

Monoglycerides (MG) are high-value glycerol derivatives with applications within the food, pharmaceutical, and cosmetic industries. Chemically, they are monoesters of hydrophilic polyols (such as glycerol) with fatty acids that contain a hydrophilic head and a hydrophobic tail, thus giving rise to their characteristic surfactant/emulsifier properties.[4] Recently, monoglycerides have been used as emulsifying components in products such as aqueous fiber finishes, lubricants, mechanical oils, water displacement oils, grinding and polishing pastes, foods, and newly biofuels.[5,6] Furthermore, monoglycerides (MG) and diglycerides (DG) have a generally recognized as safe status,[7] and some newly uncovered beneficial effects and nutritional properties have been reported.[8] Monoglycerides have similar chemical properties to biodiesel, which allows them to be used as fuel in compression ignition engines. They exhibit good lubricity[8] and a good cetane number, indicating their potential for efficient combustion and reduced emissions. Glycerol has a high energy content, and its versatile nature makes it an attractive option for biofuel production. The main challenge of glycerol and monoglycerides as biofuels is their high viscosity, which can impact their combustion efficiency and compatibility with existing fuel systems. For this reason, their production and use on a commercial scale as primary fuel sources from a medium- to long-term perspective face several obstacles, including technological and economic barriers, as well as the need for supportive policies and infrastructure development. Researchers and scientists are actively investigating ways to optimize the production processes[9] and improve the fuel properties of monoglycerides. This includes exploring different feedstocks, optimizing transesterification conditions, and evaluating additives or blending strategies to enhance their performance as biofuels. In this context, recently, the same catalytic and enzymatic methodology was developed to obtain a new second-generation biodiesel composed of fatty acid ethyl (or methyl) esters and monoglycerides (FAEE/MG or FAME/MG) blended in a 2:1 molar ratio.[10,11] This new product, which integrates glycerol as (MG) into the biofuel

Received: May 29, 2023
Accepted: July 13, 2023
Published: July 27, 2023

composition and is named Ecodiesel, has similar physicochemical properties as conventional biodiesel and also avoids the removal step of the byproduct. In that respect, it is interesting to point out that the presence of MG enhances the lubricating properties of the biofuel.[12]

Currently, there are two major industrial routes to obtain monoglycerides: the transesterification of the triglycerides with glycerol at high temperature in the presence of a basic catalyst,[13−15] and the direct esterification of glycerol with fatty acids.[1,3,14] Investigations to optimize the yield of the monoderivative in both processes are of great interest.[3]

Esterification is one of the most important reactions in the chemical industry, usually driven by acid catalysts through carbocation activation.[16] Indeed, the esterification reaction is catalyzed by homogeneous acid catalysts (sulfuric acid, AMS, or APTS),[17] H_2SO_4, H_3PO_4, *p*-toluenesulfonic acid,[4] or homogeneous metallic Sn, Ti, and Zr catalysts.[18] The use of such catalysts, when in large amounts, creates many environmental problems, such as corrosion and the difficulty of catalyst recycling or chemical problems (secondary reactions). Furthermore, the selectivity to monoglycerides is low. Important number of researchers are interested in the development of heterogeneous solid acid catalysts that resulted in the evolution of various inorganic/organic materials, including acid functionalized silica/mesoporous silica,[19,20] sulfated or mixed oxides,[21] heteropoly acids,[22] metal−organic framework-based solid acids,[23,24] ion-exchange resins having sulfonic acid groups,[25] and metal-containing molecular sieves.[26] As they are also interested in the use of the acid catalysts in the esterification reaction, such as the glycerol esterification with fatty acid by using solid cationic resins,[18,27] zeolitic materials,[28,29] and immobilized lipase.[30,31]

