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Biodiesel Production from Waste Cooking Oil Using Extracted Catalyst from Plantain Banana Stem via RSM and ANN Optimization for Sustainable Development

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Abstract: Biodiesel is a promising sector worldwide and is experiencing significant and rapid growth. Several studies have been undertaken to utilize homogeneous base catalysts in the form of KOH to develop biodiesel in order to establish a commercially viable and sustainable biodiesel industry. This research centers around extracting potassium hydroxide (KOH) from banana trunks and employing it in the transesterification reaction to generate biodiesel from waste cooking oil (WCO). Various operational factors were analyzed for their relative impact on biodiesel output, and after optimizing the reaction parameters, a conversion rate of 95.33% was achieved while maintaining a reaction period of 2.5 h, a methanol-to-oil molar ratio of 15:1, and a catalyst quantity of 5 wt%. Response surface methodology (RSM) and artificial neural network (ANN) models were implemented to improve and optimize these reaction parameters for the purpose of obtaining the maximum biodiesel output. Consequently, remarkably higher yields of 95.33% and 95.53% were achieved by RSM and ANN, respectively, with a quite little margin of error of 0.0003%. This study showcases immense promise for the large-scale commercial production of biodiesel.

Keywords: biodiesel; plantain banana stem; sustainable development; waste management; artificial neural network; circular economy; response surface methodology

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1. Introduction

Energy is a critical resource for mankind's sustainable development, and its demand continues to rise worldwide. To achieve both environmental and economic sustainability, expanding the proportion of alternate energy resources in the energy mix is essential [1]. Conventional fuels especially fossil diesel, natural gas, and coal in its various grades are considered as prevalent energy sources; however, they are regarded as finite, economically expensive, non-renewable, environmentally unsustainable, and cannot be replaced quickly on a human timescale [2]. Their use has been linked to accelerated depletion and various environmental concerns, such as global warming, irregular climate change patterns across various nations, and ozone layer weakening, which have disturbed nature's balance [3]. Therefore, researchers are focusing on identifying energy needs and environmental problems to shift toward sustainable, clean and reliable alternate energy options.

Biodiesel is an important alternate energy option. It is derived from natural and abundantly available sources such as WCOwaste animal fats, and both food-grade and non-food-grade vegetable oils [4]. Biodiesel, due to its organic and natural source of origin,

is considered non-toxic, renewable, environmentally friendly, and biodegradable. It has a high flash point value, emits little particulate matter (PM), carbon dioxide (CO_2), sulfur dioxide (SO_2), and unburnt hydrocarbons (HC), and can significantly reduce air pollution when blended with diesel fuel in vehicles [5]. However, the cost of the primary component, mainly, refined vegetable oil, poses a substantial challenge to the commercialization of biodiesel due to its higher production expenses [6]. The significant difference in cost between biodiesel derived from food-grade vegetable oils and petroleum-based diesel fuel poses a substantial obstacle [7]. Research has indicated that the replacement of fossil diesel with WCO derived biodiesel in China can theoretically lead to a reduction of up to 5.5×10^6 tons of CO_2 equivalent in life cycle greenhouse gas emissions [8]. This finding underscores the environmental benefits and potential for substantial carbon dioxide emissions mitigation through the implementation of WCO-derived biodiesel as a sustainable option to substitute conventional diesel fuel [8,9].

Finding low-cost alternate feedstock options that can replace refined food-grade oils is much more important. This is crucial to develop biodiesel at a comparatively reduced cost and in an economically viable way [10]. Among these feedstocks are options for using waste or used oil (WCO) and animal-derived fats sources. These are promising and favorable feedstocks that have gained attention in recent years [11]. WCO has been identified as a particularly attractive option due to its low cost, local availability, and abundance [12,13]. The heating value of WCO is also comparable to diesel's, making it a viable alternative fuel source [13,14]. While there are various methods for extracting methyl esters from WCO, researchers are constantly striving to improve the effectiveness of this process. One option to enhance the process efficiency of WCO conversion is employing catalysts to speed up the transesterification process [15]. The purpose of using catalysts is to improve the solubility of alcohols in the oils, leading to faster and more efficient conversion [16,17]. Among the various categories of catalysts available in the market are three major types that can be used in transesterification reactions: homogeneous, heterogeneous, and enzymatic [18]. Homogeneous catalysts are soluble in both the feedstock oil and alcohol, which directs towards a faster reaction rate [19,20].

In recent years, a growing focus of the research community has been the use of agricultural waste to develop low-cost catalysts in an environmentally sustainable way. A bulk amount of agricultural waste is generated annually from fruit and vegetable crops. The average yearly creation of biomass waste lies in the range of approximately 150 Gt., posing considerable management challenges. Further disposed-of biomass waste often has severe negative consequences due to the atmospheric accumulation of methane gas [21]. An enormous range of products including fuels, polymers, and construction materials can be derived from biomass waste materials [22]. Plantains and bananas are often treated as one of the plentiful crops globally. The production output of bananas is projected to be 28 million tons globally [23]. This massive production figure provides a depiction of the huge waste that is produced worldwide in banana and plantain cultivation. The banana and plantain stem is richer in mineral potassium compared to any other known fruit crop. This potassium can be extracted as an alkali [24,25]. The combustion phenomenon is considered the main option for directly using biomass waste, resulting in the creation of ash as a byproduct [26]. The combustion of banana trunk biomass yields ash; from which potassium oxide can be extracted. Potassium oxide is converted to KOH by its reaction with distilled water at 60 °C [27]. Banana stem-derived KOH can be employed in the WCO to biodiesel transformation process through transesterification. This banana stem-derived potassium hydroxide might help to lessen reliance on commercial-grade potassium hydroxide (KOH), and thus save a considerable amount of national exchequer [28].

