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Optimisation of Reaction Parameters in Transesterification of Waste Cooking Oil Using Response Surface Methodology

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Optimization of reaction parameters for biodiesel production is crucial to develop a more efficient and cost-effective system in the biodiesel industry. The transesterification reaction is affected by several factors, which are alcohol to oil molar ratio, reaction temperature, reaction time, and catalyst loading. In this study, the Response Surface Methodology (RSM) was utilized to obtain the optimal conditions for maximizing biodiesel yield. RSM using Box-Behnken experimental design that consists of 30 runs (number of experiments) and three blocks was developed to determine the optimal conditions of key parameters, such as (A) methanol:oil ratio (20-40); (B) catalyst loading [0.25-2% (wt/l)]; (C) reaction temperature (50-70°C); and (D) reaction time (1-15 hours). The ANOVA analysis suggested that the quadratic model is significant as the p-value for the model was < 0.0001 and the large F-value of 37.70. The lack of fit p-value of 0.0928 (p-value is not significant) implies that the model fitted all the data. The R^2 value of 0.9760 indicates that the model fitted the experimental data. Based on the F-value and p-value of the significant model terms, methanol:oil molar ratio has the largest effect on biodiesel yield compared to other parameters. The optimum conditions whereby the maximum biodiesel yield of 35.45% was obtained were methanol to oil molar ratio of 34:1; reaction temperature of 68.4 ºC; reaction time of 11.9 h; and 1.125 wt% catalyst loading. In terms of interaction, AB, AC, AD, BC, BD, and CD were found to be insignificant model terms as their p-values were higher than 0.05.

Key words: Response surface methodology; waste cooking oil; transesterification, biodiesel

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Currently, fossil fuels provide approximately 87% of the total world energy demand and are still the main source of the global energy demand and supply scenario [1]. The increasing trend in the dependency on fossil fuels to meet the increasing energy demand will also cause an increase in greenhouse gas emissions into the atmosphere, which in turn will increase severe environmental problems [2]. Therefore, it is essential to make some initiatives to save our planet for future generations.

The production of biofuels, in general, and biodiesel, in particular, is gradually becoming a vital issue due to the urgent need to decrease greenhouse gas emissions. Thus, energy concerns, growing environmental awareness, and economic considerations are the major driving forces behind the worldwide direction towards producing biodiesel from bioresources. Recent research works seek for the possibilities of using low cost and highly available bioresources or waste in the biodiesel industry. Due to increasing economic concerns and obvious environmental reasons, the transformation of non-edible oils into biodiesel should be the foremost choice to substitute fossil fuels [3]. The transesterification procedure is one of the most commonly used methods for converting vegetable oils into biodiesel. Biodiesel production by transesterification involves the reaction of vegetable oils (edible and non-edible), recycled waste vegetable oils or animal fats. The transesterification reaction is affected by several factors, which are alcohol to oil molar ratio, reaction temperature, reaction time, and catalyst loading. Therefore, several attempts have been made to investigate the effects of the above-mentioned parameters on the biodiesel yield in the transesterification reaction to determine their optimum values for maximum biodiesel yield.

Previously, an optimization study was done with the variation of one parameter at a time (one-variable-at-a-time technique), which is tedious and time-consuming [4]. Besides, this traditional technique does not show interactive effects among the reaction variables. Thus, the development of response surface methodology can be used to study the relation-

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ships among process variables and responses efficiently using a minimum number of experiments.

In this study, RSM with Box-Behnken design (BBD) was employed to optimize extraction variables for maximum biodiesel yield. The statistical model developed was used for the prediction and optimization of biodiesel yield. There were four reaction parameter variables, which were: methanol:oil ratio (20, 30, 40), catalyst loading (wt.%) (0.025, 1.125, 2), reaction temperature (50, 60, 70ºC), and reaction time (7, 11, 15 hours). A series of 30 experiments was performed with optimized variables to identify the relationship between the actual yield and the predicted yield from Design-Expert software.

MATERIALS AND METHODS

1. Material

Waste cooking oil (WCO) was collected from the restaurant area in Seksyen 7, Shah Alam, where the waste cooking oil was used for frying purposes. Prior to use, the waste cooking oil was filtered using filter papers to remove insoluble impurities and washed several times with hot water to remove salt and other soluble materials. The oil was dried at 110ºC for 24 h in the oven and stored in an airtight bottle until further studies.

2. Catalyst Preparation

Mg-Al layered double hydroxide was prepared by the alkali-free co-precipitation method adopted from [5]. It involved synthesis of catalyst precursor, activation of catalyst by calcination, and reconstruction of catalyst.

2.1. Preparation of Mg-Al LDH Precursors

Alkali-free co-precipitation method was used to synthesize LDHs with three different molar ratios, which were 4:1, 3:1, and 2:1 Mg/Al. The synthesis was prepared by mixing an aqueous solution of metallic cations (solution A) with a highly basic carbonate solution (solution B) simultaneously drop by drop under vigorous stirring at pH 8.5. Ammonium hydroxide solution was added drop by drop to maintain the pH. Solution A was prepared by mixing 1 M Mg(II) nitrate hexahydrate with 1 M aluminium nitrate nonahydrate according to different Mg/Al ratios to make up to 100 mL solutions. Solution B was 2 M ammonium carbonate in 100 mL of distilled water. The products of the co-precipitation were brought to reflux for 24 h for ageing process at 65ºC. Then, the solutions were filtered and washed with distilled water until the pH of the filtrate was 7. Next, the precursors were placed in an oven at 100ºC for 24 h.

