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Optimization of the Esterification Process of Crude Palm Oil (CPO) with Natural Zeolite Catalyst Using Response Surface Methodology (RSM)

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Abstract

Esterification is one of the important processes in the production of biodiesel. This is done to ensure that the FFA content in CPO is less than 3%. The esterification reaction can be accelerated by using natural zeolite as a catalyst. Optimization needs to be carried out to select the appropriate conditions to reach the optimal region quickly. The purposes of this research are to analyze the impact of esterification time and the natural zeolite catalyst size on the reduction of FFA levels and find the optimal parameters in the CPO esterification through RSM. Esterification is operated by maintaining the reaction temperature at 60 °C, agitation speed at 150 rpm, and using a molar ratio of methanol:CPO of 6:1. The independent variables used in the research are esterification time (90, 110, 130, 150, and 170 minutes) and natural zeolite size (20, 40, 60, 80, and 100 mesh). The optimization results using RSM indicate that the optimum points in the study are at an esterification time of 170 minutes and a natural zeolite size of 97.3909 mesh.

Keywords: esterification, CPO, natural zeolite, FFA, RSM

INTRODUCTION

Biodiesel production can use vegetable oils or animal fats as its raw materials (Musta et al., 2017). One of the raw materials that can be utilized is crude palm oil (CPO). As the second-largest producer of CPO in the world, Indonesia has significant potential to produce CPO-based biodiesel (Maulidan et al., 2020). CPO contains free fatty acids (FFA) at varying levels. The production of biodiesel from CPO requires a process to reduce the FFA content to below 3%. If the FFA content exceeds 3% and the catalyst used is an alkaline catalyst, this can cause a saponification reaction that disrupts the biodiesel production process (Demisu, 2021). The reduction of FFA levels often takes a long time, so the use of a catalyst is necessary to accelerate the reaction (Rachim et al., 2017).

Catalysts for reducing FFA levels are categorized into two types: homogeneous and heterogeneous catalysts. An example of a commonly used homogeneous catalyst is sulfuric acid (Sumari et al., 2021). However, heterogeneous catalysts such as natural zeolites are more advantageous due to their lower cost, high adsorption capacity, and ease of separation through simple methods (Roschat et al., 2016; Santoso et al., 2019). Natural zeolites contain two main compounds, namely SiO_2 and Al_2O_3. The ratio of silicon atoms to aluminum atoms (Si/Al) determines the adsorption capacity of zeolite. A lower SiO_2/Al_2O_3 ratio results in a hydrophilic zeolite surface, while a higher ratio makes the surface hydrophobic (Wang et al., 2019). The Si/Al ratio of natural zeolite varies depending on the mining location, so it is necessary to activate the zeolite to meet the required specifications.

The activation of zeolite can remove impurities that can reduce adsorption capacity. Natural zeolite can be activated using acid compounds such as HCl or base compounds such as NaOH. Acid activation increases the hydrophobicity of zeolite while reducing its water absorption capacity, whereas base activation reduces the Si/Al ratio (Al Muttaqii et al., 2019). Base activation also makes zeolite more polar, allowing it to attract polar compounds such as free fatty acids to the catalyst surface. Research using used cooking oil shows that zeolite activation with 1 M NaOH is more effective in reducing FFA levels, reaching 0.15%, compared to 1 M HCl which only reduces FFA levels by 0.2%, from an initial level of 0.4% (Putranti et al., 2018). Thus, natural zeolite activated by a basic method is more effective in reducing FFA levels.

Biodiesel production usually involves two main processes, namely esterification and transesterification. Transesterification converts triglycerides, the main component of CPO, into biodiesel and glycerol. Meanwhile, esterification aims to reduce the FFA content in CPO by converting it into methyl esters and water (Santoso et al., 2024; Ulfa & Samik, 2022). The esterification process involves conventional heating, alcohol, and a catalyst that are continuously stirred to react all the materials (Suleman et al., 2019). Research on the reduction of FFA levels in CPO using sulfuric acid catalyst at a temperature of 45 °C with independent variables of esterification time of 70, 90, 110, and 130 minutes proved that there was a decrease in FFA levels from 10.59% to 2.37% after 130 minutes (Harahap et al., 2021), which means that by using a base-activated zeolite catalyst, the longer the reaction lasts, the FFA levels can also decrease. Additionally, the size of natural zeolite affects esterification because it influences the surface area of the catalyst. Research using zeolite catalysts with mesh sizes of 10–20, 30–40, 50–60, 70–80, and 100–120 showed that at mesh 100-120, the acid value of tuna fish oil waste decreased from 2.35 mg KOH/g to 1.1 mg KOH/g (Rosyadi et al., 2021).