Experimentation design for enhancing yield and reducing production cost by mutually adjusting various influencing parameters is considered a tedious, expensive, and time-consuming task. Various statistically driven optimization tools have captured the interest of researchers in recent years [29]. The dawn of machine learning and deep learning techniques including various purpose-built algorithms have revolutionized many indus-

trial fields including biodiesel production and optimization. A substantial advancement can be observed in these algorithms in comparison with traditional machine learning methods. These techniques enable deep neural networks to adapt and enhance the working performance over time, more often in response to changing patterns of data distribution, non-stationary environments, or other evolving and unknown factors [30]. These deep learning algorithms, together with optimization algorithms, can be implemented successfully to balance complex interactions between input reaction parameters and desired output parameters such as production yield and product quality [31]. Among the various available machine learning tools, artificial neural network (ANN) is regarded as advanced and efficient tool that can be utilized in the area of biodiesel optimization studies. The ANN model is usually comprised of various simplified signal-processing components named "neurons". The neurons are interconnected, most of the time, by unidirectional communication networks. The ANN model is employed using network training methodology to predict target values with considerably higher accuracy levels [32]. ANNs have the unique ability to learn about a system without advanced information on operational correlations [25,33]. The response surface methodology (RSM) has been recognized as a valuable optimization technique in various research and industrial fields [34]. It could reduce the number of experimental conductions needed to produce statistically significant results. Generally, RSM is implemented to forecast and optimize the response parameters and input parameters, respectively. The utilization of RSM and ANNs has been extensively documented in various studies focusing on optimizing the conversion process of a diverse range of feedstock oils into biodiesel samples. In a major study by Ayoola et al., extensive research on biodiesel production and optimization was carried out utilizing crude palm kernel oil by employing RSM and ANN models. Results indicated the better performance of the RSM model for predicting biodiesel output [35]. In a research conducted by Rauf Foroutan et al., the influence of four process variables involving catalyst quantity, process temperature, reaction interval, and methanol-to-oil ratio was explored. The biodiesel yield was optimized by RSM and ANN tools. The biodiesel output observed was 98.76% and 97.75% employing RSM and ANN models, respectively [36]. Other notable examples include biodiesel production and optimization using sunflower oil, soybean oil [34], neem oil [37], cotton-seed oil [38], moringa oleifera oil [39], rape seed oil [40] and azolla filiculoides algae feedstock oil [19].

Much of the current research has centered on the commercial-grade KOH catalysts available in the market. However, this study is based on the rarely reported approach of extracting KOH from banana stems—a readily available organic waste on a global scale. The impact of independent process variables, concentration of the catalyst employed, methanol–oil ratio, and reaction duration on the biodiesel output was examined. ANN and RSM models were implemented to improve and optimize the reaction parameters for the transformation of WCO to biodiesel using a KOH catalyst derived from waste plantain banana stems. The accuracy and suitability of each model were examined on statistical grounds.

2. Materials and Methods

The biomass waste in the form of banana trunks was collected from a local orchard. Waste cooking oil (canola oil) was supplied by the cafeteria of the University of Engineering & Technology Lahore. Analytical grade methanol (99.5%) was supplied by Fischer Scientific. Whatman filter paper was purchased from a commercial market in Lahore. All other reagents were analytical grade. Glassware used included a 500 mL beaker, 500 mL volumetric flask, and 500 mL separating funnel. Other equipment included a hot plate magnetic stirrer, thermometer, and flask holding stands. All glassware used was Pyrex product. The methodology adopted to execute the present research work is elaborated in Figure 1.

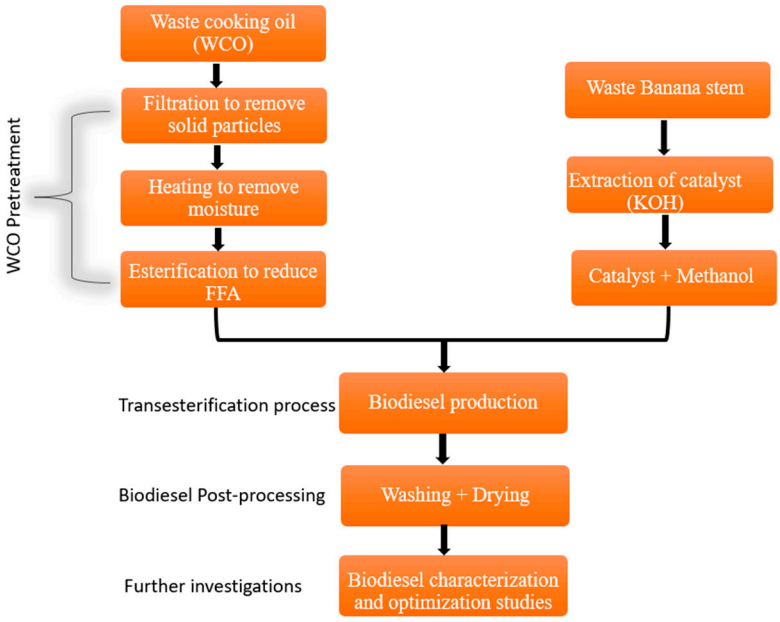

Figure 1. Proposed research methodology flowchart.

2.1. Catalyst Synthesis

2.1.1. Preparation of Banana Trunk Ash Sample

The collected banana trunk sample was first cleaned manually to remove any debris and dust particles and then washed with purified water many times. Then, the cleaned banana trunk was sun-dried for 72 h. This was followed by oven-drying at 120 °C. It was noted that the moisture contents were removed to a maximum extent after a period of 24 h. The dried sample was crushed by an industrial grinder to make a fine-powder sample. The powder sample was placed in ceramic crucibles for calcination in a high-temperature furnace at 600 °C for 3 h. This led to the decomposition of organic compounds such as lignin, cellulose, and hemicellulose, thus ensuring the removal of moisture contents along with volatile components in the form of carbon dioxide. The obtained ash was then stored in polythene bags for further extraction. The following formula can be used to obtain the percentage of ash recovered.

$$\text{Ash recovered } (\%) = \frac{\text{Weight of ash recovered}}{\text{Weight of banana trunk sample}} \times 100 \quad (1)$$

2.1.2. Extraction of Catalyst from Banana Trunk Ash

The hydrated form of potassium oxide (KOH) was extracted from the ash sample by stirring the ash in purified water. First, a 20 g sample of ash was weighed and mixed thoroughly with 10 mL/g of de-ionized water sample in a flask of 500 mL capacity. The prepared solution was further heated to 70 °C temperature for a period of 2 h. Afterward, the filtration of the sample was carried out using filter paper, and the residual solution was tested to confirm that it was neutral or almost neutral using pH paper. The filtrate was then evaporated to dryness after being heated. Figure 2 shows the flow diagram of catalyst extraction from banana waste.

