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Research Article

A Green Heterogeneous Catalyst Production and Characterization for Biodiesel Production using RSM and ANN Approach

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Abstract. In this work, naturally available moringa oleifera leaves (also known as horseradish trees or drumstick trees) are chosen as a heterogeneous catalyst in the transesterification for biodiesel production from palm oil. The dry moringa oleifera leaves are calcinated at 700 °C for 3 hours to improve their adsorbing property. The calcinated catalyst characterization analysis from XRD and EDX highlights the presence of calcium, potassium, and other elements. Response surface method (RSM) optimization and artificial neural network (ANN) modeling were carried out to elucidate the interaction effect of significant process variables on biodiesel yield. The results show that a maximum biodiesel yield of 92.82% was achieved at optimum conditions of catalyst usage (9 wt.%), molar ratio, methanol to triglyceride (7:1), temperature (50 °C) and reaction time (120 min). The catalyst usage (wt.%) was identified as a significant process variable, followed by the molar ratio. Furthermore, the biodiesel's significant fuel properties in terms of thermal, physical, chemical, and elemental match the established standards of ASTM. Finally, when the catalyst was reused for five cycles, more than 50% of the biodiesel yield was achieved.

Keywords: Moringa oleifera leaves; Calcination; Biodiesel; Optimization and Modeling

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1. Introduction

In the last few decades, the strategy for providing sustainable energy has become an ongoing discussion. Biomass selection, thermal management, and waste pyrolysis have been done to cut down on fossil fuel use (Adetunji *et al.,* 2021; Elehinafe *et al*., 2021; Sunaryo *et al*., 2021; Supriyanto *et al.*, 2019). Cleaner fuels like liquefied petroleum gas (LPG) and compressed natural gas (CNG) have been used, but they have not been able to replace conventional fuels like gasoline and diesel oil on a larger scale (Kivevele *et al.*, 2020; Munahar *et al*., 2021; Susanto & Setiyo, 2018). Ethanol has also been introduced for a long time, even from local sources (Syarifudin *et al*., 2020; Wahyu et al., 2019), but implementation on a larger scale still remains a challenge due to uncompetitive market prices. Of all the available options, biodiesel is the only renewable and compatible fuel for current internal combustion engine (ICE) technology because it can be produced from a variety of biological sources and can be applied directly without significant engine modifications (Setiyo, 2022).

The scientific studies reveal that biodiesel from locally available oils of different feedstocks matches the petro-diesel fuel properties (Karmakar *et al.*, 2010; Souza *et al*., 2018). As a result, biodiesel production and characterization research using various edible and non-edible oils are ongoing (Demir *et al*., 2019). Improved fuel properties like high cetane number, high flash point, zero sulfur, presence of molecular oxygen (>9%), non-toxicity, and biodegradability in biodiesels attracted as a feasible solution to control the toxic emissions from the diesel engines (Basha *et al*., 2009).

However, biodiesel has high viscosity (> 40 cSt) which is not recommended in diesel engines due to poor atomization (Kolakoti & Rao, 2020a; Supriyadi *et al*., 2022). Therefore, the transesterification process was implemented to reduce the viscosity (Hariyanto *et al*., 2021; Zetra *et al*., 2021) in addition to thermal cracking, micro-emulsification and blending techniques. The transesterification process has gained huge attention due to its high efficiency in biodiesel conversion (Sinha *et al*., 2008). During the transesterification process, the triglycerides in raw oils react with alcohol and a strong catalyst to form methyl or ethyl esters. Based on our

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previous studies, lower viscosity was achieved with the methanol compared to ethanol (Kolakoti & Rao, 2020a).

Catalysts play an important role in achieving maximum biodiesel output from the transesterification process. Because of their simple availability, low cost, and high catalytic activity, sodium hydroxide (NaOH) and potassium hydroxide (KOH) are the most commonly used homogeneous catalysts. However, homogeneous catalysts are corrosive and require more water during the purification process, which entails generating large amounts of wastewater and making the transesterification process more expensive (Changmai *et al.*, 2020). In addition, because of the catalyst present in the washed liquid, it cannot be effectively recollected or reused (Lee *et al.*, 2014). As a result, heterogeneous catalysts were developed to address the problems produced by homogeneous catalysts. A wide variety of heterogeneous catalysts from acid and base types are used in biodiesel production (Changmai *et al.*, 2020). Some of them are mixed metal oxides (Rashid *et al.*, 2018), Zn/Al oxides (Jiang *et al.*, 2010), La/Mn oxide (Nasreen *et al.*, 2015), KF/Cao nanoparticles (Wen *et al.*, 2010). The main advantages of using heterogeneous catalysts are recyclability/reusability, a minimum quantity of wastewater generation during the filtering process, glycerin separation is much easier and high-quality glycerin can be obtained. Moreover, sold heterogeneous catalysts from naturally available sources are less toxic, eco-friendly, and have low energy intake (Lee *et al.*, 2014; Hadiyanto *et al* 2016). Thus, the heterogeneous catalyst has gained a lot of interest and offers a cost-effective and efficient transesterification method.