In the catalytic esterification of fatty acids with glycerol, the choice of heterogeneous catalyst is important due to its role in controlling the fatty acid conversion and monoglyceride selectivity.[32] Clays are a type of fine-grained earth, primarily composed of aluminum and silicate minerals.[33] Montmorillonite clay, a natural smectite, has been found to be a useful catalyst in a variety of organic reactions after modification. Organic montmorillonite[34] and acid-activated montmorillonite have attracted substantial attention. Hashemizadeh and Zuhairi[35] showed that the monoglyceride yield of about 70% was achieved in 8 h at 130 °C using a glycerol/lauric acid molar ratio/6:1 and 3 wt % of tetra-*n*-butylammonium-modified montmorillonite catalyst. Due to its strong acidity, it was inexpensive compared to ion exchange resin, noncorrosive, reusability, and non-polluting.[36] Bouguerra Neji *et al.*[37] studied the production of fatty acid esters for the production of biodiesel with KSF (acid-activated montmorillonite). Thus, the objective of montmorillonite clay KSF-catalyzed esterification of glycerol with the present work was to study the production of a high percentage of monoglycerides by commercial oleic acid in a solvent-free system.[37,38] A Box-Behnken experimental design with three variables was used to study the response pattern and to determine the optimum combination of variables. In this context, the glycerol/oleic acid ratio, amount of catalyst (w/w %), and reaction temperature (°C) were optimized.

2. MATERIALS AND METHODS

2.1. Materials. Fatty acid oleic acid (*cis*-9-octadecenoic acid, C18:1; 99%) and the commercial clay (Montmorillonite KSF clay) were purchased from Fluka (Sigma-Aldrich, Steinheim, Germany). Glycerol (1,2,3-propanetriol, ≥99.5%) and isopropanol were purchased from Panreac (Barcelona, Spain). All these chemicals were used as received without any further purification. Acetonitrile (ACN), methanol (MeOH), and tetrahydrofuran (THF) were all from Fisher and were of HPLC grade.

2.1.1. Esterification Reaction. A continuous-type reactor composed of a three-neck flask (100 mL) equipped with a water-cooler condenser, a thermometer, and a magnetic stirrer[38] was applied to study the esterification reaction of glycerol with oleic acid. An experiment design (Box-Behnken design) was used in this work. The reaction medium was withdrawn repeatedly at a specific time interval to determine the progress of the. After finishing the esterification reaction, the spent catalyst was separated from the mixture by centrifugation. Then, the sample was diluted in the isopropanol and filtered prior to analysis by high-performance liquid chromatography (HPLC).

2.2. Method. *2.2.1. Analysis of Samples.* Samples were withdrawn and diluted in pure isopropanol to a concentration of 5 g/L, being analyzed by an HPLC JASCO 2000 series device equipped with a refraction index detector. The compounds were separated using a "Mediterranea Sea-18″ column 5 μm 15 × 0.46 cm (Teknokroma) as a stationary phase. Two methods were used in our work to analyze the samples. Oleic acid and monoglyceride (group A) were separated using a mobile phase consisting of ACN/acidic water (H_2SO_4) (95:5 v/v) for 28 min. Diglyceride and triglyceride (group B) were separated using ACN/MeOH/THF (40:40:20 v/v/v) for 29 min. The injection volume was 40 μL, and samples were eluted at a flow rate of 1 mL/min with the column temperature set at 40 °C.

3. EXPERIMENTAL DESIGN

In this study, the optimization of the esterification reaction of glycerol with oleic acid has been carried out with three important variables, which include the glycerol/oleic acid ratio (mol/mol) (A), reaction temperature (°C) (B), and catalyst amount (w/w %) (C). The effects of these variables on the yield of monoglycerides were studied with the method of the Box-Behnken design by the software of a design expert. As shown in Table 1, the three factors chosen for this study were

Table 1. Levels and Code of Variable Chosen for Box Behnken Design

variables	symbols	low level −1	central level 0	high level +1
molar ratio Gly/OA	A	1:1	2:1	3:1
reaction temperature (°C)	B	100	150	200
catalyst amount (%)	C	0.2	0 0.5	0.8

designated as and prescribed into three levels, coded +1, 0, and −1 for high, intermediate, and low values, respectively. For predicting the optimal point, a second-order polynomial model was fitted to correlate the relationship between independent variables and response (monoglycerides yield %). The equation for three factors is stated as follows

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2$$

https://doi.org/10.1021/acsomega.3c03772
ACS Omega 2023, 8, 28813−28820

where Y is the predicted response; β_0 is the constant coefficient; β_1, β_2, and β_3 are coefficients for the linear effects; β_{11}, β_{22}, and β_{33} are the coefficients for the quadratic effects; β_{12}, β_{13}, and β_{23} are the coefficients for the interaction effects; and A, B, and C are the factor codes.

