

Research Paper

Ferric sulfate modified bifunctional catalyst for methyl esters production from microwave-assisted intensification of *Delonix regia* and waste cooking oil mixture

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ARTICLE INFO

Keywords:

Bifunctional catalyst

Eggshell waste

Biodiesel

Microwave-aided transesterification

Waste cooking oil

Delonix regia seed oil

ABSTRACT

Intensification of synergistic active sites of a bifunctional catalyst promotes process efficiency in biodiesel production. In this study, a bifunctional solid catalyst was developed from waste eggshells and ferric sulfate in the presence of ammonium molybdate solution. The developed catalyst was applied in a microwave-aided process for simultaneous esterification-transesterification of *Delonix regia* seed oil and waste cooking oil mixture. Several analytical methods were utilized to examine the characteristics of the synthesized catalyst. The findings reveal that the catalyst is mainly composed of mesoporous particles featuring medium to strong acidic and basic sites, essential for its dual catalytic activity. The synthesized catalyst has a surface area of 52.38 m²/g and a pore diameter of 8.34 nm. Crystalline phase of the catalyst was dominated by both acidic (CaSO₄ and Fe₂O₃) and basic (CaO) compounds. Optimal conditions for methyl esters production in the single-step process were: MeOH/oil molar ratio of 15:1, reaction time of 5 min, and catalyst amount of 1 wt%, with a corresponding methyl esters yield of 98.52 %. Estimated specific energy consumption of 1.9 kWh/kg and specific CO₂ emissions of 1.52 kg/kg of biodiesel indicate efficient microwave energy usage in driving the reaction process while contributing to a reduced carbon footprint. The biodiesel produced has physicochemical and fuel properties that fall within ASTM D6751 and EN 14214 stipulated standards. This strategy could help improve the process economics of biodiesel production by using eggshell waste as support, leading to less reduction in ecotoxicity.

1. Introduction

The conversation around future energy sources intensifies due to the growing attention on climate change challenges, energy security, and economic stability [1]. Overcoming the deficiency between the energy demand and supply would require the hybridization of many energy sources. Renewable energy is positioned to drive global shift from conventional energy sources to sustainable energy [2]. Investment in renewable energy technologies is a strategic way for organizations and countries to reduce their carbon footprint, strengthen economic resilience, enhance energy security, and position themselves as leaders in the green economy. The production of biofuel not only alleviates global

warming concerns, but the bioproducts generated alongside provide income and employment opportunities in developing areas [3,4].

Among the biofuels, biodiesel is a liquid fuel similar to conventional diesel obtained from fossil sources. Biodiesel is a safe, clean-burning, efficient, biodegradable, and renewable fuel that can serve several purposes such as heating, transportation, electricity generation, and operation of machinery [5,6]. Additionally, biodiesel can be used alone or blended with petro-diesel at any proportion without compromising the performance of the diesel engine [7,8]. Despite several advantages in the utilization of biodiesel, large-scale production for commercial usage is limited by the cost of production which is attributed to feedstock availability, catalyst type, and higher cost of production technology

Abbreviations: ANOVA, analysis of variance; ASTM, American standard testing methods; BET, Brunauer-Emmet-Teller; BJH, Barrett-Joyner-Halenda; CaO, calcium oxide; CCRD, central composite rotatable design; DRSO, *Delonix regia* seed oil; EDX, energy-dispersive X-ray; FFA, free fatty acid; FTIR, Fourier transform infrared spectroscopy; MAT, microwave-aided technology; RSM, response surface methodology; SEM, scanning electron microscopy; TPD, temperature-programmed desorption; WCO, waste cooking oil; XRD, X-ray diffraction.

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<https://doi.org/10.1016/j.enconman.2025.119588>

Received 14 November 2024; Received in revised form 5 January 2025; Accepted 26 January 2025

Available online 29 January 2025

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[9,10]. To avoid food price inflation, biodiesel feedstocks from non-edible crops, waste cooking oil, and algae materials have been well-embraced [11–13]. Though, a single non-edible feedstock source is desirable for biodiesel production, however, relying solely on one source puts pressure on the existing plantations and degrades soil quality. Besides, feedstock from a single source is sometimes insufficient to meet the quantity required for biodiesel production even in a local region [14].