The goal of esterification is to reduce the FFA level below 3% so that the material is suitable for biodiesel production. FFA is the main impurity usually found in CPO, often exceeding 5%. The darker the oil, the higher the FFA level. This reduces the quality of biodiesel. The FFA level can be measured using the acid-base titration method.The titration is performed until the sample changes color to brick red (Pranata & Husin, 2023) .

Considering the length of the esterification process, optimization is necessary to identify the optimal conditions. This study uses RSM to analyze the influence of independent variables (x) on the response (y). RSM is an effective method for improving the efficiency of the esterification process. RSM helps determine the most appropriate process conditions and facilitates the exploration of factors to quickly achieve the optimal range (Rahman et al., 2021).

This research aims to optimize the CPO esterification process using a base-activated natural zeolite catalyst. Although several studies have been conducted to reduce the FFA content in CPO, the unique combination of variations in natural zeolite size and esterification time to be studied in this research, as well as the use of the Response Surface Methodology (RSM), has not been widely reported. Thus, this research is expected to contribute to the development of the biodiesel industry in Indonesia. The results of this research are expected to produce optimal conditions for effectively reducing FFA levels, increasing production efficiency, and generating higher quality biodiesel. In addition, this research can also serve as a reference for future studies in the development of more environmentally friendly and cost-effective heterogeneous catalysts.

METHODOLOGY

Materials and Instrumentals

The materials needed in this study are crude palm oil, natural zeolite, methanol, NaOH, distilled water, phenolphthalein, and ethanol. Meanwhile, the equipments used in this reserach are sieves (20, 40, 60, 80, and 100 mesh), magnetic stirrer, beaker glass, measuring cylinder, erlenmeyer flask, vertical condenser, pycnometer, thermometer, and GC-MS (Gas Chromatography-Mass Spectrometry)

Methods

Natural zeolite activation process

Natural zeolite is ground using a sieve according to the predetermined particle size variable. This natural zeolite is mixed with a 100 ml solution of 0.4 M NaOH in a beaker glass. This mixture is homogenized using a magnetic stirrer at a stirring speed of 150 rpm for 2 hours. This mixture is washed with distilled water until the pH reaches 7. Then, filtration is carried out with filter paper. The precipitate obtained from the filtration process is dried in an oven at 110 °C for 3 hours, and then calcined at 500 °C for 2 hours.

Esterification

CPO is first centrifuged to remove its impurities. Methanol and CPO with a molar ratio of 6:1 and activated natural zeolite are stirred with a magnetic stirrer. The stirring speed is 150 rpm, the esterification temperature is 60 °C, and the esterification time variables are 90, 110, 130, 150, and 170 minutes. The resulting mixture is centrifuged for 20 minutes at a speed of 1500 rpm. The results obtained were natural zeolite that can be reactivated and the filtrate. The analysis of FFA content in the filtrate is conducted.

FFA Levels Calculation

Titration can be used to find out the free fatty acid levels. The titration method involves heating 2 grams of the sample and 20 ml of ethanol to a temperature of 45 °C. The mixture is added with 3–5 drops of phenolphthalein indicator. The titration is

conducted with a 0.1 N NaOH solution until a color change to brick red occurs. (Herlina & Safitra, 2018).

