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Research Article

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

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**Abstract**

The production of monoglyceride or monoacylglycerol (MAG) from triglycerides and glycerol has been studied. The purpose of this research was to study the effect of using KF/CaO-MgO catalyst on MAG production with batch reactor. The effect of reaction temperature, reaction time, and catalyst loading was investigated using Response Surface Methods (RSM). The reaction temperature, reaction time, and catalyst loading were varied at 200-220 °C, 2-4 hours, and 0.1-0.3 % w/w, respectively. The maximum yield of monoglyceride 41.58% was achieved the optimum conditions of catalyst loading of 0.19 % (w/w), reaction temperature of 208.37 °C, and reaction time of 3.20 hours. 

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

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## 1. Introduction

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

Monoglycerides can be prepared by glycolysis reactions between fat and fatty acid methyl esters of palm oil. The glycolysis reactions can be carried out by biocatalyst (enzymatic glycolysis/enzymatic reactions), without catalyst (non-catalyst reaction), or by chemical catalyst (chemical glycolysis). The most common method is the catalysis reaction using alkaline catalysts such as NaOH [9], $NaOCH_3$ [10], MgO [11,12] and CaO [13]. However, the use of this alkaline catalyst has a low catalyst activity. The activity of the catalyst can be increased by dispersing a metal oxide on the surface of another metal oxide [14] (such as: CaO on the surface of MgO). Mixed metal oxides (CaO-MgO) provide stronger basic strength than pure oxide (CaO or MgO) [15]. Mixed metal oxides will also increase the surface area of the catalyst [14]. The use of im-

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pregnated mixed metal oxide catalysts is expected to increase the activity of the catalyst so that it can increase the yield of monoglycerides. Monoglyceride synthesis using KF/CaO-MgO catalyst has been studied previously [16], but optimization studies of operating conditions have not been carried out. Therefore, this research aims to study MAG production from cooking oil and glycerol using KF/CaO-MgO catalyst in batch reactor and investigate the effect of reaction temperature, reaction time, and catalyst loading. Optimization was carried out using the RSM method with STATISTICA 12.0. The optimum composition will affect the process of getting good quality of monoglycerides.

## 2. Material and Methods

### 2.1 Materials

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

### 2.2 Methods

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

The design experiment used is a central composite design (CCD) using a response surface method (RSM). This design is widely used for second-order empirical models [17]. The experimental design used was the low level, center level, and high level for each factor which included catalyst percentage, temperature and reaction time. The experimental design can be showed in Table 1.

The relationship between the $Y$ response and the $X$ independent variable is modeled as follow:

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

Where, $Y$ is the response observed (yield (%)); $\beta_0$ is regression parameters; $X_i$ is the main linear variable; $X_iX_j$ is interaction between variables; $X_i^2$ is the square of the main variable; and $i$ is 1,2,3,…,$k$. The desired response is the monoglyceride yield ($Y$). The experimental design for optimization was obtained 16 times experiment to obtain optimum monoglyceride yield. This experimental design was proposed by RSM/CCD using Statistica v.12.0 software which provided an assistance on executing response surface, optimization, and statistical analysis.

## 3. Results and Discussion

### 3.1 Experimental Design Matrix

Experimental design matrix was designed using central composite design (CCD) with response surface methodology. The Design of Experimental (DOE) was designed for a total of 16 runs, consists of 8 factorial points, 6 axial points, and 3 central points. The experimental set was arranged randomly to reduce the influence of uncontrolled factors. The use of CCD can evaluate quickly and effectively the influence of each parameter [17].

The CCD experimental design for optimizing yield of monoglyceride, based on three independent factors (catalyst loading, reaction temperature and reaction time) with a five-level structure, is presented in Table 2. Based on the experimental results, the quadratic polynomial equation is given by Equation (2), which expressed as coded units, which defines the relationship between the independent variables (catalyst loading, reaction temperature and reaction time) and response (yield of monoglyceride).