2.2. Activation of Mg-Al LDH Precursors by Calcination

The Mg-Al LDH precursors were calcined at 450ºC for 5 h to remove water molecules and carbonate compound. After calcination, all the samples must be placed inside the vacuum desiccator to avoid the catalysts from absorbing moisture because Mg-Al LDH has the characteristic of hygroscopicity.

2.3. Reconstruction of LDH by Hydrothermal Method

After calcination, the layered Mg-Al LDH catalysts collapsed. Thus, to rebuild the layers, the catalysts must undergo a reconstruction method. In this study, the hydrothermal reconstruction method was carried out as follows - first, 0.5 g of calcined catalyst was placed inside a 100 mL Teflon, and then 90 mL of deionised water was added into the Teflon. The Teflon was closed with the cap and put inside the hydrothermal reactor. The oven was set at 100ºC, and the hydrothermal reactor was then placed in the oven for 24 h. Next, the hydrothermal reactor was cooled at ambient temperature, before the cap was opened. The catalyst was filtered and then dried in an oven at 100ºC for 5 h. The dried samples must be kept properly inside the vacuum desiccator. These reconstruction steps were repeated by varying the weight of the samples (0.25 g and 0.75 g) and reconstruction time (12 h and 18 h).

3. Characterization of Waste Cooking Oil Feedstock

The key physical and chemical properties of waste cooking oil such as acid value, saponification value and water content were determined experimentally following standard ASTM test methods.

3.1. Determination of Acid Value (AV)

Acid value is the number of milligrams of KOH required to neutralize all acid in 1 g of sample. Acid value is determined by titration of the sample dissolved in a mixture of ethanol and diethyl ether, with KOH as the titrant. The acid value of the WCO was determined using the European standard EN14101 method [6]. In this method, 1 g of oil was added into a flask and dissolved in 25 mL of ethanol and 25 mL of diethyl ether, with a few drops of phenolphthalein as an indicator. This solution was then divided into three different conical flasks with 15 mL in each flask. The titration process was stopped when the solution turned to light pink in color. The formula to calculate acid value is shown in Equation 1.

$$\text{Acid value, mg KOH/g} = \frac{volume\ of\ KOH\ (mL) x\ normality\ of KOH\ (N) x\ 56.1}{weight\ of\ sample\ (g)} \quad (1)$$

3.2. Determination of Saponification Value

Saponification value is defined as the amount of alkali required to saponify a defined quantity of oil sample. It is expressed as the number of milligrams of KOH required to saponify 1 g of oil sample [7]. The measurement of saponification value involves the saponification process where triacylglycerols are split to form glycerol and free fatty acids by alcoholic alkali. The free fatty acids are neutralized, while excess alkali is back titrated with HCl in the presence of an indicator.

The saponification value of the WCO was determined using the AOCS method Cd 3a-94 [7]. In this method, 2 g of oil was weighed accurately in a 250 mL conical flask. About 25 mL of ethanolic solution of KOH (0.5 N) was added into the flask with constant stirring. About 4 mL of a solvent mixture of 1:1 ethanol and diethyl ether was later added into the flask and slightly agitated to dissolve the oil sample in the solvent mixture. The mixture was heated gently for 1 h to saponify the oil. After the mixture was cooled down to room temperature, a few drops of phenolphthalein indicator (1%) were added to the mixture and then titrated against standardize (0.5 N) HCl with vigorous stirring till the pink color disappeared for at least 30 s. Another experiment was performed under similar conditions without adding the oil sample to the mixture to determine the blank reading. The saponification value was then calculated according to Equation 2.

$$\text{Saponification value, mg KOH/g} = \frac{(blank - volume\ HCL\ used)\, x\ molarity\ of HCl\ x\ 56.1}{weight\ of\ oil\ (g)} \qquad (2)$$

3.3. Determination of Water Content

Water content is classified as one of the physicochemical properties which may affect transesterification reaction and hence biodiesel yield. A feedstock with high water content may result in a side reaction of hydrolysis of oil to form free fatty acids, which may lead to saponification reaction in the presence of the base catalyst. Therefore, to avoid the side reaction, the feedstock used for biodiesel production should be water-free or has water content lower than 0.3 wt%.

The oven method [8] was used to determine the water content. In the oven drying method, the sample is heated under specific conditions (temperature, pressure, time) and loss of weight is used to calculate the water content of the sample. In this method, an empty beaker was weighed and the weight recorded. Then, 5.0 g of WCO sample was placed in the beaker and weighed accurately. The beaker (uncovered) containing the sample was placed in the oven at 110ºC. The sample was left overnight. The sample was then removed from the oven and stored in a vacuum desiccator. The sample was weighed and the mass recorded. Replicates of the samples were prepared. The water content was calculated using Equation 3.

$$\text{Water content, \%} = \frac{weight\ before - weight\ after}{weight\ before}\ x\ 100 \qquad (3)$$

4. Esterification of Waste Cooking Oil

Esterification is a pre-treatment process where FFA are reduced by reacting the fatty acids in the presence of an acid catalyst (HCl) to form new esters. Esterification was performed in a 500 mL two-neck round bottom flask. One neck was equipped with a thermometer to measure the temperature. A water-cooled condenser was connected to another neck on the top of the round bottom flask to reduce evaporative loss of methanol. The round bottom flask was placed in paraffin oil and heated on a hot plate.

