

The Production and Optimization of Biodiesel From Microalgae Utilizing Banana Peel Ash As A Catalyst: Employing Response Surface Methodology (RSM) For Optimization

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Abstract

Dispute over the impact of biodiesel production on food security makes the use of crops and food producing plants not sustainable. Biodiesel is produced by the chemical reaction of vegetable oil or animal fat with an alcohol in the presence of either homogenous or heterogenous catalyst. However, using a homogeneous catalyst for biodiesel production is recently considered unsustainable by industries due to its single use, slow reaction rate and saponification issues due to the presence of fatty acids in the feedstock. The potential of banana peel ash as a suitable catalyst for conversion of microalgae oil to fatty acid methyl ester (FAME) in a transesterification reaction was investigated in this research. The FAME was produced through transesterification reaction. Optimization of the transesterification of microalgae oil was achieved by a four-factorial central composite design (CCD), a tool in response surface methodology (RSM) in 30 experimental runs. A second-order model was obtained to predict the biodiesel yield and free fatty acid content (FFA) as a function of the process variables. The model can be successfully employed in the biodiesel industry to maximize the yield, oxidation stability and minimize FFA of methyl esters. Based on ANOVA, the methanol to oil ratio, catalyst concentration, reaction time, and agitation speed had a significant effect on biodiesel yield and FFA. Biodiesel yield of 88.85% and FFA of 0.0068 wt.% were achieved at an optimum condition of methanol to oil ratio of 9:1 using calcined banana ash at 2.25 wt.% as catalyst and 1000 rpm agitation speed for 120 min at 60°C temperature. XRF analysis revealed that the catalytic action of banana peels was because of the potassium and calcium content when calcined at 700°C. The physicochemical properties of the microalgae oil were found to be as follows; saponification value (SV) = 310.55 mgKOH/g, peroxide value (PV) = 175.2 mgKOH/g, acid value (AV) = 2.1 mgKOH/g, iodine value (IV) = 106.45gI₂/100g, specific gravity = 0.9248, free fatty acid (FFA) = 1.05 wt.%, while those of the produced biodiesel were found to be in conformity with ASTM D6751 standards as follows; specific gravity of 0.8475, flash point of 132°C, kinematic viscosity@40°C of 4.79 cst, sulfur content of 0.0015 wt.%, diesel index of 59.2, cloud point of +2.2, initial boiling point (IBP) of 115°C, final boiling point (FBP) of 369°C. The presence of methyl ester groups in the produced biodiesel was confirmed using gas chromatography (GC). Thus, banana peel ash can be used as a green catalyst for low-cost production of biodiesel from microalgae on the industrial scale.

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I. Introduction

Global energy consumption is projected to more than double by 2050, reaching 30 Terawatts, and triple by the end of the century, reaching 46 Terawatts (Nabora et al., 2019). Additionally, the volatility of petroleum product prices further emphasizes the need for alternative energy sources. Biofuel derived from renewable resources has garnered international attention as a potential solution to global energy security issues. Biodiesel, for instance, has been promoted as a viable alternative to petroleum-based fuels due to its renewability, biodegradability, and positive environmental impact (Gimbin et al., 2013). To address energy and environmental concerns, it becomes imperative to explore stringent renewable energy sources such as plant biomass, which emits no greenhouse gases (Madvar et al., 2019). Both edible and non-edible sources can be utilized to obtain these renewable energy supplies.

The predominant method used for biodiesel production relies on homogeneous catalysts in the transesterification reaction. Nonetheless, this approach presents various drawbacks, such as environmental harm due to the discharge of alkaline wastewater. Additionally, the complexity of the synthesis process and the challenges associated with large-scale implementation hinder its practical applications (Marinković et al., 2016).

A growing body of research suggests the utilization of heterogeneous catalysts in the transesterification process of biodiesel production as an alternative to homogeneous catalysts. Heterogeneous catalysts provide numerous advantages, including non-corrosiveness, environmental friendliness, and the ability to enhance biodiesel yield (Goli & Sahu, 2018). Moreover, waste materials such as rice husk, eggshell, banana peels, and construction debris can serve as viable sources for producing heterogeneous catalysts (Wang et al., 2018).

II. Materials and Methods

2.1 Microalgae Classification and Characterization

The microalgae species used in this study was identified using the Edmondson (1959) and van Vuuren (2006) method. The oil extraction process was carried out using a Soxhlet apparatus, with n-hexane employed as the solvent. The extracted microalgae oil was subjected to various analytical characterizations, including the determination of free fatty acid (FFA) content, acid value (AV), saponification value (SV), iodine value (IV), specific gravity, pH value, and peroxide value. These analytical tests were conducted to assess the quality and properties of the microalgae oil for further biodiesel production and evaluation.

2.2 Banana Peels Ash Preparation

The process for preparing calcined banana ash (CBA) is outlined in Figure 1, as described by Gohain et al. (2017). Initially, ripe banana peels were cut into small pieces to facilitate the drying process. These pieces were then subjected to sun drying for a period of 7 days after being washed with distilled water. Subsequently, the dried banana peels were further dried in an oven for 6 hours at a temperature of 80°C.

