

Artificial Neural Networks for Modelling Biodiesel Production from Sesame Seed Oil Using Doped Heterogeneous Catalyst Prepared from Periwinkle Shell

By

Ugochukwu Jonathan Anene, Kessington Obahiagbon* and Andrew Nosakhare Amenaghawon

Abstract

This study investigated the synthesis of a bifunctional heterogeneous solid catalyst to produce environmentally benign biodiesel from sesame seed oil. The heterogeneous solid catalyst was synthesized using periwinkle shell as support material while functionalization was carried out using nickel-strontium mixed metal oxides via wet impregnation method. The synthesized catalyst was characterized using X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and Brunauer, Emmett and Teller (BET) analysis. Artificial neural networks (ANN) used to model the parametric effect of reaction time, reaction temperature, catalyst concentration and methanol to oil ratio biodiesel yield. The results obtained showed that an oil yield of 50% was obtained after extraction. The oil had a low kinematic viscosity, acid value, iodine value and peroxide values, making it a suitable feedstock for biodiesel production. Characterization of the solid catalyst revealed that it had a high surface area of 367.40 m²/g, pore diameter of 2.45 nm and pore volume of 0.198 cm³/g. ANN was adequate in modelling the process with high R² value (0.9980), adjusted R² value (0.9977) and low error values (MSE = 0.7547, RMSE = 0.868, SEP = 1.4091, MAE = 0.3348 and AAD = 0.5962). Numerical optimization gave a maximum biodiesel yield of 95.61% at corresponding reaction time, reaction temperature, catalyst concentration, and methanol to oil ratio values of 62.55 min, 77.59 °C, 3.20 wt%, and 6.50 respectively. The properties of the biodiesel sample produced at the optimized conditions were comparable with the ASTM D6571 and EN 14214 standards.

Keywords: Biodiesel, Sesame seed oil, Artificial neural networks, Modelling, Optimization

1. INTRODUCTION

Global population is continuously on the increase and this has the consequent impact of increasing demand for energy¹. The transportation sector in particular has had the most significant impact in terms of the demand for liquid fuels. Currently, the transportation sector is primarily dependent on petroleum-based sources of fuels. Reports have shown that the utilisation of petroleum-based fuels like gasoline and diesel for road transportation is not sustainable and environmentally friendly consciousness.²

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

*Corresponding author: kess.obahiagbon@uniben.edu

¹ Jones, G. A. and Warner, K. J. (2016). The 21st century population-energy-climate nexus. *Energy Policy*, 93, pp. 206-212.

² Ajala, S. O. and Betiku, E. (2015). Yellow oleander seed oil extraction modeling and process parameters optimization: Performance evaluation of artificial neural network and response surface methodology. *Journal of food processing and preservation*, 39(6), pp. 1466-1474.

The combustion of these fuels in internal combustion engines contributes to environmental pollution through the emission of greenhouse gases³. Other than greenhouse gas emissions, consumption of petroleum-based fuels has also been reported to contribute to the release of other toxic air pollutants such as volatile organic compounds (VOCs), oxides of sulphur (SO_x), nitrogen oxides (NO_x), and particulate matter⁴. Furthermore, global warming and climate change have been attributed to the release of these greenhouse gases by a number of researchers. As a result of the aforementioned problems associated with the use of petroleum-based fuels and the rising awareness of their environmental impacts, a lot of attention is now being directed to the search for energy sources that are more sustainable and environmentally friendly.

Bioenergy sources, particularly biofuels such as biodiesel, bioethanol, biogas etc have been identified as a way of drastically reducing the harmful effects associated with the emission of greenhouse gases institutions⁵. Among available biofuels, biodiesel has been identified as a viable alternative to petroleum-based diesel for powering heavy duty transport vehicles because it is renewable, biodegradable, non-toxic and environmentally friendly⁶. Biodiesel is produced via the transesterification of vegetable oils and oils of some non-edible plants. The composition of biodiesel is very similar to that of petrodiesel hence both can be blended in any proportion for use in existing diesel engines without modifications.

Homogeneous catalysts, such as bases, acids, and enzymes, are those that exist in the same phase (gas or liquid) where the reaction occurs. Most often, homogeneous catalysis involves the introduction of an aqueous phase catalyst into an aqueous solution of reactants. However, these homogeneous catalysts have several limitations such as separation problems and reduced biodiesel yield. Heterogeneous catalysts are catalysts that operate in a different phase from the reactants. Typically, heterogeneous catalysis involves the use of solid catalysts placed in a liquid reaction mixture and they are able to overcome the challenges of homogeneous catalysts. Commonly used solid base catalysts are alkaline earth metal oxides, zeolite, KNO₃ loaded on Al₂O₃, KNO₃/Al₂O₃, BaO, SrO, CaO, MgO, etc.

Sesame seed (*Sesamum indicum* L.) is one of the world's most important and oldest oil seed crops known to man⁷. It has been cultivated for centuries, particularly in Asia and Africa specially Sudan, Ethiopia and Nigeria⁸. Nearly 70% of the world production is from Asia. Africa grows 26% of the world's sesame, with Sierra Leone, Sudan, Nigeria and Uganda being key producers. Latin America grows 4% of the total world production⁷. The chemical composition of sesame shows that the seed is an important source of oil (50–60%), protein (18–25%), carbohydrates and ash⁹. The oil fraction shows a remarkable stability to oxidation due to the presence of antioxidants (sesamol, sesamolins and sesamin) together with tocopherols.

³ Gomez, L.D., Steele-King, C.G. and McQueen-Mason, S.J. (2008). Sustainable liquid biofuels from biomass: the writing's on the walls. *New Phytologist*, 178(3), pp. 473–485.

⁴ Liu, Z., Guan, D., Wei, W., Davis, S. J., Ciaia, P., Bai, J. and Andres, R. J. (2015). Reduced carbon emission estimates from fossil fuel combustion and cement production in China. *Nature*, 524(7565), p. 335.

⁵ Hajjari, M., Tabatabaei, M., Aghbashlo, M. and Ghanavati, H. (2017). A review on the prospects of sustainable biodiesel production: A global scenario with an emphasis on waste-oil biodiesel utilization. *Renewable and Sustainable Energy Reviews*, 72, 445–464.

⁶ Osorio-Tejada, J. L., Llera-Sastresa, E., & Scarpellini, S. (2017). A multi-criteria sustainability assessment for biodiesel and liquefied natural gas as alternative fuels in transport systems. *Journal of Natural Gas Science and Engineering*, 42, 169–186.

⁷ Abou-Gharbia, H. A., Shehata, A. A. Y. and Shahidi, F. (2000). Effect of processing on oxidative stability and lipid classes of sesame oil. *Food research international*, 33(5), pp. 331–340.

⁸ Casadei, E. and Albert, J. (2003). Food and agriculture organization of the United Nations.

⁹ El Khier, M. K. S., Ishag, K. E. A. and Yagoub, A. A. (2008). Chemical composition and oil characteristics of sesame seed cultivars grown in Sudan. *Research Journal of Agriculture and Biological Sciences*, 4(6), pp. 761–766.

The quantity and quality of the oil contained in the seed have been shown to depend on ecological, genetics and physiological factors such as climate, soil type, cultivars and maturity of plant respectively¹⁰.

