

Optimized Biodiesel Production from Waste Cooking Oil Using Poultry Droppings Catalyst: A Comparison of RSM and Ann

Kessington Obahiagbon* and David Ohimai Ahonkhai**

Abstract

This study developed a catalyst from poultry droppings for the synthesis of biodiesel from waste cooking oil (WCO). Poultry droppings catalyst characterization was achieved using Brunauer-Emmett and Teller (BET) analysis, fourier transform infrared spectroscopy (FTIR), scanning electron microscope and energy dispersive X-ray (SEM-EDX), X-ray fluorescence (XRF), and X-ray diffraction (XRD). Box-Behnken design (BBD) was used in designing the experiments. Response surface methodology (RSM) and artificial neural network (ANN) were compared to determine their performance in modelling and optimizing the process. The catalysts characterization revealed CaO as the largest constituent and the presence of high surface area ($286.322\text{m}^2/\text{g}$) and pore size (1.853nm). Optimum biodiesel yield of 90.4694% was achieved with a temperature of 43.92°C , reaction time of 120 minutes with a methanol/oil ratio of 6:1 and catalyst loading of 1 wt.%. RSM model was found to be very efficient with R^2 value of 0.9464. Although, comparing with ANN, ANN performed better with a higher R^2 value of 0.99669.

Keywords: Biodiesel, Box-Behnken design, Poultry droppings, Modelling

1. Introduction

The energy demand is increasing steadily due to hastened modernization and large urban growth. Conventional energy sources are depleting daily due to their non-renewability nature¹. As a result of the enormous dependence on crude oil as a key source of fuel for energy generation in Nigeria and globally, prices of fossil fuels have risen dramatically in recent years. Furthermore, the use of these traditional energy supplies contributes to global warming, which must be addressed by using alternate energy sources^{2,3}. Environmental degradation is also a problem that can be alleviated by using alternative energy sources such as biodiesel⁴.

* Occupant of Petroleum Technology Development Fund Professorial Chair in Renewable Energy, Department of Chemical Engineering, University of Benin, Benin City, Edo State, Nigeria

** Department of Chemical Engineering, University of Benin, Benin City, Edo State, Nigeria

¹Arshad, M., Bano, I., Khan, N., Shahzad, M. I., Younus, M., Abbas, M., & Iqbal, M. (2018). Electricity generation from biogas of poultry waste: An assessment of potential and feasibility in Pakistan. *Renewable and Sustainable Energy Reviews*, 81, 1241–1246. <https://doi.org/10.1016/j.rser.2017.09.007>

²Canesin, E. A., de Oliveira, C. C., Matsushita, M., Felicidade Dias, L., Reghiany Pedrão, M., & de Souza, N. E. (2014). Characterization of residual oils for biodiesel production. *Electronic Journal of Biotechnology*, 17(1), 39–45.

³Ali, N. A., Khairuddin, N., & Siddique, B. M. (2021). Eggshell waste as a catalyst for biodiesel production: A preliminary study. *IOP Conference Series: Materials Science and Engineering*, 1195(1), 012043. <https://doi.org/10.1088/1757-899x/1195/1/012043>

⁴Hiwot, T. (2017). Determination of oil and biodiesel content, physicochemical properties of the oil extracted from avocado seed (*Persea Americana*) grown in Wonago and Dilla (Gedeo zone), Southern Ethiopia. *Chemistry International*, 3(3), 311–319. <https://www.researchgate.net/publication/337102107>

Transesterification of triglycerides with alcohol using a suitable catalyst produces biodiesel⁵. Most existing biodiesel production methods employ vegetable oils as a feedstock, and it is generally catalyzed by homogeneous catalysts⁶. Using pure vegetable oil as fuel, conversion or adjustment of engine may be required. Vegetable oil can be blended also with fossil fuel, although incomplete combustion, which leads to carbon build-up in the cylinders, could be a serious issue. The chemical conversion of vegetable oils into biodiesel is preferable because of these factors⁷.

Biodiesel has been widely considered as a good option for the world's heavy reliance on fossil fuels. Although, a long-term dependence on consumable oils as biodiesel feedstock would have a negative its supply for feeding and also has amplified some issues relating to the environment such as the major soil resource loss, deforestation, and the use of much of the accessible arable land⁸. In addition, the price of sources of consumable oils has increased significantly in recent times, putting the biodiesel industry's economic viability in doubt; if it continues to depend on edible oil as feedstock⁹. A renewable fuel must be technically possible, economically realistic, ecologically friendly, and easily obtainable to qualify as a fossil fuel alternative¹⁰.

The key problems in manufacturing biodiesel to meet global demand are scarcity of resources and a functional catalytic system. Biodiesel can only become established and more accepted around the world if it is produced at a lower cost than conventional fuel¹¹. Transesterification of vegetable oil and animal fats employing homogeneous catalysts, distributed in methanol is the conventional way of creating biodiesel¹². Although, using such catalyst has a number of drawbacks, including the generation of soap, and difficulties recovering the catalyst, which necessitates a downstream treatment process of wastewater and so elevates biodiesel production

⁵Akhabue, C. E., & Okwundu, O. S. (2017). Monitoring the transesterification reaction of castor oil and methanol by ultraviolet visible spectroscopy. *Biofuels*, 10(6), 729–736.

⁶Aniya, V. K., Muktham, R. K., Alka, K., & Satyavathi, B. (2015). Modeling and simulation of batch kinetics of non-edible karanja oil for biodiesel production: A mass transfer study. *Fuel*, 161, 137–145.

⁷Sahar, Sadaf, S., Iqbal, J., Ullah, I., Bhatti, H. N., Nouren, S., Habib-ur-Rehman, Nisar, J., & Iqbal, M. (2018). Biodiesel production from waste cooking oil: An efficient technique to convert waste into biodiesel. *Sustainable Cities and Society*, 41, 220–226. <https://doi.org/10.1016/j.scs.2018.05.037>

⁸Farag, H. A., El-Maghraby, A., & Taha, N. A. (2013). Kinetic study of used vegetable oil for esterification and transesterification process of biodiesel production. *Ijcbcs*, 3(January 2013), 1–8.

⁹Tshizanga, N., Aransiola, E. F., & Oyekola, O. (2017). Optimisation of biodiesel production from waste vegetable oil and eggshell ash. *South African Journal of Chemical Engineering*, 23, 145–156.

¹⁰Liu, Q., Xin, R., Li, C., Xu, C., & Yang, J. (2013). Application of red mud as a basic catalyst for biodiesel production. *Journal of Environmental Sciences (China)*, 25(4), 823–829.

¹¹Tang, Z., Lim, S., Pang, Y., Ong, H., & Lee, K. (2018). Synthesis of biomass as heterogeneous catalyst for application in biodiesel production : State of the art and fundamental review. *Renewable and Sustainable Energy Reviews*, 92(March), 235–253. <https://doi.org/10.1016/j.rser.2018.04.056>

¹²Falowo, O. A., Oladipo, B., Taiwo, A. E., Olaiya, A. T., Oyekola, O. O., & Betiku, E. (2022). Green heterogeneous base catalyst from ripe and unripe plantain peels mixture for the transesterification of waste cooking oil. *Chemical Engineering Journal Advances*, 10(January), 100293.

costs^{13,14}. Due to this, biodiesel made with a homogeneous catalyst is not cost effective comparable with diesel made from crude oil¹⁵.