4. RESULTS AND DISCUSSION

4.1. Single-Factor Experiment. This section discusses the effect of reaction temperature, glycerol/oleic acid molar ratio, and catalyst loading on reaction products. In general, the chemical reaction is strongly dependent on the reactor temperature. Figure 1 shows the influence of reaction

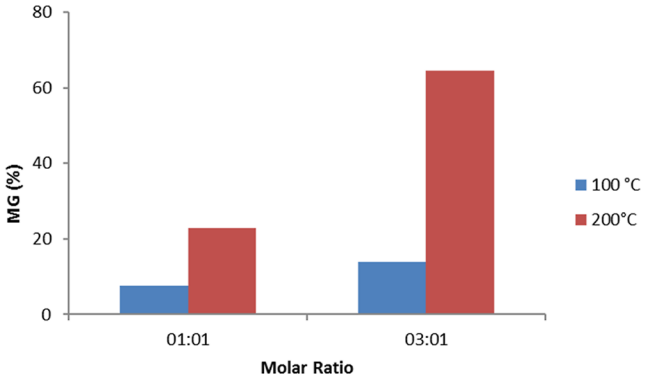


Figure 1. Effect of reaction temperature and a Gly/OA molar ratio on the monoglyceride yields. Experiments were carried out with 10 wt % of KSF catalyst for 5 h.

temperature on the monoglycerides yield where the molar ratios Gly/OA are 3:1 and 1:1, catalyst loading is 10 wt %, and the reaction time is 5 h. It can be observed that the reaction rate increases with temperature. At 100 °C and an equimolar ratio of acid and glycerol, the monoglyceride yield is low, as just reaching 7.5, and 14% with a molar ratio 3:1. The monoglyceride yield would increase with increasing temperature; for instance, at 200 °C, the monoglyceride yield could reach 22.8 and 64.6% with molar ratios of 1:1 and 3:1, respectively. This effect shows that by increasing the temperature, the mobility of the molecules increases. Therefore, molecules can reach the inner pores of the catalyst more easily.[38]

Figure 1 can also show the effect of the Gly/OA molar ratio on the esterification reaction. As can be seen, the excess of glycerol is beneficial to the synthesis of MG. When the Gly/OA molar ratio was multiplied for three 1:1 to 3:1, the concentration of monoglyceride was tripled at 200 °C (22.8 to 64.6%). In the same context, Zhao et al.[16] also found that the highest concentration of MG (42.5%) was obtained with the highest molar ratio Gly/OA 6:1 when the other variables were fixed (catalyst load 10 wt %, β-cyclodextrin/lipase mass ratio 1.5:1, initial water content 10%, reaction temperature 40 °C, agitator speed 190 r/min).

The esterification reactions were performed at different catalyst loads 4 and 16 wt % to investigate their effect to the reaction with Gly/OA molar ratios of 2:1 and 3:1 at 100 and 150 °C, respectively. It can be seen from Figure 2 that increasing the amount of catalyst from 4 to 16 wt % increased the monoglyceride yield from 7.9 to 33.8% in the first reaction with a Gly/OA molar ratio of 2:1 at 100 °C and from 37.5 to

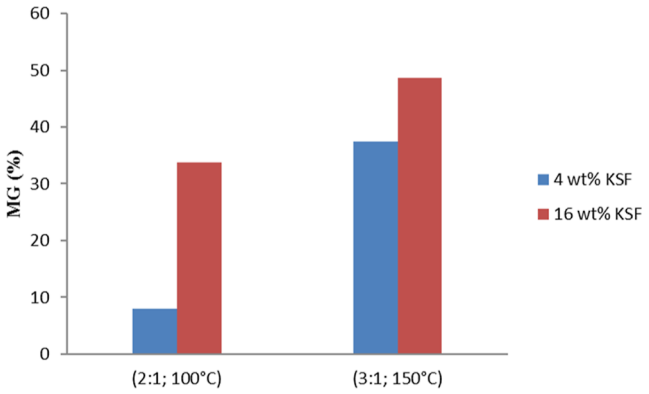


Figure 2. Effect of a catalyst concentration on the monoglyceride yields. Experiments were carried out with a 2:1, 3:1 Gly/OA molar ratio and at 100, 150 °C for 5 h.