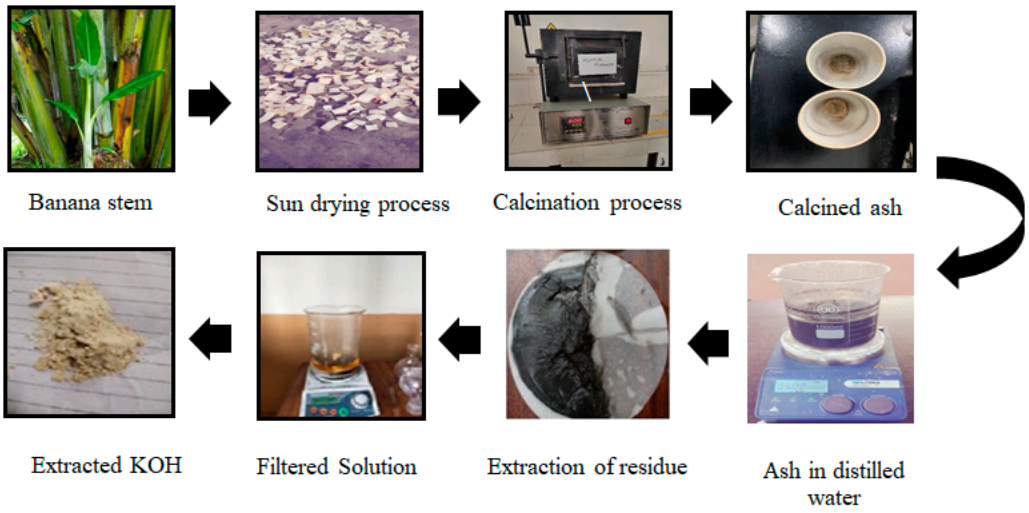

Figure 2. Flow diagram for catalyst extraction.

Following the drying process, the catalyst sample was weighed and subsequently protected within a glass container for future applications. The KOH recovered % was evaluated by the following relation.

$$\text{KOH recovered } (\%) = \frac{\text{Weight of KOH recovered}}{\text{Weight of ash sample}} \times 100 \quad (2)$$

2.2. Biodiesel Synthesis Process

2.2.1. Experimental Setup

Figure 3 indicates the experimental arrangement and process description for biodiesel production. The essential equipment for biodiesel generation includes a biodiesel reactor made of a round bottom flask. A laboratory scale hot plate stirrer is used for simultaneous heating and stirring purposes. A glass condenser was attached with the round bottom flask at one opening and a thermometer for monitoring temperature. A separating flask was used to isolate the layers of biodiesel and glycerol by density differences.

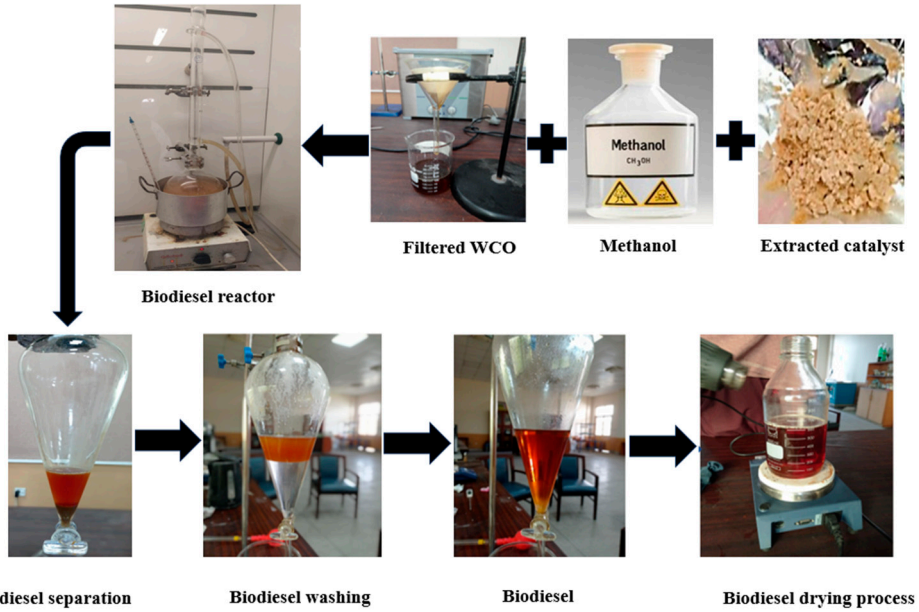

Figure 3. Experimental setup for biodiesel production.

2.2.2. Pretreatment of WCO

The WCO underwent filtration using Whatman filter paper to eliminate any suspended solid particles. Following this, the oil was heated to 100 °C to effectively eliminate any water content present. The WCO was filtered using Whatman filter paper to eliminate suspended solid particles. Afterward, oil heating was carried out at 100 °C to eliminate water contents. The titration process was followed to measure the acid value of WCO sample. This acid value of the WCO was further utilized to evaluate the free fatty acids (FFA) value. An acid value greater than 2% indicates the unsuitability of this oil for the transesterification reaction. The esterification process followed, to decrease the FFA value of the WCO sample to less than 2%. Table 1 presents the different physiochemical characteristics of the WCO sample.

Table 1. Physiochemical properties of WCO.

Characteristics	Values	Units
Oil viscosity (at 40 °C)	6.80	mm^2/s
Density (at 20 °C)	908.20	kg/m^3
Acid value	7.4	mg KOH/g
FFA	3.7	%

The FFA content of the WCO sample needs to be below 2% before its conversion into biodiesel. The acid catalysis or esterification process was followed to deal with excessive acid value by a 6:1 methanol-to-oil ratio and 2% sulfuric acid (v/v) in preheated oil at 65 °C. The mixture was agitated at 700 rpm for 3 h on a magnetic stirrer. The acid value of the WCO can be calculated by the given equation.

$$\text{Acid Value (AV)} = \frac{(56.1 \times \text{V} \times \text{N})}{\text{W}} \quad (3)$$

Here, V indicates the KOH volume used, N shows the normality of the KOH solution, and W shows the weight of the WCO used during the titration process. The reaction mixture, once the reaction is completed, was shifted to another flask for overnight settling and separation purposes. The upper layer contained esterified products (FAME products), whereas the bottom layer contained the reaction byproduct, mainly glycerol. The oil sample, after esterification process, was separated and maintained at 110 °C to ensure the removal of excessive alcohol and moisture contents.

2.2.3. Transesterification Reaction

Following the pretreatment step, the pre-esterified oil sample underwent a base catalysis process known as transesterification. The production output was directly impacted by the catalyst quantity or concentration, the methanol-to-oil molar ratio, and the reaction duration. At the start, the WCO sample was heated up to 60 °C temperature. A known quantity of KOH catalyst (7 wt%) was mixed in methanol before adding it to the preheated WCO. Throughout the process, a uniform mixing rate of 600 rpm and a constant heating at 60 °C were maintained. The resulting reaction products were subsequently transferred to another flask for settling and separation purposes, allowing glycerol and methyl esters to separate into distinct layers based on their relative densities. After replacing the layer of glycerol from the bottom of the separating flask, the remaining reaction mixture was rinsed with hot distilled water to eliminate any unused methanol, unreacted catalyst, and soap components. Finally, the methyl ester contents were subjected to heating at a temperature of 110 °C for one hour to remove any moisture content, resulting in the obtainment of a pure biodiesel sample.