Data Analysis

Free Fatty Acid (FFA) Content Analysis

The FFA content in the sample is calculated using the following equation: The equation used must be written centered with the numbering as in the following example:

$$\%FFA = \frac{(V\ NaOH \times N\ NaOH \times BM\ FFA)}{(w \times 1000)} \times 100\% \qquad (1)$$

V represents volume in ml, N denotes the normality of solution, the molecular weight of free fatty acid (palmitate acid) is 256 g/mol, and w signifies the mass of the sample in g (Herlina & Safitra, 2018)

RSM Optimization

The research results in the form of FFA content were optimized using RSM to determine the conditions of the independent variables that can produce an optimal response. RSM analysis was conducted by selecting the Composite Central Design (CCD). The program that will be used to optimize the research results is called Minitab. The optimization results will yield equations such as the following:

1. First order

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 \qquad (2)$$

2. Second order

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} {x_i}^2 + \sum_{i=1}^{k} \sum_{i=2}^{k} \beta_{ij} x_i x_j \qquad (3)$$

y is dependent variable, x is independent variable, and β is constan value (Djimtoingar et al., 2022)

Analysis of GC-MS

Analysis of GC-MS is a combined analytical technique that involves gas chromatography (GC) to separate volatile components in a sample based on differences in polarity and volatility on a capillary column coated with a stationary phase. The separated components are then identified and their molecular masses specifically determined through mass spectrometry (MS) (Gargazi et al., 2022).

RESULTS AND DISCUSSION

The Effect of Esterification Time and Particle Size on FFA Levels

The esterification of crude palm oil (CPO) aims to reduce FFA levels before proceeding to the next stage of biodiesel production. The research results show a decrease in FFA levels in CPO based on the specified variables. The obtained FFA levels are presented below:

Table 1. Results of FFA Levels Analysis (%) in CPO

Esterification time (minutes)	Catalyst size (mesh)				
	20	40	60	80	100
90	6.3573	6.2720	5.5040	5.4613	5.2053
110	6.2720	6.4853	5.6320	5.2480	5.2907
130	6.6560	5.8880	5.2480	5.2480	4.9493
150	6.3573	5.5593	5.1627	5.1200	4.7360
170	5.5040	5.3333	6.1440	5.0773	4.6080

The initial FFA content of CPO is 12,2027%. The lowest FFA value obtained is 4,608% when the esterification time was 170 minutes and the catalyst size was 100 mesh. Nevertheless, this FFA level still exceeds the maximum limit of 3% recommended for biodiesel production. The results of this study demonstrate the potential to reduce FFA levels through the adjustment of reaction time and the size of natural zeolite catalysts. However, it should be emphasized that this study focuses on evaluating the influence of esterification time and the size of natural zeolite catalysts within a certain range. Therefore, further research is needed to achieve the appropriate FFA levels for biodiesel production, including considering other variables.

The effect of esterification time and catalyst size can be observed in more detail in the following graph:

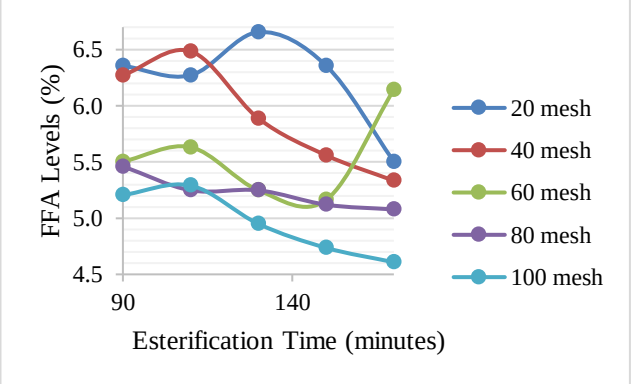

Figure 1. Graph of the Impact of FFA Levels (%) on Esterification Time (minutes) and Catalyst Size (mesh)

Based on Figure 1, the longer the esterification times and the smaller the catalyst sizes the FFA levels will be lower. Catalyst size smaller ones have a larger surface area so the conversion rate will be higher (Rahma & Hidayat, 2023). In addition, the longer the

contact with the catalyst, the more the reaction will take place, so that the FFA content will decrease (Esa & Him, 2023).