The performance of the biodiesel production process has been reported to be influenced by operating variables such as temperature, amount of catalyst, reaction time, methanol to oil ratio, stirring speed etc. Optimising these variables has the potential of enhancing biodiesel yield¹¹. An important example of a tool for modelling biodiesel production is artificial neural networks (ANNs), which are modelled after biological nervous system have emerged as promising artificial learning tool in chemical engineering. ANN is an attractive option for developing nonlinear empirical models particularly when it is not possible to develop conventional empirical models or when such models are inadequate in describing real life systems¹².

Thus, the aim of this study was to use artificial neural network to model and optimize the production of biodiesel from sesame seed oil using strontium-doped periwinkle shell as heterogeneous solid catalyst.

2. MATERIALS AND METHODS

2.1. Materials

The periwinkle shells used as precursor for the production of the heterogeneous solid catalyst were obtained from a local market in Warri, Delta State, Nigeria. The periwinkle shells were cleaned to remove impurities and fleshly portion adhered to the wall of shell by rinsing with cycles of warm water. The sesame seeds used as source of oil were obtained from a local market in Niger State, Nigeria. The seeds were separated from the chaff and dried for 5 days in the sun at ambient temperature for easy dehulling of seeds. The seeds were further dried in an electric oven at 60 °C for 5 hours so as to reduce the moisture content to an appreciable value in order to ease the extraction process. The prepared seeds were grounded using an electric mill so as to improve the surface area for extraction¹³.

2.2. Oil Extraction

The Soxhlet extraction procedure was adopted for the extraction of the sesame seed oil using n Hexane as solvent. The prepared sesame seed was weighed and then charged into the equipment in a muslin cloth placed in the thimble of the extractor. The extractor was connected to a round bottom flask containing n-hexane. The set up was completed with a condenser which was tightly fixed at the bottom. The whole setup was heated up in a heating mantle at a fixed temperature of 70 °C. Multiple runs were carried out in order to have enough amount of oil for the production of biodiesel. At the end of each run, the residue was discarded, and the extractor was charged again with fresh seed. Furthermore, the excess solvent in the oil was recovered using a rotary evaporator. The oil yield was gravimetrically determined using Equation (1).

¹⁰ Rahman, M. S., Hossain, M. A., Ahmed, G. M. and Uddin, M. M. (2007). Studies on the characterization, lipids and glyceride compositions of Sesame (*Sesamum indicum* linn.) Seed Oil. *Bangladesh Journal of Scientific and Industrial Research*, 42(1), pp. 67-74.

¹¹ Tshizanga, N., Aransiola, E. F. and Oyekola, O. (2017). Optimisation of biodiesel production from waste vegetable oil and eggshell ash. *South African Journal of Chemical Engineering*, 23, pp. 145-156.

¹² Velu, S., Velayutham, V. and Manickkam, S. (2016). Optimization of fermentation media for xanthan gum production from *Xanthomonas campestris* using Response Surface Methodology and Artificial Neural Network techniques. *Indian Journal Chemical Technology*, 23, pp. 353–361.

¹³ Betiku, E. and Adepoju, T. F. (2013). Methanolysis optimization of sesame (*Sesamum indicum*) oil to biodiesel and fuel quality characterization. *International Journal of Energy and Environmental Engineering*, 4(1), p. 9.

$$\text{Oil yield (wt\%)} = \frac{\text{mass of extracted oil}}{\text{mass of seed used}} \times 100 \quad (1)$$

2.3. Characterization of Sesame Seed Oil

The physical and chemical properties of the extracted sesame seed oil were determined to assess its suitability as a feedstock for biodiesel production. The properties investigated include density, specific gravity, peroxide value, acid value, saponification value, iodine value, viscosity, chemical composition etc according to the methods of AOAC¹⁴.

2.4. Catalyst Preparation and Characterization

Periwinkle shells were used as catalyst (CaO) precursor for this study. The periwinkle shells were crushed and then vigorously washed with water to remove any decayed flesh materials within the shell. The less dense inner wall linings floated in the water, while the denser shells sunk in the water. This step was repeated several times until all the gelatinous materials were satisfactorily removed. The shells were air dried in the sun and were then dried in an oven at 110 °C for 2 hours to remove the remaining moisture. The dried periwinkle shells were ball milled to reduce the particle size and increase the surface area. The ground shells were sieved to a size of 300 – 425 µm using a sieve mounted on a sieve-shaker. The sieve-shaker was operated for 20 minutes per batch to obtain fine particles. Calcination of the sieved periwinkle shell was carried out in a muffle furnace under static air condition at 900 °C for four hours to decompose the calcium carbonate species in the periwinkle shell into CaO molecules. At the end of the process, the calcined shells were then crushed and ground to fine powder. The resulting material was then kept in a desiccator to prevent contact with air. For the doping, exactly 50 g of the stored calcined periwinkle shell samples was measured. An aqueous solution of strontium nitrate (0.2 M) was then prepared. The measured calcined periwinkle shell sample was doped with the strontium nitrate solution using wet impregnation method and stirred at room temperature for 1 hr. The mixture was dried at 105 °C for 24 h in an electric oven and was subsequently calcined at 600 °C for 3 hrs in the furnace. This resulted in Sr/CaO catalyst which was stored in a desiccator for catalyst performance studies¹⁵.

The characteristics of the produced solid catalyst were determined by carrying out numerous characterization tests. The tests carried out include Fourier transform infrared spectroscopy (FTIR), X-ray fluorescence (XRF) Spectroscopy, X-Ray diffraction (XRD) spectroscopy, scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) analysis and these were carried out according to the standard analytical procedures.

2.5. Biodiesel Production and Characterization

The Sr/Cao catalysed transesterification reaction of sesame seed oil and methanol was carried out as a batch process in a 250 mL three-necked round bottom flask fitted with a water-cooled condenser and thermometer. The reaction was carried out under different conditions of reaction time, methanol to oil ratio, catalyst dosage, and temperature and these conditions were optimized according to a statistical experimental design procedure. For the actual transesterification reaction, the catalyst was dried in oven at 100 °C for 2 h and then dispersed in methanol at 50 °C under constant stirring for 30 min. This was followed by addition of the

¹⁴ Association of Official Analytical Chemists (AOAC). (1990). *Official methods of analysis of the Association of Official Analytical Chemists* (Vol. 1).

¹⁵ Tantirungrotechai, J., Thepwatee, S. and Yoosuk, B. (2013). Biodiesel synthesis over Sr/MgO solid base catalyst. *Fuel*, 106, pp. 279–84.

required quantity of sesame seed oil which had been preheated to the reaction temperature¹⁶. The other experimental conditions were fixed according to the experimental design. At the end of the reaction, the reaction mixture was filtered using a Whatman 42 filter paper (125 mm diameter and a pore size of 2.5 µm) followed by centrifugation to separate the catalyst. The resulting filtrate was then transferred to separating funnel and it was allowed to stand for 24 hours for separation to take place. The products separated into four distinct layers, methanol layer, biodiesel layer, glycerol layer and catalyst layer. The bottom layer (glycerol) was drained out while the methanol was recovered via rotary evaporation. The biodiesel produced was purified of impurities such as unconverted methanol, catalyst, and traces of glycerol by washing several times with warm distilled water. It was then dried afterward in an oven to eliminate residual moisture. The produced biodiesel was then stored in air tight bottle for further studies. The yield of biodiesel produced was determined according to Equation (2)¹⁷.

$$\text{Biodiesel yield} = \frac{\text{mass of biodiesel produced}}{\text{mass of sesame seed oil used}} \times 100 \quad (2)$$

The density, acid value, free fatty acid, iodine value, kinematic viscosity, saponification value of the produced biodiesel were determined according to the methods of A.O.A.C¹⁸. The chemical composition analysis was done using GC-MS.