2.3. Biodiesel Characterization

The physicochemical characteristics of the WCO and the biodiesel obtained from it (WCOB) were investigated according to international standards ASTMD6751 and BS EN 14214. These properties include the density of the oil sample, kinematic viscosity, acid value, calorific value, flash point, and cetane number. The methyl ester contents (FAME composition) were examined employing gas chromatography-mass spectrometry (GC-MS) equipment. The biodiesel sample was prepared separately and examined by GC-MS (Trace 1300, ISQLT type). A quantity of 0.05 g of biodiesel was blended with 50 mL methanol in a 50 mL capacity flask. The 0.1µL quantity of the sample thus prepared was shifted into a separate test tube before loading to the GC-MS equipment.

2.4. Experiment Design using RSM

To develop and optimize the synthesis of biodiesel, Design-Expert 13.0 of the response surface methodology tool was implemented as a statistical model. RSM proved to be an invaluable approach for refining and enhancing the biodiesel production process, ultimately improving the overall yield. The Box–Behnken technique within RSM was specifically utilized to determine the optimum values of reaction parameters, aiming to accomplish the optimum value of biodiesel generation from WCO. RSM suggests two design options, namely the central composite design (CCD) and the Box–Behnken technique (BBD). In this study, the BBD was chosen, which involves variables at three levels (+1, 0, −1) and employs a quadratic polynomial equation to create the connection between the process parameters and the response parameter. The range of operating parameters can be found in Table 2, to provide an overview of the variables considered in the optimization process.

Table 2. Operating parameters specifications.

Operating Parameters Type	Range	Units
Methanol to oil molar ratio	9:1 to 15:1	Molar ratio
Catalyst concentration	5–7	% (*w*/*w*)
Reaction time	2–3	h

To optimize the biodiesel output, a string of experiments were performed using Box–Behnken response surface design. The data generated from experimentation was analyzed on Design-Expert 13.0 and then interpreted. The transesterification phenomenon was meticulously optimized by considering three variables with three different values, leading to a total of eighteen experimental runs. To fit the data obtained from the experiments, a quadratic polynomial model was implemented. The equation for this model is provided below.

$$Yield = +90.85 + 1.01A + 3.49B + 0.2850C - 4.23AB - 0.0875AC + 0.6975BC - 0.1762A^2 - 1.99B^2 - 2.56C^2 \quad (4)$$

In this model equation, the independent parameters chosen for optimization are catalyst concentration (A) in weight percentage (wt.%), methanol-to-oil ratio (B), and reaction interval (C) in hours (h). The temperature or heating rate and stirring rate were maintained constant at 700 rpm and 65 °C, respectively.

Analysis and validation of the RSM results were performed by analysis of variance (ANOVA). This analysis was required to conclude the impact of reaction parameters as well as their combined effect on process efficiency. The *p*-value (probability value) was used to identify the impact of each reaction parameter on biodiesel production efficiency. A less than 0.05 *p*-value implies the model fitness. The F-value in ANOVA helps to determine if the differences between group means are statistically significant. A large F-value and lower *p*-value together indicate the statistical significance and suitability of the model.

2.5. Experiment Design Using ANN

One limitation of RSM is its inability to incorporate variables that are beyond control. ANNs are a fundamental component of machine learning tools that can be used to model complex relationships in data and make predictions or optimization decisions. ANN neurons possess synaptic weights connections and have the ability to store information through their interconnections [41]. The ANN technique employed a feedforward backpropagation algorithm, with three layers of neurons referred to as input, hidden, and output. This feedforward backpropagation algorithm is generally employed as a training technique for training Artificial Neural Networks (ANNs). It is considered as a foundation for various neural network models that involves regulating the network weights network to minimalize the difference between predicted output values and actual target outputs [29]. The input, hidden, and output layers had 3, 10, and 1 neuron, respectively, and utilized TANSIG, TANSIG, and PURLINE activation functions. Optimized yield response is obtained according to the function assigned either TANSIG or PURLINE and corresponding to the point for which they are trained. A total of 17 data points were compiled to create a unified dataset, with the independent input variables or the operating parameters considered for the transesterification process.

The implementation of the ANN was accomplished using MATLAB, version 2019. To assess the accuracy and suitability of the RSM and ANN models, performance indicators such as mean square error (MSE), root mean squared error (RMSE), and correlation coefficient (R^2) were employed. These evaluation metrics were established by the following three equations, providing quantitative measures of the correctness and reliability of the RSM and ANN models.

$$\mathrm{MSE} = \frac{\sum_{i=1}^{n}(xe - xp)^2}{n} \tag{5}$$

$$\mathrm{RMSE} = \left(\frac{1}{n}\sum_{i=1}^{n}(xe - xpi)^2\right)^{\frac{1}{2}} \tag{6}$$

$$\mathrm{R}^2 = 1 - \frac{\sum_{i=1}^{n}(xe - xpi)^2}{\sum_{i=1}^{n}(xei - xav)^2} \tag{7}$$

where

n = Total number of observations;
xe = Observed or noted value;
xp = Predicted value;
xav = Average value.

3. Results and Discussion

This segment incorporates the investigation of the synthesized KOH catalyst from waste banana stems using Fourier transform infrared spectroscopy (FTIR). Furthermore, the fuel characteristics of the developed biodiesel from WCO were explored through various characterization techniques. Subsequently, optimization investigations were carried out utilizing RSM and ANN models. The accuracy and appropriateness of each model were thoroughly assessed based on statistical criteria.

3.1. FTIR Analysis of Banana Ash, Banana KOH, and Pure KOH

The FTIR model was developed to recognize the presence of functional groups by assessing the information about the molecular vibrational modes in the catalyst. These curves indicate the presence of different characteristic peaks highlighting the molecular vibrations of corresponding elements present in the sample. The sample preparation techniques and types of instruments involved may influence the precise position and intensity of these peaks. The infrared spectrometry of banana ash, banana KOH, and pure KOH are shown in Figure 4 for clear identification of the stretching of different bonds.