Once thoroughly dried, the banana peels were subjected to ashing at a temperature of 700°C using an airtight Box Muffle Furnace. The resulting ash was then milled and sieved to obtain a fine powder. Finally, the calcined banana ash (CBA) was crushed and stored in a container for XRF (X-ray fluorescence) analysis.

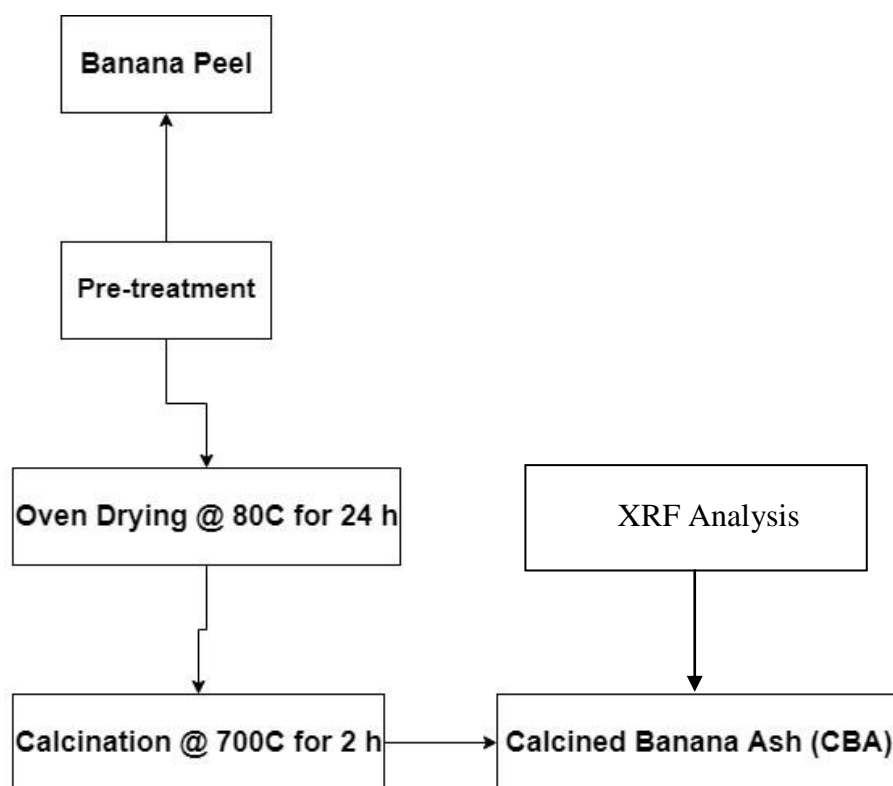


Figure 1: Block Diagram for Catalyst Preparation from Banana Peel

2.3 Production of Microalgae Biodiesel

The production processes for biodiesel, as illustrated in Figure 2 (Jitjamnong et al., 2020), involve six stages:

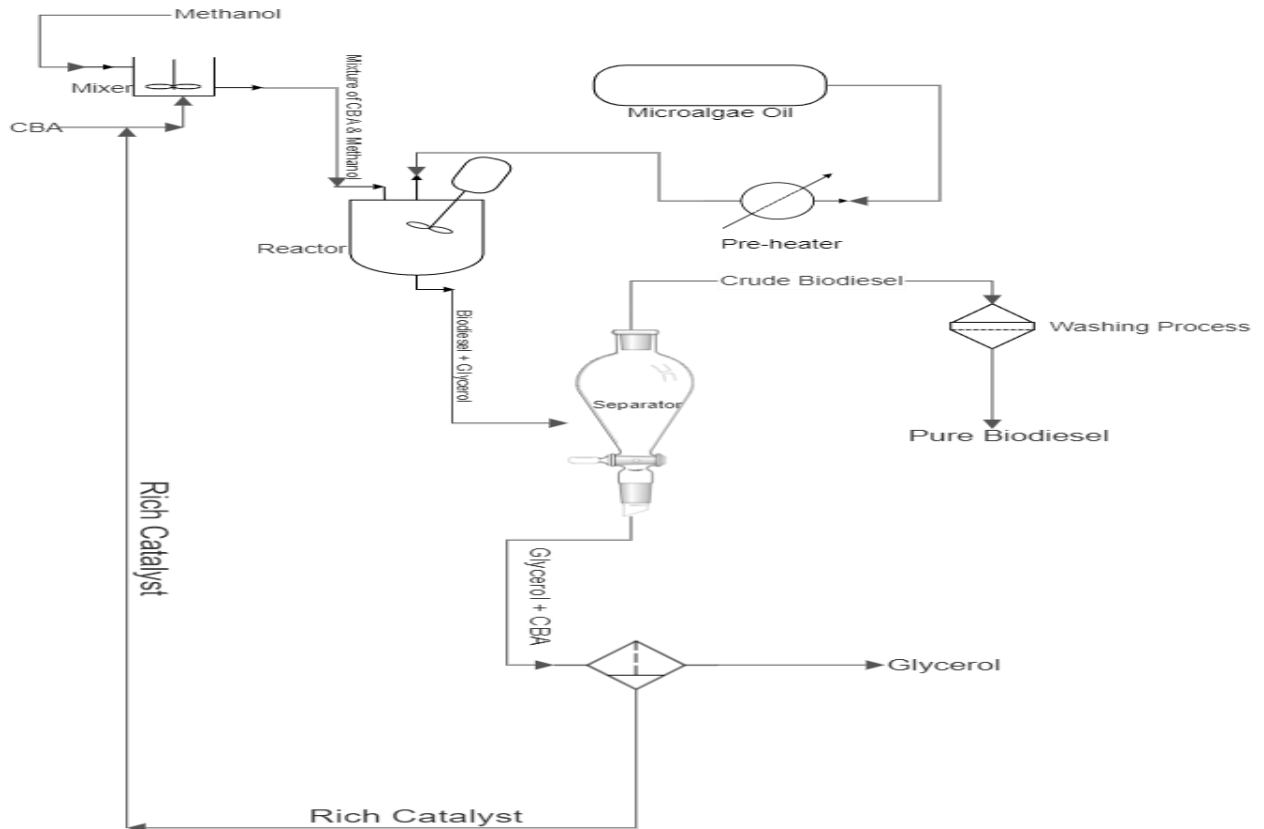


Figure 2: Process Flow Diagram for Biodiesel Production

1. Dispersion of Catalyst: The calcined banana ash (CBA), which acts as the heterogeneous catalyst, was dispersed in methanol. This step ensured proper mixing of the catalyst with the alcohol.
2. Transesterification Reaction: The mixture of calcined banana ash (CBA) and methanol was then combined with the pre-treated oil. The transesterification reaction took place, converting the triglycerides present in the oil into biodiesel and glycerol.
3. Phase Separation: After the transesterification reaction, the mixture was allowed to undergo phase separation. This separation resulted in the formation of three distinct layers, with biodiesel accumulating on the top, glycerol at the middle and catalyst settling at the bottom.
4. Washing: The biodiesel layer underwent a washing process to remove impurities and residues. This step is crucial for achieving high-quality biodiesel with improved purity.
5. Drying: Following the washing process, the biodiesel was dried to remove residual moisture. This step ensures the stability and longevity of the biodiesel.
6. Phase Separation of Glycerol and Heterogeneous Catalyst: The final stage involved separating the glycerol and the heterogeneous catalyst from the biodiesel. This separation allowed for the recovery and reuse of the catalyst while obtaining purified glycerol as a byproduct.

Biodiesel produced yield was calculated from equation (1), FFA using equation (2) and oxidation stability using EN 15751:2009 method (Indhumathi et al., 2014).

$$\text{Biodiesel Yield (\%)} = \frac{\text{weight of biodiesel produced}}{\text{weight of microalgae used}} * 100 \quad - \quad - \quad - \quad (1)$$

$$\text{(\%)}\text{FFA} = \frac{\text{biodiesel acid value}}{2} \quad - \quad - \quad - \quad (2)$$

2.4 Biodiesel characterization

Fatty acid methyl esters compositions were determined by gas chromatographic analysis using Agilent 6890 gas chromatograph unit equipped with FID. The important properties of the biodiesel produced were determined and compared with biodiesel standards (ASTM D6751).

2.5 Design of Experiment

2-levels 4 factors were considered in this research as shown in Table 1.

Table 1: 2 – Level – 4– Factor Experimental Design Plan

| Factor Level | Unit | Coded Variable | -1 | +1 |
|-----------------------|-------------|----------------|-----|------|
| Methanol to Oil ratio | molar ratio | x1 | 9:1 | 17:1 |
| Catalyst amount | wt.% | x2 | 0.5 | 5.0 |
| Time | min | x3 | 30 | 120 |
| Agitation speed | rpm | x4 | 200 | 1000 |

III. Results and Discussion

3.1 Microalgae Oil Analysis

The dried microalgae used in the study exhibited a lipid content of 10.63%. Previous research has reported varying lipid contents for different microalgae species. For instance, *Microspora* sp. has been found to contain lipid contents ranging from 12.0% to 23.0% on a dry weight basis (Abomohra et al., 2013; Kumar et al., 2015). Similarly, *Oedogonium* has been reported to have lipid contents ranging from 6.5% to 22.6% on a dry weight basis (Khan et al., 2018; Schultz-Jensen et al., 2013).

It is important to acknowledge that the lipid content and oil yield of microalgae can vary significantly due to factors such as the specific strain of microalgae, cultivation conditions (e.g., nutrient availability, light intensity, temperature), and harvesting methods employed. These variations highlight the need for careful selection and optimization of microalgae species and cultivation parameters to achieve optimal lipid production for biodiesel production.