48.6% in the second reaction with a Gly/OA molar ratio of 3:1 at 150 °C.

4.2. Development of the Regression Model Equation. *4.2.1. Box-Behnken Design Experiments.* The experimental design for oleic acid esterification with glycerol over acidic montmorillonite KSF-assisted monoglyceride production was a Box-Behnken design. In this work, the Box-Behnken design is a combination between 2^k factorial design with an incomplete block design, providing 15 experiments. The results obtained in the experiments are summarized in Table 2. As shown in the

Table 2. Design of the Response Surface Method and the Corresponding Results

	process variables			
design points	glycerol to oleic acid molar ratio	reaction temperature T/°C	catalyst amount (%)	monoglyceride yield %
1	03:01	100	0.5	14.0
2	02:01	150	0.5	45.4
3	03:01	150	0.2	37.5
4	02:01	150	0.5	46.5
5	02:01	100	0.2	7.9
6	02:01	200	0.8	41.5
7	01:01	150	0.2	38.8
8	01:01	200	0.5	22.8
9	03:01	150	0.8	48.6
10	01:01	150	0.8	23.2
11	03:01	200	0.5	64.6
12	02:01	100	0.8	33.8
13	02:01	200	0.2	62.2
14	01:01	100	0.5	7.5
15	02:01	150	0.5	46.1

table, the monoglyceride yield ranged from 7.9 to 64.6%, depending on different conditions of the experiments. Also, these results can be fitted into a second-order regression model equation by design expert software, as given in eq 1

$$Y = +45.98 + 9.06A + 15.97B + 0.08C + 8.82AB + 6.67AC - 11.64BC - 9.01A^2 - 9.74B^2 + 0.08C^2 \quad (1)$$

Coefficient $\beta_0 = 45.98$ gives the response in the central point of the domain (all $X_i = 0$), whereas β_i, β_{ii}, and β_{ij} coefficients types progress information about the influences of these three

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variables on the process. The effects of each variable and the influence of their coupling are represented in Figure 3. A

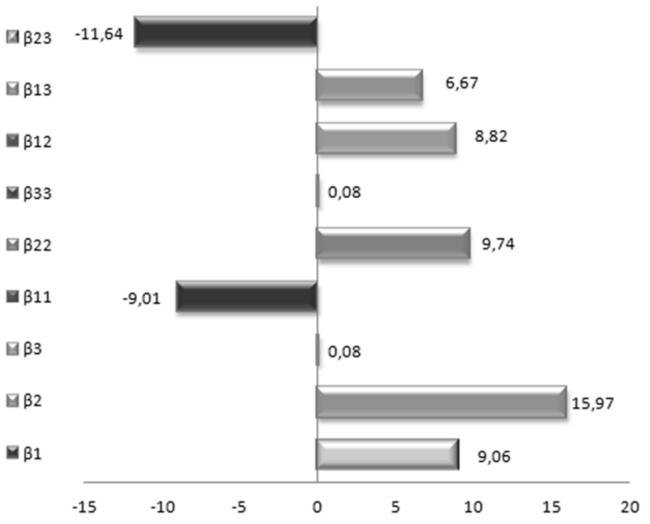

Figure 3. Graphic representation of the polynomial coefficient derived from experimental results.

positive sign of the coefficient indicates a synergistic effect, while a negative term indicates an antagonistic effect[39] upon the monoglyceride yield. Molar ratio (A), reaction temperature (B), and catalyst amount (C) have positive responses on the process. The monoglyceride yield is greatly influenced by the temperature reaction, which has the most important value (15.97). The effect of catalyst amount is negligible, while the molar ratio is the second most significant factor on the monoglyceride yield.