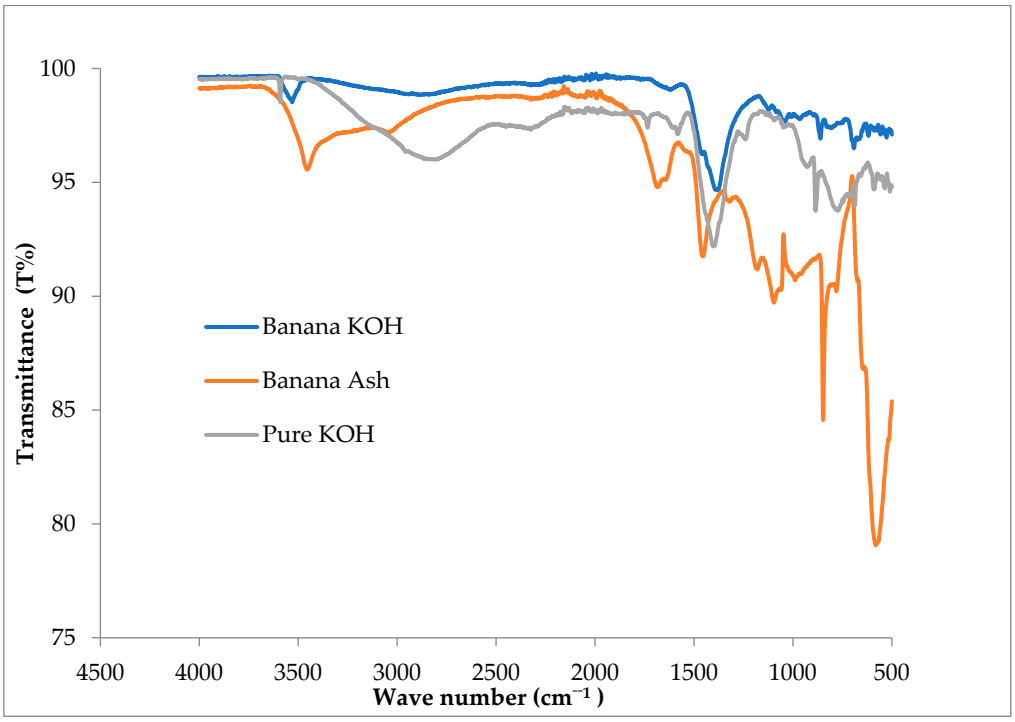

Figure 4. FTIR graphs of banana ash, banana KOH, and pure KOH.

A range of 500–4500 cm^{-1} wavenumber was selected for the development of the infrared spectrum of banana ash, banana KOH, and pure KOH. The splitting of coupling between OH-ions in the unit cell of KOH is expressed by the O-H stretching band near 3590 cm^{-1} and 1417 cm^{-1}. These O-H stretching peaks are relatively broad due to the existence of hydrogen bonding in KOH. The peaks at 1753 cm^{-1} and 1622 cm^{-1} indicate water absorption of pure KOH. A moderately sharp peak at 705 cm^{-1} suggests the K-O stretching mode for both banana and pure KOH.

A seemingly consistent and uniform pattern emerged from the FTIR curves of banana KOH, banana ash, and pure KOH within the spectral range of 4000 cm^{-1} to 1500 cm^{-1}. Seemingly, a noticeable deviation in the pattern was observed in the banana ash curve spanning 1500 cm^{-1} to 600 cm^{-1}. This divergence is primarily due to the existence of additional functional groups or impurities inherent in the banana ash sample. Given these findings, it highlights the significance of ensuring the precise preparation of samples free of impurities. Such careful preparation of samples is pivotal for upholding the credibility, reliability, and precision of FTIR outcomes. Consequently, this emphasis on sample purity is of critical importance to obtain accurate results and facilitate a robust interpretation of the FTIR data.

3.2. Physiochemical Properties of Biodiesel

The fuel characteristics of WCO-derived biodiesel (WCOB) were studied under optimal conditions following international biodiesel standards. These WCOB characteristics were compared with diesel and are reported in Table 3.

Kinematic viscosity is considered an important property of fuel due to its influence on fuel atomization quality. The slightly higher viscosity value of 5.01 against BS EN 14214 standard range of 3.5–5 is due to the relatively low unsaturation degree value. The fame components with lower values of double bonds (unsaturation degree) possess high viscosity. The density of fuel is a critical parameter as it influences the performance of engine and its combustion characteristics. Table 3 indicates the calculated value of fuel density, which further indicates its appropriateness to be used in diesel engines. The temperature at which a liquid fuel produces enough quantity of vapors to make a combustible mix with air is regarded as flash point of the fuel. The calculated value of the flash point for WCOB is

169 °C. The greater the flash point value of any fuel, the more difficult it is to ignite that fuel. This value is considerably higher than the flash point values of waste vegetable oil and diesel fuel, which ensures its safety during physical handling, transportation, and storage.

Table 3. Thermophysical characteristics of WCO, WCOB, and fossil diesel.

Properties	Unit	Method	WCO	WCOB	EN 590:2009 Diesel	ASTM D6751	BS EN 14214
Density 15 °C	Kg/m^3	ASTM D4052	903	862.1	820–845	870–900	860–900
Viscosity 40 °C	mm^2/s	ASTM D445	27.13	5.01	2–4.5	1.9–6	3.5–5
Acid value	mgKOH/g	ASTM D664	5.3	0.51	--	0.50 (max)	0.50 (max)
Calorific value	MJ/kg	ASTM D240	37.76	39.76	45.67	--	--
Cetane No.		ASTM D4737	40	61	51 (min)	47 (min)	51(min)
Flash point	°C	ASTM D93	220	169	55 (min)	93 (min)	101 (min)
Cloud point	°C	ASTM D2500		2	2	−3 To −12	--
Pour point	°C	ASTM D97		12	2	−15 To −16	--
FFA	mgKOH/g	ASTM D664	2.65	0.26	--	0.25 (max)	0.25 (max)

In conclusion, the thermophysical characteristics of WCOB indicate its relative suitability as an alternate to fossil diesel in many applications including combustion engines.

3.3. FAME Analysis

Table 4 indicates the FAME profile of WCOB obtained by employing GC-MS equipment. The overall level of unsaturated fatty acids in WCOB indicates higher value as compared to the level of saturated fatty acids. It was observed that WCOB contained 84.9% of unsaturated fatty acids as compared to 14.3% saturated fatty acids. According to BS EN 14214, the FAME components, especially its unsaturation degree, directly impact the fuel characteristics. The higher quantity of unsaturated fatty acids is also an indicator of better cold flow properties.

Table 4. Mass percentage of measured FAME contents in WCOB.

Formula	Compound	Designation	Mass (%)
$C_{17}H_{34}O_2$	Palmitic acid	C16:0	10.7
$C_{18}H_{36}O_2$	Stearic acid	C18:0	3.2
$C_{19}H_{36}O_2$	Oleic acid	C18:1	51.8
$C_{19}H_{34}O_2$	Linoleic acid	C18:2	32.9
$C_{19}H_{32}O_2$	Linolenic acid	C18:3	0.8
$C_{21}H_{42}O_2$	Arachidic acid	C20:0	0.2
$C_{21}H_{40}O_2$	Gadoleic acid	C20:1	0.2
$C_{23}H_{46}O_2$	Behenic acid	C22:0	0.2

Saturated fatty acids (%) = 14.3, Unsaturated fatty acids (%) = 84.9.