The properties of microalgae oil were determined in accordance with the ASTM and EN 14214 standards as shown in Table 2.

Table 2: Physicochemical Properties of Microalgae Oil

| Parameter | Value | Value from Literature | Reference |
|-----------------------|------------------------------|-----------------------|-------------------------|
| Saponification value | 310.55 mgKOH/g | 200 | (Ikechukwu, 2013) |
| Peroxide value | 175.2 mgKOH/g | 1.1 | (Kaur et al., 2021c) |
| Free fatty acid (FFA) | 1.05 wt.% | 0.468 – 7.14 | (Larida & Bañaga, 2021) |
| Acid value | 2.1 mgKOH/g | 1.9 | (Ikechukwu, 2013) |
| Specific gravity | 0.9248 | 0.892 | (Yuvarani et al., 2017) |
| Iodine value | 106.45 gI ₂ /100g | 102.45 | (Kaur et al., 2021) |
| pH value | 4.8 | 5.2 | (Yusuff, 2019) |

In accordance with EN 14214 (Annex B)

3.2 Catalyst characterization

K₂O concentration in calcined banana ash was found to be dominant with 47 wt.%, SiO concentration of 10.4 wt.%, CaO concentration of 8.55 wt.%, Na₂O concentration of 5.61 wt.%, BaO concentration of 0.201 wt.%, and MgO concentration of 3.21 wt.% as shown in Table 3 based on XRF (X-ray fluorescence) characterisation.

Table 3: Compositions and their abundance from the CBA

| Composition | Abundance (wt.%) |
|--------------------------------|------------------|
| Na ₂ O | 5.61 |
| MgO | 3.23 |
| Al ₂ O ₃ | 1.46 |
| SiO ₂ | 10.4 |
| P ₂ O ₅ | 3.62 |
| K ₂ O | 47.00 |
| CaO | 8.55 |

| | |
|--------------------------------|-------|
| Fe ₂ O ₃ | 0.33 |
| MnO | 0.06 |
| Elemental species | 17.92 |
| Loss of ignition | 1.82 |
| Total | 100 |

3.3 Microalgae FAME Physicochemical Properties

Some physicochemical properties of the resulting biodiesel have been determined as presented in Table 4.

Table 4: Biodiesel properties and Method of Analysis Adopted

| Property | Test method | Unit | Specification | Experimental result |
|---|---------------|---------|---------------|---------------------|
| Specific Gravity @60°F | ASTM D1298 | - | 0.820 min | 0.8475 |
| Flash Point, Pensky Martens | ASTM D93 | °C | 130 min | 132 |
| Water and sediment | D 2709 | vol.% | 0.050 max | - |
| Kinematic viscosity @40°C | D 445 | Cst | 1.9 – 6.0 | 4.79 |
| Sulfur | D 5453 | wt.% | 0.05 max | 0.0015 |
| Copper strip corrosion | D 130 | 100°C | No. 3 max | No. 1 |
| Diesel Index | ASTM D6890 | | 47 min | 59.22 |
| Cloud point | D 2500 | °C | +4 max | +2.2 |
| Carbon residue (100% sample) | D 4530 | wt.% | 0.050 max | - |
| Acid number | D 664 | mgKOH/g | 0.80 max | 0.21 |
| Free glycerine | D 6584 | wt.% | 0.020 max | - |
| Total glycerine | D 6584 | wt.% | 0.240 max | - |
| DISTILLATION-IBP | ASTM D86 | °C | REPORT | 115 |
| RECOVERED@357°C | ASTM D86 | °C | 90 min | 94 |
| DISTILLATION FBP | ASTM D86 | °C | 385 max | 369 |
| Distillation temperature at 90% recovered | D86 | °C | 360 max | 342 |
| Oxidation Stability | EN 15751:2009 | h | 6 min | 18 |
| Total Acid Number | ASTM D664 | mgKOH/g | 0.50 max | 0.15 |
| Aniline Point | ASTM D611 | °C | Report | 75 |

3.4 Modelling and Optimization of Biodiesel Production from Microalgae

From the experimental results presented in Table 5, it was observed that the maximum and minimum yield, oxidation stability and free fatty acid were 95.11% and 66.0%, 1050 min and 145 min, 0.11% and 0.05%, respectively.