In this experiment [18], 6:1 methanol to oil ratio was applied with 1 wt% of catalyst. Methanol and HCl were mixed before the mixture and oil were heated to 60-65ºC. After the temperature was reached, the mixture of methanol and HCl was added to the oil and the reaction was let to complete for 2 h. As the mixture of methanol and oil was immiscible, the reaction was stirred vigorously to ensure efficient mixing. After 2 h, the solution was brought to a rotary evaporator to remove all the methanol. The esterified oil was washed three times with hot water before transesterification and acid value determination. The acid value must be lower than 1.0 mg KOH/g of oil before being subjected to transesterification.

5. Transesterification of Waste Cooking Oil

The esterified oil was subjected to transesterification process to obtain biodiesel and glycerol. The transesterification reaction of WCO was performed in a 250 mL two-necked round bottom flask fitted with a water-cooled condenser and a thermometer. The transesterification reaction was performed using waste cooking oil, methanol, and Mg-Al LDH catalyst under different reaction parameters such as methanol: oil ratio, catalyst loading, reaction temperature, and reaction time to obtain optimum reaction conditions for maximum biodiesel production conditions. After completion of the reaction, the reaction mixture was filtered using a Whatman 42 filter paper and centrifuged to separate the catalyst. The mixture was then transferred to a separating funnel and allowed to stand for approximately 24 h. The bottom layer (glycerol) was drained and methanol was removed via rotary evaporation. The biodiesel was collected and washed with hot deionized water. Excess water was removed by oven method and the biodiesel was stored in an air-tight bottle before further studies.

The biodiesel produced from the transesterification reaction of WCO was analyzed for FAME composition with gas chromatography (GC-FID), using AGILENT 6890N FID-ECD gas chromatograph, to determine the ester content.

6. Response Surface Methodology

6.1. Design of Experiments

The parameters used for FFA reduction from WCO by Mg-Al LDH catalyst were analyzed by standard response surface methodology (RSM) with Box-Behnken Design (BBD). RSM method is suitable for the quadratic model. Generally, BBD comprises of 2n factorial points, 2n axial points, and no center points. When the number of variables increases, the number of runs for a complete replicate for the design also increases rapidly, and each variable is studied at two levels [9]. At center points, repetitions were required to evaluate the accuracy issue of the results. Since individual second-order effect cannot be estimated separately by 2n factorial design, BBD was employed and used to develop the model for FFA reduction from WCO [9,10]. In the design, the independent variable of the experiment is assumed to be continuous and regulated by experiments with negligible errors. The objective of the experimental design was to optimize the response variables (Y), which can be achieved 46 by acquiring a suitable approximation for the true correlation between independent variables and response surfaces.

In this study, the operating parameters (independent variables) chosen for the statistical experiment design are as follows: methanol:oil (A), % catalyst (B), reaction temperature (C), and reaction time (D). Hence, a total of 30 tests (16 factorial points, 8 axial points and 6 center points) were required for the four independent variables, as generated from Equation 4. The parameters and their levels were chosen based on the previous OVAT study and tabulated in Table 1.

6.2. Model Fitting and Statistical Analysis

Design Expert software (Stat-Ease, Inc., Minneapolis, USA) was used to perform regression analysis of experimental data and plot the response surfaces and contour plot at the optimized condition. ANOVA was used to determine the significance and fitness of the quadratic regression model. Besides, it was also used to define the effects of significant individual variables and the interaction between the variables and responses by graphical means in estimating the statistical parameters. The statistical significance of the second-order model was checked by the F-test, in which the calculated F-value should be greater than the tabulated F-value. The accuracy of the fitted polynomial model was determined by the coefficient of R^2. The probability of error and the significance of each regression coefficient were evaluated by the probability value (p-value) at 95% confidence interval [11, 12, 13].

The Box-Behnken experimental design is shown in Table 2 and consists of 30 runs (number of experiments) and three blocks (30 experiments must be done within three days, 10 experiments each day). This experimental design was automatically arranged by the software.

7. Biodiesel Analysis

The various physicochemical properties such as acid value, flash point, pour point, and cloud point were determined experimentally following standard test methods. Biodiesel analysis is important to ensure the biodiesel produced complies with the ASTM and EN standards.

7.1. Determination of Pour Point

Pour point is the lowest temperature, expressed as a multiple of 3ºC, at which an oil is observed to flow when cooled and examined under prescribed conditions. ASTM designation D 97-66 method was applied to determine the pour point. Firstly, a sample of the biodiesel was half-filled in a test tube. Then, the test tube was immersed in crushed ice (added with some sodium chloride to further bring down the temperature to -12ºC). Beginning at 8ºC above the

$$\text{Number of tests (N)} = 2^n + 2n + n_{\text{center point}} = 2^4 + (2 \times 4) + 6 = 30 \quad (4)$$

Table 1. Coded Parameters for the Independent Variables for Process Optimization

Parameters	Units	Levels		
		-1	0	+1
Methanol:oil	mol/mol	20	30	40
% catalyst	wt.%	0.25	1.125	2
Reaction temperature	ºC	50	60	70
Reaction time	h	7	11	15