3.4. Process Parameters Optimization Using RSM

Box–Behnken design (BBD) was implemented to find the correlation between WCOB yield and process parameters selected for the yield optimization study. This design was chosen for its efficacy in determining key process parameters. The experimental matrix of yield values corresponding to the design points, along with the values of all three variables, created by Design-Expert 13 software, are provided in Table 5.

Table 5. Box–Behnken arrangements and responses.

Trial No.	Catalyst Concentration (A)	Methanol–Oil Molar Ratio (B)	Time (C)	Biodiesel Yield	
				Actual	Predicted
1	6	12	2.5	91	90.85
2	5	12	3	87.65	87.47
3	6	12	2.5	91.10	90.85
4	6	12	2.5	90.20	90.85
5	7	15	2.5	88.90	88.96
6	6	9	3	82.15	82.39
7	6	15	2	89.05	88.81
8	5	12	2	86.55	86.73
9	7	12	3	89.50	89.33
10	6	9	2	83.33	83.22
11	5	9	2.5	80	79.94
12	7	12	2	88.75	88.93
13	6	15	3	90.66	90.77
14	6	12	2.5	90.70	90.85
15	5	15	2.5	95.33	95.4
16	6	12	2.5	91.5	90.85
17	6	12	2.5	90.6	90.85
18	7	9	2.5	90.5	90.44

The statistical accuracy and adequacy of the quadratic polynomial equation developed by RSM and the role of key influencing parameters were calculated through the analysis of variance (ANOVA) technique. Table 6 presents the outcomes, which show that the model is greatly significant. This conclusion is also supported by the large F value of 159.11 and the small *p*-value (<0.0001) for the methanol-to-oil ratio (B) parameter. The *p*-value is utilized to assess the significance of each process parameter. It can also be used to reveal the significance of the combined effect of process parameters on biodiesel yield. The *p*-value of 0.0001 suggests that the prospect of obtaining a high F value due to random variations is just 0.01%. Consequently, the process variables B (methanol-to-oil ratio), A (catalyst value), B^2 (quadratic effect of methanol amount), C^2 (quadratic effect of reaction duration), and AB (combined effect of methanol with catalyst amount), exert substantial influences on biodiesel synthesis. Among these variables, the methanol-to-oil ratio (B) holds the utmost importance in conversion efficiency of WCO to WCO-biodiesel. This is evident from its considerably higher F value of 602.12 and its lower *p*-value (<0.0001). The Lack of Fit statistic reveals that the model inadequately describes the correlation between reaction parameters B, C, A, and the WCO biodiesel yield (dependent variable). Specifically, the Lack of Fit parameters for the F value and *p* value are 0.47 and 0.7191, respectively. The *p* value of 0.7191 denotes an appropriate fit for the quadratic model used in this study.

Figure 5 demonstrates the correlation between the predicted data originated from the empirical model and the actual results attained through experiments. The correlation coefficient (R^2) and the Adj-R^2 obtained were 0.9869 and 0.9787, respectively. The minor variance between R^2 and Adj-R^2 denotes the significance and efficacy of all reaction parameters involved.

Table 6. ANOVA outcomes using Design-Expert 13 (BBD) software.

Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	*p*-Value Prob > F
Model	232.41	9	25.82	159.11	<0.0001
A-Catalyst Concentration	8.24	1	8.24	50.78	<0.0001
B-Methanol/0il	97.72	1	97.72	602.12	<0.0001
C-Time	0.65	1	0.65	4.00	0.0804
AB	71.66	1	71.66	441.52	<0.0001
AC	0.031	1	0.031	0.19	0.6755
BC	1.95	1	1.95	11.99	0.0085
A^2	0.14	1	0.14	0.84	0.3875
B^2	17.30	1	17.30	106.61	<0.0001
C^2	28.63	1	28.63	176.38	<0.0001
Residual	1.30	8	0.16		
Lack of Fit	0.28	3	0.094	0.47	0.7191
Pure Error	1.01	5	0.20		
Total	233.71	17			
R^2 = 0.9869					
Adj R^2 = 0.9787					

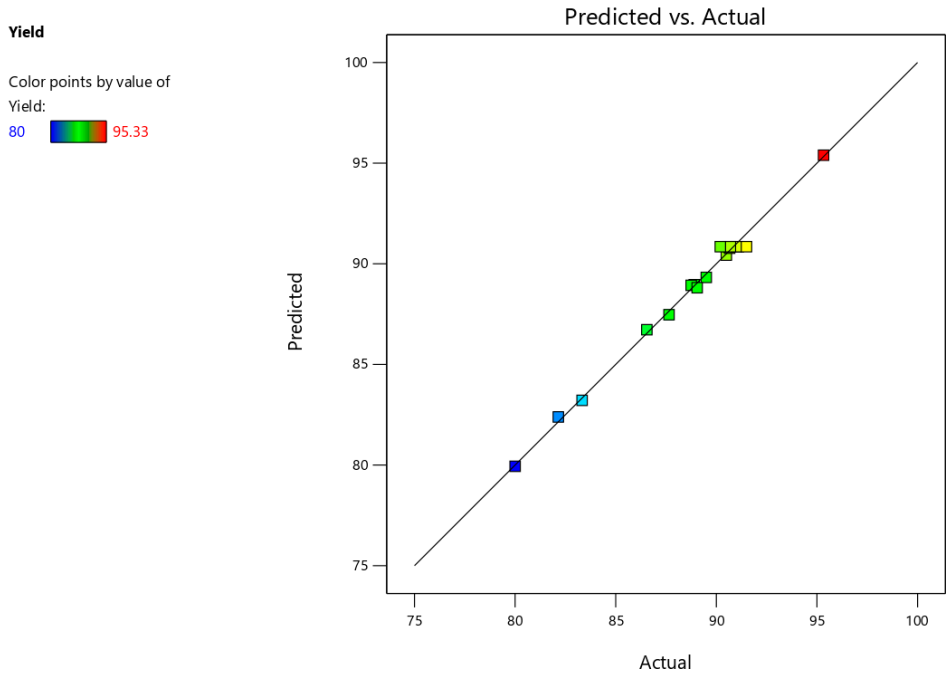

Figure 5. Predicted vs. actual FAME conversion.

Effect of Process Parameters to Optimize Biodiesel Production

The transesterification efficiency was examined by analyzing the combined effects of various process variables. Three-dimensional contour plots were implemented to visualize the interface between two independent parameters while maintaining the remaining variables at central levels. These contour plots helped establish the relationship among these parameters and establish the best levels for achieving maximum optimum yield.