Table 5: Experimental Results for the Central Composite Design Matrix for Biodiesel Production using CBA as Catalyst

| Std | Run | Space Type | A: Methanol to Oil ratio | Factors | | | Responses | |
|-----|-----|------------|--------------------------|--------------------|------------------|--------------------|-----------|-------|
| | | | | B: Catalyst Amount | C: Reaction Time | D: Agitation Speed | Yield | FFA |
| | | | (wt.%) | (min) | (rpm) | % | % | |
| 19 | 1 | Axial | 13 | 0.5 | 75 | 600 | 76.9 | 0.07 |
| 13 | 2 | Factorial | 9 | 0.5 | 120 | 1000 | 70.82 | 0.06 |
| 9 | 3 | Factorial | 9 | 0.5 | 30 | 1000 | 73.48 | 0.08 |
| 28 | 4 | Center | 13 | 2.75 | 75 | 600 | 91.92 | 0.02 |
| 29 | 5 | Center | 13 | 2.75 | 75 | 600 | 92 | 0.02 |
| 30 | 6 | Center | 13 | 2.75 | 75 | 600 | 91.91 | 0.02 |
| 10 | 7 | Factorial | 17 | 0.5 | 30 | 1000 | 90.11 | 0.06 |
| 17 | 8 | Axial | 9 | 2.75 | 75 | 600 | 88.98 | 0.04 |
| 14 | 9 | Factorial | 17 | 0.5 | 120 | 1000 | 83.95 | 0.088 |
| 15 | 10 | Factorial | 9 | 5 | 120 | 1000 | 91.68 | 0.03 |

| | | | | | | | | |
|----|----|-----------|----|------|-----|------|-------|-------|
| 26 | 11 | Center | 13 | 2.75 | 75 | 600 | 91.21 | 0.02 |
| 16 | 12 | Factorial | 17 | 5 | 120 | 1000 | 87.92 | 0.06 |
| 7 | 13 | Factorial | 9 | 5 | 120 | 200 | 86.7 | 0.06 |
| 4 | 14 | Factorial | 17 | 5 | 30 | 200 | 74.16 | 0.03 |
| 6 | 15 | Factorial | 17 | 0.5 | 120 | 200 | 80.04 | 0.05 |
| 2 | 16 | Factorial | 17 | 0.5 | 30 | 200 | 85.01 | 0.019 |
| 21 | 17 | Axial | 13 | 2.75 | 30 | 600 | 91.11 | 0.028 |
| 25 | 18 | Center | 13 | 2.75 | 75 | 600 | 92.11 | 0.02 |
| 23 | 19 | Axial | 13 | 2.75 | 75 | 200 | 90.1 | 0.017 |
| 8 | 20 | Factorial | 17 | 5 | 120 | 200 | 82.73 | 0.02 |
| 20 | 21 | Axial | 13 | 5 | 75 | 600 | 82.52 | 0.06 |
| 3 | 22 | Factorial | 9 | 5 | 30 | 200 | 78.43 | 0.11 |
| 1 | 23 | Factorial | 9 | 0.5 | 30 | 200 | 69 | 0.11 |
| 5 | 24 | Factorial | 9 | 0.5 | 120 | 200 | 66 | 0.09 |
| 22 | 25 | Axial | 13 | 2.75 | 120 | 600 | 92.91 | 0.01 |
| 11 | 26 | Factorial | 9 | 5 | 30 | 1000 | 82.63 | 0.1 |
| 12 | 27 | Factorial | 17 | 5 | 30 | 1000 | 77.98 | 0.08 |
| 27 | 28 | Center | 13 | 2.75 | 75 | 600 | 92.01 | 0.02 |
| 24 | 29 | Axial | 13 | 2.75 | 75 | 1000 | 95.11 | 0.02 |
| 18 | 30 | Axial | 17 | 2.75 | 75 | 600 | 95 | 0.005 |

3.5 Analysis of variance for the response surface model

3.5.1 Response 1: Yield

From the ANOVA table, the model terms methanol to oil ratio, catalyst concentration, reaction time, agitation speed, interaction between methanol to oil ratio and catalyst concentration, catalyst concentration and reaction time are significant and quadratic effect of catalyst amount are significant model terms while interaction between methanol to oil ratio and reaction time, quadratic effect of agitation speed are not significant model terms.

Table 6: Analysis of Variance for the Response Surface Model for Yield

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|-------------------------|----------------|----|-------------|---------|----------|-----------------|
| Model | 1970.02 | 7 | 281.43 | 894.34 | < 0.0001 | Significant |
| A-Methanol to Oil ratio | 134.37 | 1 | 134.37 | 427.01 | < 0.0001 | |
| B-Catalyst amount | 135.80 | 1 | 135.80 | 431.53 | < 0.0001 | |
| C-Reaction time | 24.13 | 1 | 24.13 | 76.67 | < 0.0001 | |
| D-Agitation speed | 95.73 | 1 | 95.73 | 304.20 | < 0.0001 | |
| AB | 365.38 | 1 | 365.38 | 1161.12 | < 0.0001 | |
| BC | 173.05 | 1 | 173.05 | 549.93 | < 0.0001 | |
| B ² | 1041.56 | 1 | 1041.56 | 3309.88 | < 0.0001 | |
| Residual | 6.92 | 22 | 0.3147 | | | |
| Lack of Fit | 6.39 | 17 | 0.3759 | 3.52 | 0.0844 | Not significant |
| Pure Error | 0.5332 | 5 | 0.1066 | | | |
| Cor Total | 1976.94 | 29 | | | | |

After polishing the model by removing the less significant terms (quadratic term of D and interaction between A and C), the new result showed that all the regression coefficients are now significant.