To present more significant information to interpret these results, Pareto analysis was used. In fact, this analysis allows calculating the percentage effect of each factor on the response according to the relation 2

$$Pi = \frac{\beta i^2}{\sum \beta i^2} \times 100 \ (i \neq 0) \tag{2}$$

The Pareto chart diagram, as depicted in Figure 4, graphically illustrates the importance of the temperature reaction on the monoglyceride yield. Guo et al.[40] also determined that reaction temperature is the most significant

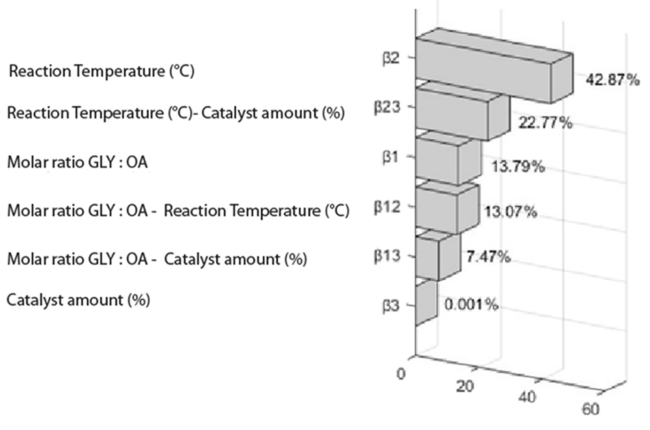

Figure 4. Graphical Pareto analysis.

variable for esterification of oleic acid using 1-butyl-3-methylimidazolium tosylate as catalyst. The strong impact of this variable is also obvious in its correlation with the other variables of the reaction. In fact, other significant coefficients are noticed in the interaction between temperature-catalyst amount (β_2, β_3) and Gly/OA molar ratio-temperature (β_1, β_2). They give positive effects on the response, based on the positive *t*-values of 22.77 and 13.07, respectively.

4.2.2. Estimation of Regression Coefficients. Table 3 shows the estimated regression coefficients for responses (% MG) that include *F* values for the model, individual terms, lack-of-fit test, and *p* value (probability of error value), which is used to check the significance of each regression coefficient. The smaller the *p* value, the bigger the significance of the corresponding regression coefficient.[41] The analysis of variance (Table 3) showed that this regression model was highly significant and clear ($P < 0.01$) with an *F* value of 27.95. Besides, the *P*-value of 0.0009 indicates that there is only 0.09% of chance that an *F*-value larger than the "model *F*-value" could occur due to the disturbance in the experiments.

4.2.3. Analysis of Variance (ANOVA) for Response. The analysis of variance for (% MG) is shown in Table 4. Another thorough study can be performed to confirm the adjustment of this model; it is done to determine the values of the determination coefficient (R^2) and the adjusted coefficient (R^2 adj.). The suitability of the model was further confirmed by R^2, which was calculated to be 0.981, indicating that 98.1% of the variability in the response could be predicted by the model. The coefficients of determination R^2 (0.981), predicted R^2 (0.731), and adjusted R^2 (0.945) are close to unity, concluding that the regression model provides an accurate description of the experimental data, indicating a successful correlation among the esterification reaction variables.

Figure 5 shows the comparison between the experimental MG % against predicted values by using the proposed model. Computation of the linear correlation coefficient suggested a reasonable agreement between the experimental and model values over the entire factor space under consideration.

4.3. Interactions between Process Variables. The purpose of this work was to determine the optimum conditions leading to the highest monoglyceride yield. Figures 6 to 8 shows the 3D response surfaces of the influence of interactions between different variables on the yield of monoglycerides.