In Figure 6a, a 3D surface plot illustrates the response surface curve depicting the relationship between catalyst concentration and reaction duration on biodiesel output. Maintaining a methanol-to-oil ratio of 15:1 and a reaction temperature of 65 °C, increasing the catalyst concentration to 5 wt.%, and keeping the reaction duration at the mid-level value of 2.5 h caused an improved biodiesel output of up to 95.33%. However, raising the catalyst concentration to 7 wt.% while maintaining the same reaction duration caused

a decline in biodiesel yield to 88.90%. Furthermore, maintaining the catalyst quantity at the mid-level of 6 wt.% and enhancing the reaction duration to an increased level of 3 h gradually increased the biodiesel yield to 90.66%. It is worth noting that higher catalyst concentrations and extended reaction times may favor triglyceride saponification, resulting in soap formation, which significantly affects biodiesel generation.

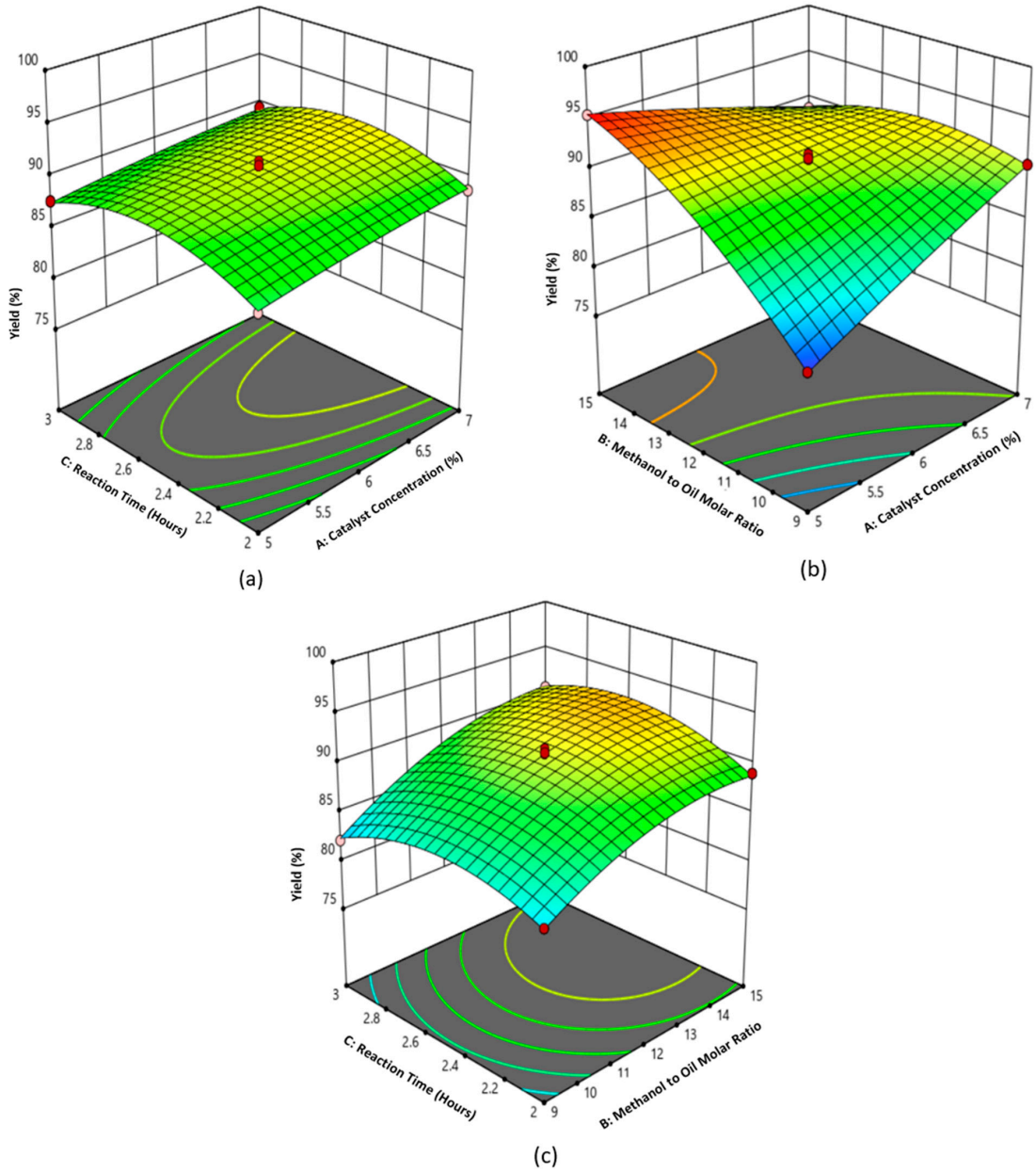

Figure 6. Contour plots of yield response and process variables: (**a**) catalyst concentration and reaction duration, (**b**) methanol to oil molar ratio and catalyst concentration, (**c**) methanol to oil molar ratio and reaction duration.

In Figure 6b, the influence of the methanol-to-oil ratio and catalyst quantity on production output of biodiesel is highlighted, considering fixed values of reaction temperature and reaction duration. Biodiesel output increases as the molar ratio of methanol-to-oil rises to 15:1, while maintaining the concentration value of catalyst at its mid-value. The maximum WCOB output was observed at a catalyst quantity of 5 wt.%, reaching 95.33%. Nonetheless, the experimental matrix in Table 5 specifies that as the molar ratio value of methanol-to-oil stays unchanged at 15:1 and the catalyst amount is at its maximum value

of 7 wt.%, the biodiesel output is reduced to 88.90%. Therefore, catalyst concentration acts as a critical factor in enhancing biodiesel output, although excessive catalyst quantity can lead to the formation of emulsified mixture and consequent phase separation.

Figure 6c shows that a decrease in the molar ratio value of methanol-to-oil from 15:1 to a minimum value of 9:1 decreases the biodiesel yield from 95.33 to a minimum value of 80%. Selecting amid-point value of 12:1 for this factor and decreasing the transesterification reaction duration from 2.5 h to 2 h accelerates the transesterification rate, thus producing more biodiesel yield. This, as a whole process, indicates that a higher methanol-to-oil ratio value acts as a considerable factor in enhancing the biodiesel production output. The optimum value of the molar ratio of methanol-to-oil was estimated at 12:1. A further decrease in this molar ratio to less than 12:1 lowered the WCOB output.