Table 7: Comparing Regression Models by Backward Elimination of less Significant Terms

| Model | Number of Parameters | R ² | Adjusted R ² | p-value |
|---|----------------------|----------------|-------------------------|---------|
| Yield = 91.95 + 2.73A + 2.75B + 1.16C + 2.31D - 4.78AB - 0.2675AC + 3.29BC - 12.39B ² + 0.5037D ² | 9 | 0.9975 | 0.9964 | 0.0001 |
| Yield = 92.03 + 2.73A + 2.75B + 1.16C + 2.31D - 4.78AB + 3.29BC - 12.03B ² | 7 | 0.9965 | 0.9954 | 0.0001 |

The coefficient estimate shows the anticipated change in response for each unit change in factor value when the other factors were held constant. The intercept in an orthogonal design is the overall average response of all the runs. Based on the factor settings, the coefficients modify the average around it. The modified equation can be used to make predictions about the response for given levels of each factor.

3.5.2 Effect of methanol to oil ratio, catalyst amount, and reaction time on biodiesel yield

Reference to Figure 3a, the yield increases with both methanol to oil ratio and catalyst concentration. However, both methanol to oil ratio and catalyst concentration has a strong effect on the yield, this can as well be link to the modified regression equation that given a unit shift in both methanol to oil ratio and catalyst amount holding other variables constant, the yield increases on average of 2.73% and 2.75% respectively. Because these factors have positive influences on the reaction, Figure 3b reveals that the maximum FAME yield greater than 90% was attained when the methanol to oil ratio and catalyst amount were increased to 17:1 and 2.75 wt.%, respectively as reported by Mathiyazhagan & Ganapathi (2011), the transesterification reaction requires 3 mol of alcohol for one mol of triglycerides to produce three mol of fatty acid ester and one mol of glycerol. Excess amount of alcohol increases conversion of fats into esters thereby increasing the biodiesel yield to a certain point. However, further increasing the amount of alcohol does not affect the yield positively rather it reduces it in addition to the increase in the cost of alcohol recovery. In addition to this the ratio of alcohol to oil may vary with catalyst used. However, because the quadratic term has a negative sign, an increase in the values of the variables beyond a particular range result in a slight decreased in FAME yield. As Santos *et al.* (2014) observed, the increase in reaction rate for triglyceride conversion to FAME was due to an increase in the number of active sites; however, an excess of catalyst can disrupt the oil-methanol-catalyst mixture and cause a phase separation, which inhibits the reaction due to diffusion.

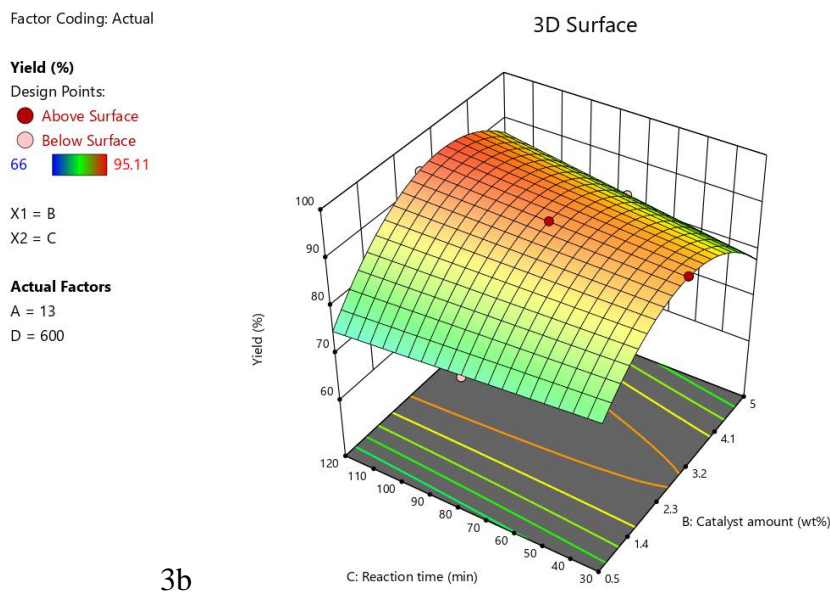
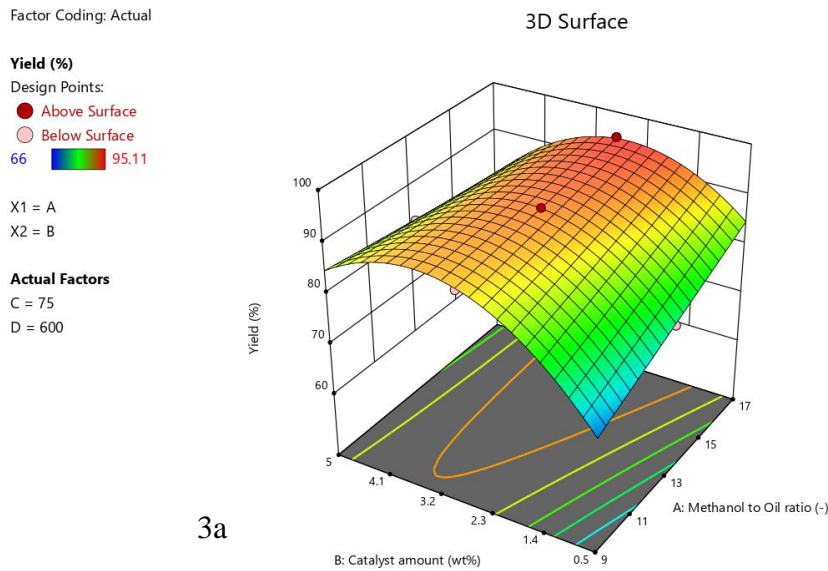