Table 2. The Box-Behnken Experimental Design

Block	Run	(A) Methanol:oil	(B) % catalyst	(C) Reaction temp, ° C	(D) Reaction time, h
Day 1	1	40	2	60	11
Day 1	2	20	0.25	60	11
Day 1	3	30	1.125	60	11
Day 1	4	30	1.125	70	15
Day 1	5	30	1.125	50	7
Day 1	6	20	2	60	11
Day 1	7	40	0.25	60	11
Day 1	8	30	1.125	70	7
Day 1	9	30	1.125	50	15
Day 1	10	30	1.125	60	11
Day 2	11	30	1.125	60	11
Day 2	12	20	1.125	60	15
Day 2	13	30	2	70	11
Day 2	14	40	1.125	60	7
Day 2	15	30	0.25	70	11
Day 2	16	20	1.125	60	7
Day 2	17	30	0.25	50	11
Day 2	18	40	1.125	60	15
Day 2	19	30	1.125	60	11
Day 2	20	30	2	50	11
Day 3	21	30	1.125	60	11
Day 3	22	30	2	60	15
Day 3	23	20	1.125	70	11
Day 3	24	40	1.125	50	11
Day 3	25	40	1.125	70	11
Day 3	26	30	2	60	7
Day 3	27	30	0.25	60	7
Day 3	28	30	0.25	60	15
Day 3	29	20	1.125	50	11
Day 3	30	30	1.125	60	11

expected pour point, then at each thermometer reading that is a multiple of 3°C, the test tube was removed from the crushed ice and carefully tilted until it was just enough to ascertain whether there was a movement of the oil in the test tube. The pour point was reached and the temperature was recorded when the biodiesel did not flow when the test tube was tilted horizontally for 5 sec. The pour point is 3°C higher than the thermometer reading.

7.2. Determination of Cloud Point

Cloud point is the temperature, expressed as a multiple of 1°C, at which a cloud or a haze of wax crystals appears at the bottom of the test jar when an oil is cooled under prescribed conditions. The cloud point was determined using ASTM D 2500-66 (Reapproved 1976). The biodiesel sample was half-filled in a test tube. The test tube was tightly closed by the cork carried the thermometer. The sample was immersed in crushed ice (added with some calcium chloride to bring down the temperature to -12°C). The temperature of the biodiesel was cooled to at least 14°C above the approximate cloud point. At each thermometer reading, the test tube was quickly removed without disturbing the oil and the presence of a cloud was observed.

7.3. Determination of Flash Point

Flash point is one of the most important physicochemical properties that establish the potential for fire and explosion of combustible/flammable materials such as fuel [14]. Therefore, the knowledge of flash point is necessary for the handling, storage, and safety of fuels and flammable liquids, and limits the level of unreacted alcohol in the finished fuel. Flash point is related to vapor pressure of a flammable liquid and is defined as the lowest temperature at which it can form a combustion mixture with air. A sample of the biodiesel was first placed in an aluminium container. The biodiesel sample was then heated to 28°C below the temperature of probable flash point (if the probable flash point is 100°C, so the sample is heated to 72°C). Then, the sample continued to be heated. For each successive 2°C, a flame was passed across the center of the container. If a flash does not appear, it means that the sample has not yet reached its flash point. The observed flash point was recorded when a flash appeared at any point on the surface of the oil. The flash point was measured using ASTM D92-78 procedure [14].

Table 3. Physicochemical Properties of WCO

Properties	**Units**	**Experimental values**	**General properties of WCO (Chan et al., 2014)**
Acid value	mg KOH/g	2.62	3.6
Saponification value	mg KOH/g	201.3	207
Mean molecular mass	g/mol	847.1	835
Water content	wt %	0.201	1.9

RESULTS AND DISCUSSION

Physicochemical Properties of WCO

Generally, the quality of an oil is expressed in terms of its physicochemical properties such as acid value, saponification value, and water content. These properties of the feedstock affect not only the biodiesel produced but also the selection of catalyst type and reaction conditions suitable for its transesterification reaction to get the maximum biodiesel yield. The results of physicochemical properties of the WCO are presented in Table 3. It was found that the values of the properties obtained in this study were similar to a previous study [15]. The presence of FFA and water in the feedstock have been reported to have significant effects on the transesterification reaction in the presence of a base catalyst [16, 17]. An oil with a high FFA content of more than 0.5% and a water content of more than 0.3% will result in soap formation. Thus, separation of biodiesel from the reaction mixture becomes difficult, hence lowering the biodiesel yield and quality.

Table 4. Box-Behnken Design of Actual and Predicted Response of Biodiesel Yield

Block	Run	Factor				Response	
		A	B	C	D	Actual	Predicted
Day 1	1	40	2	60	11	25	23
Day 1	2	20	0.25	60	11	9	10
Day 1	3	30	1.125	60	11	35	36
Day 1	4	30	1.125	70	15	37	34
Day 1	5	30	1.125	50	7	23	25
Day 1	6	20	2	60	11	6	7
Day 1	7	40	0.25	60	11	27	25
Day 1	8	30	1.125	70	7	31	32
Day 1	9	30	1.125	50	15	32	31
Day 1	10	30	1.125	60	11	34	36
Day 2	11	30	1.125	60	11	35	33
Day 2	12	20	1.125	60	15	11	9
Day 2	13	30	2	70	11	30	29
Day 2	14	40	1.125	60	7	19	21
Day 2	15	30	0.25	70	11	27	28
Day 2	16	20	1.125	60	7	7	5
Day 2	17	30	0.25	50	11	25	27
Day 2	18	40	1.125	60	15	23	24
Day 2	19	30	1.125	60	11	32	33
Day 2	20	30	2	50	11	20	19
Day 3	21	30	1.125	60	11	34	32
Day 3	22	30	2	60	15	21	24
Day 3	23	20	1.125	70	11	9	9
Day 3	24	40	1.125	50	11	23	22
Day 3	25	40	1.125	70	11	28	29
Day 3	26	30	2	60	7	18	18
Day 3	27	30	0.25	60	7	26	23
Day 3	28	30	0.25	60	15	24	25
Day 3	29	20	1.125	50	11	8	8
Day 3	30	30	1.125	60	11	33	33