2.6. Design of Experiment

A Box-Behnken factorial design with four factors and three levels, including five center points was used for fitting a second-order response surface. The experimental runs were randomized to minimize the effects of unexpected variability in the observed responses. Based on the preliminary experiments and literature review¹⁹, the high and low values of temperature were chosen as 50 °C and 80 °C, respectively. The catalyst concentration was designated “high” at 10 % and “low” at 3 %. Similarly, the alcohol-to-oil ratio was taken as “high” at 14:1 and “low” at 3:1. The central points were 65 °C, 6.5%, 8.5:1 and 105 minutes for reaction temperature, catalyst concentration, alcohol-to-oil molar ratio and reaction time respectively as shown in Table 1. Design Expert® 7.0.0 (Stat-ease, Inc. Minneapolis, USA) software was used.

Table 1: Range of variables used for Box Behnken design for transesterification reaction

Variables	Symbol	Unit	Levels		
			-1	0	+1
Reaction time	X ₁	Min	60	105	150
Reaction temperature	X ₂	°C	50	65	80
Catalyst dosage	X ₃	%	3.0	6.5	10.0
Methanol to oil ratio	X ₄	-	3:1	8.5:1	14:1

2.7. Artificial Neural Network Modelling

Artificial neural networks (ANN) was used to model and optimize the biodiesel production process. This was accomplished using a commercial ANN Software, NeuralPower, version 2.5

¹⁶ Betiku, E. and Adepoju, T. F. (2013). Methanolysis optimization of sesame (*Sesamum indicum*) oil to biodiesel and fuel quality characterization. *International Journal of Energy and Environmental Engineering*, 4(1), p. 9.

¹⁷ Sani, J., Samir, S., Rikoto, II, Tambuwal, A.D., Sanda, A., Maishanu, S.M. and Ladan M.M. (2018). Production and Characterization of Heterogeneous Catalyst (CaO) from Snail Shell for Biodiesel Production Using Waste Cooking Oil. *Innovative Energy and Research*, 6(2), pp. 2–5.

¹⁸ Association of Official Analytical Chemists (AOAC). (1990). *Official methods of analysis of the Association of Official Analytical Chemists* (Vol. 1).

¹⁹ Enweremadu, C. C. and Mbarawa, M. M. (2009). Technical aspects of production and analysis of biodiesel from used cooking oil-A Review. *Renewable and Sustainable Energy Reviews*, 13, pp. 2205-2224.

(C.P.C-X Software USA). Because it is not always possible to know apriori, the most suitable network for modelling a process, it is usually useful to investigate different network options. For this work, the dependent variable (biodiesel yield) was predicted using a multilayer full feed forward (MFFF) and a multilayer normal feed forward (MNFF) neural network both with two hidden layers to determine which was more suitable. Furthermore, because it is also not possible to know before hand, the best training algorithm for a particular network, it is also useful to evaluate a number of training algorithms to determine which is most suitable for a particular process. For this work, the two network architectures chosen were trained using different training algorithms including such as incremental back propagation (IBP), batch back propagation (BBP), quick propagation (QP), generic algorithm (GA), and Levenberg-Marquadt (LM) algorithm. For each of these learning algorithms, 70% of the experimental data was used for training the network for it to get used to the experimental data, 15% of the experimental data was used for validating the model and the remaining 15% was then used for testing the network. The training algorithm that best describes the biodiesel production process was selected based on their R^2 and RMSE values. Validation of the data predicted by the ANN model was done by using the trained network to generate output response for the last 15% input data without knowledge of their actual responses, and the generated responses were then compared with their actual responses²⁰.

3. RESULTS AND DISCUSSION

3.1. Characterisation of Sesame Seed Oil

Table 1 displays the characteristics of sesame seed oil, which is utilized as a feedstock for biodiesel manufacturing. The characterisation tests were performed to determine the oil's appropriateness as a feedstock for biodiesel production. The oil yield obtained throughout the extraction process was 50%. The value falls between the 44 to 54% range reported by Saydut et al.²¹. The significant oil yield observed suggests that sesame seed may be used as a long-term oil feedstock for biodiesel synthesis. The extracted oil was light yellow in color and had a liquid physical condition at room temperature. This is consistent with earlier studies²¹. The oil's moisture content was determined to be 0.46%. This number is comparable to that reported by Younis et al.²². Moisture content is significant because excessive moisture level promotes microbial development during storage and may interfere with biodiesel generation during transesterification²³. Density and specific gravity were calculated to be 895.8 kg/m³ and 0.896, respectively. This is a sign of oil unsaturation, as rising degrees of unsaturation are associated with high density and specific gravity values. The oil's viscosity was determined to be 5.92 mm²/s. This figure is much lower than the values published by Younis et al.²² (33.6 mm²/s) and Sabarinath et al.²⁴ (35.9 mm²/s). High viscosity results in low volatility and poor cold flow characteristics, which is why oils are not suited as direct fuels in diesel engines²¹. The peroxide

²⁰ Betiku, E., Okunsolawo, S.S., Ajala, S.O. and Olatunde, S.O. (2014). Performance evaluation of artificial neural network coupled with generic algorithm and response surface methodology in modeling and optimization of biodiesel production process parameters from shea tree (*Vitellaria paradoxa*) nut butter. *Renewable Energy*. 76, pp. 408-417.

²¹ Saydut, A., Duz, M. Z., Kaya, C., Kafadar, A. B. and Hamamci, C. (2008). Transesterified sesame (*Sesamum indicum* L.) seed oil as a biodiesel fuel. *Bioresource Technology*, 99(14), pp. 6656-6660.

²² Younis, K. A., Gardy, J. L. and Barzinji, K. S. (2014). Production and characterization of biodiesel from locally sourced sesame seed oil, used cooking oil and other commercial vegetable oils in Erbil-Iraqi Kurdistan. *American Journal of Applied Chemistry*, 2(6), pp. 105-111.

²³ Banerjee, A. and Chakraborty, R. (2009). Parametric sensitivity in transesterification of waste cooking oil for biodiesel production—A review. *Resources, conservation and recycling*, 53(9), pp. 490-497.