In recent years, eco-friendly heterogeneous catalysts from biomass and agricultural wastes are gaining wide popularity due to effective waste management and promoting sustainable green chemistry. They also transcend the limitations of homogeneous catalysts and demonstrate exceptional catalytic reaction activity under moderate circumstances. The heterogeneous catalysts are tested on different oils and the available reports reveal that a maximum biodiesel yield of 91% from waste cooking oil was achieved with calcinated waste chicken eggshells catalyst (Kolakoti & Satish, 2020). Similarly, 96% soybean oil biodiesel yield was achieved for Wei *et al.* (2009) with the waste eggshells catalyst calcinated at 1000 °C. Muthusamy and Subramaniapillai (2020) achieved the highest ceiba pentandra oil biodiesel yield of 99.36% with the banana peduncle base heterogeneous catalyst. Fan *et al.* (2019) introduced a novel alkaline catalyst from waste banana peel and the reported results reveal that calcinated banana peel catalyst showed strong alkalinity, better catalytic performance, and recyclability. Likewise, the other heterogeneous catalysts from wood ash (Sharma *et al.*, 2012), rice and peanut husk (Dai *et al.*, 2014), and waste rubber seed shell (Onoji *et al.*, 2017) are also successfully utilized in biodiesel production.

From the above discussions, it was evident that heterogeneous catalysts from naturally available biomass have a great significance in mitigating the challenges in homogeneous catalysts. Therefore, in this study, calcinated moringa oleifera leaves are chosen as a heterogeneous catalyst. Moringa plants are widely grown in tropical countries like India, Central America, and Africa. They are rich in vitamins (A, B1, B2, B3, B6, C and folate) and minerals (potassium, calcium, and magnesium) and have many medical applications (Gopalakrishnan *et al.*, 2016). So, our present study focuses on the catalyst preparation viz calcination technique and its characterization to elucidate the elemental compositions and reuse capabilities. Palm oil was chosen with this heterogeneous catalyst for biodiesel production and response surface method (RSM) optimization and artificial intelligence (AI) modeling was also carried out to predict the biodiesel yield like we did in our previous work (Kolakoti *et al.*, 2021, 2022). The right combination of catalyst, molar ratio, temperature, and reaction time is expected to produce optimal biodiesel yields.

2. Materials and Methods

2.1. Materials

Moringa oleifera leaves were obtained from locally available trees and purified palm oil (free fatty acid content ≤ 2%) was purchased from a local supermarket in Visakhapatnam, India. Different glassware, filter papers (Whatman), distilled water, temperature-controlled hot plat magnetic stirrer, muffle furnace, are used from our fuel's laboratory and analytical grade chemicals (99.8% pure) methanol (CH_3OH) and etc., are obtained from the Sigma-Aldrich chemicals in Bangalore, India.

2.2. Catalyst Preparation

Fresh moringa oleifera leaves were washed with distilled water to remove the attached impurities and residues and then dried under natural heat (sunlight) for three days. After drying for three days, the moisture on the leaves disappears and the bright green color moringa oleifera leaves turn into dull olive-green color. The dried leaves were separated from the stems and then placed in a hot air oven for one day to remove any traces of moisture presence. Finally, dried leaves were pulverized to a fine power with the help of micro vibratory ball mill equipment. The fine powder of moringa oleifera leaves calcined in a muffle furnace at 300 °C, 500 °C and 700 °C for three hours each with a heating rate of 5 °C/min. After careful physical observation of the ashes from different temperatures, the moringa oleifera leaves were completely decomposed at 700 °C. Therefore, the ashes collected at 700 °C were used as a heterogeneous catalyst for biodiesel production and different characterization analyses like X-Ray Diffraction (XRD) and Energy Dispersive X-Ray Analysis (EDX) were conducted for the catalyst calcinated at 700 °C. Fig 1 shows the preparation stages of heterogeneous catalysts from moringa oleifera leaves.

2.3. Design of Experiments (DoE)

Process factors such as alcohol consumption, catalyst concentration, reaction duration, and temperature all play a part in achieving optimal biodiesel output from the transesterification process (Onoji *et al.*, 2017). Therefore, the experiments were conducted based on a DoE in Minitab-19 statistical software, as shown in Table 1. The Response Surface Method (RSM) optimization approach with Box-Behnken assistance and 27 experiments were done at random by altering the process variables according to the DoE. By altering the input process variables, the mathematical Equation (1) was employed to estimate the output response yield.

Fig 1. Preparation of moringa oleifera leaves as heterogeneous catalyst.

Table 1
Process variables and their ranges as per DOE.

Process variables	Units	Symbol	Low	Mid	High
Time maintained	Min	A	120	180	240
Temperature maintained	°C	B	40	50	60
Methanol to Oil ratio	-	C	4:1	7:1	10:1
Catalyst usage	Wt.%	D	3	6	9

$$Yield = A_0 + \sum_{i=1}^{k} A_i X_i + \sum_{i=1}^{k} A_{ii} X_i^2 + \sum_{j=i+1}^{k} \sum_{i=1}^{k} A_{ij} X_{ij} \quad (1)$$

Where: A_0 and A_i represents the intercept and regression of the first-order coefficient in RSM and A_{ii} and A_{ij} represents the quadratic regression coefficient for its factor and regression coefficient among the ith and jth input parameters. X_i and k denotes the independent input parameter and no of input parameters.