Blending different vegetable oils solves the problem of the unavailability of the feedstock. Additionally, blending various oil feedstocks at the right proportion has been shown to negate the disadvantages caused by a single oil feedstock [9,15]. Mixing of oil feedstocks in various ratios changes both the acid value and the chemical composition of the feedstock, thereby decreasing the harsh conditions required for the pre-treatment step [15]. The sustainability of biodiesel requires a complementary nature of all components that make up the fuel, including feedstocks. *Delonix regia* trees are found in many tropical parts such as roadsides, parks, school premises, and temple grounds. It contains 15–25 seeds, and the oilseed has ~ 30–33 wt% oil content [16]. Fig. 1 shows the tree, seeds, and oil of *Delonix regia* seeds. Despite the availability and abundance of *Delonix regia* seeds, only a few studies have produced biodiesel from its oil [8,17–19]. On the other hand, millions of tons of waste cooking oil (WCO) are generated worldwide, representing a vast feedstock for a circular economy.

The conventional biodiesel production from triglycerides having high free fatty acid (FFA) first involves an esterification process in the presence of acid catalysts to reduce the acid value to < 2 mg KOH/g oil [20], followed by transesterification in the presence of a base catalyst to produce methyl/ethyl esters depending on the alcohol used. Currently, certain nanocatalysts can achieve the same conversion in a single-step. The utilization of nanocatalyst accelerates the transesterification process by lowering the activation energy of the reactants, all while remaining stable and undamaged throughout the reaction [21]. Metal oxide compounds have high catalytic activity since they have abundant acidic and basic sites, and they can be applied in the trans(esterification) process several times without losing catalytic activity [22]. Ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) is a heterogeneous catalyst with acidic properties, and it has been applied in several transesterification reactions, including inter-esterification [23]. $\text{Fe}_2(\text{SO}_4)_3$ is an active modifier that could enhance catalytic activity since it has both acidic and oxidizing properties [24,25]. In the current context, $\text{Fe}_2(\text{SO}_4)_3$ can enhance the performance of a bifunctional catalyst, creating multiple acidic sites on the catalyst surface, and enhancing the catalyst to expedite the reaction involving high FFA-content feedstock [26]. For instance, Akhabue, et al. [27] incorporated an acidic group into a bifunctional catalyst by loading ferric sulfate on poultry droppings. Falowo, et al. [26] modified calcined eggshells with ferric sulfate to synthesize a bifunctional catalyst utilized in a single conversion of WCO.

Enhancement of the active sites of a catalyst is vital to its

performance. For example, loading 20 % molybdenum oxide on silica support increases the strength of the Bronsted acid sites in the bifunctional catalyst developed for tinidazole synthesis [28]. Fe-Mo-based bifunctional catalyst applied in the one-step preparation of methylal led to high conversion [29]. The presence of $\text{Fe}_2(\text{MoO}_4)_3$ on the catalyst enables electron transfer between the lattice oxygen and the metal ion, thereby leading to a high catalytic rate. AlKahlaway, et al. [22] synthesized ferric molybdate nanocatalyst for the transesterification of oleic acid. A conversion of 90.5 % and 92.5 % was achieved at 3 wt% and 5 wt %, respectively, due to a considerable number of Lewis-acid sites.