²⁴ Sabarinath, S., Prabha Rajeev, S., Rajendra Kumar, P. K. and Prabhakaran Nair, K. (2020). Development of fully formulated eco-friendly nanolubricant from sesame oil. *Applied Nanoscience*, 10(2), pp. 577-586.

value was found to be 2.8 meq O₂/g. This is comparable to the 2.7 meq O₂/g value found by Gharby et al.²⁵. This low peroxide number indicates that the oil has strong oxidative stability, which means it may be stored for long periods of time without turning rancid²⁶. The sesame seed oil's iodine value was discovered to be 106.4 g/100g. The iodine value is also used to determine the oxidative stability of oils. Oils with high iodine concentrations are more unsaturated and consequently have lower oxidative stability. This study's result is lower than that reported by Dim et al.²⁶ (113 g/100g). The oil's free fatty acid content was determined to be 1.97%. The free fatty acid level also indicates the oil's stability. A high free fatty acid concentration is undesirable for biodiesel synthesis since it might cause the oil to be converted to soap. The saponification value gives a measure of the chain length of the molecules making up the oil and thus, its average molecular weight. A value of 175 mg/g was obtained for the oil sample used in this study which is comparable with the values reported in literature²⁷. Figure 1 and Table 2 show the findings of the fatty acid content profile of sesame seed oil as determined by gas chromatography and mass spectrometry. As illustrated in Figure 1, there were six distinct peaks, each corresponding to a fatty acid content of the oil. Table 2 summarizes the specifics of the peaks. The oil's primary fatty acids were vaccenic acid, stearic acid, and oleic acid, in quantities of 45.18%, 37.08%, and 10.11%, respectively. Palmitic acid (1.32%), isopalmitic acid (4.92%), and arachidic acid (1.38%) were also present. Similar findings have also been published²⁷.

Table 1: Properties of sesame seed oil

Properties	Value
Yield	50%
Colour	Light yellow
Physical state at room temperature	Liquid
Density	895.8 kg/m ³
Specific gravity	0.896
Kinematic viscosity @ 40 °C	5.92 mm ² /s
Peroxide value	2.8 meq O ₂ /g
Acid value	3.93 mg KOH/g
Free fatty acid value	1.97%
Saponification value	175 mg KOH/g
Iodine value	106.40 g I ₂ /100 g oil

²⁵ Gharby, S., Harhar, H., Bouzoubaa, Z., Asdadi, A., El Yadini, A. and Charrouf, Z. (2017). Chemical characterization and oxidative stability of seeds and oil of sesame grown in Morocco. *Journal of the Saudi Society of Agricultural Sciences*, 16(2), pp. 105-111.

²⁶ Dim, P. E., Adebayo, S. and Musa, J. (2013). Extraction and characterization of oil from sesame seed. *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, 4(2), pp. 752-757.

²⁷ Nzikou, J. M., Mvoula-Tsiéri, M., Ndangui, C. B., Pambou-Tobi, N. P. G., Kimbonguila, A., Loumouamou, B. and Desobry, S. (2010). Characterization of seeds and oil of sesame (*Sesamum indicum* L.) and the kinetics of degradation of the oil during heating. *Research Journal of Applied Sciences, Engineering and Technology*, 2(3), pp. 227-232.

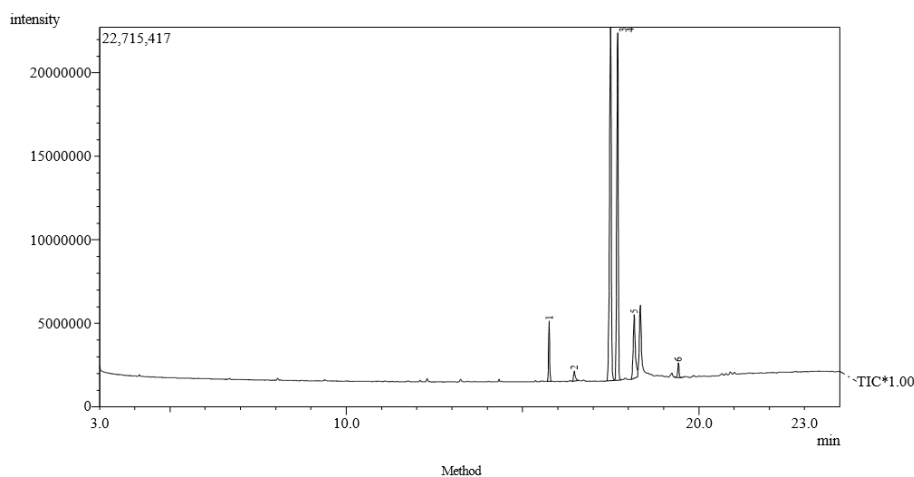


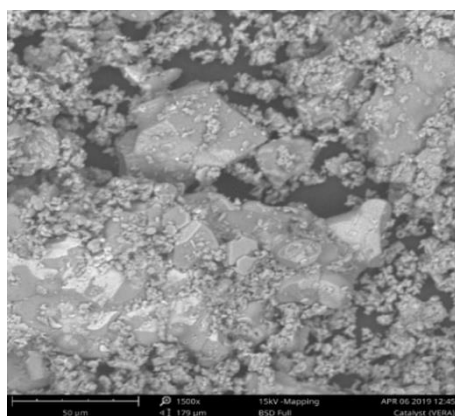
Figure 1: GC-MS of sesame seed oil

Table 1: Composition of sesame seed oil

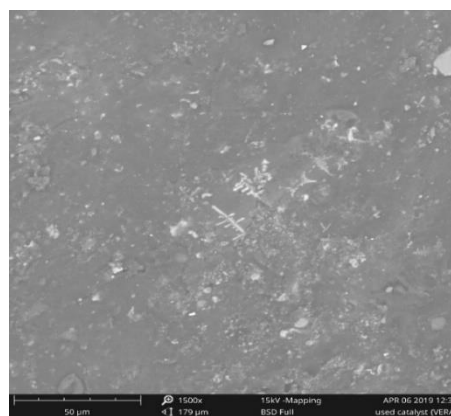
Fatty acid	Chemical formula	Retention time (min)	Area (%)
Isopalmitic acid	$C_{16}H_{32}O_2$	15.752	4.92
Palmitic acid	$C_{16}H_{32}O_2$	16.467	1.32
Vaccenic acid	$C_{18}H_{32}O_2$	17.498	45.18
Stearic acid	$C_{18}H_{36}O_2$	17.698	37.08
Oleic acid	$C_{18}H_{34}O_2$	18.167	10.11
Arachidic acid	$C_{20}H_{40}O_2$	19.419	1.38

3.2. Characterisation of Prepared Catalyst

Figure 2a shows the SEM images depicting the surface morphology of the solid catalyst before it was used to catalyze the transesterification reaction while Figure 2b shows the SEM images of the catalyst after using it to catalyze the transesterification reaction at different magnifications. The micrographs shown in Figure 2a indicates that prior to usage, the catalyst's surface was characterized by large undefined and irregular pores which are necessary as attachment sites for the reactants. The smaller grain sizes and porous nature of the catalyst could potentially indicate a high surface area which is necessary for heterogeneously catalyzed reactions²⁸. Figure 2b shows that after the catalyst was used to catalyze the transesterification reaction, the distinct pores observed in the virgin catalyst were no longer visible.



(a)



(b)

²⁸ Tang, X. and Niu, S. (2019). Preparation of carbon-based solid acid with large surface area to catalyze esterification for biodiesel production. *Journal of industrial and engineering chemistry*, 69, pp. 187-195.