However, as seen in Figure 1, FFA content does not always decrease with increasing esterification time or decreasing catalyst size. In fact, there is a point where FFA content increases. This increase in FFA can occur due to the hydrolysis reaction of triglycerides which are the main components in CPO, because the esterification reaction produces water as a by-product which then reacts with triglycerides and breaks them down into FFA (Mohyuddin et al., 2016). The data presented in the graph above may not always be accurate and may contain a certain level of error. Data variations due to this error are presented in the following graph:

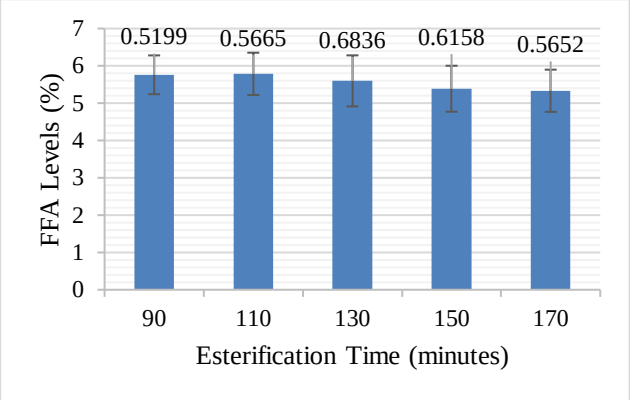

Figure 2. Graph of Standard Deviation of FFA Levels (%) at Certain Esterification Time (minutes)

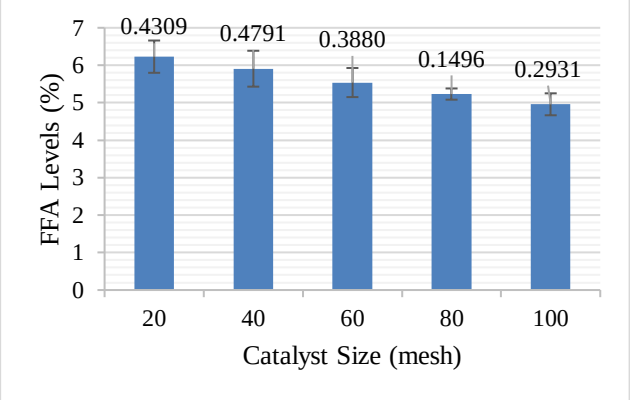

Figure 3. Graph of Standard Deviation of FFA Levels (%) at Certain Catalyst Sizes (mesh)

Figure 2 shows the average and data distribution or standard deviation for time certain esterification. Based on this image, the average FFA content gradually decreased along with time. Standard deviation shows the spread of data. The standard deviations respectively at 90, 110, 130, 150, and 170 minutes are 0.5199; 0.5665; 0.6836; 0.6158, and 0.5652. If it gets smaller standard deviation, the smaller the probability the occurrence of errors in measurement. The smallest standard deviation was observed at 90 minutes of esterification, with a value of 0.5199, while the largest was seen at 130 minutes, with a value of 0.6836.

Figure 3 shows the average and distribution of data, or standard deviation, for a given catalyst size. From the image, the average FFA content also decreases as the catalyst size variable increases. The standard deviations respectively at 20, 40, 60, 80, and 100 mesh are 0.4309; 0.4791; 0.3880; 0.1496, and 0.2931. The smallest standard deviation in the figure is observed for the 80 mesh catalyst size at 0.1496, while the largest is for the 40 mesh catalyst size at 0.4791.

A linear decrease is theoretically beneficial, since increasing the esterification time and reducing the catalyst size will result in a greater reduction in FFA content. However, this is not the case in an industrial setting. In industry, increasing the esterification time means increasing the residence time, which leads to higher reactor tank costs and inefficiencies. In addition, smaller catalyst sizes require higher costs for crushing and refining. Small catalysts are also difficult to separate (Rahma & Hidayat, 2023). These factors highlight the need for process optimization to determine the optimal esterification time and catalyst size, so that it is feasible for industrial applications.

Optimization of FFA Levels Using Response Surface Methodology

This research produces 25 data points of FFA levels, but some data points have significant discrepancies. If all these data points are optimized, the resulting model might not accurately predict the response value. Therefore, optimization is performed only with the 13 data points that have small discrepancies so that the resulting model can predict the response value more accurately. The 13 optimized FFA data, as shown in Table 2.

