

Enhancement of metal-oxides bifunctional catalyst applied in biodiesel production from waste cooking oil via microwave-aided and conventional heating methods

Olayomi Abiodun Falowo^{a,*}, Babatunde Oladipo^{b,*}, Oluwajuwonlo Adewole^a, Tunde V. Ojumu^b

^a Department of Chemical Engineering, Landmark University, P.M.B.1001, Omu-Aran, Kwara State, Nigeria

^b Department of Chemical Engineering, Cape Peninsula University of Technology, Bellville, Cape Town 7535, South Africa

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ABSTRACT

The present study developed metal-oxides bifunctional catalyst from eggshell waste, ferric sulfate, and zinc sulfate. The developed catalyst was applied to optimize biodiesel production from waste cooking oil (WCO) using Box-Behnken design by comparing the activity of the catalyst in microwave-aided technology (MAT) and conventional heating technology (CHT). Characterization analysis revealed that the catalyst was dominated by the crystalline phase of ZnO while the surface area and pore diameter of the catalyst were 14.24 m²/g and 9.81 nm, respectively. The synthesized catalyst contained mesoporous particles with strong acidic and basic active sites. Optimal conditions established for maximum biodiesel yield were methanol/oil molar ratio (15:1), catalyst loading (1 wt%), and reaction time (62 min) at a constant temperature of 70 °C for the CHT process with a corresponding biodiesel yield of 90.45 %. For the MAT process, the optimal conditions established were methanol/oil molar ratio (15:1), catalyst loading (2.5 wt%), and reaction time (20 min), at a constant irradiation power of 450 W, with a corresponding biodiesel yield of 98.7 %. Using the synthesized catalyst, the MAT process produced a higher WCO biodiesel yield at a shorter reaction time compared to the CHT process. The properties of the fuel produced indicate that it met biodiesel standards.

1. Introduction

Economic and social development across the world is mainly driven by energy. The global primary energy consumption to date has been from fossil fuels, leading to increased energy-related CO₂ emissions in the last 40 years (Kober et al., 2020). Environmental consequences from fossil fuels and growing energy demand prompted the adoption of alternative, sustainable, and renewable energy technologies (Joshi et al., 2017). Renewable energy technologies are at different stages of development, thereby limiting the applicability of many discoveries on a large scale. However, some are fully embraced due to their cleanliness, technological advancement, raw materials availability, and cost-effectiveness in several countries worldwide. The utilization of biofuels as a renewable energy offers several advantages for both society and the environment, such as being biodegradable and non-toxic, reducing greenhouse gas emissions, and promoting a circular economy, thereby contributing to a cleaner environment (Malode et al.,

2021; Oraegbunam et al., 2020).

Improving resources and advancing technology for biofuel production is crucial for its commercialization (Falowo and Oladipo, 2023). Biodiesel is generally considered superior to other forms of liquid fuel, such as bioethanol, in terms of environmental impact and potential applications, particularly in diesel engines and heavy-duty transport. Unlike bioethanol, which can contribute to the corrosion and degradation of engine components due to its hygroscopic nature and lower lubricity, biodiesel acts as a natural lubricant, reducing friction and wear in engines (Betiku et al., 2024). The compatibility of biodiesel with existing diesel infrastructure makes it more feasible for large-scale implementation in transportation, agriculture, and industrial sectors, whereas bioethanol often requires engine modifications and is primarily used in spark-ignition engines. Generally, biodiesel production is through a transesterification process, in which triglycerides react with short-chain alcohols (mostly methanol or ethanol) in the presence of homogeneous or heterogeneous catalysts (Betiku et al., 2018). However, one of the limitations of biofuel production is the unavailability of

* Corresponding authors.

E-mail addresses: falowo.olayomi@lmu.edu.ng (O.A. Falowo), oladipob@cput.ac.za (B. Oladipo).

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Nomenclature

Acronym	analysis of variance
ANOVA	analysis of variance
BBD	Box-Behnken design
BET	Brunauer-Emmet-Teller
BJH	Brunauer-Joyner-Halenda
CaO	calcium oxide
CHT	conventional heating technology
EDX	energy-dispersive X-ray
FTIR	Fourier transform infrared spectroscopy
MAT	microwave-aided technology
R^2	coefficient of determination
RSM	response surface methodology
SEM	scanning electron microscopy
TPD	temperature-programmed desorption
WCO	waste cooking oil
XRD	X-ray diffractometer
ZnO	zinc oxide

sufficient feedstocks to meet industrial production (Joshi et al., 2017). To this end, different feedstocks (non-edible, waste, mixed, and genetically synthesized triglycerides) have been investigated as potential feedstocks, such as rubber seed oil (Oladipo and Betiku, 2020), micro-algae biomass (Pandit and Fulekar, 2017), Karanja and palm oil (Kumar et al., 2023), and waste cooking oil (Falowo et al., 2022). Waste cooking oil (WCO) is ideal for biodiesel production compared to other non-edible feedstocks due to its cost-effectiveness, higher availability, and lower land-use impact, as it does not contribute to deforestation or biodiversity loss associated with the cultivation of oilseed crops.

The impact of technology on biodiesel production is profound, as it directly influences reaction kinetics, feedstock utilization, and overall yield, ultimately determining the economic and environmental feasibility of the process. Conventional heating methods, such as the use of a hot plate, are widely employed in biodiesel production due to their simplicity, accessibility, and ability to provide controlled thermal energy for transesterification reactions (Gude and Martinez-Guerra, 2018). Exploration of alternative technologies beyond conventional heating in biodiesel production is essential to enhance efficiency, reduce energy consumption, and improve overall process sustainability. Technological advancements, such as microwave-aided heating, offer a more efficient approach by enabling rapid and uniform energy distribution at the molecular level, reducing reaction time, and enhancing catalyst performance (Rhithuparna et al., 2024). Investigating these technologies is crucial for optimizing biodiesel production by identifying methods that maximize conversion efficiency while minimizing resource input. Thus, comparison between microwave-aided and conventional heating methods could provide critical insights into their respective advantages and limitations, allowing for the development of improved catalytic systems and energy-efficient processes.

Catalysts enhance biodiesel production by accelerating reactions, improving yield, and reducing energy consumption (Atadashi et al., 2013; Thangaraj et al., 2019). A bifunctional catalyst offers a significant advantage by facilitating both esterification and transesterification reactions within a single catalytic system (Munywali et al., 2022). This dual functionality is particularly beneficial for converting low-quality feedstocks like WCO, which typically contain high free fatty acid (FFA) content. Unlike conventional single-function catalysts that require pre-treatment steps to reduce FFAs before transesterification, the bifunctional catalyst eliminates the need for additional processing, thereby enhancing reaction efficiency and reducing production time (Aderibigbe et al., 2023; Mansir et al., 2018). Bifunctional catalyst has potential cost advantages. By combining esterification and

transesterification in a single step, it reduces the need for multiple catalysts and additional processing steps, leading to lower operational costs (Mulyatun et al., 2022).

Currently, several soluble catalysts used in biodiesel production are being transformed into active, recyclable forms through modification. For example, in sorghum oil transesterification, 96 % of biodiesel was obtained in a batch reactor using a ZnO catalyst (Kumar and Kant, 2014). After this process, the catalyst remains unrecoverable. Though ZnO is a fascinating catalyst, it is highly soluble in methanol, making the recovery a big challenge. Doping and impregnation of ZnO with other active metal oxides improve its catalytic performance as well as its reusability (Yusuff et al., 2021). In another study, ZnO was doped with ferric sulfate to produce a ferromagnetic zinc oxide nanocomposite that yielded 91 % biodiesel from castor oil (Baskar and Soumiya, 2016). Due to ZnO affinity for other metals, ZnO nanoparticles, when doped with transition metals such as Co, Cu, Ni, Fe, and Mn, generate excellent nano-catalysts for biodiesel production, with a pseudo-first-order kinetics (Dasta et al., 2022). Transition metal oxide catalyst synthesized through Mn-doped ZnO produced 97 % biodiesel (Baskar et al., 2017). Furthermore, a ZnO-supported Ag-nanoparticle catalyst was applied to palm oil transesterification; a biodiesel of 97 % was obtained from the conversion (Laskar et al., 2020). Nanocomposite of Cu and ZnO acted as a heterogeneous catalyst in the transesterification of WCO to produce 97.71 % biodiesel (Gurunathan and Ravi, 2015). ZnO, along with an industrial waste product, coal fly ash, was utilized to develop a catalyst and achieved a biodiesel yield of 83.17 % in the transesterification of used cooking oil (Yusuff et al., 2021). Asri et al. (2018) in their study converted Kesambi oil to 92.29 % biodiesel yield using an alumina-supported ZnO catalyst. Jayaraman et al. (2022) combined ZnO nanoparticles with tungsto phosphoric acid to develop a solid acid catalyst in a single-stage WCO transesterification. In their study, a biodiesel yield of 94 % was produced at the optimum condition, and the methyl ester was fired in a compression ignition engine. Additionally, ferric sulfate is an important solid acid catalyst for esterification reaction (Ajala et al., 2020b; Falowo et al., 2020). Meanwhile, in our previous study, Falowo et al. (2024) reported a bifunctional catalyst development from waste eggshells and ferric sulfate. It was observed that ~90% biodiesel production was achieved, yielding methyl ester less than many of these reported values. Thus, this necessitates the development of an active bifunctional catalyst from zinc oxide and ferric sulfate anchored on waste eggshell support for the direct esterification-transesterification process of WCO.