2.4. Transesterification Process

This experimental study used the transesterification process to convert raw palm oil into biodiesel using calcinated moringa oleifera leaves as heterogeneous catalysts and methanol as alcohol (see Fig 2). Initially, 1 liter of raw palm oil was heated on a temperature-controlled magnetic stirrer. Methanol and catalyst of varying quantities as per the design conditions in Table 1 were mixed with the oil to initiate the reaction process. By adding the catalyst and alcohol, the separation of triglycerides into the methyl esters and glycerin appears in the reaction process after a certain reaction time. Then the mixture was transferred to a separating funnel and allowed to settle overnight for a clear appearance of methyl ester and glycerin. The high-density glycerin was removed from the separating funnel and leftover methyl ester (biodiesel) was washed with deionized water. Due to the heterogeneous catalyst usage, the washing process was easy with limited wastage (approximate 1.5-liter of deionized water was utilized for cleaning the methyl esters) and the catalyst was recovered after every usage and dried and storied for recyclability test. By varying the process parameters as per the design conditions in Table 1 a total of 27 experiments were conducted randomly and the experimental biodiesel yield was calculated with Equation (2) and presented in Table 2.

$$\text{Biodiesel yield}(\%) = \frac{\text{Weight of the Biodiesel}}{\text{Weight of the Raw oil}} \times 100 \quad (2)$$

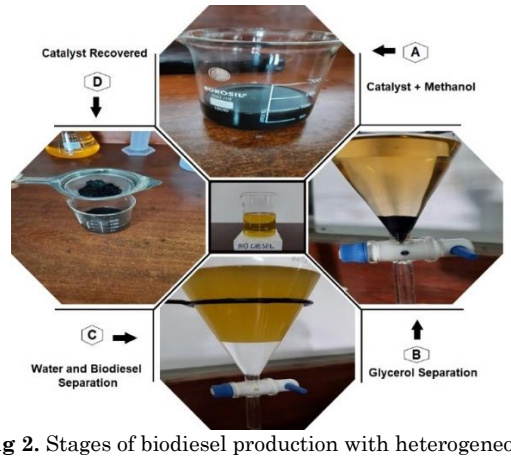

Fig 2. Stages of biodiesel production with heterogeneous catalyst.

2.5. ANN Modeling

Artificial Intelligence (AI) tools like neural networks, fuzzy logic, genetic algorithm etc., are gaining popularity in recent times due to their highly accurate prediction capabilities and solving most complex nonlinear problems. Due to their exceptional qualities, they are widely used in predicting the output results in biodiesel production. Available literature (Sewsynker-Sukai *et al.*, 2017) on utilizing these tools in biodiesel production reveals that compared to statistical tools, AI tools show a better performance in estimating the biodiesel yield. Therefore, an attempt was made in this study to use an artificial neural network (ANN) tool in MATLAB-R20A software to predict biodiesel yield. The ANN works similarly to the human brain, where many neurons (processing units) are connected to one another and form a large network of communication for solving complex problems. The entire working process of the network happens with training and learning. The detailed working of the models can be found in the literature (Kolakoti, 2020). In this investigation, a three-layer feed-forward backpropagation network model (Lavenberg) was chosen, as shown in Fig 3, which consists of input, hidden, and output layers.

Table 2
Design of experiments and biodiesel yield.

Exp. Runs	A	B	C	D	Exp. Yield	RSM. Yield
1	180	40	4	6	74.46	74.61
2	180	50	4	3	71.12	70.28
3	180	50	10	9	88.96	91.14
4	120	50	10	6	89.1	88.19
5	240	40	7	6	81.69	81.68
6	240	50	4	6	78.12	78.82
7	240	50	10	6	82.91	82.34
8	240	60	7	6	79.65	80.97
9	180	50	7	6	89.93	89.13
10	180	50	7	6	88.12	89.13
11	180	60	10	6	85.12	83.82
12	120	50	4	6	73.56	73.92
13	180	50	7	6	89.34	89.13
14	180	40	7	3	75.49	76.94
15	180	40	7	9	91.87	90.01
16	180	60	7	9	90.86	89.21
17	180	60	4	6	72.21	70.81
18	180	50	4	9	85.57	86.58
19	120	60	7	6	81.12	82.47
20	180	60	7	3	76.69	78.35
21	120	40	7	6	81.12	81.14
22	120	50	7	9	85.98	87.08
23	120	50	7	9	87.87	87.08
24	180	40	10	6	79.16	79.40
25	120	50	7	3	89.12	87.97
26	180	50	10	3	83.19	83.52
27	240	50	7	3	76.11	74.64

The experimental data of four process variables (A, B, C & D) from Table 2 was trained as input to the network and experimental biodiesel yield as output. During the training process, twenty neurons were chosen for the hidden layer by trial-and-error technique and the training of the algorithm was stopped when a low mean square error (MSE) was achieved in the output (Equation.3). Furthermore, the total experimental data (100%) was divided for training (70%), testing (15%), validation (15%), and the tan-sigmoid function (Equation 4) was used for input and hidden layers. The accuracy of the chosen models is based on the correlation coefficient values (R^2), the highest R^2 represents the better accuracy of the model, and they are calculated using Equations 5 and 6.

$$MSE = \frac{1}{n}\sum_{i=1}^{n}(X_{p,i} - X_{a,i})^2 \quad (3)$$

$$tansig(X) = \frac{e^{X} - e^{-X}}{e^{X} + e^{-X}} \quad (4)$$

$$R = \frac{\sum_{i=1}^{n}(X_{p,i} - X_{p,avg})(X_{a,i} - X_{a,avg})}{\sqrt{[\sum_{i=1}^{n}(X_{p,i} - X_{p,avg})^2][\sum_{i=1}^{n}(X_{a,i} - X_{a,avg})^2]}} \quad (5)$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(X_{a,i} - X_{p,i})^2}{\sum_{i=1}^{n}(X_{p,i} - X_{a,avg})^2} \quad (6)$$

Where the terms n represents the number of experimental data, $X_{p,i}$, $X_{a,i}$ represents the estimated and experimental values, $X_{a,avg}$, $X_{p,avg}$ represents the average experimental and estimated values, respectively.