Figure 2: SEM images of catalyst before transesterification reaction (a) before and (b) after reaction

The XRD patterns of the catalyst before and after usage is presented in Figures 3a and 3b respectively. The major peaks present in the diffractograms is indicative of the predominating presence of calcium containing compounds. This was observed for both the virgin and used catalyst. The presence of calcite peaks indicates the presence of calcite containing 56.03% CaO as a dominant constituent of the catalyst which is in line with the fact that CaCO_3 is a dominant constituent of periwinkle shell. The presence of portlandite peaks indicate the presence of Ca(OH)_2 which contains 75.69% CaO. This contributed to the catalytic activity of the catalyst. In comparing the virgin and used catalyst, it was found that the intensity of the peaks decreased after the catalyst had been used for transesterification. This indicates that the active sites of the catalyst had become occupied.

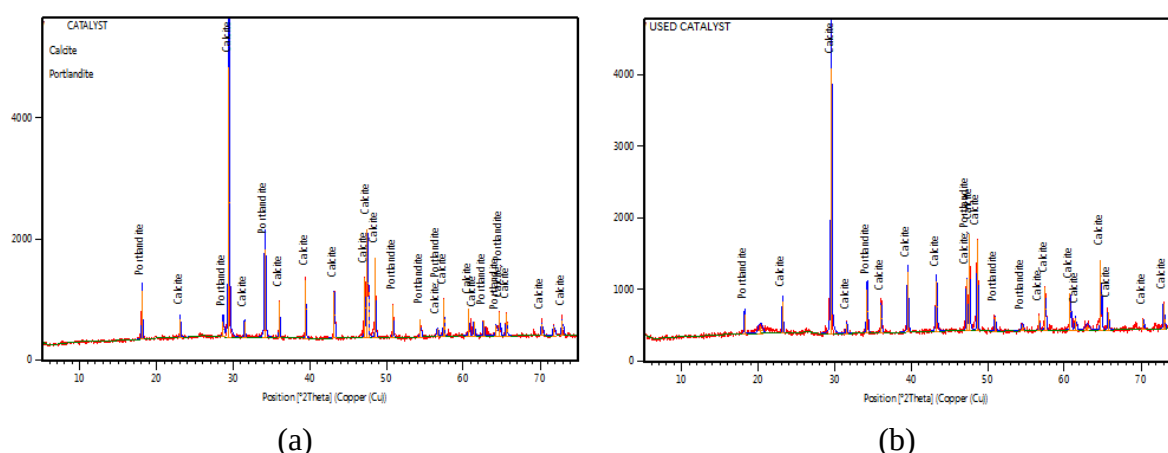


Figure 3: XRD pattern of catalyst (a) before and (b) after transesterification reaction

The functional groups on the surface of the catalyst before and after usage were elucidated via their respective FTIR spectra. Figure 4a shows the FTIR spectra of the virgin catalyst before usage and it shows that the virgin catalyst sample presents a broad peak at 1408.9 cm^{-1} , a set of prominent peaks at 872.2 cm^{-1} , 711.9 cm^{-1} , 3641.6 cm^{-1} and other peaks at 2877.5 cm^{-1} , 2504.8 cm^{-1} , 1994.1 cm^{-1} , 1636.3 cm^{-1} and 1356.8 cm^{-1} . For the used catalyst, Figure 4b shows the spectra of the sample. A shift in the location of the major peaks and an increase in some of the minor peaks was observed. The prominent peak changed to the position 1412.7 cm^{-1} , 1539.4 cm^{-1} , 2922.2 cm^{-1} , 711.9 cm^{-1} , 872.2 cm^{-1} , 1572.9 cm^{-1} and other peaks at 3369.8 cm^{-1} , 2851.4 cm^{-1} , 1110.7 cm^{-1} , 1043.7 cm^{-1} and 3008.0 cm^{-1} showing a slight decrease in the transmittance. Table 4.6 shows the corresponding chemical species of the peaks. There was a significant number increase in peaks for the catalyst after biodiesel production.

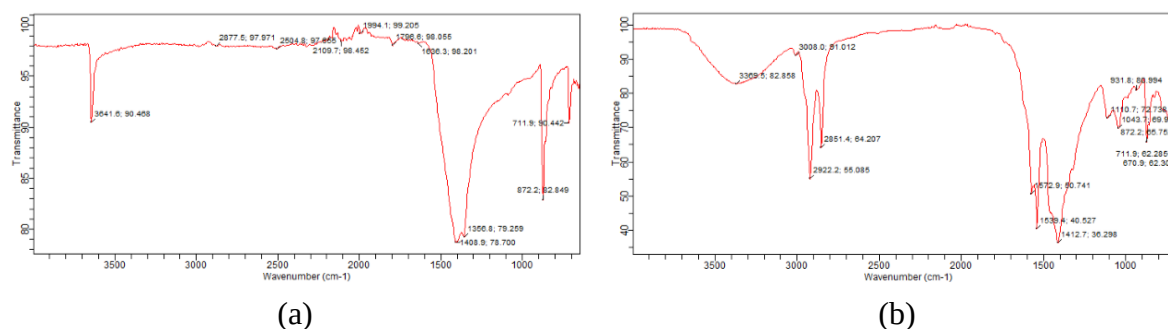


Figure 4: FTIR spectra of catalyst (a) before and (b) after transesterification reaction

Brunauer, Emmett and Teller (BET) analysis was carried out on the prepared bifunctional solid catalyst to determine the surface area, pore diameter and pore volume. The result obtained for

catalyst showed a surface area of 367.40 m²/g, pore diameter of 2.45 nm and pore volume of 0.198 cm³/g. The high surface area and pore volume may be attributed to the effect of calcination which completely removed the adsorbed species and the moisture content that filled up the pores of the catalyst resulting to an increase in surface area and pore volume of the catalyst.

3.3. ANN Modelling of Biodiesel Production

The most suitable transfer function was chosen as the one with the highest R² value and lowest RMSE value. In this regard, it was found that the hyperbolic tangent transfer function was most suitable for developing the ANN model because it was characterized by the highest R² value (0.9960) and lowest RMSE value (1.2766) compared to the others (Table 3). Several training algorithms such as incremental back propagation, batch back propagation, quick propagation, generic algorithm, and Levenberg-Marquardt algorithm were assessed to determine the most suitable one and the results are shown in Table 4. The best training algorithm was chosen as the one that displayed the highest R² value and lowest RMSE value. In this regard, it was found that the incremental back propagation algorithm was the most suitable for training the network and this was on the basis of the fact that it had the highest R² value (0.9967) and lowest RMSE value (0.1626) when compared with the other training algorithms. Different numbers of neurons were used for the network and the impact on the predictive performance of the network was assessed on the basis of the R² value and RMSE value. As shown in Figure 5, when the number of neurons was increased from 1 to 3, the R² value increased while the RMSE was observed to decrease. This is an indication that the predictive capability of the network was increasing. However, increasing the number of neurons beyond 3 did not result in any change in the R² and RMSE values showing that the predictive capability of the network was not enhanced beyond 3 neurons. Thus, the optimum number of neurons for the network was chosen as 3. The results shown in Table 4 indicates that the multilayer full feed forward network trained with the incremental back propagation algorithm was most suitable as it was characterized by the highest R² value (0.9967) and lowest RMSE value (0.1626). Thus, for a neural network with four input factors, 3 neurons in both hidden layers and 1 factor in the output layer, the corresponding optimum neural networks will be 4-3-3-1. The network architecture for predicting biodiesel yield is represented schematically as shown in Figure 6.