The objective of the present study was to improve the catalytic performance of a bifunctional catalyst from waste eggshells and ferric sulfate by enhancing the metal oxide features of the synthesized catalyst. Zinc oxide was doped with ferric sulfate on the calcined waste eggshell to obtain a highly active bifunctional catalyst and characterized using several techniques (FTIR, XRD, PSD, BET, SEM-EDX, TPD). In addition, Box-Behnken design and optimization of biodiesel production from WCO using the synthesized bifunctional catalyst were investigated by comparing two production techniques (microwave-aided and conventional heating) in one-pot biodiesel synthesis. Physicochemical properties of the biodiesel produced were compared with the ASTM D6751 and EN 14214 biodiesel standards.

2. Materials and methodology

2.1. Materials

Eggshell waste and WCO were collected from Landmark University cafeteria kitchen. Analytical grade methanol was purchased from Sigma-Aldrich (USA). Other reagents such as Wij's solution, potassium hydroxide, ethanol, diethyl ether, phenolphthalein, cyclohexane, sodium thiosulphate, potassium iodide, and starch were also of analytical grade and used without further purification.

2.2. Preparation and development of bifunctional catalyst

Eggshell waste collected was thoroughly cleaned by washing with distilled water, and the size was reduced by grinding. The waste eggshells were dried in a temperature-controlled oven (DHG-9053A) at 105 °C until a constant weight was achieved. The pulverized eggshell waste was calcined in a muffle furnace (Vecstar, LF3 UK) operated at 800 °C for 3 h. After calcination, the sample was cooled and milled into powder. The bifunctional catalyst was prepared by adopting a co-impregnation method according to the steps outlined in Falowo et al. (2024); 1 g of calcined eggshell was added to the solution of 0.5 M ferric sulfate in a molar ratio of 1:1. The slurry generated was allowed to mix for 2 h before 1 g of zinc sulfate was added to it. The resulting slurry was placed on a hot plate (Stuart US152) equipped with a magnetic stirrer and allowed to stir for 6 h at 80 °C. After the modification procedure, the slurry was decanted, washed with distilled water, and oven-dried at 100 °C until constant weight was achieved. The solid synthesized material was further calcined at 500 °C for 2 h. Finally, the resultant solid was cooled, pulverized, and sieved with an 80 mm mesh size to remove larger grains. The bifunctional catalyst synthesized was stored in an air-tight crucible for further analysis and application.

2.3. Bifunctional catalyst characterization

Features of the synthesized bifunctional catalyst were investigated to obtain information on the structure, functional groups, morphology, particle size, surface area, porosity, crystallinity, elemental constituents, as well as its acidity and basicity. The surface morphology and elemental composition of the bifunctional catalyst were measured using a scanning electron microscopy (SEM) instrument (NeoScope™ JCM-7000). Elemental composition was analyzed using an energy-dispersive X-ray (EDX) analyzer (JEOL JED-2300) attached to the SEM. Functional groups of the catalyst were ascertained using a Fourier transform infrared (FTIR) spectrometer (Perkin Elmer UATR Two). Crystalline phases of the bifunctional catalyst were obtained using an X-ray diffractometer, XRD (Bruker D2 Phaser). The strength of the acidic and basic sites of the catalyst was determined by ammonia (NH₃) and carbon dioxide (CO₂) temperature-programmed desorption (TPD), respectively, using a Micromeritics AutoChem™ 2950 HP with a thermal conductivity detector (TCD) for measuring the desorbed gases. Particle size instrument (Microtrac S3500 Laser Diffraction) was used to measure the particle size distribution (PSD) of the catalyst in the dry dispersion unit. Total surface area of the catalyst was determined using the Brunauer–Emmett–Teller (BET) method with corresponding N₂ adsorption-desorption isotherms on a Micromeritics Tristar II 3020. Barrett–Joyner–Halenda (BJH) model was employed to estimate the average pore size distribution.

2.4. One-pot synthesis of biodiesel using the synthesized bifunctional catalyst

Triglyceride conversion to biodiesel in the presence of an alkali-based catalyst is possible if the FFA of the oil is ≤1 % (Khan et al., 2020). FFA content of oil >1 % reacting with methanol in the presence of a base catalyst will lead to soap formation in a process called saponification (Oladipo et al., 2019). Based on the physicochemical properties of WCO determined in this study, particularly its kinematic viscosity (6.99 mm²/s) and acid value (3.78 mg KOH/g), a pretreatment step was necessary to reduce the FFA value to ≤1 % and prevent soap formation. Consequently, before its full conversion to biodiesel, the WCO underwent two processes: esterification and transesterification. These reactions were conducted in a single step using the synthesized bifunctional catalyst in a 500 mL three-neck round-bottom flask equipped with a reflux condenser. For the conventional heating method, a known amount of methanol was added to a known volume of WCO in a reactor placed on a hotplate with a magnetic stirrer, and then, a known

weight of catalyst was charged to initiate the reaction according to the process condition specified by the design matrix. This same procedure was followed for the one-pot biodiesel synthesis in the microwave-aided trans(esterification) method. The set-up was performed in a modified microwave reactor (Severin MW 7820) aided with an external stirrer (GallenKamp, Handilab SS-425). After the completion of the reaction using either of the employed heating technologies, the reaction mixture was allowed to cool and then centrifuged using a centrifuge machine (Mcl 90–2) to recover the catalyst. The biodiesel was washed several times to remove unreacted methanol and glycerol. After washing, the purified biodiesel was dried with sodium sulfate, and the amount obtained was determined gravimetrically according to Eq. 1.

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

2.5. Experimental design for one pot-synthesis biodiesel production

Modeling and optimization of biodiesel production from WCO were performed using the Box-Behnken design (BBD) of response surface methodology (RSM). The effect of process parameters (methanol/oil molar ratio, catalyst loading, and reaction time) on biodiesel yield was analyzed through BBD. The experimental ranges for the three variables considered in conventional heating technology (CHT) are as follows: reaction time (30–90 min), methanol/oil molar ratio (5:1–15:1 v/v), and catalyst loading (1–3 wt%), under a constant temperature of 70 °C. Whereas for microwave-assisted technology (MAT), reaction time (5–20 min), methanol/oil molar ratio (5:1–15:1 v/v), and catalyst loading (1–5 wt%) were considered in the reaction process, under a constant heating power of 450 W. A total of 15 experiments were generated using BBD, with biodiesel yield as the response variable. Each experiment was conducted in duplicate, and the average biodiesel yield was recorded. Analysis and optimization of biodiesel yield were performed using Design-Expert software (version 13.0.1, Stat-Ease).

2.6. Physicochemical and fuel properties of WCO and biodiesel produced

Physicochemical and fuel properties of the WCO and biodiesel produced using the synthesized bifunctional catalyst were determined by the standard methods of the Association of Official Analytical Chemists (AOAC) (Oladipo and Betiku, 2019; Oladipo et al., 2020).

2.7. Model optimization, validation, and catalyst recyclability test

Biodiesel yield was optimized along with the process factors (reaction time, methanol/oil molar ratio, and catalyst loading) using the numerical optimization approach of RSM. The fitness of the regression model was validated by conducting experiments at the predicted optimal process conditions. Following each reaction cycle, the recovered catalyst was thermally treated at 105 °C for 30 min to restore its active sites and preserve pore volume, both of which are crucial for maintaining its catalytic efficiency (Falowo et al., 2025). The catalyst reusability test for biodiesel production was thereafter performed at the optimal conditions.