3. Results and Discussions

3.1. Characterization of Palm Biodiesel

As the biodiesels are desired to compete with current petro-diesel fuel, the obtain biodiesel from the transesterification process using heterogeneous catalyst must meet the specified fuel standards of ASTM. Therefore, significant fuel properties related to thermal, physical, chemical, and elemental properties are measured as per the ASTM standards and presented in Table 3. The thermal properties especially high cetane number, high flash, and fire points in biodiesel represent the good quality of combustion and ease of storing and transporting during their usage. Similarly, low heating value than diesel fuel can regulate achieving the high combustion pressure and temperatures. On the other hand, the kinematic viscosity related to a physical property was observed higher than diesel fuel. This may occur due to the presence of free fatty acids (FAC), saturated and unsaturated compositions in biodiesel (Islam *et al.*, 2015; Kolakoti & Rao, 2019). Like kinematic viscosity, density in biodiesel is also more due to the variations in FAC profiles. The chemical and elemental properties like the acid number, sulfur content, and molecular oxygen reveal that high molecular oxygen of 11.12% and no trace of sulfur was reported for neat palm biodiesel. The reported fuel properties are compared with the available literature (Kolakoti & Rao, 2019, 2020b) and observed there is a relatively close agreement.

3.2. Fatty Acid Composition (FAC) Analysis

The FAC compositions from chromatography (GCMS-QP2010SE) analysis as shown in Table 4 reveals the presence of unsaturated fatty acids is more in palm oil biodiesel (±55.27 wt.%) and the total saturated FAC was observed as ±44.73 wt.%. The highest contributed FAC was observed as oleic acid (44.32 wt.%), which is an unsaturated FAC as shown in Fig 4. The FAC has a significant influence on biodiesel fuel properties especially kinematic viscosity, density, heating value, cloud and pour points. Similarly, the chain length and bonding in FAC also have a significant influence on fuel properties. For instance, long-chain FAC with high unsaturated levels increases the viscosity and density (Islam et al., 2015; Kolakoti & Rao, 2019). Furthermore, the quality of combustion will be improved with high cetane index fuels and biodiesel possess high cetane number than diesel fuel (Satya *et al.*, 2019). The high cetane number in biodiesel is due to the presence of long-chain monounsaturated FAC (Satya *et al.*, 2019). Similarly, the exhaust emissions from biodiesel-fueled engines are also depended on the variation in FAC. For instance, the presence of highly unsaturated FAC like linolenic acid in biodiesel increases NOx emissions (Kolakoti & Rao, 2019).

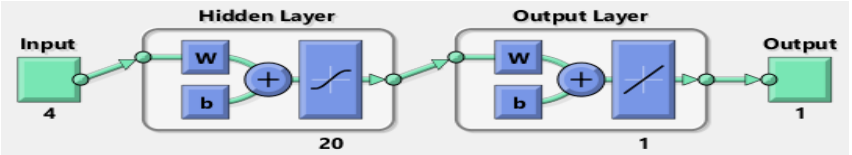

Fig 3. ANN network architecture.

Table 3
Palm oil biodiesel significant fuel properties comparison with diesel fuel.

Properties	Neat PBD	Neat Diesel Fuel	Limits	ASTM-
Heating value (Mj/kg)	38.54	42.6	35-43	D240
Flash point (°C)	152	90	130 min	D93-16
Fire point (°C)	168	100	-	D93-16
Cetane number	58	50	47 min	D613
Pour point (°C)	-3.19	-13	-15 to 10	D7346-15
Cloud point (°C)	2.11	0	-3 to 12	D2500
Density (kg/m^3)	880	830		D1298
Kinematic viscosity (mm^2/s)	4.12	2.98	1.90-6.0	D445
Acid number (mg/KOH)	0.17	0.07	0.80 max	D664
Molecular oxygen (wt.%)	11.12	-	-	D5291
Sulfur content (wt.%)	-	0.162	-	D5291

Table 4
FAC in palm oil biodiesel from chromatography (GCMS).

Fatty Acid Name	Structure	Wt (%)
Palmitic	C16:0	37.48
Oleic	C18:1	44.32
Linoleic	C18:2	9.17
Linolenic	C18:3	1.78
Stearic	C18:0	3.13
Myristic	C14:0	1.97
Caprylic	C8:0	0.39
Arachidic	C20:0	0.97
Lauric	C12:0	0.79
Total Saturated		44.73 (Wt.%)
Total Unsaturated		55.27 (Wt.%)