Experimental Design and Results

A series of 30 runs of experiments were performed in a randomized order and the experimental yields or responses of each run are tabulated in Table 4. The statistical model developed was used for the prediction and optimization of biodiesel yield. The final equation in terms of coded factors for biodiesel production is shown in Equation 5.

$$\text{Yield} = +\,5.82 + 1.02(A) - 0.18\,(B) + 0.26\,(C) + 0.22(D) + 0.089(AB) + 0.081(AC) - 0.058(AD) + 0.20\,(BC) + 0.13(BD) - 0.087(CD) - 1.56(A^2) - 0.57(B^2) - 0.13(C^2)\ 0.39(D^2) \qquad (5)$$

Selection of Model Analysis

The RSM software generated a series of models which were linear, two factorial interaction (2FI), quadratic, and cubic polynomial that fitted to the response, as well as suggesting the best-fitted model as shown in Table 5. According to the sequential model sum of the square, the best model to fit the response is the quadratic model due to its highest order polynomial (p-value = < 0.0001) with significant of additional terms and the model was not aliased. The suggested model for analysis was determined by the sequential model sum of the square must significant (p-value < 0.05) and insignificant (> 0.05) lack of fit. As reported by a previous report, p-value less than 0.05 indicates the significant model terms [18].

Lack of fit techniques were evaluated to check the adequacy of the models. It should be noted that the lack of fit value should be insignificant for the model to fit well in the experimental design [19].

A significant lack of fit may occur due to the exclusion of several important terms from the model or the presence of large abnormal residuals arising from fitting the model [12]. Interestingly, the lack of fit of the current model was non-significant (p-value > 0.05), as shown in Table 6, suggesting that the model satisfactorily fitted to the experimental data. Furthermore, the model developed also showed a high coefficient determination of (Adj $R^2 = 0.9501$), justifying an excellent correlation between the independent variables. On the other hand, a relatively lower value of the coefficient of variation (CV = 3.22%) was obtained, indicating a high degree of precision and reliability of the model [12].

Table 5. Sequential Model Sum of Squares

Source	**Sum of squares**	**df**	**Mean square**	**F-value**	**p-value, Prob > F**	
Mean	678.26	1	678.26			
Block	0.58	2	0.29			
Linear	14.15	4	3.54	4.28	0.0098	
2FI	0.34	6	0.056	0.051	0.9993	
Quadratic	17.87	4	4.47	72.88	< 0.0001	Suggested
Cubic	0.68	8	0.085	3.71	0.0827	Aliased
Residual	0.12	5	0.023			
Total	712.00	30	23.73			

Table 6. Lack of Fit Test

Source	**Sum of squares**	**df**	**Mean square**	**F-value**	**p-value, Prob > F**	
Linear	18.97	20	0.95	69.47	0.0024	
2FI	18.63	14	1.33	97.48	0.0015	
Quadratic	0.76	10	0.076	5.54	0.0928	Suggested
Cubic	0.074	2	0.037	2.71	0.2124	Aliased
Pure error	0.041	3	0.014			

Analysis of Variance (ANOVA) and Regression Analysis

Statistical analysis of variance was performed to investigate the significance and fitness of the model and the effects of the individual independent variables and their interaction on the response. Based on Table 7, the value of R^2 of 0.9760 indicates that the model fits the experimental data (the closer the R^2 to the unity, the better the model). Daud et al. (2018) reported that the value of R^2 must be > 0.75 to indicate the fitness or suitability of the model. The predicted R^2 of 0.8233 is in reasonable agreement with the adjusted R^2 of 0.9501 as the difference between these two is less than 0.2. The adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. As the adequate precision obtained in this analysis was 18.856, this indicates an adequate signal, thus this model could be used to navigate the design space.

Table 7. The Value of Regression Coefficient

Term	Value
R^2	0.9760
Adjusted R^2	0.9501
Predicted R^2	0.8233
Adequate precision	18.856

The summary of ANOVA for the quadratic model is provided in Table 8. The p-value serves as a tool to check the significance of each coefficient. Always note that the smaller the p-value (probability of error value) and the larger the F-value, the more significant is the parameter reflecting the relative importance of the term attached to that parameter. The p-value less than 0.05 (p-value < 0.05) indicates the significant term while p-value larger than 0.05 (p-value > 0.05) implies the insignificant term toward the corresponding response.

From the ANOVA analysis, as shown in Table 8, it could be observed that the quadratic model was significant as the p-value for the model was < 0.0001 and had a large F-value of 37.70. The lack of fit p-value of 0.0928 (p-value is not significant) implied that the model was fitted to all the data (not significant lack of fit is good). The suitability of the model was also tested using the regression coefficient.