3. Results and discussion

3.1. Characterization of the synthesized catalyst

The surface morphology of the bifunctional catalyst is presented in Fig. 1. The SEM image (Fig. 1a) reveals the agglomeration of small grains distributed across the surface of the catalyst. At low magnification (×1000, 10 μm), the particles appear compact and uniform with several cavities dispersed throughout. This indicates that these porous structures are beneficial for catalytic activity, as they facilitate the diffusion of triglyceride molecules, promoting efficient mass transfer and reaction

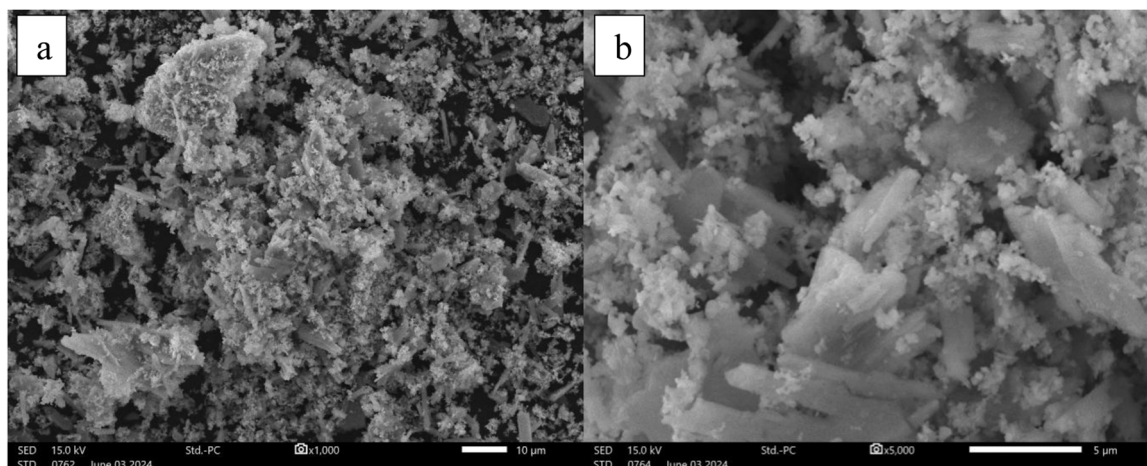


Fig. 1. Surface morphology of the synthesized bifunctional catalyst at different magnifications: (a) $\times 1000$ at $10\ \mu\text{m}$ and (b) $\times 5000$ at $5\ \mu\text{m}$.

kinetics. A higher magnification ($\times 5000$, $5\ \mu\text{m}$) in Fig. 1b provides a closer view of the surface of the catalyst, showing rod-like particles surrounded by small grains. This suggests that there are sufficient active sites for reacting molecules to maximize their interaction with each other (Betiku et al., 2017).

As reported in Goli and Sahu (2018), metal oxides like CaO make up the largest proportion of the calcined eggshell composition. Additionally, the calcination temperature of the biomass plays a crucial role in determining the percentage of CaO in the final calcined sample. The elemental composition of the newly synthesized bifunctional catalyst is as follows: C (5.44 %), O (24.37 %), S (2.69 %), Ca (10.42 %), Fe (10.49 %), and Zn (46.59 %). The most abundant element in the catalyst is Zn, while Ca and Fe elements are in equal proportion (Fig. 2). Traditionally, CaO nanocatalysts are dominated by Ca and O (Pandit and Fulekar, 2017), meanwhile, the weight fraction of Fe (18.5 %) and Ca (20.7 %) in our previous work (Falowo et al., 2024) was higher than the amount obtained in this study. This might be attributed to the incorporation of ZnO into the new catalyst, thereby decreasing the percentage mass of Fe and Ca. Generally, co-precipitation is used in the transition metal oxide catalyst synthesis (Baskar et al., 2017). For example, homogeneous precipitation was used in ZnO@Ag NPs catalyst synthesis (Laskar et al., 2020). However, it was evident from this study that biomass-metal oxide catalyst synthesis can be successfully achieved via co-impregnation.

The diffractogram of the synthesized bifunctional catalyst is depicted in Fig. 3, revealing 4 distinct crystalline phases in varying proportions. The identified phases are zinc oxide (ZnO) at 2θ values of 31.6° , 34.5° ,

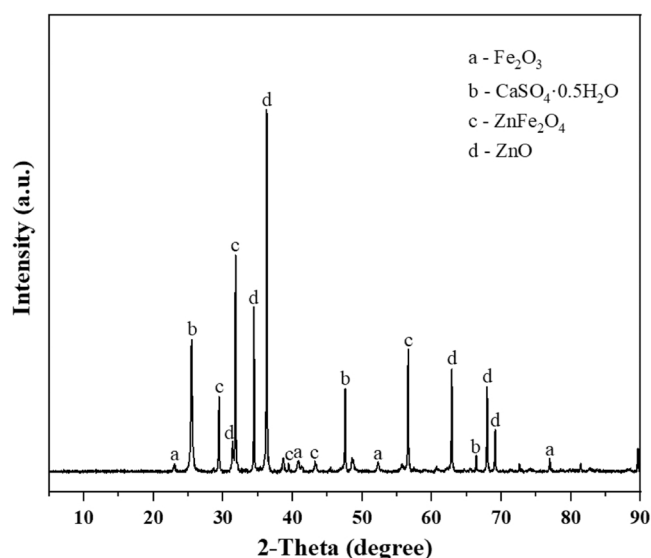


Fig. 3. Diffraction pattern of the synthesized bifunctional catalyst.

36.3° , 62.8° , 67.9° , and 69.1° ; franklinite (ZnFe_2O_4) at 29.4° , 31.8° , 39.5° , 43.2° , and 56.7° ; bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) at 25.5° , 47.6° , and 66.4° ; and hematite (Fe_2O_3) at 23.1° , 40.8° , 52.3° , and 77° (Ajala et al., 2020a). From the XRD pattern, ZnO and ZnFe_2O_4 are the dominant crystalline phases, consistent with previous findings on zinc sulfate-doped materials, where overlapping diffraction peaks of franklinite and ZnO nanoparticles were observed (Baskar and Soumiya, 2016). The formation of multiple crystalline phases may be attributed to the surface chemistry and the high microporosity of the support material (Yang et al., 2020), which can influence nucleation and crystal growth. Additionally, differences in thermodynamic stability, solubility, and diffusion kinetics during catalyst synthesis likely contributed to phase development. The presence of ZnFe_2O_4 , a ternary spinel oxide, plays a significant role in catalytic performance due to its unique electron distribution across tetrahedral and octahedral sublattices, which can enhance redox properties and active site availability (Levy et al., 2000). The synergistic interaction between these crystalline phases results in a bifunctional catalytic system with both acidic and basic properties. This system can influence reaction pathways through electron transfer mechanisms while improving catalytic stability and durability. The elemental composition confirmed via EDX analysis further supports these findings.

The TPD technique is an effective method for identifying active sites

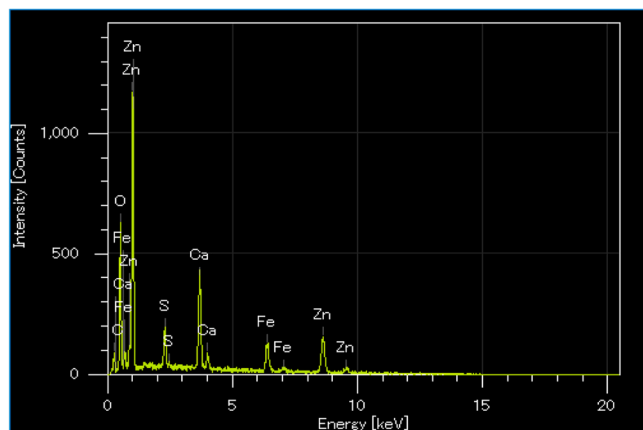


Fig. 2. Pictogram of the elemental composition of the bifunctional catalyst.