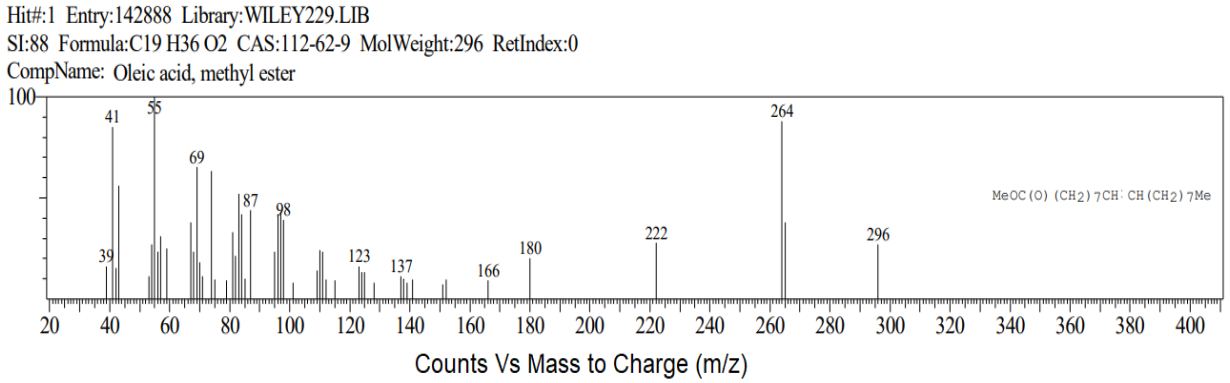

Fig 4. Oleic acid FAC from chromatography analysis.

3.3. XRD Analysis

The calcinated (700 °C) moringa oleifera leaves powder was tested in X-Ray Diffraction (XRD) to identify the crystalline compounds. From Fig 5, the sharp peaks were identified, which reveal the presence of better crystallinity at 2θ. According to Fig 4, the peaks located at 2θ = 28.86 °C, 69.27 °C and 89.39 °C represent the presence of calcium compounds like CaO. Furthermore, the peaks located at 2θ = 33.39 °C and 47.86 °C represent potassium compounds, and the peak at 2θ = 56.94 °C represents magnesium compounds. In general, calcium carbonate ($CaCO_3$) was present in renewable materials like eggshells, oysters, conch shells, etc. If they are used as a heterogeneous catalyst without calcination will result in low biodiesel yield due to poor inactive phase with low basicity of the catalyst. Therefore, calcination at high temperatures (>500 °C) helps the conversion of $CaCO_3$ to CaO and removes the water and volatile substances. Available studies on naturally available materials of eggshells (Kolakoti & Satish, 2020) and banana peel (Muthusamy & Subramaniapillai, 2020; Wei *et al.*, 2009) show an improvement of crystalline compounds of calcium, potassium, magnesium, etc., after calcination. Therefore, calcination at 700 °C improves the adsorbing property of the moringa oleifera leaves; thus, more fatty acids bind to the catalyst surface, decrease the reaction time, and promote better biodiesel yield. The conversion of $CaCO_3$ to CaO in heterogeneous catalysts does not always occur at high temperatures, several studies identify that calcination can occur at a temperature of 500 - 600 °C (Aleman-Ramirez *et al.*, 2021; Kolakoti & Satish, 2020). The conversion temperatures and time are always varied on the type of catalysts. For instance, the catalyst obtained from different animal bones will have different temperatures and the catalyst obtained from plant leaves will have different temperatures.

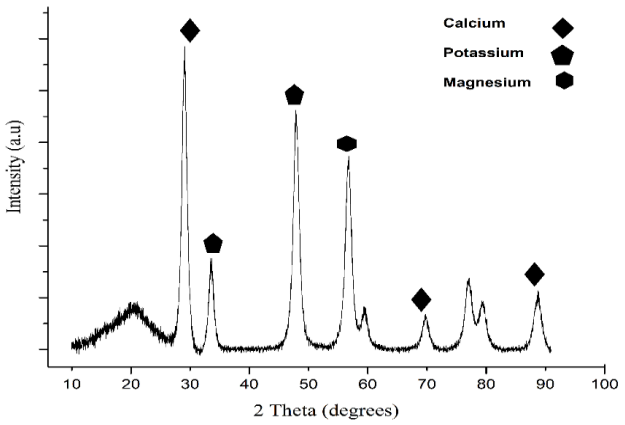

Fig 5. XRD spectrum of calcinated moringa oleifera leaves powder.

3.4. EDX Analysis

Energy Dispersive X-ray (EDX) analysis was carried out for calcinated (700^{0}C) moringa oleifera leaves powder to analyze the elemental compositions. From Fig 6, five major elements are identified namely potassium(K), Oxygen(O), Carbon (C), Calcium (Ca) and Magnesium (Mg) with a contribution of 11.39 wt.%, 29.62 wt.%, 28.72 wt.%, 27.86 wt.% and 2.41wt.%, respectively. Most of the reported literature exhibits the EDX analysis before and after the calcination of catalyst at different temperatures and reveals the elemental compositions are varied (increase or decrease) after the calcination. However, the main elements like potassium, calcium and etc., which play a significant role in the transesterification process, are improved after the calcination process and the same is reported in the present investigation. The improvement in some elements may acclaim due to crystalline and lattice rearrangement. The reported results in the present investigation are in convergence with the available literature (Fan *et al.*, 2019; Muthusamy & Subramaniapillai, 2020); therefore, calcinated moringa oleifera leaves powder could be an efficient heterogeneous catalyst as it has significant elemental compositions for improving the catalytic activity during the biodiesel production from different feedstocks.