As a result, a new process is necessary that is cheaper, more eco-friendly, and also streamlines the process of removing the catalyst from the products is needed. Hence, heterogeneous catalysts are being used as a preferable option for low-cost, long-term commercial biodiesel production. Using solid heterogeneous catalysts in manufacturing biodiesel minimizes wastewater produced during the purification of biodiesel. Also, there is the benefit of being able to recover the catalyst and also reuse^{16,17}.

Furthermore, cost of consumable oil, which makes up a substantial portion of the overall biodiesel manufacturing cost, is high; hence a low-grade feedstock like WCO would be recommended¹⁸. Also, with increased human population, demand for poultry birds as edible food has gradually increased and thus, more poultries have been established to meet such increasing demand. In turn, with this increase there is an increase in the amount of wastes generated by poultry birds. Continuous disposal of such wastes could result in pollution within the environment. Hence, using poultry droppings as catalyst would help the environment and reduce production cost of biodiesel¹⁹.

Production of biodiesel is dependent on multiple process factors such as feedstock of catalyst, catalyst loading, reaction time, temperature, methanol/oil ratio, agitation speed etc. RSM and ANN can be used in optimizing process variables affecting biodiesel yield and thereby creating a more cost effective process. RSM is a tool for statistical modelling and designing experiments with multivariable. RSM enables lowered number of experiments when compared with the conventional one-factor-at-a-time method for the same number of process factors. Empirical

¹³Marinković, M., Waisi, H., Blagojević, S., Zarubica, A., Ljupković, R., Krstić, A., & Janković, B. (2022). The effect of process parameters and catalyst support preparation methods on the catalytic efficiency in transesterification of sunflower oil over heterogeneous KI/Al₂O₃-based catalysts for biodiesel production. *Fuel*, 315(November 2021).

¹⁴Chumuang, N., & Punsuvon, V. (2017). Response Surface Methodology for Biodiesel Production Using Calcium Methoxide Catalyst Assisted with Tetrahydrofuran as Cosolvent. *Journal of Chemistry*, 2017.

¹⁵Akhabue, C. E., Osa-Benedict, E. O., Oyedoh, E. A., & Otoikhian, S. K. (2020). Development of a bio-based bifunctional catalyst for simultaneous esterification and transesterification of neem seed oil: Modeling and optimization studies. *Renewable Energy*, 152, 724–735.

¹⁶Amenaghawon, A. N., Evbarunegbe, N. I., & Obahiagbon, K. (2021). Optimum biodiesel production from waste vegetable oil using functionalized cow horn catalyst: A comparative evaluation of some expert systems. *Cleaner Engineering and Technology*, 4, 100184.

¹⁷Ali, B., Yusup, S., Quitain, A. T., Alnarabiji, M. S., Kamil, R. N. M., & Kida, T. (2018). Synthesis of novel graphene oxide/bentonite bi-functional heterogeneous catalyst for one-pot esterification and transesterification reactions. *Energy Conversion and Management*, 171, 1801–1812. <https://doi.org/10.1016/j.enconman.2018.06.082>

¹⁸Dhanasekaran krishnan. (2012). A kinetic study of biodiesel in waste cooking oil. *African Journal of Biotechnology*, 11(41), 9797–9804. <https://doi.org/10.5897/ajb12.507>

¹⁹Babaei, K., Bozorg, A., & Tavasoli, A. (2021). Hydrogen-rich gas production through supercritical water gasification of chicken manure over activated carbon/ceria-based nickel catalysts. *Journal of Analytical and Applied Pyrolysis*, 159(September), 105318. <https://doi.org/10.1016/j.jaap.2021.105318>

models for describing processes can also be developed using RSM. However, RSM has certain limitations such as being a local tool for optimization where the model developed may not be useful for extrapolation not within the range of experiments²⁰.

2. Materials and Methods

2.1. Materials

WCO used in this study was collected from a local restaurant within Benin City, Nigeria. The collected WCO was first filtered with muslin cloth to remove traces of food particles and then heated at 100°C to lower the content of moisture. The properties of the WCO used are shown in Table 1. Poultry droppings used for catalyst production was obtained from the University of Benin model farm, Benin City, Nigeria. Analytical grade reagents used were purchased from a vendor within Benin City, Nigeria.

Table 1: Physiochemical properties of WCO

Property (Unit)	Value
FFA (%)	4.63
Density (g/cm ³)	0.91
pH	5.17
Iodine value (g I ₂ /100g)	108.6
Saponification value (mg KOH/g)	215.99
Peroxide value (meq/kg)	17.3
Viscosity (m Pas @40°C)	39

2.2. Catalyst preparation

Fresh poultry droppings was collected and then sun-dried for several days to remove any remaining moisture and then grinded. The powdered dry poultry droppings was then heated to 300°C in a carbonization process for 4 hours to remove any remaining odor. The sample was then soaked with 0.1M KOH for 24 hours, dried in the sun for 1 hour, and in an oven at 100°C for 1 hour, and finally calcined for 6 hours in a muffle furnace at 900°C. The catalyst was kept in a desiccator, to allow cooling and then kept in an airtight container for further use.

2.3. Catalyst characterization

The physicochemical properties of the poultry droppings catalyst were assessed using various characterization tests. The BET analysis determined the surface area and pore properties. FTIR spectroscopy analysis showed the bond structure and interaction. SEM-EDX analysis showed the

²⁰Elfghi, F. M. (2016). A hybrid statistical approach for modeling and optimization of RON: A comparative study and combined application of response surface methodology (RSM) and artificial neural network (ANN) based on design of experiment (DOE). *Chemical Engineering Research and Design*, 113, 264–272.
<https://doi.org/10.1016/j.cherd.2016.05.023>

surface structure and elemental composition. XRF analysis determined the composition of oxides. And XRD analysis, determined the crystalline phases of the catalyst.

2.4. Biodiesel production and characterization

2.4.1. Two-step biodiesel production

The WCO had an FFA of $4.63 \pm 0.05\%$, which was high. Therefore, lowering the FFA to less than 2% was necessary by esterification reaction before transesterification reaction.

2.4.1.1. Acid-catalyzed esterification step

Using catalyst prepared from poultry droppings for biodiesel production, the WCO went through an acid-catalyzed esterification process to get FFA content lower than 2%. Use of oil with FFA content greater than 2%, leads to the formation of soap and difficulty in product separation, thereby resulting in lower biodiesel yield. As a result, before the transesterification step, an esterification pre-treatment step of the WCO was conducted using sulphuric acid and methanol. 5g of sulphuric acid was mixed with 150g of methanol. This mixture was added slowly to 500g of the WCO. The mixture was then agitated for 1 hour at 60°C using a magnetic stirrer. After that, the mixture was separated into two layers in a separating funnel overnight. After which, the new FFA of the oil was determined.