on a catalyst and gaining insights into catalytic reaction mechanisms. Fig. 4 shows the CO₂-TPD and NH₃-TPD thermograms, illustrating the strength of the basic and acidic sites of the synthesized bifunctional catalyst, respectively. The curve pattern of the sample constituting the main CO₂ desorption peaks was detected between 60 °C and 900 °C (Fig. 4a). The total basicity of the catalyst was determined to be 23.3 μmol CO₂/g. The desorption profile of CO₂ on the catalyst revealed a prominent peak at 747 °C, signifying strong basic sites. This peak suggests substantial CO₂ adsorption on high-energy O²⁻ anions (Lee et al., 2014), a characteristic typically observed at temperatures > 500 °C. However, there was the absence of weak and medium basic site peaks, which may be due to the composition and synthesis conditions of the bifunctional catalyst, hence, inherently favoured the formation of strong basic sites. The presence of the strong basic sites will help enhance the transesterification process of WCO by efficiently facilitating the deprotonation of methanol molecules, thereby generating highly nucleophilic methoxide ions (Oladiipo et al., 2024). The desorption band of NH₃-TPD was observed between 250 °C and 900 °C (Fig. 4b). The total acidity of the catalyst was determined to be 22.7 μmol NH₃/g. The high-temperature NH₃ desorption peak at 737 °C indicates the presence of strong acid sites, suggesting that the transition metal sulfates (Fe₂(SO₄)₃ and ZnSO₄) are well-dispersed on the eggshell support. This dispersion is facilitated by strong electrostatic interactions and the chemical affinity between the sulfate groups and the calcium-rich surface of the eggshell. Furthermore, the Fe³⁺ and Zn²⁺ provide the Lewis acidic sites to promote the activation of carbonyl groups in fatty acids, while the SO₄²⁻ group stabilizes the metal cations and supports their catalytic activity. The near-equal levels of total basicity (23.3 μmol CO₂/g) and acidity (22.7 μmol NH₃/g) in the bifunctional catalyst suggest a well-balanced acid-base profile promoting cooperative interactions, which can improve reaction rates for both esterification and transesterification processes in a single-step conversion.

The BET surface area, pore diameter, and pore volume of the synthesized bifunctional catalyst are 14.24 m²/g, 9.81 nm, and 0.039 cm³/g, respectively. The catalyst developed in this study has a sufficiently high surface area to facilitate high catalytic performance. While the surface area in this present study is slightly lower than the 16.4 m²/g reported for CaO nanocatalyst by Pandit and Fulekar (2017), the pore diameter is significantly larger than the 5.07 nm reported in their study. Larger pores enable faster diffusion of large triglyceride molecules into the catalyst structure, enhancing contact with active sites and promoting higher reaction rates. Rahman et al. (2021) reported BET surface area for CaO from eggshell waste and CaO/ZnO catalyst as 2.96 m²/g and 13.71 m²/g, respectively. Impregnation of calcined material with metal

oxide enhanced the surface properties of the catalyst, as the impregnation process widened the pore volume. Fig. 5 shows the N₂ adsorption and desorption isotherms of the synthesized catalyst. The isotherm is similar to Type IV, which indicates the bifunctional catalyst has mesoporous pores. This isotherm is generated from the interaction between the adsorbent mesopore surface and gas molecules, which leads to capillary condensation. The hysteresis loop associated with the formation of this isotherm is H3 type (Sing, 1985). From the BJH pore size distribution (Fig. 5 (inset)), the pore size of 9.81 nm obtained for the catalyst falls within the mesoporous range (2–50 nm) (Sing, 1985). This further supports that the sample is a mesoporous material, providing highly active sites for reaction. Hence, a material of this nature is well-suited for applications in heterogeneous catalysis, adsorption, and energy storage.

The plot of percentage volume against the particle size of the synthesized catalyst is shown in Fig. 6. The fine end of the distribution shows that 10 % of the catalyst particles have a size of 0.71 μm (D10). These fine particles may lead to high dispersion in the oil, potentially influencing the kinematic viscosity of the biodiesel due to their rapid dissolution (Ilangoan et al., 2021). The median particle size (D50) is 2.61 μm, indicating that half of the catalyst particles are below this size. This moderate particle size, combined with a mesoporous structure (pore size of 9.81 nm), provides an optimal balance between surface

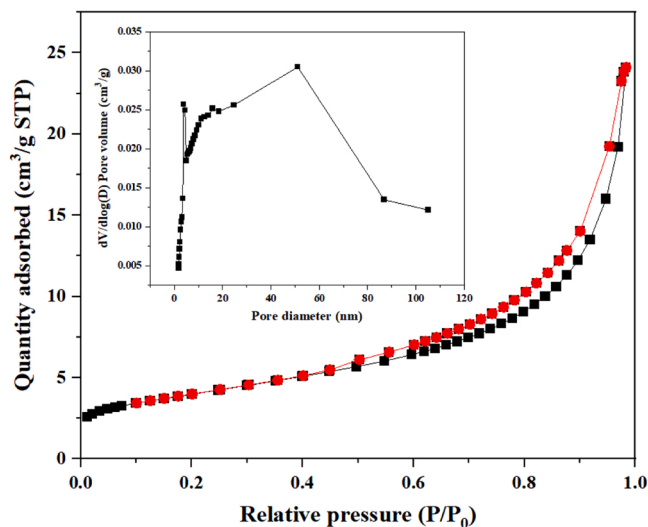


Fig. 5. N₂ adsorption-desorption isotherm and pore-size distribution (inset).

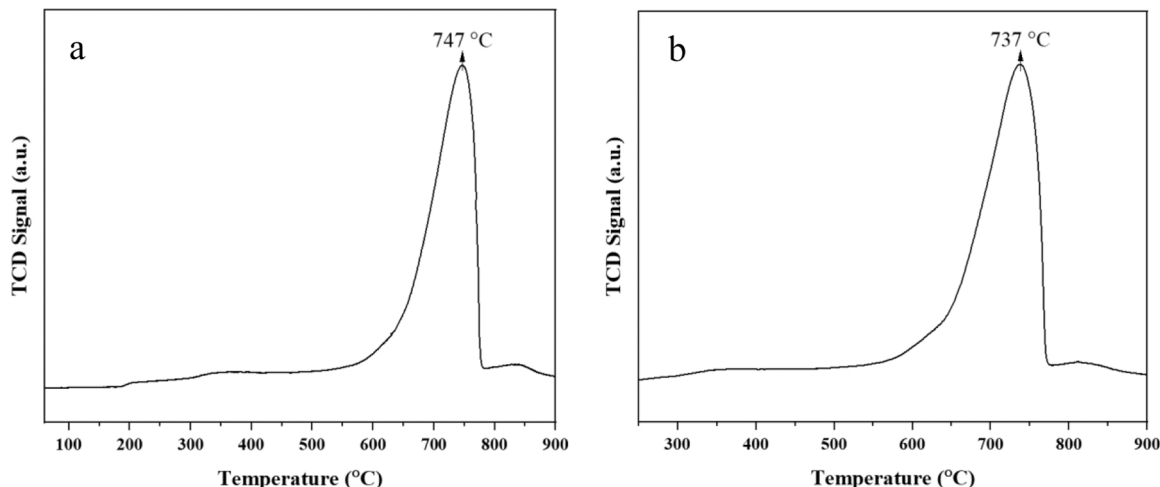


Fig. 4. (a) CO₂-TPD and (b) NH₃-TPD of the bifunctional catalyst.

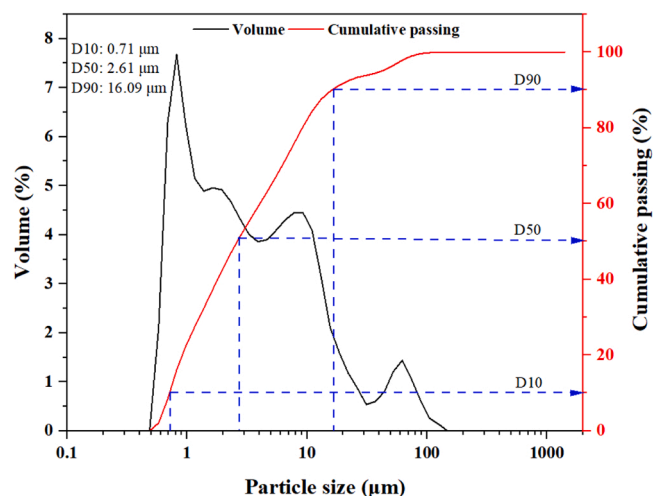


Fig. 6. Particle size distribution of the synthesized catalyst.

area exposure and mass transport, enhancing catalytic efficiency while preventing excessive aggregation. At 90 % cumulative passing, the particle size is $\leq 16.09 \mu\text{m}$ (D90), meaning the majority of particles fall within the 0–16.09 μm range, with only 10 % exceeding this size. The presence of larger particles (D90 = 16.09 μm) contributes to structural stability, reducing catalyst loss due to agglomeration while maintaining sufficient surface reactivity for effective esterification and transesterification reactions.