3.5. Analysis of Variance

The experimental and RSM predicted biodiesel yield as shown in Table 1 reveals the significant information on the process variables and their effect on biodiesel yield under various conditions. The most contributing process variable in achieving better biodiesel yield can be identified with the analysis of variance (ANOVA), as shown in Table 5. The table comprises process variables with their interactions, degree of freedom (DF), P and F values. The lowest P-value denotes a significant parameter in biodiesel yield. From Table 5, both C (molar ratio) and D (catalyst usage) are significant with the lowest P-values (<0.0001). However, by considering the highest F-value (130.85), catalyst usage (D) was determined as an influencing process variable in biodiesel production. Furthermore, the chosen model accuracy was determined with the coefficient correlation value (R^2), which is 96.71%. This shows that more than 96% of the chosen data was consistent with the observed results. Finally, a regression Equation (7) was developed to calculate the biodiesel yield for future experiments.

3.6. Interaction Analysis of Process Variables

From the ANOVA analysis, the significant process variable in the transesterification process was identified as catalyst usage followed by molar ratio. The individual influence of the process variables on biodiesel yield was analyzed using box plots, as shown in Fig 7. These plots represent the contribution of individual parameters on biodiesel yield by considering other parameters as constant. Each box in the individual plots represents the lower hinge (LH), upper hinge (UH), and median (M) values. The variation of catalyst usage on biodiesel yield, as shown in Fig 7a, reveals that with the increase in catalyst usage, the biodiesel yield increased and it was observed at 9 (wt.%) the UH, LH, and M was recorded as 90.86%, 85.98%, and 88.41%, respectively. This shows that for heterogeneous catalysts, more amount of catalyst was required to convert the triglycerides into methyl esters.

$$\text{Yield (\%)} = -104.9 + 0.124\,A + 5.411\,B + 12.08\,C - 1.97\,D - 0.000542\,A^2 - 0.05611\,B^2 - 0.7062\,C^2 + 0.0122\,D^2 - 0.00085\,A{\times}B - 0.01493\,A{\times}C + 0.03569\,A{\times}D + 0.0684\,B{\times}C - 0.0184\,B{\times}D - 0.2411\,C{\times}D \quad (7)$$

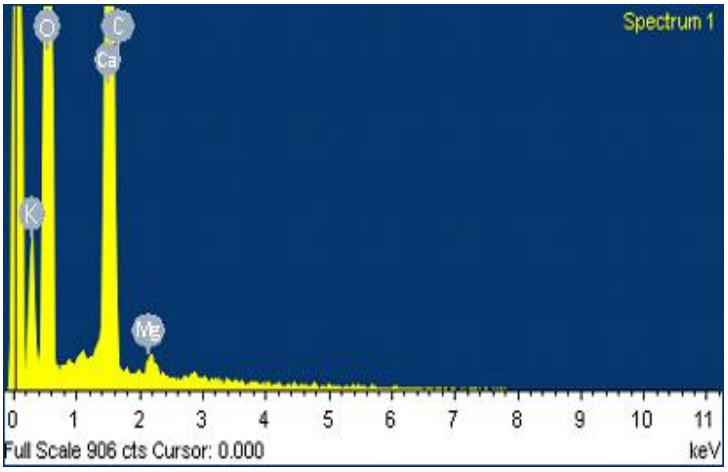

Fig 6. EDX spectrum for calcinated moringa oleifera leaves powder.

Table 5
ANOVA results (R^2= 96.71%; R^2(Adj)= 92.87%)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	14	991.10	70.793	25.18	<0.0001
Linear	4	631.63	157.907	56.17	<0.0001
A	1	0.60	0.602	0.21	0.652
B	1	0.29	0.288	0.10	0.754
C	1	237.63	237.630	84.53	<0.0001
D	1	367.86	367.864	130.85	<0.0001
Square	4	322.06	80.516	28.64	<0.0001
A^2	1	18.89	18.891	6.72	0.024
B^2	1	164.86	164.859	58.64	<0.0001
C^2	1	211.54	211.543	75.25	<0.0001
D^2	1	0.06	0.060	0.02	0.887
2-Way Interaction	6	186.92	31.153	11.08	<0.0001
A×B	1	1.04	1.040	0.37	0.554
A×C	1	28.89	28.891	10.28	0.008
A×D	1	120.08	120.077	42.71	<0.0001
B×C	1	16.85	16.851	5.99	0.031
B×D	1	1.22	1.221	0.43	0.522
C×D	1	18.84	18.836	6.70	0.024
Error	12	33.74	2.811		
Lack-of-Fit	9	30.25	3.361	2.89	0.207
Pure Error	3	3.49	1.163		
Total	26	1024.83			