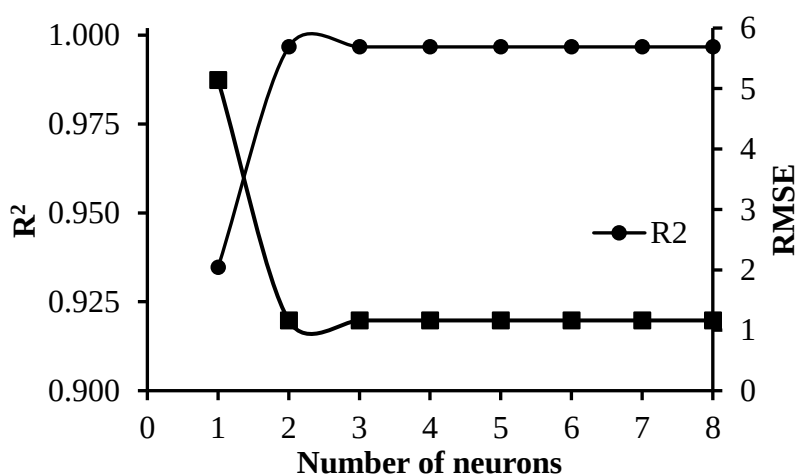


Figure 5: Selection of optimum number of neurons

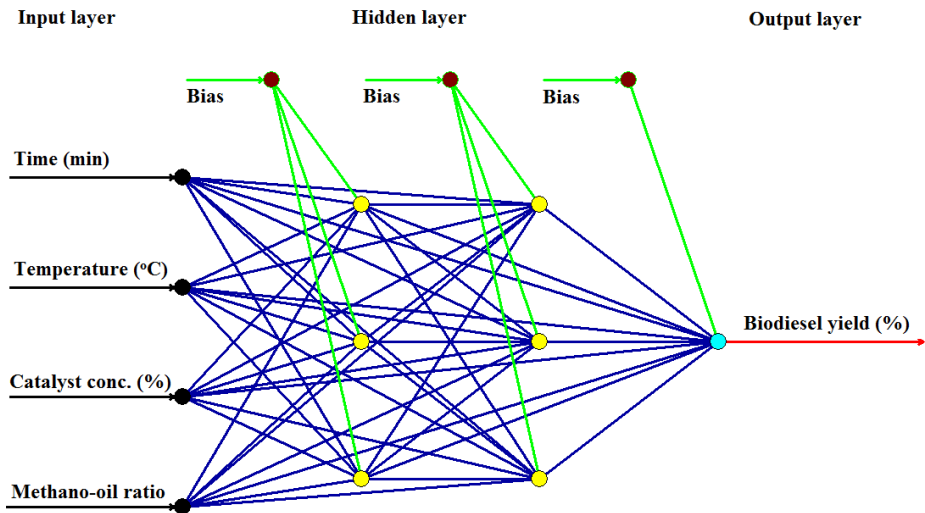


Figure 6: Optimum ANN configuration for biodiesel production

Table 3: Selection of best transfer function

Transfer function	R^2	RMSE
Sigmoid	0.9702	3.4672
Hyperbolic-tangent	0.9960	1.2766
Gaussian	0.7220	10.5980
Linear	0.6127	12.5080
Threshold linear	0.2082	17.8850
Bipolar linear	0.2240	17.7060

Table 4: Selection of best network configuration and training algorithm

Network architecture	Learning algorithm	R^2	RMSE
MNFF	IBP	0.9960	1.2766
	BBP	0.9861	2.3731
	QP	0.9653	3.7430
	GA	0.9601	4.0159
	LM	0.9967	1.1627
MFFF	IBP	0.9967	0.1626
	BBP	0.9941	1.5442
	QP	0.9868	2.3101
	GA	0.9761	3.1084
	LM	0.9966	1.1658

The predictions of the ANN model was validated by comparing them with those obtained from the actual experiments and the results are shown in Table 5. The values predicted by the ANN model were very similar to those of the experiments indicating validity and reliability of the ANN model. The goodness of fit statistics for the ANN model representing biodiesel yield are presented in Table 6. The results show that the ANN prediction was characterised by very high R^2 and adjusted R^2 (R^2 and adjusted $R^2 \sim 1.0000$). This shows that there was almost a perfect fit between the ANN model predictions and the experimental values. The model was also characterized by small error values.

Artificial Neural Networks for Modelling Biodiesel Production from Sesame Seed Oil Using Doped Heterogeneous Catalyst Prepared from Periwinkle Shell

Table 5: Experimental and ANN predicted results for biodiesel yield

Run	Factors								Responses	
	Coded values				Actual values				Biodiesel yield (%)	
	X ₁	X ₂	X ₃	X ₄	X ₁	X ₂	X ₃	X ₄	Experimental observation	ANN prediction
1	0	-1	1	0	105	50	10.0	8.5	21.5	21.5
2	0	1	-1	0	105	80	3.0	8.5	83.0	83.0
3	0	0	0	0	105	65	6.5	8.5	58.0	55.8
4	-1	1	0	0	60	80	6.5	8.5	88.5	88.5
5	0	0	0	0	105	65	6.5	8.5	58.8	55.8
6	-1	-1	0	0	60	50	6.5	8.5	45.2	45.2
7	0	0	0	0	105	65	6.5	8.5	57.0	55.8
8	1	0	-1	0	150	65	3.0	8.5	87.3	87.3
9	1	-1	0	0	150	50	6.5	8.5	74.0	74.0
10	-1	0	0	1	60	65	6.5	14.0	70.0	70.0
11	0	0	-1	1	105	65	3.0	14.0	75.6	75.6
12	1	0	0	1	150	65	6.5	14.0	71.4	71.4
13	-1	0	0	-1	60	65	6.5	3.0	73.7	73.7
14	0	0	-1	-1	105	65	3.0	3.0	88.0	88.0
15	1	0	1	0	150	65	10.0	8.5	21.3	21.3
16	0	-1	-1	0	105	50	3.0	8.5	74.5	74.5
17	1	0	0	-1	150	65	6.5	3.0	65.7	65.7
18	0	1	1	0	105	80	10.0	8.5	33.8	33.8
19	0	-1	0	1	105	50	6.5	14.0	79.2	79.2
20	0	-1	0	-1	105	50	6.5	3.0	48.7	48.7
21	0	1	0	1	105	80	6.5	14.0	67.3	67.3
22	-1	0	-1	0	60	65	3.0	8.5	62.5	62.5
23	0	1	0	-1	105	80	6.5	3.0	88.4	88.4
24	0	0	1	-1	105	65	10.0	3.0	21.3	21.3
25	-1	0	1	0	60	65	10.0	8.5	41.7	41.7
26	1	1	0	0	150	80	6.5	8.5	49.8	49.8
27	0	0	0	0	105	65	6.5	8.5	53.4	55.8
28	0	0	1	1	105	65	10.0	14.0	52.9	52.9
29	0	0	0	0	105	65	6.5	8.5	51.7	52.9