FTIR spectrum of the bifunctional catalyst synthesized from the impregnation of ZnO and $\text{Fe}_2(\text{SO}_4)_3$ is depicted in Fig. 7. The absorption bands identified at 594 cm^{-1} and 612 cm^{-1} correspond to the stretching vibrations of metal-oxygen bonds of Fe–O and Zn–O, respectively. These metal oxides provide the acid-base catalytic sites, which are responsible for enhancing the bifunctional behaviour of the catalyst. This was also reported in CaO/ZnO catalyst after impregnation (Rahman et al., 2021). Moreover, the peak located at 672 cm^{-1} is likewise ascribed to the co-existence of the Ca–O and Zn–O stretching vibration band. The bands identified at 875 cm^{-1} and 1446 cm^{-1} correspond to out-of-plane bending and asymmetric stretching vibration, respectively, of the C–O bond in carbonate (CO_3^{2-}) species, contributing to the basicity, which is important for transesterification. The peaks at 1098 cm^{-1} and 1146 cm^{-1} are attributed to the S=O stretching vibrations, confirming sulfate

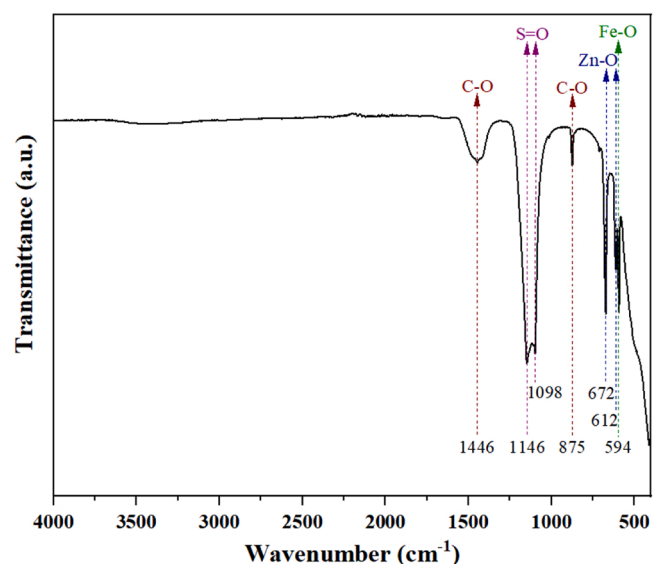


Fig. 7. FTIR spectrum of the synthesized bifunctional catalyst.

groups that introduce acidic sites for esterification.

3.2. Biodiesel yields under the conventional heating technology (CHT)

The process variables from the BBD of RSM applied for the one-pot synthesis of biodiesel from WCO, as well as the response yields (actual and predicted biodiesel yields), are presented in Table 1. Biodiesel yield obtained using the synthesized functional catalyst ranged from 71.64–90.69 %, under a constant temperature of 70 °C. Compared to our previous study (Falowo et al., 2024), there was a significant improvement in catalytic performance. In our earlier study, 6 out of 9 experiments produced a biodiesel yield between 63.4 % and 71.5 %, which is lower than the minimum yield recorded in this current study. This suggests that the newly developed catalyst exhibits enhanced activity. Biodiesel yield percentage based on regression analysis can be presented in coded form as given in Eq. 2.

$$\text{WCO biodiesel yield (\%)} = 85.28 + 3.33A - 1.81B + 0.908C + 3.81AC + 4.02BC - 6.91C^2 \quad (2)$$

where, A, B, and C represent process factors namely; methanol/oil molar ratio, catalyst loading, and reaction time, respectively. A positive sign suggests that a unit increase in the process factor would increase the biodiesel yield by the stoichiometric value, while a negative sign means that a unit increase in the process factor leads to a decrease in biodiesel yield by the stoichiometric value.

ANOVA of the experimental study for the CHT process is presented in Table 2. Generally, according to Fischer's test, any model term having a p -value ≤ 0.05 is significant. The regression model of the experimental study is significant at a 95 % confidence level, with $p < 0.0001$ indicating that the tendency of obtaining a large F -value due to noise is 0.01 %. The methanol/oil molar ratio (A), catalyst loading (B), and quadratic effect of reaction time (C^2) are significant. The linear term of the reaction time (C) was statistically insignificant, however, its interactive terms (AC and BC) were significant. The major contributor to the biodiesel yield was the methanol/oil molar ratio, as evident in its F -value. Stoichiometrically, the transesterification reaction requires 3 moles of alcohol to 1 mol of triglyceride. However, because the reaction is reversible, an additional mole of methanol is added to shift the equilibrium to favour biodiesel production (Rahman et al., 2021).

The plot of predicted biodiesel yields against actual biodiesel yields is shown in Fig. 8. The two responses are close to each other, thereby validating the reliability of the regression model in establishing a correlation between the independent variables and the biodiesel yield.

Table 1
BBD matrix, experimental, and predicted biodiesel yields under CHT.

Run	A: Methanol/ oil molar ratio (v/v)	B: Catalyst loading (wt%)	C: Reaction time (min)	Experimental biodiesel yield (wt%)	Predicted biodiesel yield (wt%)
1	15	3	60	87.33 $\pm$ 0.79	86.81
2	5	1	60	84.46 $\pm$ 0.47	83.76
3	15	2	90	87.85 $\pm$ 0.91	86.43
4	5	3	60	80.86 $\pm$ 0.46	80.14
5	10	1	30	84.14 $\pm$ 0.35	83.30
6	10	2	60	84.44 $\pm$ 0.41	85.28
7	10	3	90	80.15 $\pm$ 0.76	81.49
8	10	3	30	72.34 $\pm$ 0.18	71.64
9	10	2	60	84.45 $\pm$ 1.02	85.28
10	5	2	90	73.25 $\pm$ 0.86	72.15
11	15	1	60	90.69 $\pm$ 0.63	90.43
12	5	2	30	77.01 $\pm$ 0.72	77.94
13	10	1	90	75.89 $\pm$ 0.35	77.08
14	15	2	30	76.39 $\pm$ 0.53	77.01
15	10	2	60	84.75 $\pm$ 0.63	85.28

Table 2
ANOVA for the BBD model under CHT.

Sources	Sum of squares	Degree of freedom	Mean square	F-value	p-value
Model	422.26	6	70.38	47.15	<0.0001
A–Methanol/oil molar ratio	88.98	1	88.98	59.61	<0.0001
B–Catalyst loading	26.28	1	26.28	17.61	0.0030
C–Reaction time	6.59	1	6.59	4.41	0.0688
AC	57.91	1	57.91	38.80	0.0003
BC	64.48	1	64.48	43.20	0.0002
C ²	178.02	1	178.02	119.26	<0.0001
Residual	11.94	8	1.49		
Lack of Fit	11.88	6	1.98	63.80	0.0155
Pure Error	0.0621	2	0.0310		
Cor Total	434.20	14			

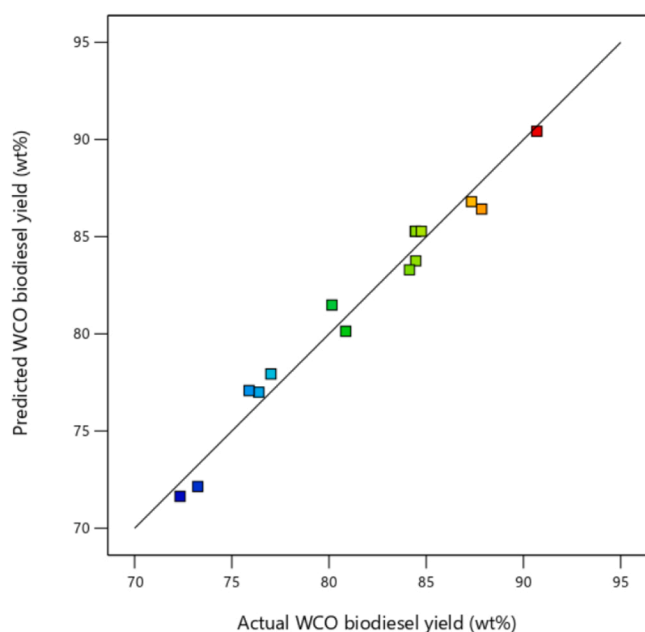


Fig. 8. Plot of predicted versus actual WCO biodiesel yields under CHT.