2.4.1.2 Transesterification of the esterified WCO

Transesterification was carried out following the procedure; 50g of WCO was poured into a 250-ml conical flask and placed on a hot plate magnetic stirrer, and heated to a specific temperature, a specific weight of the catalyst was dissolved in a specific volume of methanol and then transferred into the WCO in the conical flask. The specific values were in consonance with the experimental data generated using BBD. In conclusion of the reaction, the mixture in the conical flask was poured into a separating funnel and left overnight to allow separation of the glycerol and biodiesel. The biodiesel was washed thrice using hot distilled water to ensure removal of any impurities²¹. The washed biodiesel was then dried in an oven. The yield of biodiesel produced was calculated using Equation (1).

$$\text{Biodiesel yield} = \frac{\text{mass of biodiesel produced}}{\text{mass of WCO used}} \times 100 \quad (1)$$

2.5. Experimental design and RSM modelling

RSM using BBD was used to design the experiment using Design Expert 13. The effect of four process variables (methanol/oil ratio, catalyst loading, reaction temperature and reaction time) on the response (biodiesel yield) was explored. Table 2 shows the coded and actual levels of the BBD variables.

²¹Reda, A. (2014). Production and characterization of biodiesel from the traditional tannery fleshing wastes. *J. Sci. & Technol*, 7(1), 1–13.

Table 2: Coded and actual levels of BBD variables

Process variables	Units	Factor	Coded Low	Mean	Coded High
Methanol/oil ratio	Mol/mol	A	6	12	18
Catalyst loading	Wt.%	B	1	3	5
Reaction temperature	°C	C	40	55	70
Reaction time	Min.	D	60	90	120

The relationship of the process (independent) variables and the response is given by a second-order polynomial as shown in Equation (2).

$$Y_i = b_o + \sum b_i X_i + \sum b_{ij} X_i X_j + \sum b_{ii} X_i^2 + e_i \quad (2)$$

Where,

Y_i denotes the predicted response,

b_o is the value at intercept,

b_i is the coefficient of first order,

b_{ii} is the quadratic effect coefficient,

b_{ij} is the interacting effect coefficient,

X_i and X_j are the process variables that affect the response, and

e_i is the experimental random error.

This resulted in generation of 29 experimental runs which were performed in the Laboratory randomly, to avoid any systematic error in the outcomes.

2.6. ANN modelling

ANNs are effective and nonlinear instruments. Because most real-life problems are nonlinear, the nonlinearity of ANN makes them relevant. The system's essence is derived from the mimicking of the human neurological system. ANNs may learn from previously given data, in this case the data generated from BBD by constructing input-output mappings for parameter prediction. Biodiesel yield was predicted by using the Multilayer Full Feed Forward (MFFF) and Multilayer Normal Feed Forward (MNFF) neural networks. ANN was trained using the data obtained from BBD by different learning algorithms such as Incremental Back Propagation (IBP), Quickprob (QP), Genetic Algorithm (GA), Batch Back Propagation (BBP) and Levenberge-Marquadt Algorithm (LM). ANN system was made up of three layers: input comprising of four neurons, hidden, and output comprising of one neuron. There may be more than one concealed layer in some other circumstances.

2.7. Comparative performance of RSM and ANN

The performance of RSM and ANN was evaluated using standard statistical indicators such as coefficient of determination (R^2), mean square error (MSE), root mean square error (RMSE), standard error of prediction (SEP), mean absolute error (MAE) and average absolute deviation

(AAD) as shown in Equations (3) – (8). The results obtained were used in comparing the performance of both expert systems to determine superiority.

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

$$MSE = \frac{1}{n} \sum_{i=1}^n (x_{p,i} - x_{a,i})^2 \quad (4)$$

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (x_{p,i} - x_{a,i})^2} \quad (5)$$

$$SEP = \frac{RMSE}{x_{a,ave}} \times 100 \quad (6)$$

$$MAE = \frac{1}{n} \sum_{i=1}^n |(x_{a,i} - x_{p,i})| \quad (7)$$

$$AAD = \frac{1}{n} \left(\sum_{i=1}^n \left(\frac{|(x_{a,i} - x_{p,i})|}{x_{a,i}} \right) \right) \quad (8)$$

Where,

n is the number of experimental runs,

$x_{p,i}$ is the estimated values,

$x_{a,i}$ is the experimental values,

$x_{a,ave}$ is the average experimental values,

3. Results and Discussions

3.1. Catalyst characterization

3.1.1. BET analysis

An important physical analysis of the catalysts prepared was conducted by the application of BET surface analysis technique. The poultry droppings catalyst had surface area of 286.322m²/g, pore diameter of 1.853 nm and pore volume of 0.188 cc/g. High surface area gives solid catalysts active sites adequate room to attach to and for the reaction to take place. Additionally, good pore characteristics allow for faster diffusion of reactants and products from the pores to the reaction sites and to the catalyst surface²². The nitrogen physisorption isotherm and pore distribution are shown in Figures 1 and 2 respectively.

²²Madai, I. J., Chande Jande, Y. A., & Kivevele, T. (2020). Fast rate production of biodiesel from neem seed oil using a catalyst made from banana peel ash loaded with metal oxide (Li-CaO/Fe₂(SO₄)₃). *Advances in Materials Science and Engineering*, 2020. <https://doi.org/10.1155/2020/7825024>