Table 6: Goodness of fit analysis of ANN model

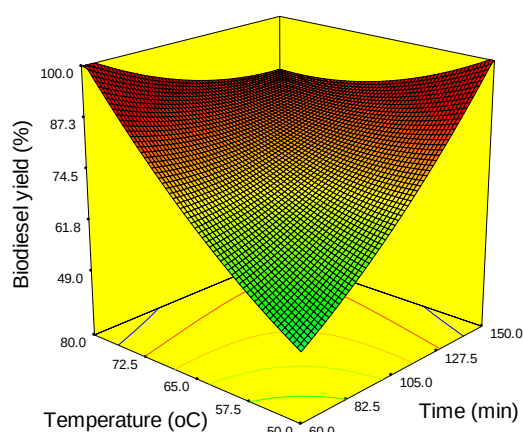
Parameter	ANN
R ²	0.9980
Adjusted R ²	0.9977
MSE	0.7547
RMSE	0.8688
SEP (%)	1.4091
MAE	0.3348
AAD (%)	0.5962

3.4. Effect of Inputs on Biodiesel

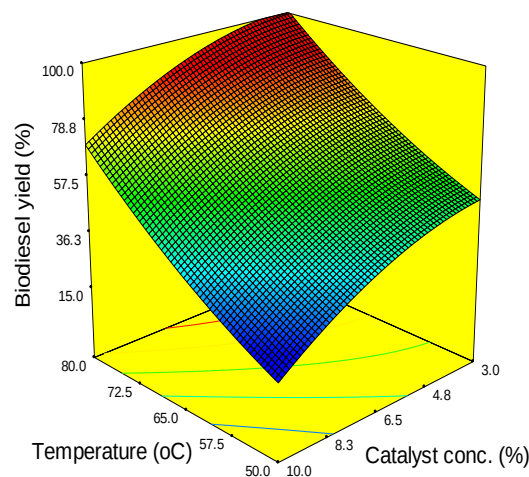
Figure 7a shows the effect of the interaction between reaction temperature and time on the biodiesel yield. It was found that within the specified temperature range, an increase in reaction temperature resulted in increase in the biodiesel yield. This is indicative of the fact that increasing the reaction temperature favoured forward reaction for biodiesel production. As reported previously, increase in biodiesel yield with increase in reaction temperature is consistent with the provisions of the Arrhenius equation, which indicates increase in rate of reaction with increase in temperature²⁹.

With respect to reaction time, Figure 7a shows that increasing the reaction time favoured the forward reaction which was manifested in the increase in biodiesel yield. This observation could be linked to the progressive conversion of the triglycerides in the oil to fatty acid methyl esters (biodiesel) in the course of reaction. Some previous reports showed that providing sufficient time during the transesterification reaction drives the reaction forward to completion for biodiesel production³⁰. Figure 7b shows the effect of catalyst concentration on biodiesel yield. It was observed that a catalyst concentration of 3.2 wt% was sufficient to obtain maximum biodiesel yield. The trend observed indicates that increasing the catalyst concentration beyond 3.2 wt% resulted in a decrease in biodiesel yield which could be attributed to poor mixing characteristics in the reaction mixture made up of the solid catalyst as well as the polar (methanol) and nonpolar (oil and biodiesel) phases³¹.

The effect of methanol to oil ratio was investigated in the range of 3 to 14 as shown in Figure 7c. It was observed that a methanol to oil ratio of 6.5 was sufficient to obtain maximum biodiesel yield. The trend observed indicates that increasing the methanol to oil ratio beyond 6.5 resulted in a decrease in biodiesel yield. Previous reports in the literature have shown that the use of excess methanol results in low biodiesel yield as a result of an increase in the polarity of the reaction mixture which increases the solubility of glycerol and thus favours the reverse reaction during transesterification³².



(a)



(b)

²⁹ Issariyakul, T., Kulkarni, M.G., Dalai, A.K. and Bakhshi, N.N. (2007). Production of biodiesel from waste fryer grease using mixed methanol/ethanol system. *Fuel Processing Technology*, 88, pp. 429-436.

³⁰ Yaakob, Z.M., Mohammad, M., Alherbawi, M., Alam, Z. and Sopian, K. (2013). Overview of the production of biodiesel from waste cooking oil. *Renewable and Sustainable Energy Reviews*, 18, pp. 183-184.

³¹ Jazie, A. A., Pramanik, H., Sinha, A. S. K. and Jazie, A. A. (2013). Egg shell as eco-friendly catalyst for transesterification of rapeseed oil: optimization for biodiesel production. *International Journal of Sustainable Development and Green Economics*, 2(1), pp. 27-32.

³² Ramírez-Verduzco, L. F., Rodríguez-Rodríguez, J. E. and del Rayo Jaramillo-Jacob, A. (2012). Predicting cetane number, kinematic viscosity, density and higher heating value of biodiesel from its fatty acid methyl ester composition. *Fuel*, 91(1), 102-111.

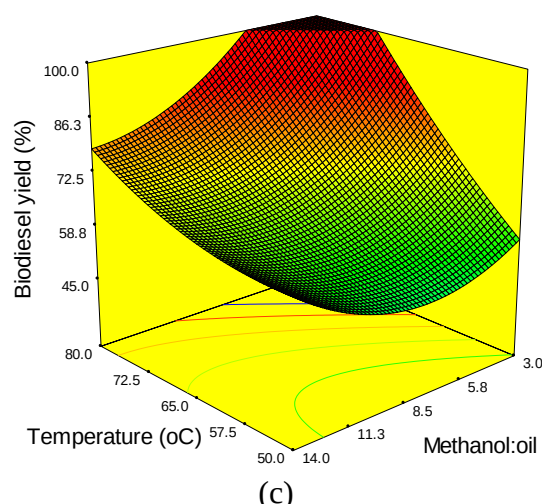


Figure 7: 3D plots showing the effect of process inputs on biodiesel production

3.5. Optimization of Biodiesel

The optimization results gave a maximum biodiesel yield of 95.61% at corresponding reaction time, reaction temperature, catalyst concentration, and methanol to oil ratio values of 62.55 min, 77.59 °C, 3.20 wt%, and 6.50 respectively. This was obtained with a desirability value of 1 indicating 100% acceptability of these optimum results. These results were validated by carrying out triplicate experiments at the recorded optimum conditions. The mean value of the triplicate experiments (95.43%) comparable to the predicted maximum value of 95.61%. Comparison of the optimized biodiesel production conditions with those of previous studies shows that there was some level of agreement (Table 7).