Figure 6 shows the effect of reaction temperature and Gly/OA molar ratio on the monoglyceride yield with a 10 wt % catalyst load after 5 h. The monoglyceride yield linearly increases with the increase in reaction temperature from 100 to 200 °C and substrate molar ratio from (1:1) to (3:1). The lowest Gly/OA molar ratio (1:1) results in 7.5−22.8% MG for 100−200 °C. As well as, the Gly/OA molar ratio increases to its maximum (3:1), percentage of MG increases in an important way in the range of 14 to 64.6% for 100 to 200 °C.

A high substrate molar ratio can accelerate the reaction rate and spend shorter time before reaching equilibrium.[42] This is consistent with the results reported by Koh et al. that the high molar ratio of the substrate (capric acid and glycerol) could obtain a high TG yield.

The response surface presented in Figure 7 shows the effect of catalyst load how is another important parameter and Gly/OA molar ratio on the synthesis of monoglycerides at the constant reaction temperature of 150 °C for 5 h. An equimolar ratio of acid and glycerol can produce 38.8% of MG with a 10 wt % catalyst load, while an increase of 16% KSF load causes a

https://doi.org/10.1021/acsomega.3c03772
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Table 3. Estimated Regression Coefficients for Response

source	sum of squares	DF m	mean square	*F* value	prob > *F*	
model	4339.7	9	482.19	27.95	0.0009	significant
A	718.6	1	718.60	41.66	0.0013	
B	2040.9	1	2040.88	118.31	0.0001	
C	0.0	1	0.05	0.00	0.9602	
AB	310.9	1	310.94	18.02	0.0081	
AC	178.2	1	178.19	10.33	0.0236	
BC	541.8	1	541.78	31.41	0.0025	
A^2	261.8	1	261.80	15.18	0.0115	
B^2	329.1	1	329.12	19.08	0.0072	
C^2	0.0	1	0.02	0.00	0.9720	
residual	86.3	5	17.25			
lack of fit	85.7	4	21.42	37.11	0.1224	not significant
pure error	0.6	1	0.58			
cor total	4426.0	14				
R-square %						

Table 4. Analysis of Variance for Monoglyceride Yield

variable	value
R^2	0.981
R^2 adjusted	0.945
SD	4.153
mean	36.03
coefficient of variation, %	11.53
press	1191
predicted R^2	0.731
adequate precision	16.28

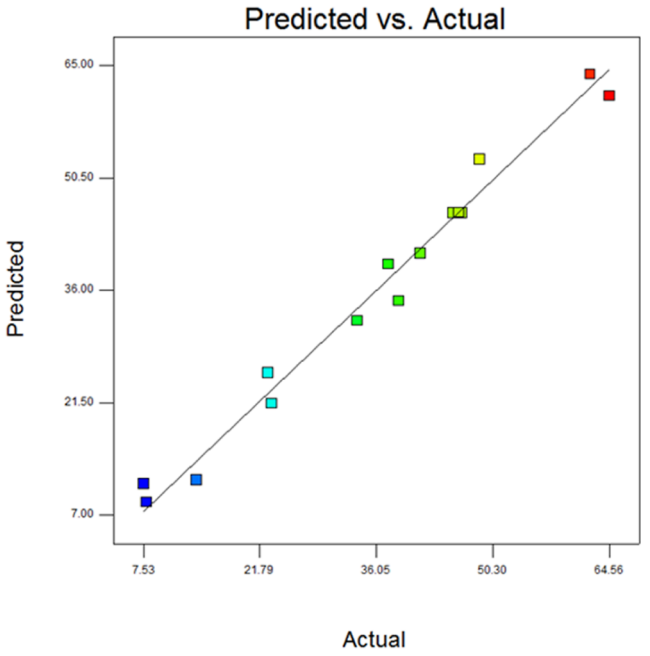

Figure 5. Predicted versus actual MG (%) yield.