Figure 3: Effect of Methanol to Oil Ratio, Catalyst Amount, and reaction Time on Biodiesel Yield

3.5.3 ANOVA for reduced quadratic model for FFA

Table 8 presents the sources of variation and their corresponding sums of squares, degrees of freedom, mean squares, F-values, and p-values. The model has been found to be significant at a high confidence level, indicating that it is a good fit for the data. The factors A (Methanol to Oil ratio), C (Reaction time), AD, B², AC, BC, D (Agitation speed), and B (Catalyst amount) all have significant effects on the response variable FFA. However, the Lack of Fit test is not significant, which indicates that the model is adequate and that there is no need to add further terms. Overall, the results suggest that the use of banana peel as a catalyst in the production of biodiesel from microalgae has a significant impact on reducing the levels of free fatty acids in the final product.

Table 8: Analysis of Variance for the Response Surface Model for FFA

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|-------------------------|----------------|----|-------------|---------|----------|-----------------|
| Model | 0.0288 | 8 | 0.0036 | 210.25 | < 0.0001 | Significant |
| A-Methanol to Oil ratio | 0.0040 | 1 | 0.0040 | 232.76 | < 0.0001 | |
| B-Catalyst amount | 0.0003 | 1 | 0.0003 | 19.21 | 0.0003 | |
| C-Reaction time | 0.0012 | 1 | 0.0012 | 71.95 | < 0.0001 | |
| D-Agitation speed | 0.0003 | 1 | 0.0003 | 16.80 | 0.0005 | |
| AC | 0.0022 | 1 | 0.0022 | 130.23 | < 0.0001 | |
| AD | 0.0045 | 1 | 0.0045 | 263.81 | < 0.0001 | |
| BC | 0.0018 | 1 | 0.0018 | 104.13 | < 0.0001 | |
| B ² | 0.0145 | 1 | 0.0145 | 843.15 | < 0.0001 | |
| Residual | 0.0004 | 21 | 0.0000 | | | |
| Lack of Fit | 0.0003 | 16 | 0.0000 | 0.8493 | 0.6371 | not significant |
| Pure Error | 0.0001 | 5 | 0.0000 | | | |
| Cor Total | 0.0292 | 29 | | | | |

3.5.4 Reduced Model for Natural Variables

FFA = 0.273358 – 0.014949 × Methanol to Oil ratio – 0.042755 × Catalyst amount – 0.000750 × Reaction time – 0.000127 × Agitation speed + 0.000066 × Methanol to oil ratio × Reaction time + 0.000011 × Methanol to oil ratio × Agitation speed – 0.000104 × Catalyst amount × Reaction time + 0.008966 × Catalyst amount².

The coefficient of methanol to oil ratio is negative, indicating that increasing this ratio will decrease the FFA yield. This makes sense, as higher methanol concentrations can lead to excess methanol reacting with the oil instead of converting the fatty acids into methyl esters. The coefficient of catalyst amount is also negative, meaning that increasing the amount of catalyst will decrease the FFA yield. This suggests that too much catalyst can overreact with the oil, reducing the number of fatty acids that can be converted into methyl esters. The coefficient of reaction time is negative, indicating that longer reaction times can decrease the FFA yield. This may be due to the breakdown of the fatty acids over time, leading to lower yields of methyl esters. The coefficient of agitation speed is also negative, meaning that higher agitation speeds can reduce the FFA yield. This could be due to increased mixing causing more of the fatty acids to react with excess methanol or the catalyst instead of being converted to methyl esters. The two positive coefficients involving the methanol to oil ratio suggest that the relationship between this variable and FFA yield is not straightforward. The effect of the ratio may depend on other factors, such as reaction time or agitation speed. Overall, the equation provides a useful tool for predicting the FFA yield based on various factors in the biodiesel production process. It highlights the importance of carefully controlling these variables to optimize the conversion of fatty acids to methyl esters. The model can predict experimental results with 98.8% confidence with only 8.72% variation in the data as shown by the R² and coefficient of variation (CV) in Table 9. Also, 50.168 signal to noise ratio indicate an adequate signal, the difference between the predicted and adjusted R² as shown in Table 9 is within the recommended value of less than 0.2 (Anderson & Whitcomb, 2007).