**Table 1.** Experimental ranges and levels of factors

| Factors ($X_i$) | Range and levels ($X_i$) | | | | |
|---|---|---|---|---|---|
| | -α | -1 | 0 | +1 | +α |
| Catalyst loading ($X_1$), %wt | 0.03 | 0.10 | 0.20 | 0.30 | 0.37 |
| Reaction temperature ($X_2$), °C | 193.18 | 200.00 | 210.00 | 220.00 | 226.82 |
| Reaction time ($X_3$), hours | 1.32 | 2.00 | 3.00 | 4.00 | 4.68 |

$$Y = -2750.60 + 299.09X_1 - 434.98X_1^2 + 25.08X_2 - 0.06X_2^2 + 98.58X_3 - 4.57X_3^2 - 0.14X_1X_2 - 9.92X_1X_3 - 0.33X_2X_3 \quad (3)$$

The accuracy of the model is assessed from the coefficient of determination, $R^2$ [18]. The $R^2$ value describes a good agreement between the experimental and predicted values. In this study, the $R^2$ value obtained is 0.9028 implies that 90.28% of the total variation in the response is justified by the model. The three variables (catalyst loading, reaction temperature, reaction time) have an effect > 90 % of the models.

3.2 Optimization of Monoglyceride by Regression Analysis

Adequacy of the model was examined by analysis of variance (ANOVA) [18] as presented in Table 3. In the ANOVA Table, the *F*-value model is 60.45 which is greater than the tabulated *F*-value of 3.49 at a significance level of 90%. This fact shows that this model is efficiently assured in predicting experimental results.

The regression coefficients, *t*-values, and *p*-values for the linear, quadratic, and variable interaction effects is listed in Table 3. The significance of variable effects on response can be confirmed through *p*-value compared with significance level (alpha). The table shows that in

**Table 3**. Significant regression coefficient for monoglyceride

| Factors | Regression Coeff. | *t*-value | *p*-value |
|---|---|---|---|
| $X_0$ | -2750.6000 | -6.2609 | 0.0008 |
| $X_1$ | 299.0900 | 1.0203 | 0.3469 |
| $X_{11}$ | -434.9800 | -4.5665 | 0.0038 |
| $X_2$ | 25.0800 | 6.1262 | 0.0009 |
| $X_{22}$ | -0.0600 | -5.9224 | 0.0010 |
| $X_3$ | 98.5800 | 4.3303 | 0.0049 |
| $X_{33}$ | -4.5700 | -4.7044 | 0.0033 |
| $X_{12}$ | -0.1400 | -0.1367 | 0.8957 |
| $X_{13}$ | -9.9200 | -0.9521 | 0.3778 |
| $X_{23}$ | -0.3300 | -3.1369 | 0.0201 |
| *Error* | 8.6933 | | |
| $R^2$ | 0.9028 | | |

**Table 2**. Experimental design matrix and experimental results (yield of monoglyceride)

| Run | Independent Variables | | | Yield of Monoglycerides (%) | |
|---|---|---|---|---|---|
| | Catalyst loading (%wt), $X_1$ | Reaction temperature (°C), $X_2$ | Reaction time (hours), $X_3$ | Actual | Predicted |
| 1 | 0.10 | 200.00 | 2.00 | 27.58 | 28.04 |
| 2 | 0.10 | 200.00 | 4.00 | 37.07 | 37.51 |
| 3 | 0.10 | 220.00 | 2.00 | 31.72 | 33.50 |
| 4 | 0.10 | 220.00 | 4.00 | 30.61 | 29.90 |
| 5 | 0.30 | 200.00 | 2.00 | 30.19 | 29.38 |
| 6 | 0.30 | 200.00 | 4.00 | 38.19 | 34.89 |
| 7 | 0.30 | 220.00 | 2.00 | 36.24 | 34.28 |
| 8 | 0.30 | 220.00 | 4.00 | 28.68 | 26.71 |
| 9 | 0.03 | 210.00 | 3.00 | 36.55 | 34.66 |
| 10 | 0.37 | 210.00 | 3.00 | 29.10 | 33.09 |
| 11 | 0.20 | 193.18 | 3.00 | 30.16 | 31.33 |
| 12 | 0.20 | 226.82 | 3.00 | 28.07 | 29.04 |
| 13 | 0.20 | 210.00 | 1.32 | 33.15 | 32.74 |
| 14 | 0.20 | 210.00 | 4.68 | 31.77 | 34.34 |
| 15 | 0.20 | 210.00 | 3.00 | 46.89 | 46.45 |
| 16 | 0.20 | 210.00 | 3.00 | 46.33 | 46.45 |

both the linear and square parameters, the effects of the prominent variables are significant on response, with *p*-values < 0.05. Similarly, the response levels of the interactions of independent variables are also significant with *p*-values < 0.05. All *p*-value data on monoglyceride production have a significance level of < 5% except $X_1$, $X_{12}$, and $X_{13}$, which indicates that the variable has a significant impact on the model.