3.5. ANN Model Development for Yield Optimization

Figure 7 indicates the outcome achieved by performing regression analysis by employing the ANN tool by employing data presented in Table 5. The ANN model was able to attain a maximum WCOB yield of 95.53% when the mean squared error (MSE) approached 0.01876. The determination coefficient (R^2) for both the RSM and ANN models are 0.9866 and 0.9932, respectively. For the ANN model, the calculated values for mean squared error (MSE) and root mean squared error (RMSE) are 0.0721388 and 0.2686, respectively, while for the RSM model, the values are 0.081505 and 0.28549, respectively. The higher R^2 value (0.9932) and the lower RMSE value (0.2686) for the ANN model in comparison to the corresponding values of the RSM model (R^2 value of 0.9866, and RMSE value of 0.28549) indicate a relatively better fitness of the ANN than the RSM model. The neurons of the central hidden layer were adjusted until the MSE was decreased to 0.01876.

Figure 8 expresses the yield % by both the ANN and RSM models. The WCOB yield output indicates slight differences among the experimental values and the values estimated by the RSM and ANN models.

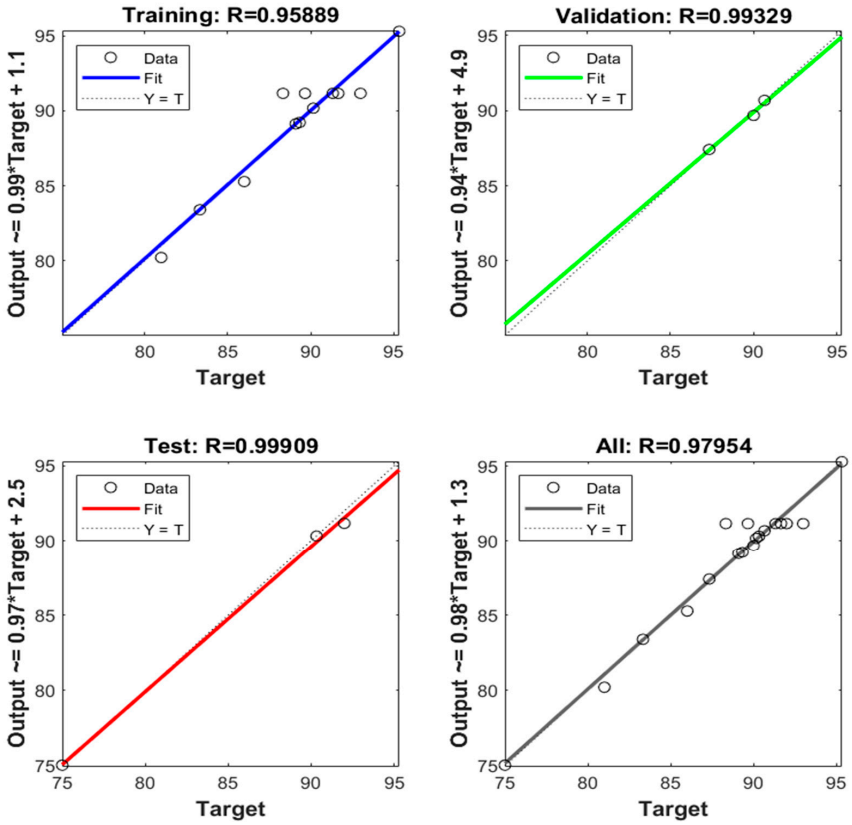

Figure 7. Regression analysis of the ANN model.

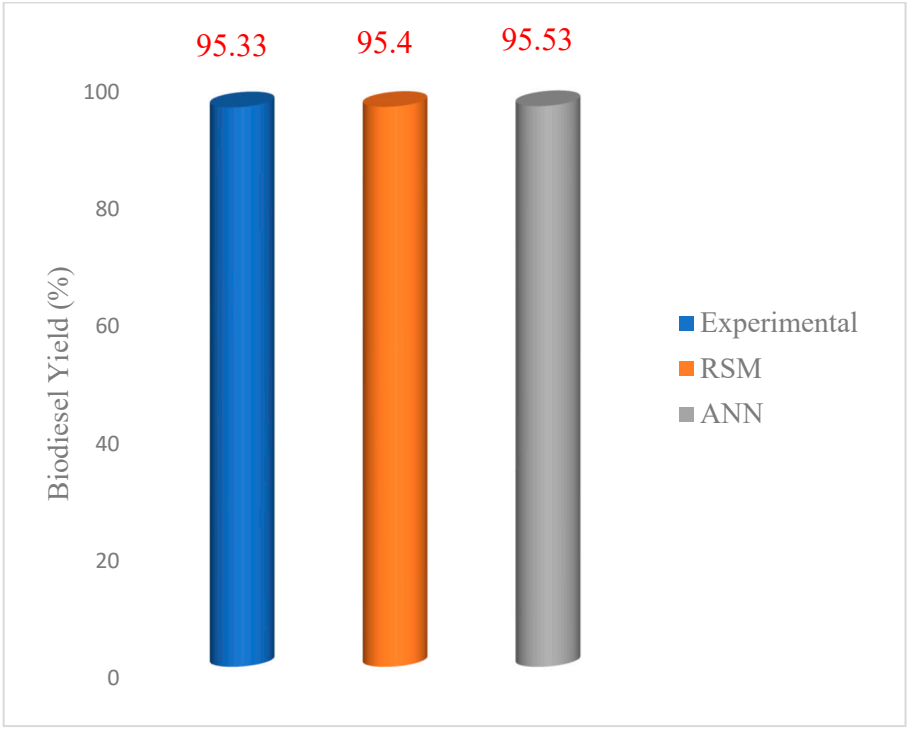

Figure 8. Comparison of experimental, RSM, and ANN yield.

4. Conclusions

In this article, a biodiesel generation and optimization study on WCO was accomplished utilizing a banana stem-derived KOH catalyst through a transesterification reaction. The GCMS analysis of WCO biodiesel was conducted to evaluate the FAME composition. The fatty acid contenets, both saturated and unsaturated, were also evaluated using GC-MS analysis.. The FFA value of WCO was reduced from 2.65 mg KOH/g to 0.26 mg KOH/g after its conversion to biodiesel by the transesterification process. Biodiesel yield optimization was achieved by employing RSM and ANN models. The optimum value of biodiesel yield was observed at process conditions of 65 °C temperature, a 15:1 molar ratio value of methanol-to-oil, a 5 wt.% concentration of the catalyst, and a 2.5 h value of reaction duration. The maximum predicted biodiesel output was 95.40% using RSM and 95.53% using ANN, with a practical biodiesel yield obtained experimentally of 95.33%. The employed RSM and ANN models predicted the biodiesel yield output with better accuracy and faster computational speed. The RSM and ANN models showed minor errors of 0.003% and 0.005%, respectively, compared to the practical findings, indicating a significant accuracy level of the models used in this study. The measured fuel characteristics of WCOB were compared with and met the requirements according to ASTM D6751 and BS EN14214 standards. Future scope of this research includes engine performance evaluation, environmental impact, and combustion characteristic studies.

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