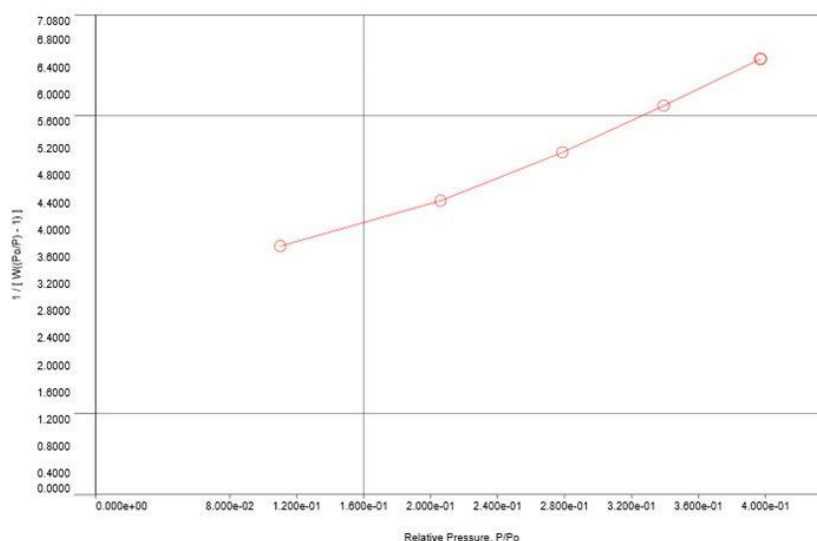


Figure 1: Nitrogen physisorption isotherm for poultry droppings catalyst

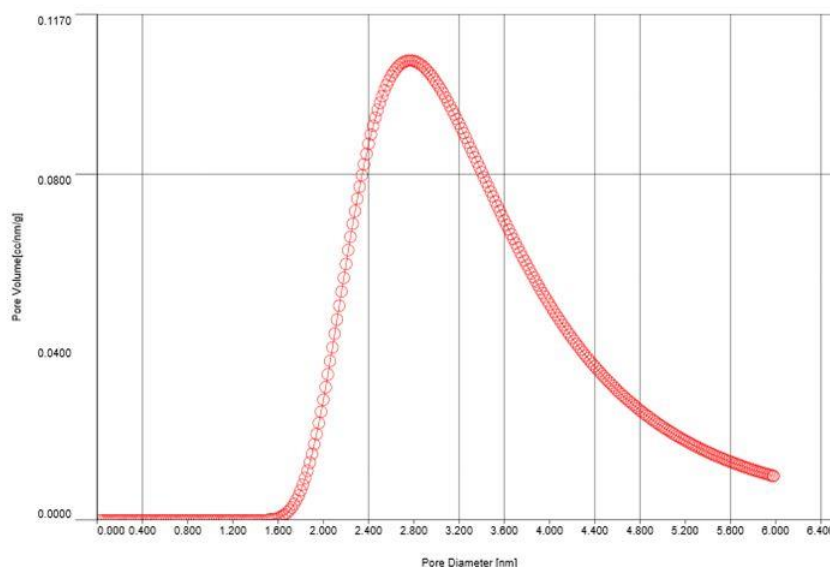


Figure 2: Pore size distribution for poultry droppings catalyst

3.1.2. FTIR analysis

The FTIR spectra of poultry droppings catalyst is shown in Figure 3. The catalyst spectrum shows distinguishing peaks at 3645.3cm^{-1} , 1420.1cm^{-1} , 1039.9cm^{-1} , 875.9cm^{-1} , and 674.6cm^{-1} . The absorption peak of the catalyst at wavenumber of 3645.3cm^{-1} can be attributed to the hydroxyl group stretching found. The presence of this peak can be as a result of moisture presence on the catalyst surface²³. The O-H out of plane vibration overlapped with the molecule's

²³ Etim, A. O., Betiku, E., Ajala, S. O., Olaniyi, P. J., & Ojumu, T. V. (2018). Potential of ripe plantain fruit peels as an ecofriendly catalyst for biodiesel synthesis: Optimization by artificial neural network integrated with genetic algorithm. Sustainability (Switzerland), 10(3). <https://doi.org/10.3390/su10030707>

fingerprint absorption, the presence of an aromatic phosphate group resulting from the P=O stretch, and the carbonyl groups from transitional metals can be responsible for the observed peaks. Peaks within $3400\text{--}3446\text{cm}^{-1}$, $2800\text{--}2950\text{cm}^{-1}$, $1640\text{--}1690\text{cm}^{-1}$, $1380\text{--}1410\text{cm}^{-1}$, and $550\text{--}570\text{cm}^{-1}$ as seen in the catalysts could be traced to the presence of metal oxides such as CaO and some other oxides of aluminum and magnesium²⁴. These FTIR results correspond with the XRD results obtained.

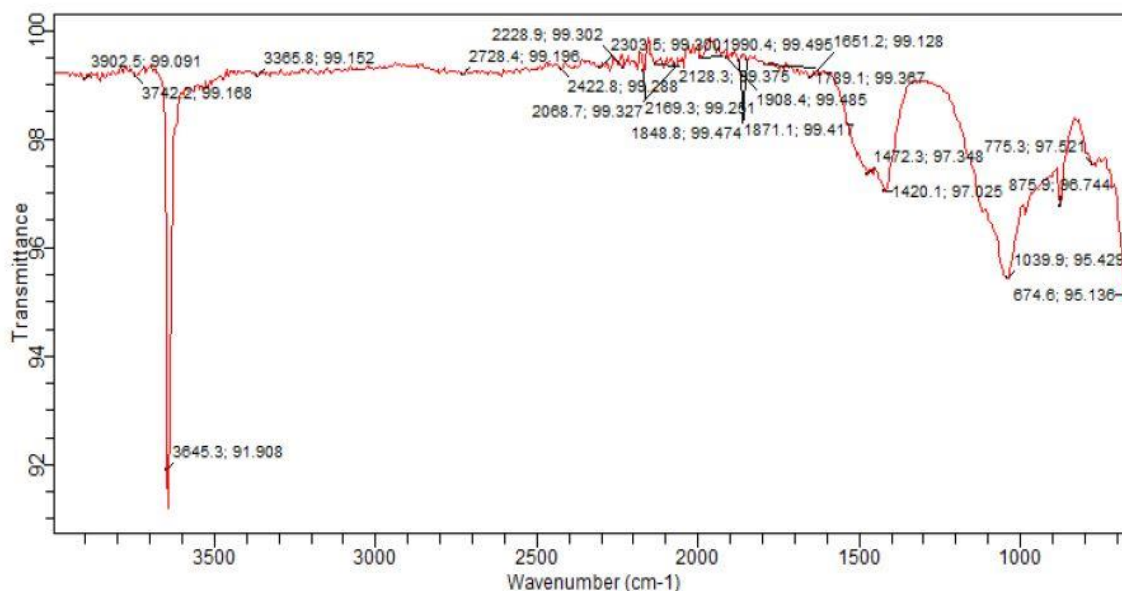


Figure 3: FTIR spectra of poultry droppings catalyst

3.1.3. SEM-EDX analysis

Morphologies of poultry droppings catalysts in different magnifications are shown in Figure 4. SEM determined the surface morphology the catalyst. The image of the catalyst from SEM analysis shows particle agglomerations, although a lot smaller particles are seen around it. The surface area observed corresponds with the BET analysis results.

The EDX patterns showed on Figure 5 indicates that the catalyst had within it metals like calcium, potassium, magnesium, aluminum and silicon. The actual weight concentration of these metals and the other elements present are shown in Table 3. The metals present in the catalyst are very reactive and this can explain the catalytic behavior of the catalysts.

²⁴Amenaghawon, A. N., Obahiagbon, K., Isesele, V., & Usman, F. (2022). Optimized biodiesel production from waste cooking oil using a functionalized bio-based heterogeneous catalyst. *Cleaner Engineering and Technology*, 8(April), 100501. <https://doi.org/10.1016/j.clet.2022.100501>

Optimized Biodiesel Production from Waste Cooking Oil Using Poultry Droppings Catalyst: A Comparison of RSM and ANN