Figure 1 (Pareto chart) shows that the reaction temperature has a significant effect on the product yield. Among the three variables, reaction temperature has a significant effect on the product yield. Other variables, namely reaction time and catalyst loading, have a significant effect but not as high as the reaction temperature.

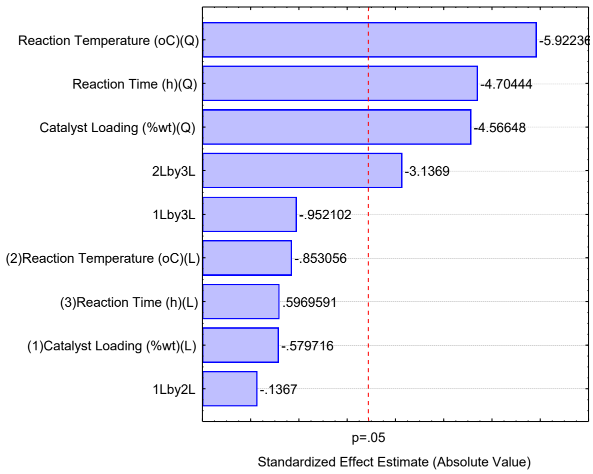


**Figure 1**. Pareto chart of effect of variables for monoglycerides conversion (Q: Quadratic, L: Linear)

### 3.3 Response Surface Plot

The optimum condition of monoglycerides can be seen from the responses were represented in Figures 2-7 in three dimensions (3D) or as contour plots that can help visualize the surface shape of the response. The contour is the constant response curve drawn in $X_i$, $X_j$, and keeping all the other variables fixed. Each contour corresponds to a certain height of surface response. From the surface contours, it can be seen where the optimum position or condition is reached, which in 3D or eclipse lies at the top and on the contour lines on the smallest part inside the contour surface [19].

#### 3.3.1 Reaction temperature vs catalyst loading

Surface optimization and contour graphs (Figures 2 and 3) shows the effect of reaction temperature and catalyst loading on glycerolysis reaction. The lowest and highest temperature conditions were reached at 193 $^o$C and 226 $^o$C, respectively with catalyst loading of 0.2% wt. At the lowest temperature conditions (193 $^o$C), the yield of monoglycerides is 30.16%. This is because the glycerolysis reaction has not reached its optimum condition. The optimum conditions achieved at a temperature of 210 °C with a 0.2 % catalyst can produce monoglyceride of 36.89 %. However, at too high a temperature of 226 °C there was a decrease in yield, the results obtained were 26.24 %. This fact shows

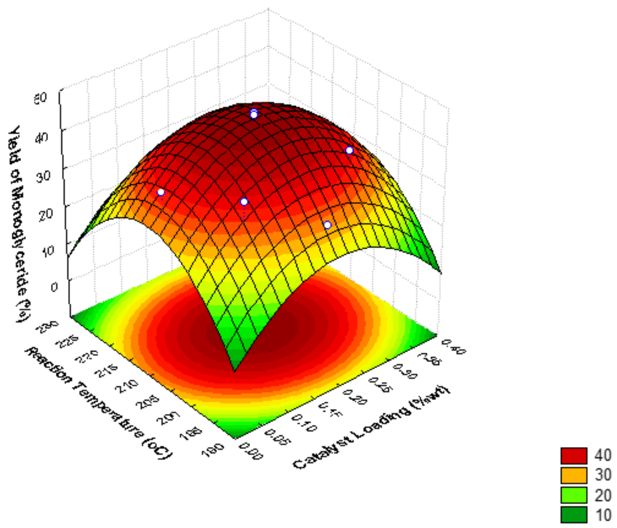


**Figure 2.** 3-D graphics response surface plot showing the effect of catalyst loading versus reaction temperature on the yield of monoglycerides at fixed time 3 hours.