Improvement of process technology in biodiesel production requires the synthesis of environmentally friendly catalysts with bifunctional properties and subsequent utilization of suitable triglycerides from different sources. A bifunctional catalyst synthesized from graphene oxide and silicon carbide was applied in a binary mixture of rapeseed oil and oleic oil [30]. The SiC-NaOH/GO catalyst applied in microwave-assisted transesterification and esterification of the oil mixture produced 92 % biodiesel. The catalyst was reported to possess high microwave absorptive properties that facilitate reaction rate in the internal and external surface of the catalyst. Production techniques are crucial to net biodiesel production costs. Various intensification techniques, including ultrasonic, microwave irradiation, hydrodynamic cavitation, incorporating co-solvents or mass transfer catalysts, and utilizing supercritical synthesis conditions, have been experimented to reduce or eliminate the issue of mass transfer limitation, aiming to enhance the biodiesel production process compared to a conventional technique [31]. Among these, microwave irradiation technology is considered the most promising approach for biodiesel production, as it accelerates reaction kinetics through volumetric heating, leading to substantial reductions in both reaction time and energy consumption [32,33]. Besides the highlighted technology, interaction and the quadratic effects of process factors involved during production are also essential for biodiesel optimization. The influential parameters such as methanol/oil molar ratio, temperature, catalyst amount, irradiation power, and reaction time can be investigated using response surface methodology (RSM) to ensure improvement in biodiesel production regarding accuracy, process economics, and efficiency [34]. Among the experimental designs, the central composite rotatable design (CCRD) can examine experimental points at the borderline and has a high number of degree of freedom than Box-Behnken for the same number of factors [35]. CCRD has been applied to optimize process factors and biodiesel yield from oil in several studies [14,36–38].

This study builds upon our previous investigation of a bifunctional catalyst developed from calcined waste eggshell and ferric sulfate, which achieved a biodiesel yield of 89.9 wt% within 45 min [26]. Recognizing the potential of bifunctional catalysts, we sought to address the ongoing need for designing improved acid-base catalysts capable of achieving higher biodiesel yields and operational versatility. The current work thus focuses on enhancing the stability and activity of the

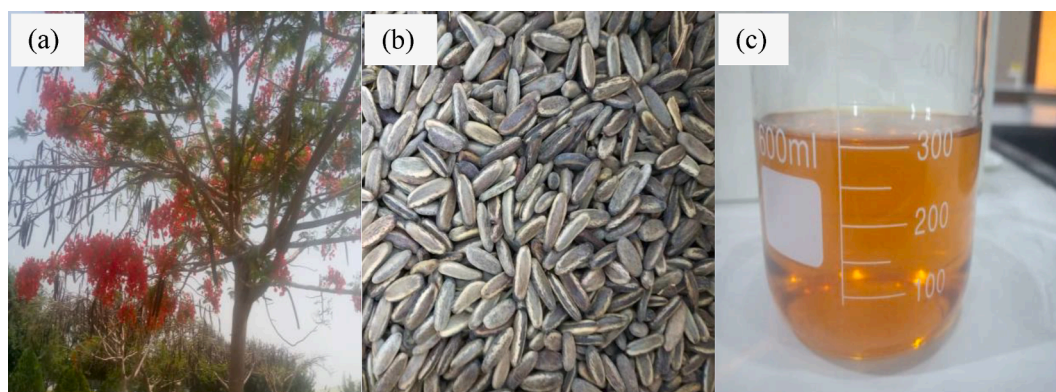


Fig. 1. (a) *Delonix regia* tree, (b) seeds, and (c) oil.

$\text{CaSO}_4/\text{Fe}_2\text{O}_3$ catalyst utilized in the esterification-transesterification of WCO. To achieve this, we introduced ammonium molybdate alongside ferric sulfate, creating a synergistic effect that improved the performance of the catalyst in single-step biodiesel production from a mixed feedstock of WCO and *Delonix regia* seed oil (DRSO). This approach leverages a novel tuning of process routes and catalyst composition, offering insights into the synthetic design of nanomaterials with enhanced catalytic properties from otherwise weaker precursors. Characterizations such as particle size distribution (PSD), scanning electron microscopy (SEM)/energy dispersive X-ray (EDX), Brunauer-Emmett-Teller (BET)/Barrett-Joyner-Halenda (BJH), X-ray diffraction (XRD), Fourier transform infrared radiation (FTIR), and temperature-programmed desorption (TPD) were investigated for the dual properties of the catalyst. The enhanced modified-bifunctional catalyst was utilized in microwave-assisted biodiesel production from an oil mixture using the CCRD of RSM.