Table 7: Optimization results

Variable	Value
Reaction time	62.55 min
Reaction temperature	77.59 °C
Catalyst concentration	3.20 wt%
Methanol-oil ratio	6.50
Maximum biodiesel yield	95.61%

3.6. Characterisation of Biodiesel

The characteristics of the biodiesel sample produced at the optimized conditions were compared with the ASTM D6571 and EN 14214 standards and the results are summarized in Table 8. It was observed that generally the optimized biodiesel sample had properties that were in conformity with the ASTM D6571 and EN 14214 standards. For instance, the biodiesel sample had a low acid value of 0.29 mg KOH/g oil. This value was less than the recommended maximum value of 0.5. The low acid value obtained indicates that when used as fuel, the biodiesel will pose little or no corrosion problems³³. The biodiesel sample was light yellow in colour. Although there is no standard for colour with respect to biodiesel, the colour obtained was attributed to the colour of the oil feedstock which was also light yellow. The biodiesel sample existed as a liquid under ambient conditions and this was linked to its low kinematic

³³ Yesilyurt, M. K., Cesur, C., Aslan, V. and Yilbasi, Z. (2020). The production of biodiesel from safflower (*Carthamus tinctorius* L.) oil as a potential feedstock and its usage in compression ignition engine: A comprehensive review. *Renewable and Sustainable Energy Reviews*, 119, 109574.

viscosity of 3.97 mm²/s which was within the limits specified by the ASTM D6571 and EN 14214 standards. A high cetane number (95.09) and higher heating value (44.60 MJ/kg) is indicative of very good ignition properties and energy content respectively. Both values were within the recommended standards. The iodine and saponification values were both obtained as 7.9947 g/100g and 115 mg/g respectively. The iodine value is used as an indicator of oxidative stability. Biodiesel samples with high iodine values have a higher degree of unsaturation and thus reduced oxidative stability. This means that the biodiesel sample will undergo rancidity during storage. However, the low iodine value obtained in this study which was less than the maximum value of 120 stipulated by the EN 14214 standard means that the biodiesel sample will not deteriorate during storage. The saponification value gives a measure of the chain length of the molecules making up the oil and thus, its average molecular weight. A value of 115 mg/g was obtained for the biodiesel sample obtained in this study was comparable with the recommended standards. The pour point -18 °C was within the ASTM specification. The pour point obtained in this study is good enough for the biodiesel to be used in colder regions. The cloud point of -15 °C obtained in this study is within the ASTM specification. Cloud point measures the lowest temperature for biodiesel utility. When the cloud point is below the stipulated limit, biodiesel tend to solidify and form crystals which restrict free movement of engine parts³⁴.

Table 8: Summary of biodiesel properties

Properties	Biodiesel	ASTM D6751	EN 14214
Physical state at room temperature	Liquid	Not specified	Not specified
Colour	Golden yellow	Not specified	Not specified
Kinematic viscosity @ 40 °C	3.97 mm ² /s	1.9 to 6.0	3.5 to 5.0
Density	881.2 kg/m ³	Not specified	Not specified
Saponification value	115 mg/g	Not specified	Not specified
Acid value	0.29 mg KOH/g	<0.5	<0.5
FFA	0.145%	Not specified	Not specified
Iodine value	7.99 g/100g	Not specified	<120
Average molecular weight	1467.2 g/mol	Not specified	Not specified
Cetane number	95.09	≥47	≥51
Flash point	195 °C	>130	>120
Pour point	-18 °C	<0	<0
Cloud point (°C)	-18 °C	Not specified	Not specified
Specific gravity	0.88	Not specified	Not specified
Higher heating value	44.60 MJ/kg	Not specified	≥35

4.9.2. Fatty Acid Profile

The chromatogram showing the fatty acid profile of the biodiesel sample produced at the optimized conditions is shown in Figure 8. The details of the major peaks corresponding to the identified compounds are summarized in Table 9. The results show that the fatty acid compositional profile of the biodiesel sample was dominated by saturated fatty acids such as palmitic acid (42.30%), vaccenic acid (36.23%), nonadecylic acid (7.42%) and isopalmitic acid (4.67%). The only unsaturated fatty acid was oleic acid which accounted for only 8.13%. The fatty acid methyl ester profile is one of the key factors that determine the suitability or otherwise

³⁴ Alamu, O. J., Akintola, T. A., Enweremadu, C. C. and Adeleke, A. E. (2008). Characterization of Palm-Kernel oil Biodiesel produced through NaOH catalysed transesterification process. *Scientific Research and Essay*, 3(7), pp. 308-311.

of any feedstock for use in biodiesel fuel production³⁵. The predominance of saturated fatty acids in the biodiesel is desirable because of the tendency to impart oxidative stability to the biodiesel.

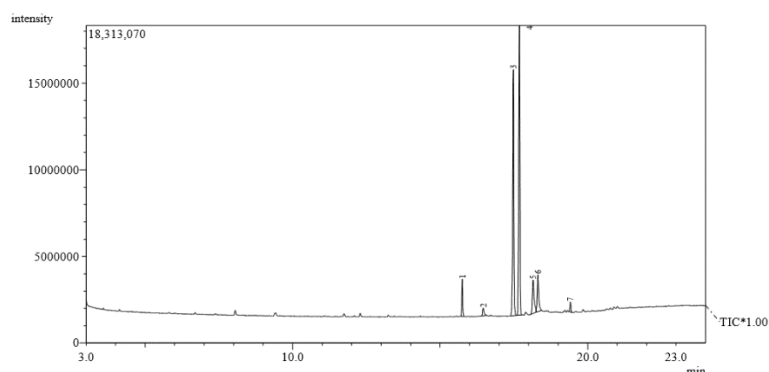


Figure 8: GC-MS results of biodiesel produced at optimized conditions

Table 9: Fatty acid profile of produced biodiesel

Fatty acid	Nature	Chemical formula	Retention time (min)	Area (%)
Isopalmitic acid	Saturated	C ₁₆ H ₃₂ O ₂	15.750	4.67
Vaccenic acid	Saturated	C ₁₈ H ₃₄ O ₂	17.481	36.23
Nonadecylic acid	Saturated	C ₁₉ H ₃₈ O ₂	18.314	7.42
Palmitic acid	Saturated	C ₁₆ H ₃₂ O ₂	17.684	42.30
Oleic acid	Unsaturated	C ₁₈ H ₃₄ O ₂	18.150	8.13
Arachidic acid	Saturated	C ₂₀ H ₄₀ O ₂	19.417	1.25

4. CONCLUSION

Oil with a high enough yield has been extracted from sesame seed for the purpose of biodiesel production. Sesame seed oil is a suitable oil feedstock for biodiesel production as seen from its desirable physical properties and fatty acid compositional properties which indicated that it contained mainly saturated fatty acids. A bifunctional heterogeneous catalyst for efficient biodiesel production was successfully synthesized from periwinkle shell, a waste biomass material. The synthesized solid catalyst was highly functional as elucidated from its physical and chemical characteristics which showed that it contained the major elements and oxides needed for the transesterification of triglycerides to biodiesel. Biodiesel was successfully produced from sesame seed oil using the bifunctional heterogeneous catalyst with a very high yield indicating the efficiency of the catalyst. The biodiesel production was successfully modelled using artificial neural network while the optimum biodiesel yield was obtained as 95.61% at corresponding reaction time, reaction temperature, catalyst concentration, and methanol to oil ratio values of 62.55 min, 77.59 °C, 3.20 wt%, and 6.50 respectively. The biodiesel sample produced at the optimized conditions has very desirable characteristics which were very comparable with the ASTM D6571 and EN 14214 standards.

³⁵ Sokoto, M. A., Hassan, L. G., Dangoggo, S. M., Ahmad, H. G. and Uba, A. (2011). Influence of fatty acid methyl esters on fuel properties of biodiesel produced from the seeds oil of Curcubita pepo. *Nigerian Journal of Basic and Applied Sciences*, 19(1), pp. 81-86.

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