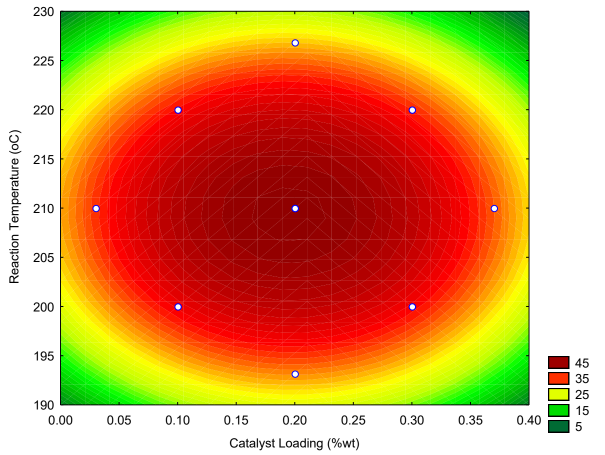


**Figure 3.** 2D graphics contour surface plot showing the effect of catalyst loading versus reaction temperature on the yield of monoglycerides at fixed time 3 hours.

glycerolysis carried out at a temperature of 220 °C using an alkaline catalyst will produce a dark-colored product and a different flavors so that have an impact on the results obtained [20].

3.3.2 Reaction time vs catalyst loading

Figures 4 and 5 shows the effect of the catalyst loading on the glycerolysis reaction time. The addition of a catalyst can reduce the activation energy of the glycerolysis reaction and accelerate the reaction [21]. The addition of the catalyst was carried out between 0.03 to 0.37 %wt at a fixed temperature of 210 °C. The addition of a catalyst amount of 0.03 % produce monoglyceride yield about 35.00 %. However, excess catalysts can reduce conversion and decrease the ability of triglyceride to dissolve glycerol [1]. The monoglyceride yield obtained was 27.03 %. Addition of excess catalyst can cause a side reaction which is a saponification reaction to oil which causes a decreased monoglyceride content [22]. The optimum percentage of catalyst for this reaction is 0.2 %.

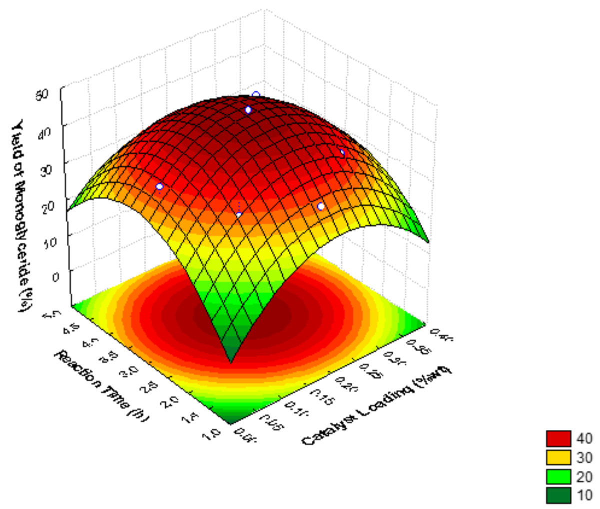


**Figure 4**. 3-D graphics response surface plot showing the effect of reaction time versus catalyst loading on the yield of monoglycerides at fixed temperature 210 °C .

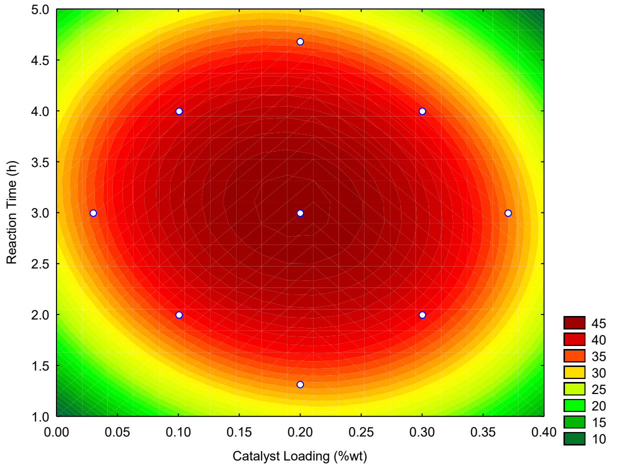


**Figure 5**. 2D graphics contour surface plot showing the effect of reaction time versus catalyst loading on the yield of monoglycerides at fixed temperature 210 °C.