Optimization using RSM is useful for optimizing the esterification process to obtain the desired FFA content. This response can be predicted with the polynomial equation that has been obtained. This equation can show that the catalyst size and the esterification time are independent variables that can affect the response. Here is the resulting equation:

$$y = 9.241 - 0.0538x_1 - 0.0181x_2 + 0{,}000212{x_1}^2 + 0{,}000029{x_2}^2 + 0{,}000074x_1x_2$$

Where y is free fatty acid (%), x_1 is catalyst size (mesh), and x_2 is esterification time (minutes)

Table 2. FFA Levels for Optimization Process

Catalyst size (mesh)	Esterification time (minutes)	FFA levels (%)
20	130	6.6560
20	150	6.3573
40	90	6.2720
40	130	5.8880
60	110	5.6320
80	90	5.4613
80	110	5.2480
80	130	5.2480
80	150	5.1200
80	170	5.0773
100	90	5.2053
100	110	5.2907
100	130	4.9493

Table 3. *Model Summary* from *Response Surface Regression* for FFA Levels

S	R-sq	R-sq(adj)	R-sq(pred)
0.0904659	98.43%	97.32%	93.40%

Based on Table 3, The obtained values of R-sq, R-sq(adj), and R-sq(pred) are 98.43%, 97.32%, and 93.40%, respectively. The increase in the R-sq value indicates that the model's ability is increasingly accurate in predicting response values. However, the closer the R-sq value is to 0, the worse the model is at depicting the relationship between the variables (Djimtoingar et al., 2022). The R-sq value must be at least 0.75 for the model to be considered good (Muzakhar et al., 2023). R-sq(adj) is the modification of R-sq that consider the amount of independent variables in the model. If there are independent variables that do not need to be included in the regression model, the R-sq(adj) value tends to decrease or remain the same as R-sq (Venkatachalam et al., 2021).

Based on Table 4, the optimum conditions were obtained at a natural zeolite catalyst size of 97.3909 mesh and an esterification time of 170 minutes. This affects the predicted FFA content obtained, which is 4.989%. The composite desirability obtained is 0.976587. Generally, the range of desirability values is from 0 to 1. The closer the desirability value is to 1 or equal to 1, the closer the response value is to the desired value (Pal & Gauri, 2018).

Table 4. Optimization Results Output with Minitab Software

Parameters						
Response	Goal	Lower	Target	Upper	Weight	Importance
FFA (%)	Minimum		4.94933	6.656	1	1

Solution

Solution	Catalyst size (mesh)	Esterification time (minutes)	FFA Levels (%) Fit	Composite Desirability
1	97.3909	170	4.98929	0.976587

Multiple Response Prediction

Variable	Setting
Catalyst size (mesh)	97.3909
Esterification time (minutes)	170

Response	Fit	SE Fit	95% CI	95% PI
FFA Levels (%)	4.989	0,123	(4.698, 5.281)	(4.628, 5.351)

Table 5. Optimization Results Output with Minitab Software if the Target is Set to Less Than 3%

Parameters						
Response	Goal	Lower	Target	Upper	Weight	Importance
FFA (%)	Target	2.691	2.99	6.656	1	1

Solution

Solution	Catalyst size (mesh)	Esterification time (minutes)	FFA Levels (%) Fit	Composite Desirability
1	96.7677	170	4.98930	0.454636

Multiple Response Prediction

Variable	Setting
Catalyst size (mesh)	96.7677
Esterification time (minutes)	170

Response	Fit	SE Fit	95% CI	95% PI
FFA Levels (%)	4.989	0.121	(4.704, 5.274)	(4.633, 5.346)

Based on Table 5, the target has been set to less than 3% (2.99%) when operating Minitab software to find optimal conditions. However, the optimization results still show an FFA level response of 4.989%. This is because none of the research data that were optimized is below 3%, so the optimization results (FFA levels) also cannot be predicted to be below 3%.

The Pareto Diagram generated through the Minitab application is as follows:

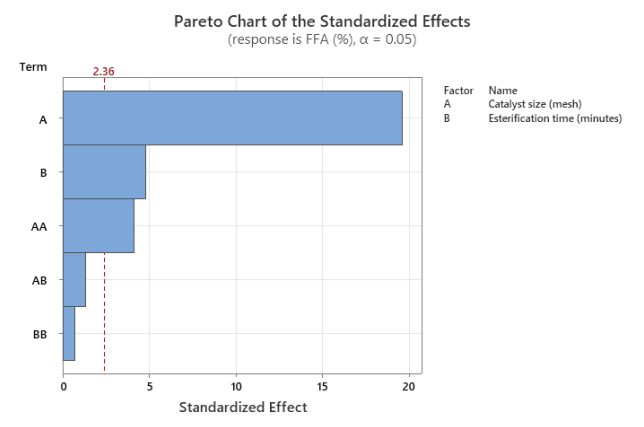

Figure 4. Pareto Diagram for the Analysis of Independent Variables on the Reduction of FFA Levels

The Pareto diagram aims to facilitate the identification of independent variables or factors that have a significant impact on the resulting response (Farrag et al., 2022). Based on Figure 4, the variable of catalyst size has a greater effect than the variable of esterification time on the reduction of FFA levels. This can be seen from the bar representing catalyst size is longer than the bar representing esterification time.