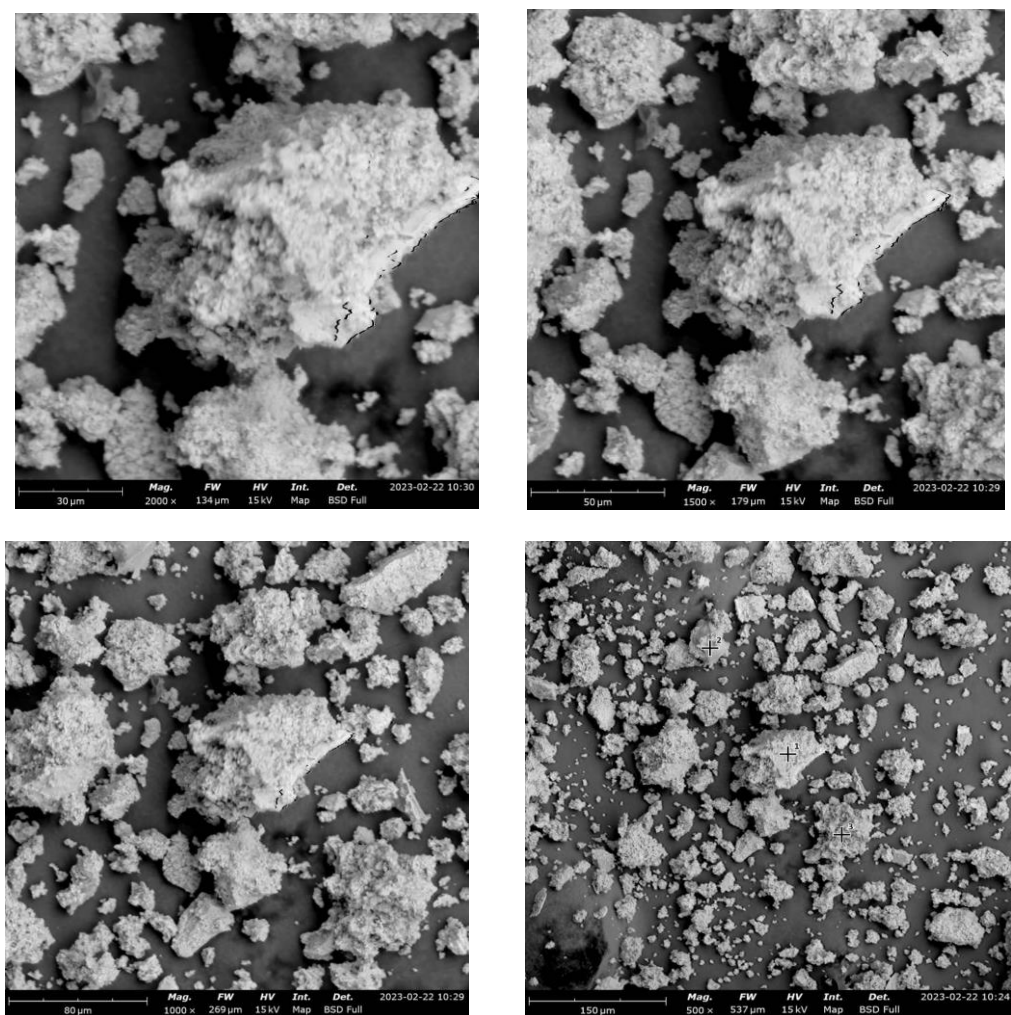


Figure 4: SEM images of poultry droppings catalyst

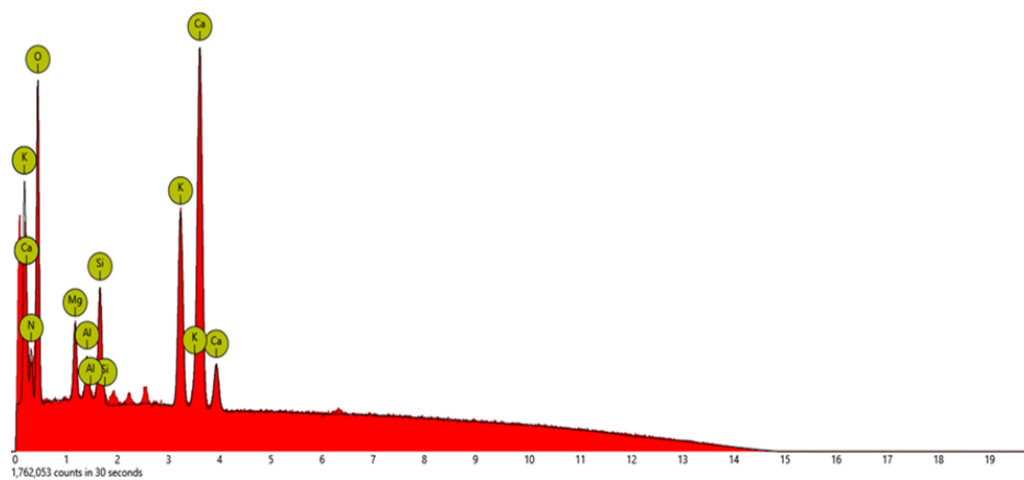


Figure 5: EDX pattern of poultry droppings catalyst

Table 3: Elemental composition of poultry dropping catalyst obtained from EDX

Element number	Element name	Element symbol	Weight Concentration (%)
8	Oxygen	O	54.99
7	Nitrogen	N	7.38
20	Calcium	Ca	19.80
19	Potassium	K	9.48
12	Magnesium	Mg	3.82
14	Silicon	Si	2.98
13	Aluminum	Al	1.55

3.1.4. XRF analysis

The elemental composition of the catalyst determined by XRF is shown in Table 4. The data obtained shows that CaO had the largest proportion (78.886%) of the component oxides of the catalyst. CaO is a highly desired catalyst for biodiesel production due to its low toxicity and its ability to enhance transesterification due to its catalytic capabilities²⁵. Some other metallic oxides present in considerable quantities in the catalyst are SiO₂, Al₂O₃ and Fe₂O₃.

Table 4: XRF data for poultry droppings catalyst

Component	Concentration (%)
Silicon oxide (SiO ₂)	11.502
Vanadium pentoxide (V ₂ O ₅)	0.055
Chromium oxide (Cr ₂ O ₃)	0.011
Manganese oxide (MnO)	0.092
Iron (iii) oxide (Fe ₂ O ₃)	2.215
Cobalt tetraoxide (Co ₃ O ₄)	0.043
Nickel oxide (NiO)	0.005
Copper oxide (CuO)	0.048
Niobium pentoxide (Nb ₂ O ₃)	0.011
Tungsten oxide (WO ₃)	0.017
Phosphorus oxide (P ₂ O ₅)	0.972
Trioxosulphate (SO ₃)	0.864
Calcium oxide (CaO)	78.886
Potassium oxide (K ₂ O)	0.769
Barium oxide (BaO)	0.060
Aluminum oxide (Al ₂ O ₃)	3.226
Tantalum pentoxide (Ta ₂ O ₅)	0.011
Titanium oxide (TiO ₂)	0.242
Zinc oxide (ZnO)	0.080
Chlorine (Cl)	0.418
Zirconium oxide (ZrO ₂)	0.083
Tin oxide (SnO ₂)	0.388

²⁵Jung, J. M., Oh, J. I., Baek, K., Lee, J., & Kwon, E. E. (2018). Biodiesel production from waste cooking oil using biochar derived from chicken manure as a porous media and catalyst. *Energy Conversion and Management*, 165, 628–633.

3.1.5. XRD analysis

Figure 6 shows the XRD data for poultry droppings catalyst. Figure 6 show a sharp spectra indicating considerable crystallinity. The peaks were clearly seen at 2θ of 9.24° , 18.42° , 24.34° , 27.00° , 34.46° , 50.42° and 60.12° for the catalyst. The main characteristic peaks are attributed to the presence of portlandite ($\text{Ca}(\text{OH})_2$), calcite (CaCO_3), lime (CaO), quartz (SiO_2), albite ($\text{NaAlSi}_3\text{O}_8$) and muscovite ($\text{H}_2\text{KAl}_3(\text{SiO}_4)_3$).