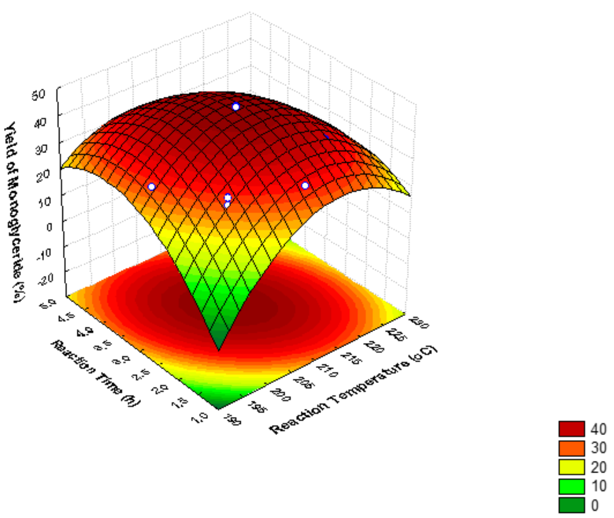


**Figure 6**. 3-D graphics response surface plot showing the effect of reaction time versus reaction temperature on the yield of monoglycerides at fixed catalyst 0.2 %wt.

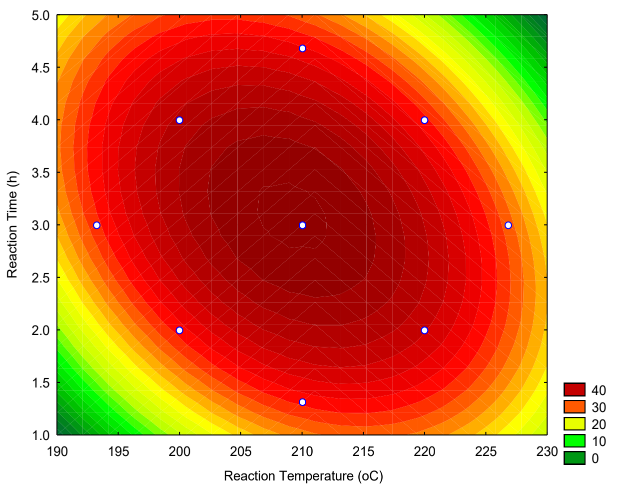


**Figure 7.** 2D graphics contour surface plot showing the effect of reaction time versus reaction temperature on the yield of monoglycerides at fixed catalyst 0.2 %wt.

### 3.3.3 Reaction time vs reaction temperature

The optimum reaction time is affected by temperature, amount of catalyst, type of solvent and other operating conditions. Figures 6 and 7 show the optimization and contour of the surface from the effect of reaction time and reaction temperature. Increased reaction time and reaction temperature can increase the yield of monoglyceride. At the same reaction temperatures (210 °C), the optimum reaction time obtained is 3 hours. This is in accordance with the research conducted by Prakoso and Sukanti [23] that the optimum time to producing monoglycerides is 3 hours with glycerolysis reaction temperature at 200 °C. Monoglyceride yield obtained of 23.51%. At the lowest reaction time of 1 hour, the monoglyceride yield obtained was 22.59%. Meanwhile, at the highest reaction time of 4 hours, monoglyceride yield of 20.54% was obtained. The highest time conditions get lower results. This is due to the glycerolysis reaction is a reversible reaction so that after reaching equilibrium, an increase in reaction time will reduce the yield of monoglycerides [10].

### 3.4 Finding Optimum Operation Conditions

The optimum condition of the synthesis of monoglycerides was 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. The relationship between the catalyst loading and reaction temperature on the yield of monoglycerides has a maximum stationary area. This is due to determining the range of data selection code (point -1, 0, +1) must be considered to get the optimum point. Optimization of monoglycerides shows that the optimum conditions are catalyst loading of 0.19 % (w/w), reaction temperature of 208.37 °C and reaction time of 3.20 hours with levels of monoglycerides obtained 41.58 %.