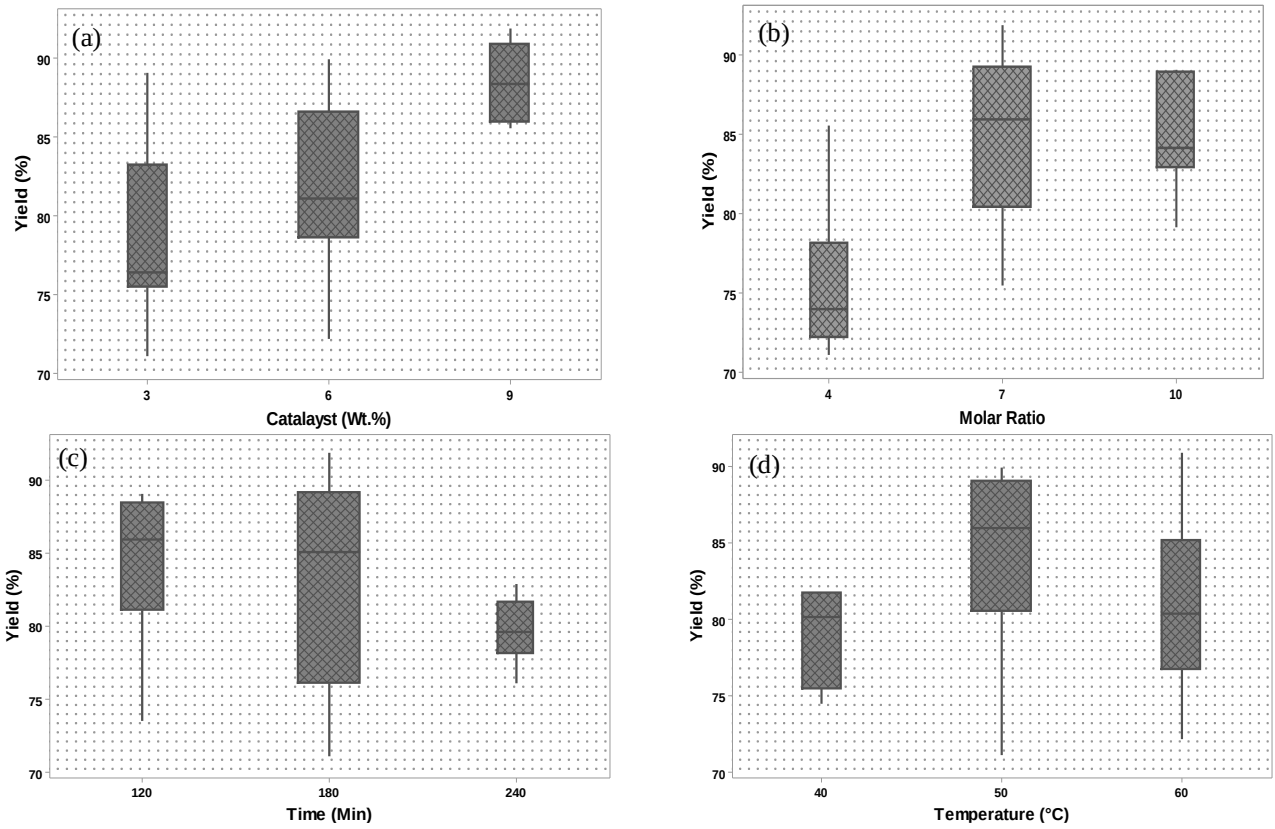

Fig 7. (a) Box plot for variation of catalyst usage on biodiesel yield; (b) Box plot for variation of molar ratio on biodiesel yield; (c) Box plot for variation of reaction time on biodiesel yield; (d) Box plot for variation of temperature on biodiesel yield

Similar results are also observed with calcinated eggshells (Kolakoti & Satish, 2020) and banana peduncle (Muthusamy & Subramaniapillai, 2020). Furthermore, the effect of molar ratio (in Fig 7b), reaction time (in Fig 7c) and temperature (in Fig 7d) on biodiesel yield reported that, at optimum conditions of 7:1, 180 minutes and 50 °C maximum biodiesel yield (UH) of 89.23%, 89.12%, and 89.03% was achieved. On the other hand, low biodiesel yield was observed at maximum temperature and reaction duration due to the escape of alcohol from the reaction process due to the low boiling point (Kolakoti, 2020; Sewsynker-Sukai *et al.*, 2017).

3.7. Comparison of ANN and RSM Models

In RSM optimization, the accuracy of the model was determined with the coefficient of correlation (R^2) value, whereas in ANN modeling, the accuracy of the model was determined with R values (Kolakoti, 2020). From Figure 8, the training (R=0.99), validation (R=0.98) and test (R=0.99) results are close to one. This shows that the chosen ANN network was highly accurate in predicting the biodiesel yield from the 27 experiments. A comparative graph was drawn for the experimental RSM and ANN biodiesel yield results, as shown in Figure 9 shows that both RSM and ANN results match the experimental values with low error (≤ 2%). As per the ANN modeling, the biodiesel yield was predicted as 92.97%, whereas in RSM, it was 91.14% at varying conditions, as shown in Table 6. Therefore, the final experiments are conducted under these conditions for validation, and it was observed that 92.82% biodiesel yield was achieved at the optimum conditions of 9 wt.% catalyst usage (D), 7:1 molar ratio (C), 50 °C reaction temperature (B) and 180 minutes of reaction time (A). The same optimized conditions are used for the reusability analysis of the catalyst.

3.8. Reusability Analysis

The catalyst reusability is one of the major advantages of heterogeneous catalysts. In this experimental investigation, the catalyst was recovered after each usage and washed with methanol and dried in a vacuum oven at 50 °C before reutilization. A comparative plot was drawn for the catalyst reutilization capability for five successive experiments, as shown in Fig 10. It was observed that after the five consecutive usages of the catalyst, the biodiesel yield remains above 50%. The reported results in the present investigation were observed higher than waste eggshells catalysts (Kolakoti & Satish, 2020) and lower than waste banana peel (Fan et al., 2019) and waste rubber seed shell catalysts (Onoji *et al.*, 2017).