3.3. Effect of process variables on biodiesel yield under CHT

The three-dimensional (3D) synergistic surface plots of process variables with respect to WCO biodiesel yield (wt%) are shown in Fig. 9. It can be observed that increased catalyst loading in the reaction led to marginal biodiesel yield (Fig. 9a). However, significant biodiesel yield

was observed when the methanol/oil molar ratio was increased within the range investigated. Outili et al. (2020) reported that green chemistry balance is achieved at a low catalyst amount. In this study, biodiesel yield was at its highest when the catalyst loading was at its minimum and the methanol/oil ratio was at its maximum. Increasing the catalyst amount and methanol/oil molar ratio in the reaction mixture led to a decrease in biodiesel yield. Erchamo et al. (2021) reported that methanol addition above the optimum value would inactivate the catalyst, favouring the backward reaction of the transesterification process. In Fig. 9b, increasing the reaction time beyond 60 min had a counterproductive influence on biodiesel yield. The interactive effect of reaction time and methanol/oil was pronounced when the methanol/oil molar ratio was at its highest and the reaction time was 60 min. Increasing the reaction time to 90 min led to a decrease in biodiesel yield. Since transesterification is an equilibrium-driven process, excessive methanol can shift the reaction equilibrium, leading to undesired side reactions such as reverse transesterification (i.e., the conversion of biodiesel back into triglycerides or partial glycerides). This phenomenon likely explains the decline in WCO biodiesel yield observed at extended reaction times in the presence of excessive methanol. A similar observation was noted in the transesterification of Pongamia oil, relating biodiesel yield to reaction time and methanol/oil molar ratio (Dwivedi and Sharma, 2015). Meanwhile, Fig. 9c revealed that at the highest level of time and catalyst amount, biodiesel yield was not favoured. From the plot, biodiesel yield is a function of reaction time, and it only increased to a certain extent (60 min). Longer reaction time beyond the optimum time may cause hydrolysis of ester and consequently reduced biodiesel yield (Erchamo et al., 2021). At the highest level of catalyst amount and reaction time, mass transfer resistance within the reaction mixture might be the prevailing circumstance, leading to low biodiesel yield (Mahesh et al., 2015).

3.4. Biodiesel yields under the microwave-aided technology (MAT)

The process factors, levels, actual, and predicted biodiesel yields are presented in Table 3. Biodiesel yields from WCO using the synthesized bifunctional catalyst in a microwave-assisted process ranged from 87.08–98.31 %, under a constant heating power of 450 W. This production technology resulted in a significant increase in biodiesel yields. It has been reported that microwave-assisted reactions benefit from accelerated chemical reactions due to the direct accessibility of heat to the reactants (Falowo et al., 2025; Khan et al., 2021). In addition to an increased biodiesel yield, the reaction time was significantly reduced. Irrespective of the alcohol utilized for a study that applied MAT and CHT, shorter reaction times and higher biodiesel yields were key benefits of microwave-assisted reaction over the conventional heating method (Pham et al., 2022).

The regression equation of biodiesel yield in coded factors using

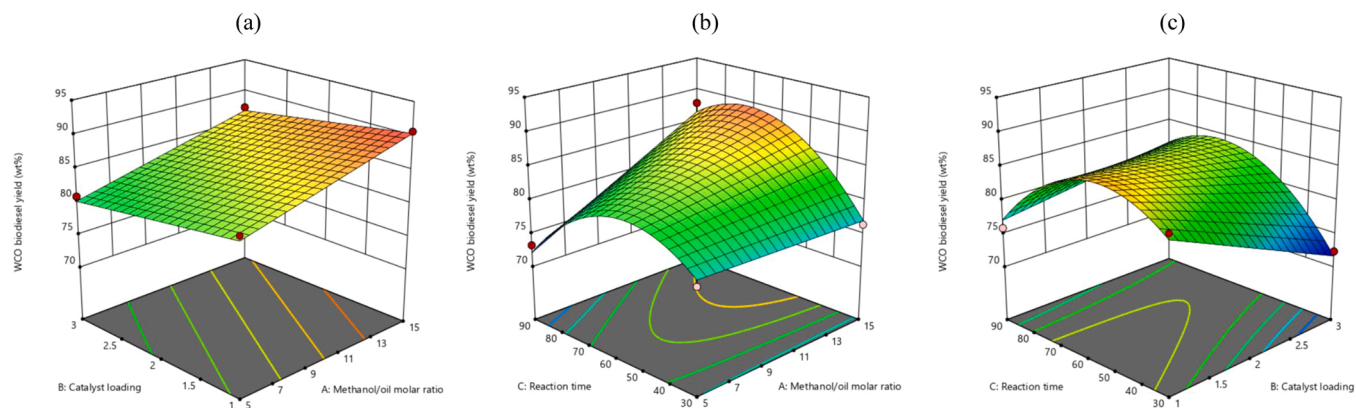


Fig. 9. 3D synergistic surface plots of process variables with respect to WCO biodiesel yield (wt%) under CHT.

Table 3

BBD matrix, experimental, and predicted biodiesel yields under MAT.

Run	A: Methanol/ oil molar ratio (v/v)	B: Catalyst loading (wt%)	C: Reaction time (min)	Experimental biodiesel yield (wt%)	Predicted biodiesel yield (wt%)
1	5	1	12.5	80.07 ± 0.32	79.33
2	10	1	5	87.08 ± 1.10	87.96
3	10	3	12.5	95.85 ± 0.47	95.52
4	5	3	20	89.67 ± 0.19	90.00
5	10	5	20	92.19 ± 0.21	92.45
6	15	5	12.5	87.19 ± 0.55	88.00
7	10	5	5	92.05 ± 0.42	91.03
8	15	3	5	94.49 ± 0.42	94.14
9	10	3	12.5	94.32 ± 0.87	95.52
10	10	1	20	89.56 ± 0.65	89.38
11	15	1	12.5	93.34 ± 0.23	93.38
12	5	5	12.5	90.89 ± 0.27	90.81
13	10	3	12.5	96.34 ± 0.30	95.42
14	5	3	5	90.43 ± 0.75	90.86
15	15	3	20	98.31 ± 0.56	97.85

MAT is presented in Eq. (3).

$$\text{WCO biodiesel yield}(\%) = 95.52 + 2.78A + 1.53B + 0.71C - 4.24AB + 1.15AC - 2.32A^2 - 5.32B^2 \quad (3)$$

where, *A*, *B*, and *C* represent methanol/oil molar ratio, catalyst loading, and reaction time, respectively. Model terms having a positive (+) sign had a synergistic effect on biodiesel yield, whereas model terms having a negative (-) sign had an adverse effect on biodiesel yield.

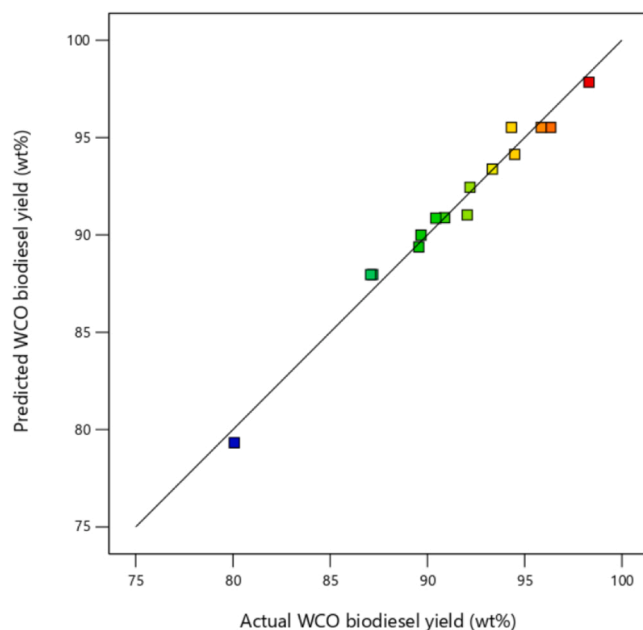
ANOVA of the experimental study for the MAT process is presented in Table 4. Any model term having a *p*-value ≤ 0.05 is considered significant within the experimental region investigated. Based on this value, the methanol/oil molar ratio (*A*) exhibited a very strong impact on biodiesel yield. Catalyst loading (*B*) significantly affects biodiesel yield, while the reaction time (*C*) is not statistically significant within the region chosen in this study.