The optimum condition is also found by a model of desirability. The optimization results

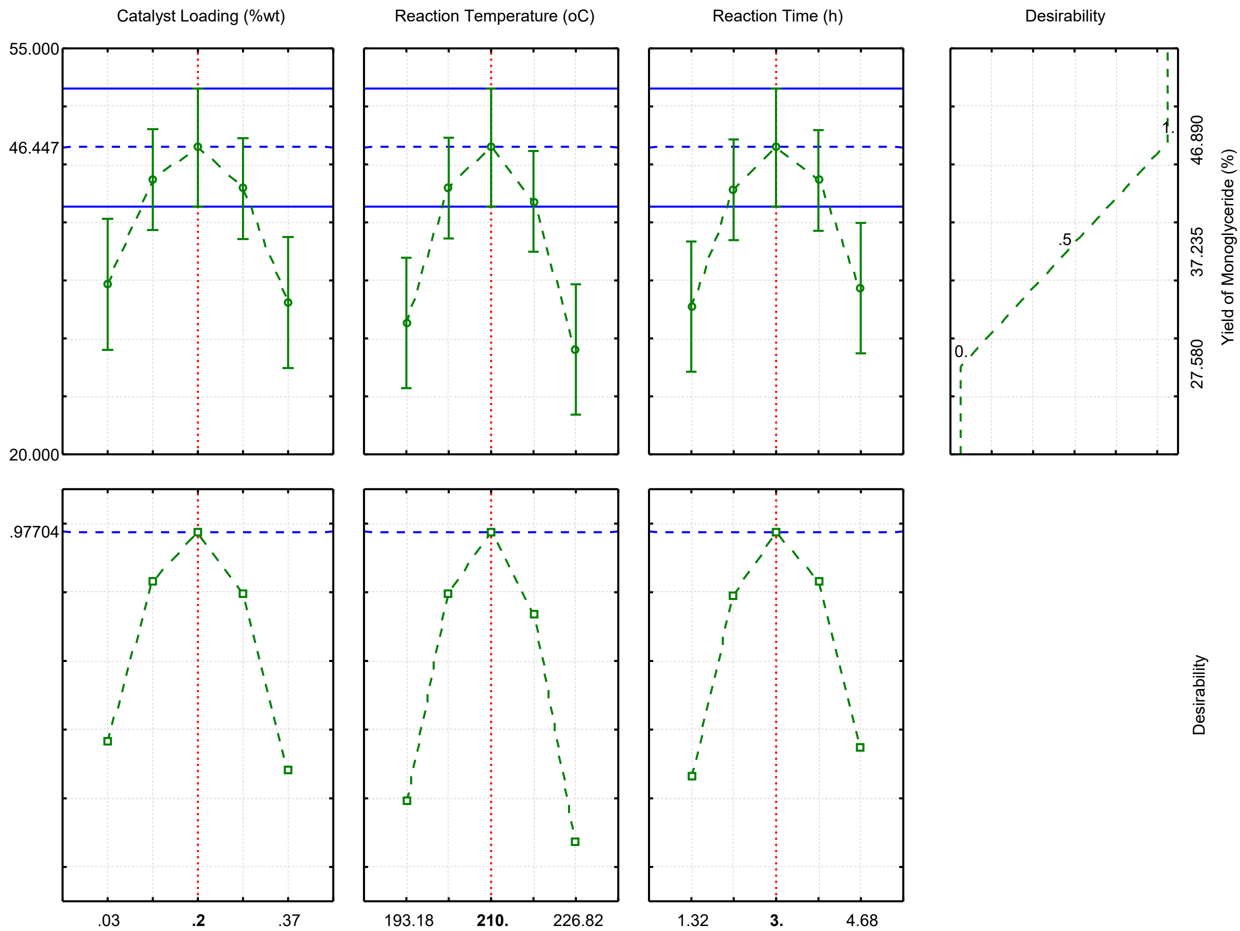


**Figure 8.** Profiles for predicted values and desirability.

are shown in Figure 8. The optimum conditions were obtained at catalyst loading of 0.2 % (w/w), reaction temperature of 210 °C and reaction time of 3 hours. Monoglycerides obtained at 46.45%.

## 4. Conclusion

Optimization of monoglyceride reaction using KF/CaO-MgO catalyst was solved by Response Surface Method (RSM). There are three variables that were optimized, i.e. catalyst loading, reaction temperature and reaction time to achieve optimum yield of monoglyceride. The Pareto graph shows that the reaction temperature gives the most significant effect compared to the other two variables. Optimization of monoglycerides showed that the optimum conditions were catalyst loading of 0.19 % (w/w), reaction temperature of 208.37 °C and reaction time of 3.20 hours with optimum monoglycerides yield of 41.58 %.

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