Table 9: Statistical Analysis Results of FFA

| | | | |
|------------------|--------|--------------------------------|---------|
| Std. Dev. | 0.0041 | R² | 0.9877 |
| Mean | 0.0475 | Adjusted R² | 0.9830 |
| C.V. % | 8.72 | Predicted R² | 0.9683 |
| | | Adeq Precision | 50.1677 |

From Table 10, it can be concluded that interaction between methanol to oil ratio and reaction time, interaction between methanol to oil ratio and agitation speed and quadratic effect of catalyst amount were most effective in increasing the responses while the rest of the model terms affect the response negatively.

Table 10: Table of Effect of Variable on FFA

| Factor | Estimated Effect |
|---|------------------|
| Methanol to oil ratio | -0.014949 |
| Catalyst amount | -0.042755 |
| Reaction time | -0.000750 |
| Agitation speed | -0.000127 |
| Methanol to oil ratio × Reaction time | +0.000066 |
| Methanol to oil ratio × Agitation speed | +0.000011 |
| Catalyst amount × Reaction time | -0.000104 |
| Quadratic effect of Catalyst amount | +0.008966 |

3.5.5 Effect of Methanol to Oil Ratio and Reaction Time on FFA

Figure 4 shows that as the methanol to oil ratio increases from 9:1 to 17:1, the FFA percent decreases slightly i.e., from 0.07497 to 0.04679% because as more methanol is used as a reactant in the transesterification reaction, the contact between FFA in the oil and methanol becomes stronger. This demonstrates that the ratio of methanol to oil has an antagonistic influence on FFA. This is in line with the findings of Santya *et al.* (2019). Which revealed that the FFA% decreases as the volume percentage of methanol to oil increases, this phenomenon is due to the interaction between FFA in the oil and methanol is enhanced as more methanol is added as the reactant in the transesterification reaction. Increase in reaction time has little or no effect on FFA however, a more significant decrease in FFA is observed as reaction time increases with a corresponding increase in methanol to oil ratio.

Factor Coding: Actual

FFA (%)

Design Points:

● Above Surface
○ Below Surface
0.005  0.11

X1 = A

X2 = C

Actual Factors

B = 2.75

D = 600

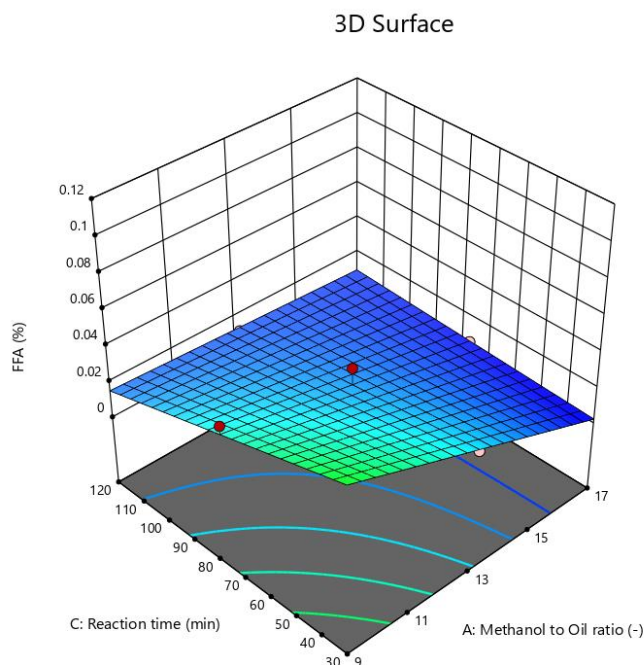


Figure 4: Effect of Methanol to Oil Ratio and Reaction Time on FFA

IV. Conclusions

Biodiesel from microalgae was successfully produced using calcined banana peel ash as a catalyst by transesterification reaction. Optimization of process variables affecting biodiesel yield and free fatty acid was achieved using 30 experimental runs through Central Composite Design (CCD) of Response Surface Methodology (RSM). Investigation of the physicochemical parameters of the produced biodiesel revealed that it is in conformity with ASTM D-6751 standards. Extraction and characterization of the microalgae oil was done using standard methods and found to have a free fatty acid (FFA) of 1.05 wt.%, acid value of 2.1 mgKOH/g, specific gravity of 0.9248 and a pH value of 4.8. A second-order model was obtained to predict the biodiesel yield and free fatty acid (FFA) as a function of process variables. The model can be successfully employed in

the biodiesel industry to maximize the yield and minimize of methyl esters. Based on ANOVA results, the methanol to oil ratio, catalyst concentration, reaction time, and agitation speed had a significant effect on biodiesel yield and FFA. An optimum biodiesel yield of 88.85% and FFA of 0.0068 wt.% was achieved with methanol to oil ratio of 9:1 using calcined banana peel of 2.25 wt.% as catalyst and 1000 rpm agitation speed for 120 min at 60°C temperature.

Data Availability

The raw data as well as the processed data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest related to this research study.

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