Moreover, the interactive terms; *AB* and *AC* are significant, indicating that they impact biodiesel yields. The *F*-value of the model is 47.54, implying that the model is significant, and there is a 0.01 % chance that a model *F*-value this large can occur due to noise. Following observations from the *p*-value, *A*, *B*, *AB*, *AC*, *A*², and *B*² are significant model terms. The lack of fit is insignificant relative to the pure error in the model. Non-significance of lack of fit is desirable since this model is expected to fit (Islam Shishir et al., 2016). The plot of predicted biodiesel yield against experimental biodiesel yield is shown in Fig. 10, which suggests a good agreement between them. This can be ascribed to the alignment of data points close to the diagonal line, signifying the adequacy of the regression model.

Table 4

ANOVA for the Box-Behnken model under MAT.

Source	Sum of squares	Degree of freedom	Mean square	<i>F</i> -value	<i>p</i> -value
Model	281.22	7	40.17	47.54	<0.0001
A–Methanol/oil molar ratio	61.99	1	61.99	73.36	<0.0001
B–Catalyst loading	18.82	1	18.82	22.27	0.0022
C–Reaction time	4.03	1	4.03	4.77	0.0652
AB	72.00	1	72.00	85.19	<0.0001
AC	5.24	1	5.24	6.21	0.0415
A ²	19.92	1	19.92	23.57	0.0018
B ²	105.15	1	105.15	124.42	<0.0001
Residual	5.92	7	0.8451		
Lack of Fit	3.70	5	0.7390	0.6657	0.6916
Pure Error	2.22	2	1.11		
Cor Total	287.13	14			

**Fig. 10.** Plot of predicted versus actual WCO biodiesel yields under MAT.

3.5. Effect of process factors on biodiesel yield under MAT

The plot of biodiesel yield against the impact of catalyst amount and methanol/oil molar ratio is presented in Fig. 11a. It can be seen that biodiesel yield increased with an increase in both catalyst loading and methanol/oil molar ratio. The effect becomes pronounced because of the high catalyst tendency to form methoxy radicals from methanol, which in turn react with triglyceride molecules to form biodiesel (Nayak and Vyas, 2019). However, at the highest catalyst amount, its impact on biodiesel yield is not complementary when compared to the methanol/oil molar ratio. At the highest catalyst amount in the presence of excess methanol, gel formation and increased viscosity of the reaction mixture can affect the reaction rate (Erchamo et al., 2021), leading to a reduced biodiesel yield. Moreover, reaction time and methanol/oil molar ratio had the highest impact on biodiesel yields (Fig. 11b). As the reaction time increased, biodiesel yield increased marginally since a sufficient amount of time is needed for proper dispersion of the reaction mixture (Mahesh et al., 2015). However, it can be observed that increasing the methanol/oil molar ratio from 5:1–10:1, and then to 15:1, led to a considerable increase in biodiesel yield with time.

3.6. Comparison of statistical model parameters

Model accuracy parameters for WCO biodiesel production under CHT and MAT are presented in Table 5. The coefficient of variation (C.V.) is a measure of deviation from the mean value (Islam Shishir et al., 2016). The C.V. obtained under MAT is very low (< 10 %), indicating a high degree of precision and reliability of experimental biodiesel yield (Nayak and Vyas, 2019). In MAT, the coefficient of determination (*R*²), predicted *R*², and adjusted *R*² values are very close to each other, which demonstrates the fitness of the regression model (Pham et al., 2022). The difference between the predicted *R*² and adjusted *R*² is lower than the maximum allowable value of 0.2 (Iwuka et al., 2023) in both CHT and MAT. This observation rules out any overfitting and gives a more accurate measure of model fit, as well as predicting model responses of future data. Adequate precision assesses the signal-to-noise ratio. A value above 4 is desirable as it demonstrates that the model is useful for optimization and can be used to navigate the design space for a reliable prediction. The higher the adequate precision value, the stronger the signal, which means the model will make good predictions that are

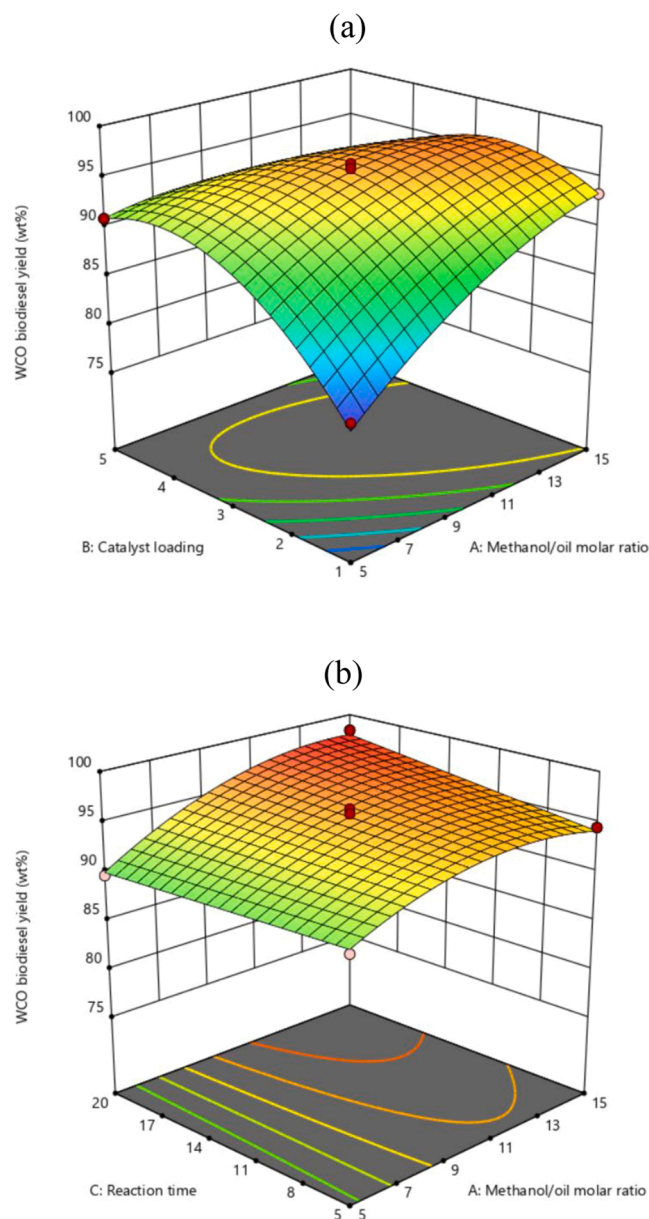


Fig. 11. 3D synergistic surface plots of process variables with respect to WCO biodiesel yield (wt%) under MAT.

Table 5
Model accuracy parameters comparing CHT and MAT.

Parameters	Value (CHT)	Value (MAT)
Standard deviation	1.22	0.92
Mean	81.60	91.46
Coefficient of variation (C.V.)	1.50	1.01
Coefficient of determination (R^2)	0.97	0.98
Adjusted R^2	0.95	0.96
Predicted R^2	0.84	0.91
Adequate Precision	22.51	25.58

within tolerance. Adequate precision values obtained for the statistical models in this study are high enough to account for future prediction. The computed parameters of the model from MAT are statistically attractive and have a better value than those obtained under CHT.

3.7. Optimization of biodiesel yields in CHT and MAT processes

One of the objectives of this study was to optimize biodiesel conversion from WCO. The performance criterion involved maximization of biodiesel yield and minimization of process factors due to consideration for energy utilization and green chemistry. The process factors predicted by BBD-RSM for optimum biodiesel yield from WCO in the CHT process are methanol/oil molar ratio of 15:1, catalyst loading of 1 wt%, and reaction time of 62 min, with a corresponding yield of 90.50 %. For the MAT process, the process factors established for optimum biodiesel yield from WCO are methanol/oil molar ratio of 15:1, catalyst loading of 2.5 wt%, and reaction time of 20 min, with a corresponding biodiesel yield of 98.93 %. The predicted optimal reaction conditions by BBD-RSM were ascertained by conducting laboratory experiments with one-pot biodiesel production from WCO. Biodiesel yields of 90.39 % and 98.90 % were obtained for the CHT and MAT processes, respectively. The low absolute relative error obtained between the predicted and actual biodiesel yield confirms the adequacy of the model in optimizing the one-pot biodiesel production using the synthesized bifunctional catalyst.