ANOVA can be used to examine the significance of changes in independent variables on the response value. The level of significance is stated by the P-value. if there is significance in the change of the independent variable towards the response, it is stated with P<0.05. Meanwhile, no significance is stated with P>0.05 (Muzakhar et al., 2023). Based on table 6, the catalyst size and esterification time have significant effect on the reduction of FFA levels.

Residual plot for the decrease in FFA levels produced as follows:

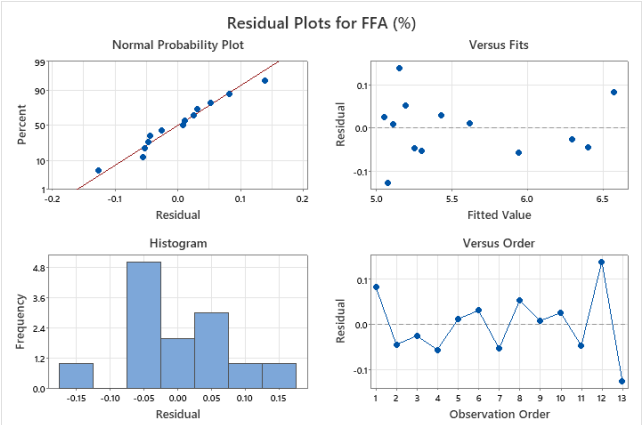

Figure 5. Residual Plots for FFA (%)

There are four types of residual plots presented in the figure, namely the normal probability plot, histogram, residual versus fit, and residual versus order. The normal probability plot is better than the histogram residual when the goal is to observe the normality of the residual distribution. This is because the histogram requires a minimum of 20 data points to provide an accurate depiction of the distribution. Meanwhile, the normality of the residual distribution

Table 6. Analysis of Variance (ANOVA)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	3.60040	0.72008	87.99	0.000
Linear	2	3.34076	1.67038	204.10	0.000
Catalyst size (mesh)	1	3.13061	3.13061	382.52	0.000
Esterification time (minutes)	1	0.18900	0.18900	23.09	0.002
Square	2	0,13813	0,06907	8,44	0,014
Catalyst size (mesh)* Catalyst size (mesh)	1	0.13784	0.13784	16.84	0.005
Esterification time (minutes)* Esterification time (minutes)	1	0.0389	0.00389	0.48	0.513
2-Way Interaction	1	0.01461	0.01461	1.79	0.223
Catalyst size (mesh)* Esterification time (minutes)	1	0.01461	0.01461	1.79	0.223
Error	7	0.05729	0.00818		
Total	12	3.65769			

on the normal probability plot can be seen from the spread of data points. The distribution of data points that tends to form a straight line on a normal probability plot is a characteristic of normally distributed data. The residual versus fit plot provides an illustration that the residuals are scattered randomly around the horizontal zero line on the residual versus fit plot without forming a particular pattern. This indicates that the model is quite good at predicting response values. Meanwhile, the residual versus order plot shows that the distribution of data points is random without forming any specific pattern around the horizontal zero line on the plot, so the residual from the first observation does not affect the residual value of subsequent observations (Muzakhar et al., 2023).

Based on Figure 5, the normal probability plot has shown that the data is normally distributed because the data distribution tends to form a straight line. Then, the residual versus fit plot also shows the distribution of data points randomly so that the resulting model has good predictive ability. In additon, the residual versus order plot also shows the random distribution of data. This means there is no influence between the residuals from each observation.