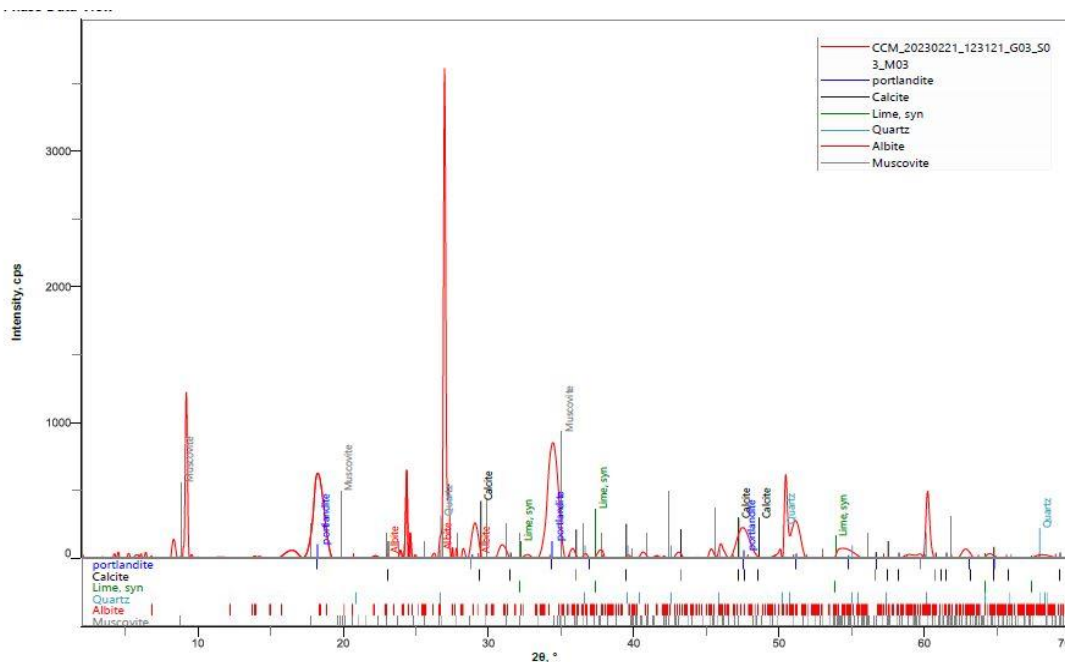


Figure 6: XRD pattern for poultry droppings catalyst

3.2. Optimization by RSM

Four variables were optimized: methanol/oil ratio, catalyst loading, reaction temperature and reaction time. Table 5 shows the experimental design of the transesterification reaction of WCO to produce biodiesel with the experimental and predicted responses. Equation (9) represents the quadratic model (coded-basis).

$$\text{Yield}_{\text{CM}} = 37.323 - 3.128A - 14.832B + 2.938C + 0.027D + 0.27AB + 0.022AC + 0.002AD + 0.045BC + 0.007BD - 0.006CD + 0.004A^2 + 1.053B^2 - 0.027C^2 + 0.002D^2 \quad (9)$$

When an independent variable in a regression equation has a positive sign, it implies that increasing the variable will result in an increase in the response, whereas a negative sign would cause a decrease in the response²⁶. From Equation (9), reaction temperature (C), reaction time (D), interaction factors (AB, AC, AD, BC and BD) and quadratic factor (A^2 , B^2 and D^2) have

²⁶Ocholi, O., Menkiti, M., Auta, M., & Ezemagu, I. (2018). Optimization of the operating parameters for the extractive synthesis of biolubricant from sesame seed oil via response surface methodology. *Egyptian Journal of Petroleum*, 27(3), 265–275. <https://doi.org/10.1016/j.ejpe.2017.04.001>

positive effects on the percentage yield of biodiesel while methanol/oil ratio (A), catalyst loading (B), interaction factor (CD) and quadratic factor (C^2) had negative effects on the percentage biodiesel yield from the poultry droppings catalyzed process. Analysis of variance (ANOVA) used to find the importance of the model is given in Table 4.

P-value and F-value are demonstrated the model significance and its consistency, respectively. According to Table 6, F-value is 17.67 and the p-value is <0.0001 means the designed model is significant.

Table 5: Transesterification experimental design with RSM and ANN response

Run	Methanol/oil ratio (mol/mol)	Catalyst loading (wt%)	Reaction temperature ($^{\circ}\text{C}$)	Reaction time (min.)	Experimental yield (%)	RSM yield (%)	ANN yield (%)
1	18.00	1.00	55.00	90.00	68.13	67.07	68.129
2	6.00	3.00	55.00	60.00	70.9	72.5	70.901
3	12.00	3.00	55.00	90.00	67.75	66.98	66.984
4	12.00	3.00	40.00	120.00	71.4	70.34	71.402
5	12.00	1.00	70.00	90.00	63.3	64.9	63.3
6	6.00	3.00	70.00	90.00	59.66	61.26	59.66
7	18.00	3.00	55.00	60.00	61.81	61.28	61.811
8	12.00	3.00	70.00	120.00	59.62	58.55	59.619
9	12.00	3.00	55.00	90.00	66.94	66.98	66.984
10	12.00	3.00	55.00	90.00	67.49	66.98	66.984
11	12.00	3.00	55.00	90.00	65.25	66.98	66.984
12	18.00	5.00	55.00	90.00	61.81	65.01	61.811
13	6.00	3.00	55.00	120.00	74.07	75.67	74.071
14	12.00	5.00	70.00	90.00	59.58	59.05	59.578
15	12.00	5.00	55.00	120.00	71.42	70.89	71.42
16	6.00	5.00	55.00	90.00	70.15	69.08	70.15
17	6.00	3.00	40.00	90.00	69.76	71.36	69.757
18	18.00	3.00	70.00	90.00	55.07	54.54	55.08
19	12.00	5.00	40.00	90.00	63.09	62.56	63.091
20	12.00	1.00	55.00	120.00	77.04	78.64	77.04
21	12.00	1.00	40.00	90.00	72.26	73.85	72.262
22	18.00	3.00	55.00	120.00	66.24	65.71	66.238
23	6.00	1.00	55.00	90.00	89.5	84.17	89.499
24	18.00	3.00	40.00	90.00	57.43	56.9	57.425
25	12.00	1.00	55.00	60.00	74.06	75.66	74.059
26	12.00	3.00	55.00	90.00	67.49	66.98	66.984
27	12.00	3.00	40.00	60.00	62.05	60.99	62.05
28	12.00	3.00	70.00	60.00	61.37	60.3	61.369
29	12.00	5.00	55.00	60.00	66.8	66.27	66.799

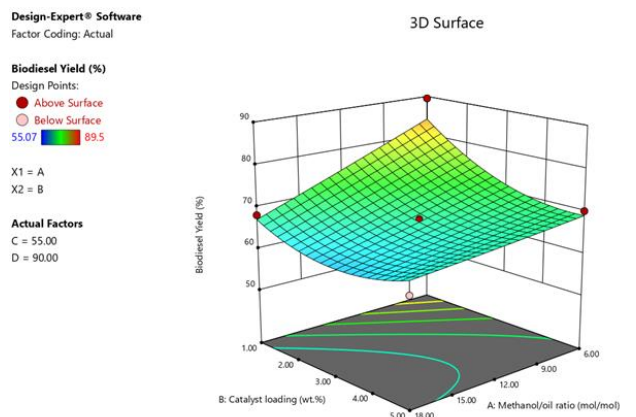
Table 6: ANOVA data for the RSM model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1276.23	14	91.16	17.67	< 0.0001	significant
A-Methanol/oil ratio	336.55	1	336.55	65.23	< 0.0001	
B-Catalyst loading	220.51	1	220.51	42.74	< 0.0001	
C-Reaction temperature	116.50	1	116.50	22.58	0.0003	
D-Reaction time	43.32	1	43.32	8.40	0.0117	
AB	42.45	1	42.45	8.23	0.0124	
AC	14.98	1	14.98	2.90	0.1105	
AD	0.3969	1	0.3969	0.0769	0.7856	
BC	7.43	1	7.43	1.44	0.2502	
BD	0.6724	1	0.6724	0.1303	0.7235	
CD	30.80	1	30.80	5.97	0.0284	
A ²	0.1198	1	0.1198	0.0232	0.8811	
B ²	115.09	1	115.09	22.30	0.0003	
C ²	241.88	1	241.88	46.88	< 0.0001	
D ²	18.03	1	18.03	3.49	0.0826	
Residual	72.24	14	5.16			
Lack of Fit	68.13	10	6.81	6.63	0.0416	significant
Pure Error	4.11	4	1.03			
Cor Total	1348.47	28				