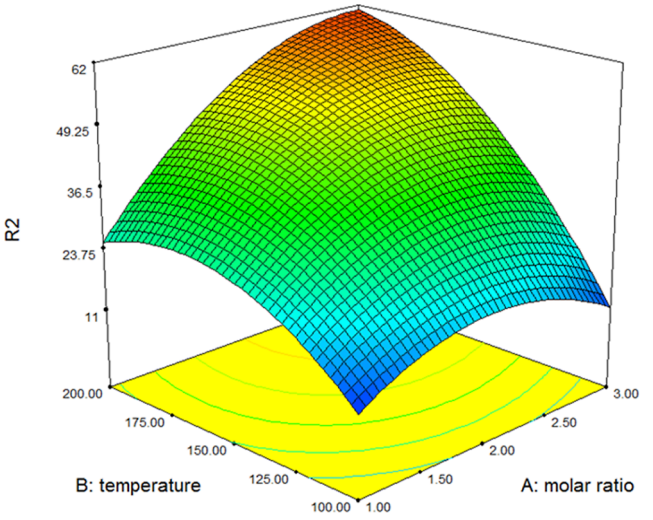

Figure 6. Effects of reaction temperature and molar ratio on monoglyceride yield with 10 wt % KSF after 5 h.

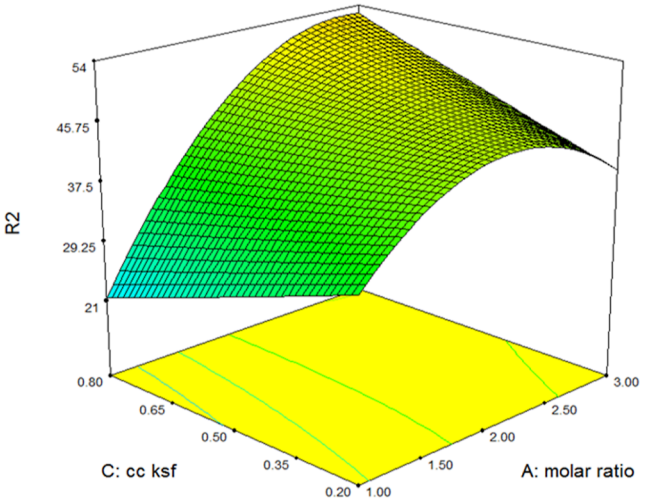

Figure 7. Effects of amount of catalyst and molar ratio on monoglyceride yield at 150 °C after 5 h.

slight decrease in % MG (23.2%). Increasing the Gly/OA molar ratio to (3:1) leads to a high selectivity for the monoglyceride formation of 48.6% with a 16 wt % catalyst load.

The effect of the reaction temperature and catalyst concentration on monoglyceride yield is shown in Figure 8. The maximum MG yield was achieved at reaction temperature of 200 °C and 16 wt % KSF (the Gly/OA molar ratio was fixed to 2:1). The MG yield at the low level of KSF load and high level of reaction temperature was higher than that at the high

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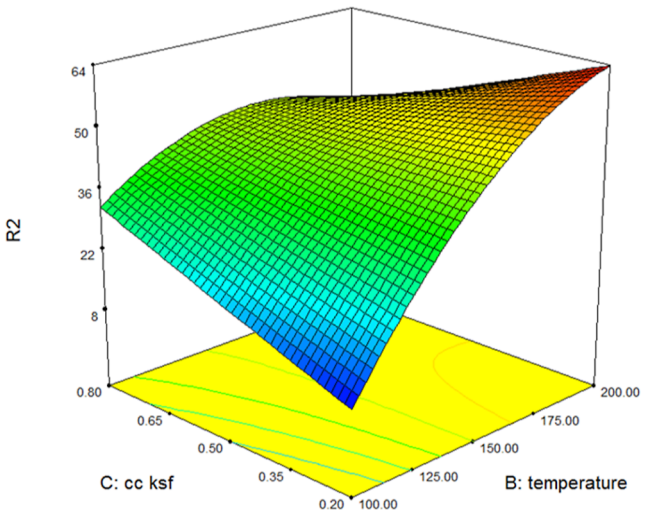

Figure 8. Effects of amount of catalyst and reaction temperature on monoglyceride yield with a Gly/OA molar ratio after 5 h.

level of KSF load and low level of reaction temperature: 62.2−33.8% MG, respectively. This fact indicates that reaction temperature has a more relevant influence on the esterification reaction than that of KSF catalyst load.[43]

4.4. Optimization Process. The optimum reaction variables (Gly/OA molar ratio, reaction temperature, and catalyst concentration) and corresponding % MG were forecast with the help of a quadratic response model. Three independent experimental runs to confirm the predictability of the model were conducted for each optimum condition.