The superior catalytic performance observed under MAT can be attributed to the unique interaction between microwave energy and the synthesized bifunctional metal-oxide catalyst. Microwave irradiation induces rapid and volumetric heating, which contrasts with the slower, surface-based heat transfer in CHT (Rhithuparna et al., 2024). In our catalyst system, the presence of polar metal oxides such as ZnO and Fe₂O₃ facilitates efficient microwave absorption due to their high dielectric loss characteristics. This leads to the generation of localized hotspots on the surface of the bifunctional catalyst, which accelerate the reaction by rapidly increasing the temperature at the active sites without significantly raising the bulk temperature (Nomanbhay and Ong, 2017). These thermal hotspots enhance the energy available for bond activation, lower the activation energy barrier, and promote faster conversion of triglycerides to biodiesel (Palma et al., 2020). Furthermore, the oscillating electromagnetic field associated with microwave radiation improves dipolar rotation and molecular collision frequency, which enhances mass transfer between the reactants and the active sites (Palma et al., 2020). This is particularly beneficial in heterogeneous catalysis, where internal diffusion limitations often restrict reaction rates (Ruhul et al., 2015). These mechanistic insights highlight the advantages of integrating MAT with heterogeneous catalyst systems for efficient and sustainable biodiesel production, as demonstrated in this current study.

3.8. Physicochemical properties of WCO and WCO biodiesel

The qualities of biodiesel produced from WCO using CHT and MAT

Table 6
Physicochemical and fuel properties of WCO and its biodiesel.

Properties	WCO	WCO biodiesel (MAT)	WCO biodiesel (CHT)	EN 14214	ASTM D6571
Kinematic viscosity (mm ² /s)	6.99	4.6	4.93	3.5–5.0	1.9–6.0
Density (kg/m ³)	960	890	895	860–900	860–900
Water and sediment	0.46	0.03	0.03	-	0.05 max
Saponification value (mg KOH/g oil)	280.5	282	281	-	-
Acid value (mg KOH/g oil)	3.78	0.36	0.46	0.5 max	0.5 max
Iodine value (g I ₂ /100 g oil)	20.49	23.4	24.63	120 max	-
Cetane number	56.86	55.3	53.5	51 min	47 min
Calorific value (MJ/kg)	38.76	40.55	39.6	-	-

were compared to values specified by EN and ASTM standards (Table 6). The kinematic viscosity and density of biodiesel are vital parameters influencing the combustion performance and fuel ignition quality in diesel engines (Yadav and Sharma, 2018). The values obtained are within the limit specified for biodiesel standards. The acid values of the produced biodiesel are below the maximum value specified, indicating that the fuels are less corrosive and can be stored and transported safely (Ala'a et al., 2021). The biodiesel samples exhibited high calorific values, comparable to the energy density of conventional diesel fuel (~ 42 MJ/kg), a critical parameter for ensuring adequate engine power output (Verma et al., 2021). Biodiesel from the MAT process has improved yields and better fuel properties than biodiesel produced from the CHT process.

3.9. Catalyst reusability

The reusability of a catalyst is vital to the process economics of catalyst-design operations in industrial biodiesel production (Yadav and Sharma, 2018). The performance of the bifunctional catalyst in this study (Fig. 12) surpassed the catalytic longevity reported by Falowo et al. (2024) and compared favourably with other ZnO-based catalysts. For example, recyclability tests of ZnO@Ag NPs revealed stable performance for up to 5 successive cycles without appreciable activity loss (Laskar et al., 2020), while copper-doped ZnO catalysts demonstrated good reusability up to 5 cycles (Gurunathan and Ravi, 2015). Yusuff et al. (2021) also showed that CFA-ZnO retained its activity over 4 cycles with negligible performance degradation. In this present study, the bifunctional catalyst applied in the MAT and CHT processes exhibited an 8.2 % and 11.2 % reduction in biodiesel yield, respectively, after the 5th cycle. The observed decline in catalytic activity after multiple reaction cycles is likely associated with agglomeration of catalyst particles over time, which may reduce the available surface area and block active sites (Yuan et al., 2024). Likewise, the accumulation of unconverted glycerides on the catalyst surface could also contribute to catalyst poisoning, further hindering access to the active sites of metal oxide-based catalysts (Mukhtar et al., 2022). The relatively lower decline in biodiesel yield observed in MAT can be attributed to superior thermal management, which mitigates deactivation mechanisms such as active site leaching by reducing thermal stress on the catalyst.

Although a detailed quantitative techno-economic analysis is beyond the scope of this current study, a qualitative assessment of the MAT process relative to the CHT offers valuable insights into its economic potential. Under optimized reaction conditions, the MAT process demonstrated significantly reduced reaction times when compared with CHT in this study. This translates to improved thermal efficiency, lower energy consumption, and shorter biodiesel production cycles (Rhithuparna et al., 2024). These factors can contribute to decreased operational costs by minimizing energy input and increasing batch throughput. Moreover, the enhanced reaction kinetics under microwave irradiation not only accelerated the transesterification process but also improved the overall conversion efficiency, resulting in a biodiesel yield higher than that obtained via CHT. This further supports the economic viability of MAT as a more efficient and productive alternative for biodiesel production (Nomanbhay and Ong, 2017). While these qualitative indicators point toward promising cost and energy advantages of MAT over CHT, our future work will focus on developing a detailed economic model to quantify these benefits under various operational scenarios.

4. Conclusion

This study successfully synthesized a bifunctional catalyst from eggshell wastes, doped with $\text{Fe}_2(\text{SO}_4)_3$ and ZnSO_4 . The synthesized catalyst has mesoporous pores with a high surface area. The catalyst showed the presence of strong basic and acidic sites, with active crystalline phases that consisted of ZnO , Fe_2O_3 , ZnFe_2O_4 , and $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. Application of the synthesized bifunctional catalyst to

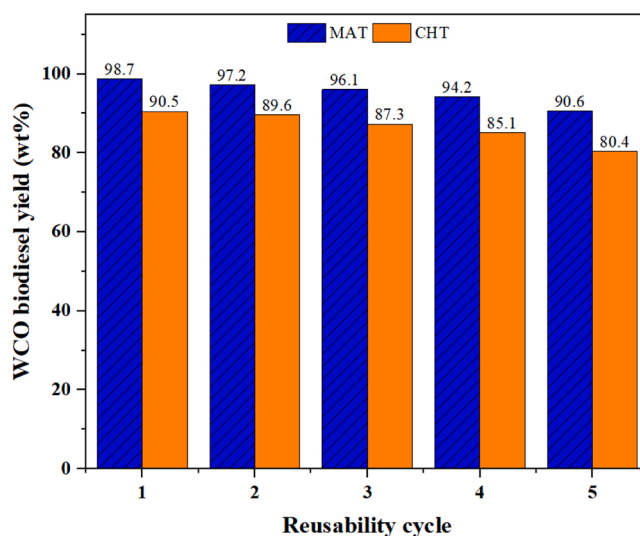


Fig. 12. Biodiesel yields from the bifunctional catalyst reusability test.

the simultaneous esterification-transesterification of WCO produced a considerable amount of biodiesel. Moreover, in the presence of the catalyst, biodiesel yields obtained from microwave-aided technology (MAT) were considerably higher than the yields obtained from conventional heating technology (CHT). This study showed that the production efficiency of biodiesel can be improved using technology with a high-energy source. The optimal conditions established for biodiesel yield were methanol/oil molar ratio (15:1), catalyst loading (1 wt%), and reaction time (62 min) at a constant temperature of 70 °C for the CHT process, with a corresponding biodiesel yield of 90.45 %. Whereas methanol/oil molar ratio (15:1), catalyst loading (2.5 wt%), and reaction time (20 min) at 450 W produced 98.7 % of biodiesel under MAT. The biodiesel produced was within the specifications for biodiesel standards (ASTM D6571 and EN 14214).

CRediT authorship contribution statement

Olayomi Abiodun Falowo: Writing – original draft, Visualization, Supervision, Formal analysis, Data curation, Conceptualization. **Babatunde Oladipo:** Writing – review & editing, Writing – original draft, Visualization, Validation, Formal analysis, Data curation. **Oluwajunwonlo Adewole:** Validation, Methodology, Investigation. **Tunde V Ojumu:** Writing – review & editing, Software, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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