Based on Table 8, all the individual independent variables, which were A (methanol:oil), B (catalyst loading), C (temperature) and D (time), have significant effects on biodiesel yield. Based on the F-value and p-value of the significant model terms, methanol:oil molar ratio has the largest effect on biodiesel yield compared to other parameters. The ranking of the significant terms for individual variables is as follows; methanol:oil > temperature > time > catalyst loading.

In terms of interaction, AB, AC, AD, BC, BD, and CD were found to be insignificant model terms as their p-values were higher than 0.05. The squared terms of the independent variables A^2, B^2, and D^2 showed a significant quadratic effect toward biodiesel yield as the p-values shown in Table 7 are less than 0.05, which are < 0.0001, <0.0001 and 0.0011, respectively. The C^2 term indicates an insignificant term as the p-value is greater than 0.05.

Table 8. ANOVA for Response Surface Quadratic Model

Source	Sum of squares	df	Mean square	F-value	p-value, Prob > F	
Block	0.58	2	0.29			
Model	32.36	14	2.31	37.70	<0.0001	Significant
A-methanol:oil	12.40	1	12.40	202.24	<0.0001	Significant
B-catalyst loading	0.39	1	0.39	6.38	0.0253	Significant
C-temperature	0.78	1	0.78	12.78	0.0034	Significant
D-Time	0.57	1	0.57	9.36	0.0091	Significant
AB	0.031	1	0.031	0.51	0.4869	
AC	0.026	1	0.026	0.43	0.5242	
AD	0.014	1	0.014	0.22	0.6445	
BC	0.16	1	0.16	2.67	0.1263	
BD	0.073	1	0.073	1.19	0.2953	
CD	0.030	1	0.030	0.49	0.4970	
A2	16.75	1	16.75	273.15	<0.0001	Significant
B2	2.23	1	2.23	36.44	<0.0001	Significant
C2	0.11	1	0.11	1.80	0.2022	
D2	1.05	1	1.05	17.20	0.0011	Significant
Residual	0.80	13	0.061			
Lack of fit	0.76	10	0.076	5.54	0.0928	Not significant
Pure error	0.041	3	0.014			
Cor total	33.74	29				

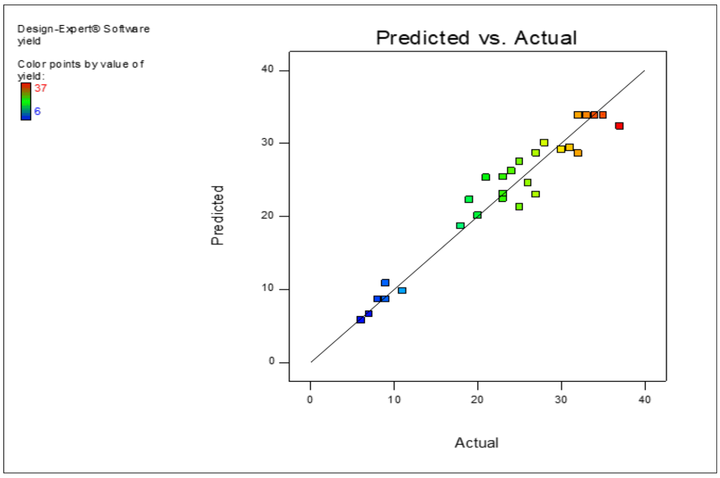

Figure 1. Predicted yield versus actual yield of biodiesel

The adequacy of the reaction model was investigated based on the residuals. Residual is the difference between the observed response and the predicted response, where a good model fitted to experimental data must present low residual values [18, 19]. Figure 1 shows the plot of predicted versus actual biodiesel yields, which verified that the predicted response agreed with the actual or observed data. This result revealed that a linear line was obtained, indicating that this model provided a good approximation to the experimental yields.

Effect of Methanol:Oil Ratio and Catalyst Loading

The interaction effects between methanol:oil ratio and catalyst loading are presented in Figure 2. A strong interaction was observed between methanol:oil ratio and catalyst loading due to the elliptical shape, as shown in Figure 2(b). Based on 3D curved Figure 2(a), with the increase in methanol:oil ratio concerning catalyst loading, the yield of biodiesel was increased. However, further increase of methanol:oil ratio from 35 to 40 approximately resulted in a decrease of yield. Further increase of catalyst loading from 1.3% to 2.0% also led to the decrease of biodiesel yield. Based on the contour plot illustrated in Figure 2(b), maximum yield (30% and above) could be achieved in a specific range of methanol:oil ratio, which was within 30-35; while catalyst loading did not give a specific range, but instead a broad range around 0.6 to 1.65. This result leads to the lower p-value of catalyst loading (B term), which was 0.0253 compared to methanol:oil ratio (A term), which was < 0.000. Thus, catalyst loading showed less sensitivity towards biodiesel yield compared to methanol:oil ratio.