Thirteen solutions are given in Table 5, which could predict the maximum % MG at optimum conditions. The solution

Table 5. Solutions of Optimum Parameters Generated by Design Expert Software

solutions	molar ratio (GLY/OA)	temperature (°C)	Cc KSF (wt %)	% MG	desirability
1	3:1	200	0.29	68.56	0.9752
2	299:1	200	0.29	68.56	0.9750
3	3:1	200	0.28	68.72	0.9745
4	298:1	200	0.29	68.56	0.9745
5	297:1	200	0.3	68.56	0.9745
6	293:1	200	0.31	68.56	0.9733
7	3:1	200	0.25	69.14	0.9729
8	287:1	200	0.31	68.56	0.9715
9	3:1	200	0.22	69.67	0.9708
10	3:1	200	0.2	70.01	0.9695
11	283:1	200	0.3	68.56	0.9649
12	245:1	200	0.29	68.56	0.9523
13	3:1	200	0.42	66.42	0.8122

number 10 was chosen to verify the predicted results of the model. Under these optimum conditions: reaction temperature 200 °C, Gly/OA molar ratio 3:1, and 4 wt % KSF load, 70% MG was obtained. To confirm the prediction of the model, the optimal conditions were tested with another reaction for the production of monoglycerides. The % MG of actual experience was 71.8%, which was close to the predicted value.

Figure 9 shows the evolution of the reaction products and the disparition of oleic acid percentage versus time at the optimum condition validated by the Box-Behnken model. It

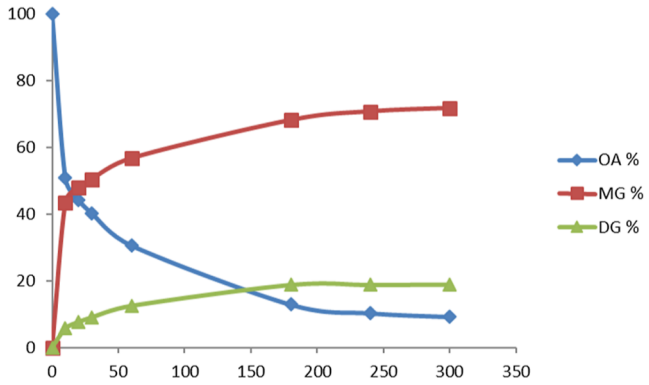

Figure 9. Esterification time courses of glycerol and oleic acid.

can be observed that after 60 min, the conversion of oleic acid decreases to 30.6%, whereas % MG and % DG increase to 56.8 and 12.6%, respectively. At the end of the reaction, the maximum MG yield was 71.8% when only 19% of DG was obtained and no TG product was observed, so the conversion of oleic acid was achieved with a high selectivity to MG production (80%).

5. CONCLUSIONS

This work investigates the use of glycerol in the esterification with oleic acid for the production of monoglycerides using an industrial KSF catalyst. Experimental design methodology has been used to examine the effect of temperature, molar ratio, and catalyst amount on the production of monoglycerides. Factorial designs demonstrated that the temperature reaction and the Gly/OA molar ratio are the most influential parameters on the monoglyceride yield. Through the response surface optimization, the optimal operating conditions are obtained; under this condition, the experimental monoglyceride yield was 71.8%, which agrees well with the predictive value.

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https://doi.org/10.1021/acsomega.3c03772
ACS Omega 2023, 8, 28813−28820

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank the Ministry of Higher Education and Scientific Research of Tunisia (Contract programe LR14ES08) for the support of this research and for giving us the opportunity to work on it. The authors also would particularly like to thank Professor Mohamed Hedi Frikha who, although no longer with us, continues to inspire us by his example and who has always believed in our ability to succeed in the academic arena.

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https://doi.org/10.1021/acsomega.3c03772
ACS Omega 2023, 8, 28813−28820