Optimization using the RSM method can be visualized with contour plot and surface plot. The shapes of the contour plot and surface plot obtained from this research are as follows:

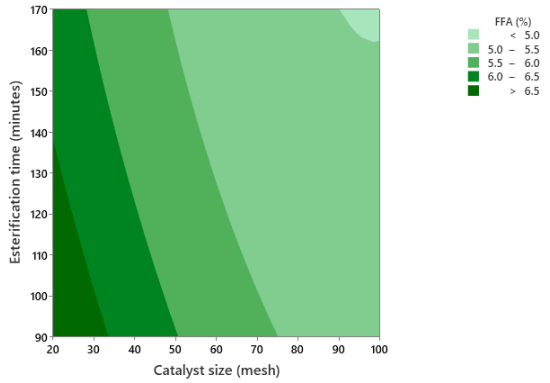

Figure 6. Contour Plot of FFA Levels (%) vs Esterification Time (minutes) and Catalyst Size (mesh)

Contour plot has a two-dimensional shape that illustrates the interaction between independent variables and dependent variables. (Muzakhar et al., 2023). Based on Figure 6, the independent variable values that can produce an optimal response are the independent variable in the 5th layer with a catalyst size range of 90 – 100 mesh and an esterification time range of 160 – 170 minutes. This is indicated by the lightest green color on the contour plot.

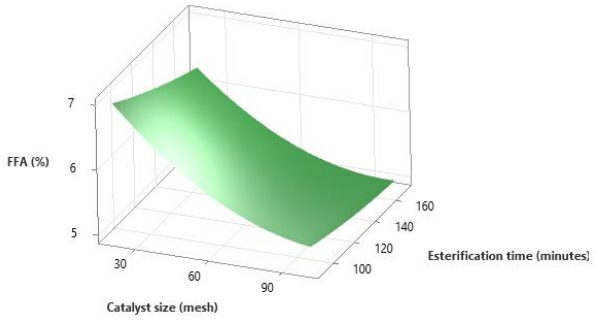

Figure 7. Surface Plot of FFA Levels (%) vs Esterification Time (minutes) and Catalyst Size (mesh)

Surface plots have a three-dimensional shape. This plot is used to identify optimal points such as maximum or minimum saddle point. The maximum point indicates a maximum response, the minimum point indicates a minimum response, and the saddle point indicates a response surface that rises in one direction and falls in another (Winarni et al., 2021). The surface plot generated above does not yet show the minimum, maximum, or saddle points.

Identification of Esterification Products with GC-MS

Optimization with RSM shows that the optimal reaction conditions are achieved at a catalyst size of 97.3909 mesh and a reaction time of 170 minutes. Therefore, GC-MS analysis was conducted on samples obtained from the nearest practical reaction conditions, which used a catalyst size of 100 mesh and a reaction time of 170 minutes. The GC-MS results are as follows:

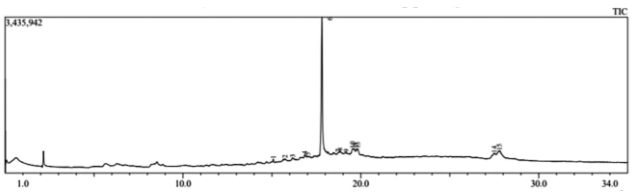

Figure 8. Chromatogram of the Esterification Products

Gas chromatography (GC) analysis shows the presence of 15 different components in the sample. This is marked by 15 peaks on the chromatogram. Variations in retention time and area indicate significant compound diversity. Compounds with the

largest area show the highest concentration in the sample. This means that the compound is dominant in the sample (Earlia et al., 2019).

Table 7. Free Fatty Acids Detected through GC-MS

Peak	Component	Retention time (minutes)	%Area
8	nonahexacontanoic acid	18.824	1.32%

Peaks indicating the presence of free fatty acids were detected at peak 8. The GC-MS analysis results show that free fatty acids are present in the sample, but in very small amounts. This is indicated by the low area percentage at the peaks where free fatty acids are present.

CONCLUSION

The research results show that longer reaction esterification times and smaller catalyst sizes reduce FFA levels. This research also indicates that the lowest FFA content obtained is 4.608% at the natural zeolite size of 100 mesh and esterification time of 170 minutes. Meanwhile, the optimization results conducted using Response Surface Methodology show the optimum conditions of this study are the variable of natural zeolite size 97.3909 mesh and esterification time of 170 minutes with an FFA levels response of 4.989%.

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