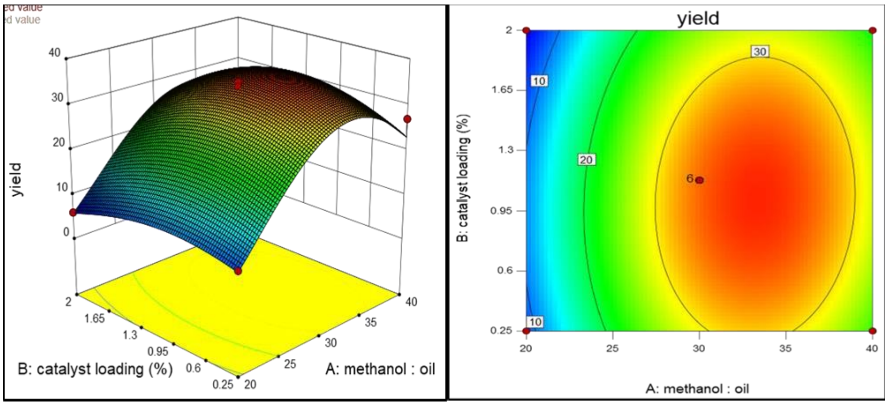

Figure 2. (a) 3D curve of interaction between methanol:oil ratio and catalyst loading on % biodiesel yield at constant reaction temperature = 60ºC, time = 11 h; (b) Contour plot for the interaction between methanol:oil ratio and catalyst loading on % biodiesel yield at constant reaction temperature = 60ºC, time = 11

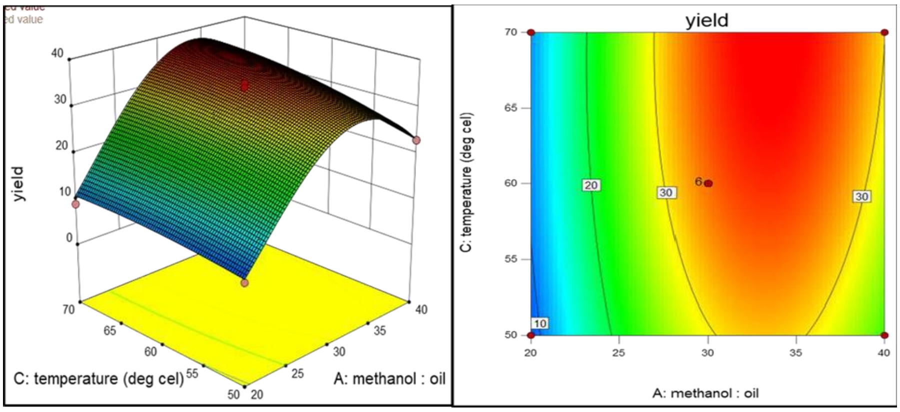

Figure 3. (a) 3D curve of interaction between methanol:oil ratio and temperature on % biodiesel yield at constant catalyst loading = 1.125%, time = 11 h; (b) Contour plot for the interaction between methanol:oil ratio and temperature on % biodiesel yield at constant catalyst loading = 1.125%, time = 11 h

Effect of Catalyst Loading and Temperature

Figure 3 shows the interaction effect of methanol:oil ratio and temperature. Elliptical contour was not observed for this interaction, meaning that methanol:oil ratio and temperature have no significant interaction. The 3D surface response (Figure 3(a) showed that increment of methanol:oil ratio from 20 to 35 increased the biodiesel yield significantly, as the curve observed. But, the 3D surface response curve for temperature was not as obvious as methanol:oil ratio. Again, this situation is proved by comparing the p-values of temperature and methanol:oil ratio. Methanol:oil ratio has a higher p-value compared to temperature, thus it strongly influenced biodiesel yield compared to temperature.

Effect of Methanol:Oil Ratio and Time

Figure 4 demonstrates the relationship between methanol:oil ratio and time. As mentioned in the previous discussion, methanol:oil ratio has the greatest influence on biodiesel yield, as shown in the resulting strong 3D curve. Based on Figure 4(a), an increase in reaction time increased biodiesel yield. The contour diagram shows that biodiesel yield above 30% can be obtained within 9 h to 13 h (red zone) reaction time.

Effect of Catalyst Loading and Temperature

The graphs of dimensional surface and contour plot were plotted for the response of two factors such as catalyst loading and temperature. Figures 5(a) and (b) show the 3D plot and contour plot for the effect of catalyst loading and temperature on the yield of biodiesel. It was observed that the conversion increased with increasing catalyst loading and temperature. Based on the contour plot in Figure 5(b), the high conversion (yield greater than 35%, red zone) was obtained at catalyst loading around 1.10% with a temperature around 65ºC. The biodiesel yield decreased to 30% (yellow zone) at catalyst loading around 1.5% and temperature 58ºC.

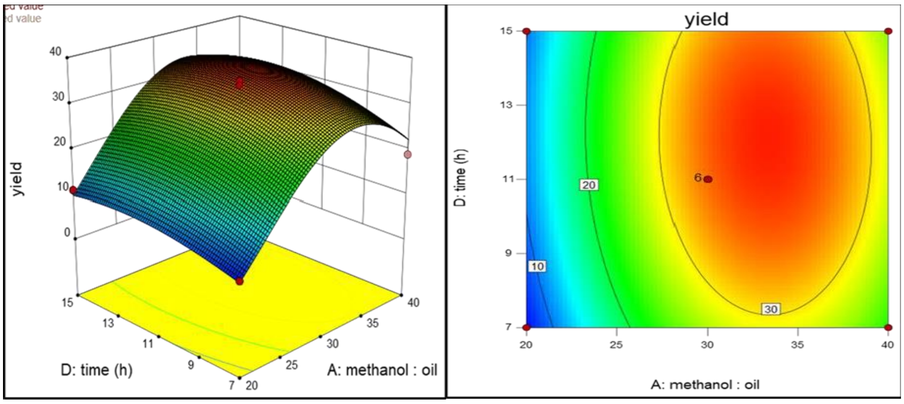

Figure 4. (a) 3D curve of interaction between methanol:oil ratio and time at constant catalyst loading = 1.125%, temperature = 60ºC; (b) contour plot of interaction between methanol:oil ratio and time at constant catalyst loading = 1.125%, temperature = 60ºC