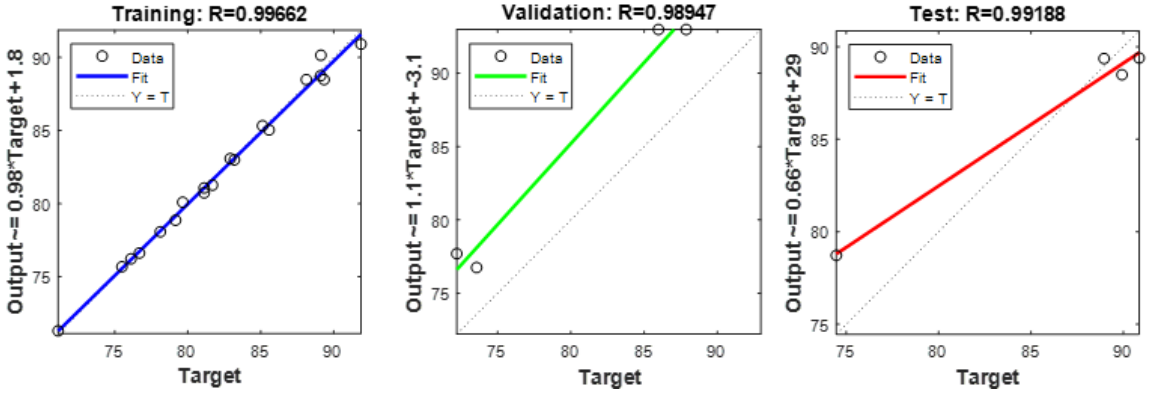

Figure 8. ANN training results.

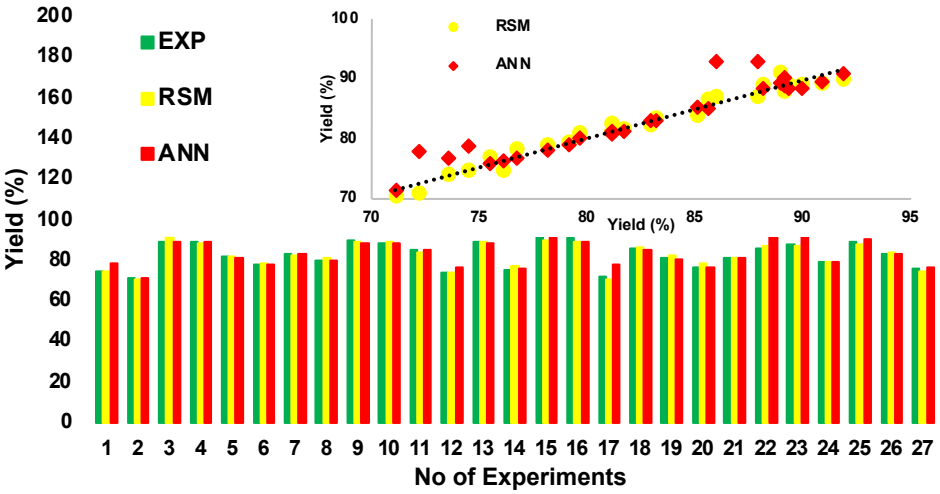

Figure 9. Comparative plot for RSM and ANN yield results

Table 6
Validation of RSM and ANN experimental results

	A (Min)	B (°C)	C	D (Wt.%)	Yield (%)	Validation Yield (%)
RSM	180	50	10	9	91.14	91.91%
ANN	120	50	7	9	92.97	92.82%

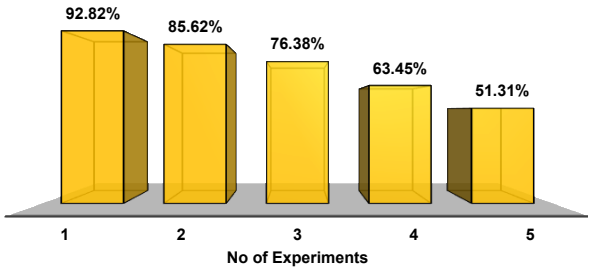

Fig 10. Catalyst reusability test.

4. Conclusions

The calcinated *moringa oleifera* leaves as a heterogeneous catalyst were successfully used in the transesterification process to convert the raw palm oil into palm methyl ester. Calcination of moringa oleifera leaves up to 700°C for three hours shows its complete decomposition and the characterization of calcinated catalyst from XRD and EDS analysis reveals the presence of significant elements like calcium and potassium. Maximum biodiesel yield of 92.82% was achieved at optimum conditions of catalyst usage (9wt.%), the molar ratio (7:1), temperature (50 0°C), and reaction time (180 min). Both RSM and ANN perform reasonably well in predicting the biodiesel yield with a high coefficient of correlation values (R and R^2). However, ANN shows dominance over RSM with a high R-value close to one. From ANOVA analysis, catalyst usage (wt.%) was identified as an influencing parameter in achieving maximum biodiesel yield in the transesterification process followed by the molar ratio. The thermal, physical, chemical, and elemental fuel properties of biodiesel match the established fuel standards (ASTM). The reusability of the catalyst revealed that more than 50% of the biodiesel yield was achieved after five consecutive usages, and also, low wastage of distilled water was observed in the cleaning process.

Calcinated moringa oleifera is a potential low-cost and effective heterogeneous catalyst that can promote a novel green method for biodiesel production. The naturally available green heterogeneous catalyst utilization helps to achieve promising results. As a future scope, these catalysts are suggested to test with various low-cost feedstocks like waste cooking oils and their oxidation stability to estimate the overall production cost for biodiesel commercialization.

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