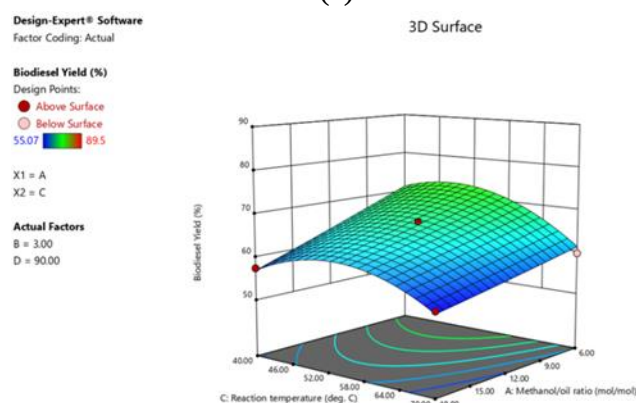
The quality of model fit is assessed by the coefficient of determination (R^2). The fit statistics data showed that the R^2 and adjusted R^2 values were 0.9464 and 0.8929 respectively. The difference of less than 0.2 indicates that the predicted R^2 and adjusted R^2 values corresponds. Therefore, this model could be used in the theoretical prediction of the biodiesel production process.

3.2.1. Effect of input variables on biodiesel yield

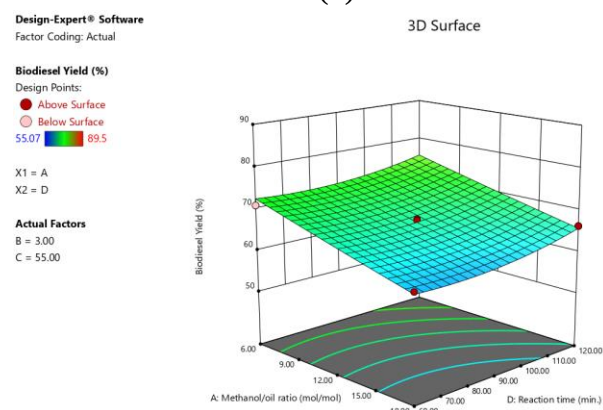
The effects of process parameters on biodiesel production were analyzed by three- dimensional (3D) surface plots. Figure 7 shows the 3D surface plots representing two independent variables while keeping other variables constant. According to the Table 6, methanol/oil ratio, catalyst loading and reaction temperature are the most significant variables for biodiesel production using poultry droppings catalyst, with methanol/oil ratio being the dominating factor, having the highest sums of squares. The three-dimensional plots show the interactions between the variables and biodiesel conversion. The optimum yield of biodiesel of 90.4694% was achieved at a temperature of 43.92°C, reaction time of 120 minutes with a methanol/oil ratio of 6:1 and catalyst loading of 1 wt.%.



(a)



(b)



(c)

Figure 7: 3D plots showing the interaction between (a) Methanol/oil ratio and catalyst loading (b) Methanol/oil ratio and reaction temperature and (c) Methanol/oil ratio and reaction time

3.3. ANN analysis

Four nodes at the input layer, representing the four input parameters, two hidden layers, and one node at the output layer, representing the single response (biodiesel yield), made up the network architecture employed in this study. The Hyperbolic Transfer Function (Tanh) was found to have better performance for transesterification. This was determined by testing various transfer functions, including Sigmoid, Gaussian, Hyperbolic tangent, Bipolar linear, Threshold liner, and linear functions, iteratively at 10000 epochs. Table 7 shows the R^2 and RMSE values for the different transfer functions. It can also be seen that Tanh provided the highest R^2 of 0.95997, and the lowest RMSE value of 1.3885.

Table 7: R^2 and RMSE values for various transfer functions

Transfer function	R^2	RMSE
Sigmoid	0.61316	4.3163
Tanh	0.95997	1.3885
Gaussian	0.77878	3.264
Linear	0.53162	4.7491
Threshold linear	-	6.9397
Bipolar linear	0.53318	4.7415

The varying R^2 and RMSE values for various learning methods using the MNFF and MFFF network designs are displayed in Table 8. The best training approach for predicting the biodiesel yield out the various approaches (IBP, BBP, QP, GA, and LM) was LM with R^2 value of 0.99669 and RMSE of 0.39919.

Table 8: Training of the different network structures

Network architecture	Learning algorithm	R^2	RMSE
MNFF	IBP	0.96074	1.3751
	BBP	0.96417	1.3136
	QP	0.98831	0.75037
	GA	0.91871	1.9786
	LM	0.99669	0.39919
MFFF	IBP	0.99162	0.63542
	BBP	0.99356	0.55681
	QP	0.99309	0.57673
	GA	0.99502	0.44318
	LM	0.99641	0.41594

The network structure of the neural network employed is shown in Figure 8. The optimal training method was ultimately determined to be two hidden layers with five nodes.

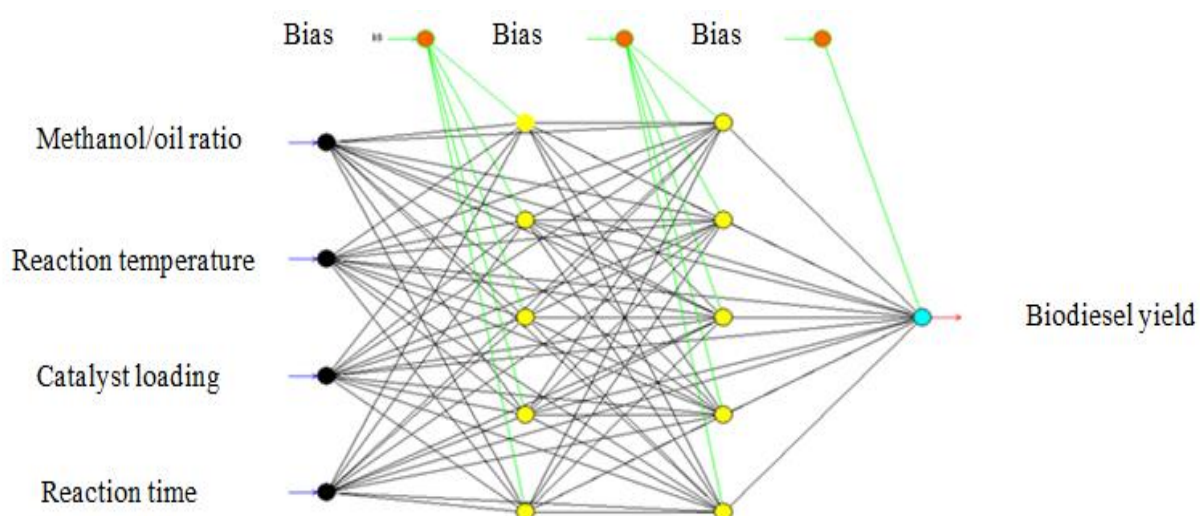


Figure 8: Architecture of the Neural Network for biodiesel production using poultry droppings as catalyst