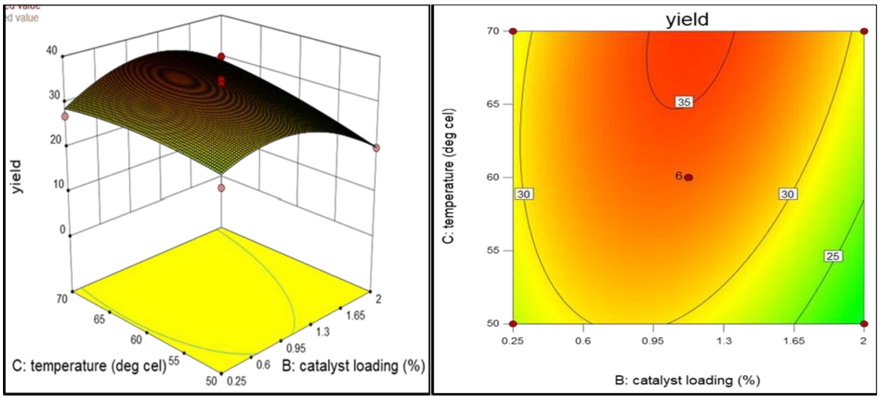

Figure 5. (a) 3D curve of interaction between catalyst loading and temperature at constant methanol:oil ratio = 30:1 and time = 11 h; (b) contour plot of interaction between catalyst loading and temperature at constant methanol:oil ratio = 30:1 and time = 11 h

Physicochemical Properties of Synthesized Biodiesel Fuel

Biodiesel is one of the promising candidates to substitute petroleum-based fuel in the near future due to its renewability and environmentally friendly behaviors. The physical and chemical properties of biodiesel fuel play an important role to determine its quality for the successful international trade in biofuels for transport. Therefore, it is essential to produce biodiesel with physical and chemical properties similar to those prescribed by the international standard specifications to ensure the safe and satisfactory diesel engine operation. The properties of biodiesel may vary from country, depending on the type of feedstock available for biodiesel production. Several countries have adopted their own standard specifications for biodiesel to ensure its quality, such as Austria fuel standard specification (ON C1191) and Czech Republic fuel standard specification (CSN 6507).

The properties of the biodiesel obtained from the WCO via transesterification reactions at the optimized reaction conditions along with the standard specifications of the American Standards for Testing and Materials (ASTM D-6751) and European Standards (EN 14214) are summarized in Table 9. Flash point (FP) is the lowest ignition temperature of volatile fuel vapors when exposed to an ignition source. According to the ASTM standards, biodiesel possesses a higher flash point than conventional petro-diesel, which signifies that biodiesel has better safety aspects in storage and transit when compared to petro-diesel [20]. The FP of the WCO biodiesel was found to be 185°C. Cloud point (CP) is the lowest possible temperature at which wax crystals are visible and cloudy. CP of biodiesel fuel also varies according to the type and fatty acid composition of the feedstocks [20]. The CP of the WCO biodiesel was found to be 9.9°C. Pour point (PP) is the minimum temperature at which a fuel loses its flow characteristics and this fuel needs to have a high pour point value to be suitably used in cold flow operation [20]. The PP of the WCO biodiesel was found to be 17°C.

As known biodiesel properties are very similar to petroleum-based diesel, it has immense potential to replace petroleum-based diesel without any modification in the diesel engine. Thus, it can be said that the WCO used in this study has the potential to be used in large scale biodiesel production using a suitable catalyst system based on the properties shown in Table 9. However, further analysis of physicochemical properties such as cetane number, calorific value, and % mass of triglycerides must be done on the synthesized biodiesel to ensure the reliability of the biodiesel.

Table 9. Physicochemical Properties of Synthesized Biodiesel compared to others studies

Properties	Units	ASTM D-6751	EN 14214	Synthesized Biodiesel	Vafakish and Barrari (2017)	Marinkovic et al., (2016)	Shohaimi and Marodzi (2017)
Acid value	mg KOH/g	≤0.5	<0.5	0.17	0.30	0.12	0.81
Moisture content	%	<0.05	<0.05	0.03	0.22	0.06	0.35
Flash point	ºC	>120	100-170	185	160	168	172
Pour point	ºC	Not specified	Not specified	17	15	17	14
Cloud point	ºC	Not specified	Not specified	9.9	7.6	8.2	6.3

CONCLUSION

The RSM results indicated that the Mg-Al LDH catalyst provides the best biodiesel yield (37.45%) at the optimum conditions of methanol to oil ratio of 34.6:1, reaction temperature of 68.4ºC, the reaction time of 11.9 h, and catalyst loading of 1.125 wt%. These optimal values may be attributed to the presence of the most optimal strength of the catalytic active sites for the transesterification reactions in the WCO. The fuel properties of the prepared biodiesel have been found to comply with the ASTM and EN standard specifications, which were acid value of 0.17 mg KOH/g, moisture content of 0.03%, flash point of 185ºC, pour point of 17ºC, and cloud point of 9.9ºC.

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