3.4. Comparison of RSM and ANN models

RSM and ANN models were compared based on their statistical values such as R^2 , MSE, RMSE, SEP, MAE, and AAD. Table 9 shows the results of the statistic values for the RSM and ANN models. ANN had the highest R^2 value of 0.99669. Also, the values of RMSE, SEP, and MAE gotten from both models indicates that ANN had lower error values than RSM. Hence, ANN model is the more suitable than RSM for optimizing the biodiesel production using poultry droppings as catalyst. Figure 9 shows the predicted biodiesel yield vs. experimental biodiesel yield obtained from RSM and ANN. Moreover, the figure gives that the ANN predicted values closely aligned to the experimental results than that of RSM. These results also show that the ANN has better performance than the RSM.

Table 9: Comparison of RSM and ANN

Parameters	RSM	ANN
R^2	0.9464	0.99669
MSE	2.4916	0.1416
RMSE	1.5785	0.39919
SEP	2.3578	0.5622
MAE	1.22	0.1239
AAD	1.7747	0.1867

Optimized Biodiesel Production from Waste Cooking Oil Using Poultry Droppings Catalyst: A Comparison of RSM and ANN

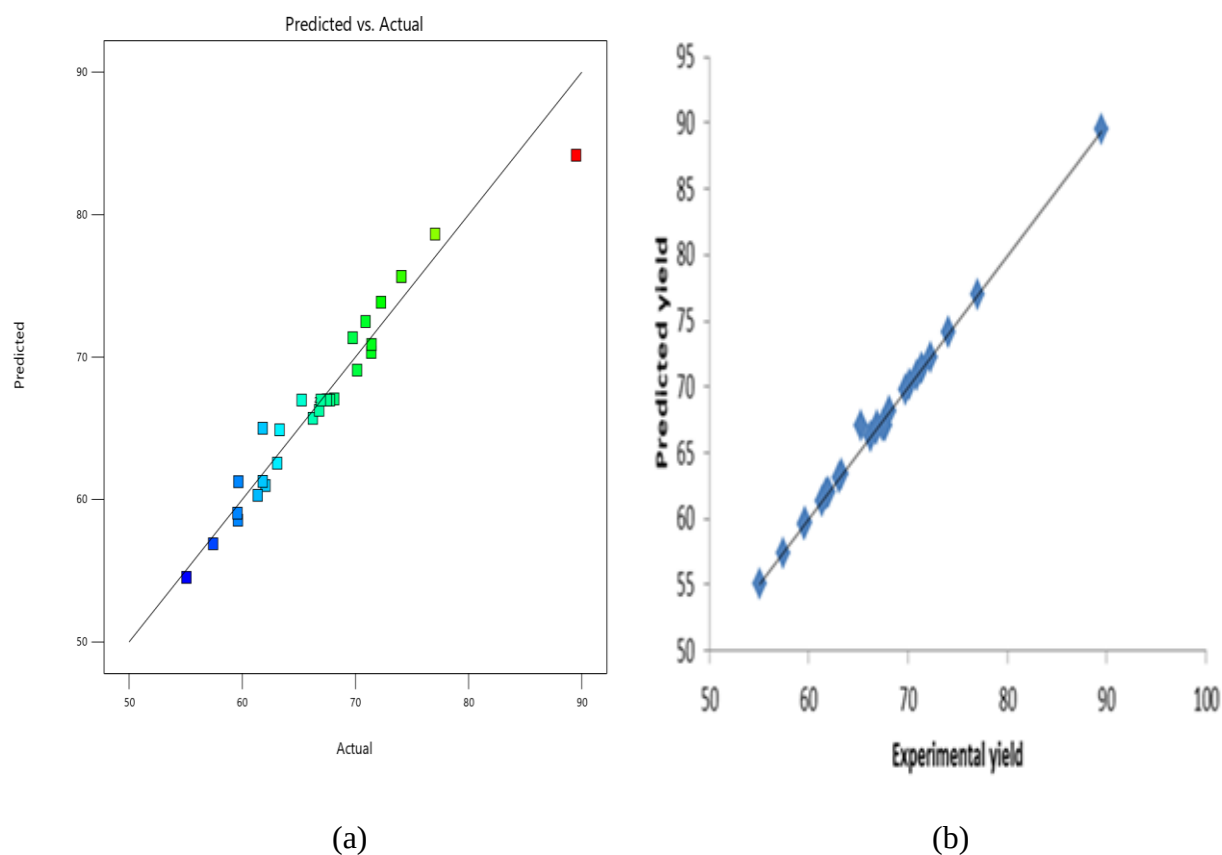


Figure 9: Predicted vs. experimental yield using (a) RSM (b) ANN

3.5. Biodiesel characterization

Table 10 summarizes the various properties tested and their corresponding values obtained for the biodiesel produced using poultry dropping catalyst as compared to ASTM D6751 and EN14214 standards of biodiesel. Low FFA percentage contributes to improved oxidative stability and longer shelf life, while low acid value indicates minimal corrosiveness of the biodiesel which would cause no engine damage. High thermal stability indicates a fuel with a high flash point, which makes it safe for transportation. The fuel's calorific value indicates that it also contains a lot of energy. The presence of a high cetane number demonstrates that the fuel is of good quality and will burn cleanly. Low fuel viscosity results in good fuel flow, which makes fuel atomization during spraying simple.

Table 10: Physicochemical properties of biodiesel produced and standards of biodiesel

Properties (Unit)	Value	ASTM D6751	EN14214
Acid value (mg KOH/g)	0.24	0.8max	0.5max
Flash point (°C)	133	100 to 170	>120
Calorific value (MJ/kg)	36.42	-	>35
Cetane number	57.17	>47	>51
Viscosity (mm ² /s) at 40°C	4.87	1.9 to 6	3.5 to 5

4. Conclusion

Biodiesel was produced from WCO using poultry droppings as catalyst. The characterization results of the catalyst indicated that poultry droppings can be utilized as a solid heterogeneous catalyst for the biodiesel production. Furthermore, RSM and ANN methods were successfully utilized for the prediction and optimization of process parameters for production of biodiesel using the poultry droppings as catalyst. From the results obtained, the optimum yield of biodiesel of 90.4694% was achieved at a temperature of 43.92°C, reaction time of 120 minutes with a methanol/oil ratio of 6:1 and catalyst loading of 1 wt.%. The predictive capability of both expert systems were determined using statistical values (R^2 , MSE, RMSE, SEP, and MAE). The acquired results were used to compare their effectiveness and to determine superiority. From the results, ANN was a better predictive tool with higher R^2 value of 0.99669 compared to that of RSM with R^2 value of 0.9464.