2. Materials and experimental methods

2.1. Materials

WCO and waste eggshells were collected from Landmark University cafeteria kitchen, Omu-Aran, Nigeria. DRSO was extracted using *n*-hexane in a Soxhlet extractor. *n*-hexane was used for its high oil solubility and non-polar nature, which enhance extraction efficiency and facilitate effective solvent recovery [39]. Other materials include analytical-grade methanol, ethanol, ammonium molybdate, diethyl ether, potassium hydroxide, sodium hydroxide, ferric sulfate, Wij's solution, and potassium iodide. All reagents used are of analytical grade and were used without further purification.

2.2. Development of CaO precursor from waste eggshells

Waste eggshells were thoroughly washed with distilled water and oven-dried in a heating dryer (DHG -9053A) at 105 °C until constant weight was achieved. The dried eggshells were pulverized to reduce them to small sizes. The resulting sample was calcinated in a muffle furnace (Vecstar, LF3 UK) at 800 °C for 3 h [26]. The thermally treated sample was allowed to cool and then pulverized into fine particles using mortar and pestle. A mesh sieve of 80 mm was used to obtain the calcined fine samples as CaO precursor, which were thereafter stored in an airtight jar.

2.3. Development of bifunctional catalyst

The bifunctional catalyst synthesis route reported in Falowo, et al. [26] was adopted. Typically, a bifunctional catalyst was prepared from calcined waste eggshells and ferric sulfate using the wet impregnation method. First, 1 g of CaO precursor was dissolved in 0.1 M of ammonium molybdate, placed on a hotplate at 80 °C and left for 30 min. After complete dissolution, 1 g of ferric sulfate was added to the resultant slurry on a hotplate with a magnetic stirrer (Stuart CD162, England) at 80 °C and allowed to mix for 4 h. The wetted sample was decanted after the process and washed with distilled water to remove any unreacted excess salts or byproducts formed during the synthesis process. The purified sample was then dried at 105 °C in an oven dryer and calcined at 500 °C for 2 h in a muffle furnace. The synthesized bifunctional catalyst was stored in an airtight jar for further analysis and subsequent usage for one-pot methyl ester production.

2.4. Physicochemical attributes of the bifunctional catalyst

The developed bifunctional catalyst was characterized to evaluate its properties. Surface morphology of the catalyst was investigated using SEM instrument (NeoScope™ JCM-7000). Elemental composition of the synthesized catalyst was determined using EDX analyzer (JOEL JED-

2300) attached to the SEM. Diffraction crystalline phases of the synthesized catalyst were obtained using XRD diffractometer (Bruker D2 Phaser). Acidic and basic sites of the catalyst were determined by NH_3 - and CO_2 -TPD, respectively, using a Micromeritics AutoChem™ 2950 HP with a thermal conductivity detector (TCD) for measuring the desorbed gases. Particle size distribution was measured on Microtrac S3500 Laser Diffraction. Total surface area of the catalyst was determined using the BET method with corresponding N_2 adsorption-desorption isotherms on a Micromeritics Tristar II 3020. BJH model was employed to estimate the average pore size distribution. Functional groups of the catalyst were identified using FTIR spectrometer (Perkin Elmer UATR Two).

2.5. Physicochemical determination and blending of DRSO and WCO oil mixture

Preliminary investigation revealed that DRSO had a low acid value (2.6 mg KOH/g oil) compared to WCO (9.7 mg KOH/g oil). The blending of WCO and DRSO was initiated in a 50:50 (v/v) ratio, thereby reducing the high FFA of WCO. To ensure thorough feedstock mixing, the oil mixture was heated to 105 °C for 30 min on a magnetic hot plate under sufficient stirring. The physical and chemical attributes determined for the DRSO and WCO blend include the FFA, acid value, iodine content, saponification content, density, kinematic viscosity, caloric value, cetane number, and specific gravity. Physicochemical tests were conducted according to AOAC methods [14].

2.6. One-pot synthesis of biodiesel from oil blend

Simultaneous esterification and transesterification process of the oil blend and methanol using the bifunctional catalyst was conducted experimentally. Microwave-assisted methyl esters synthesis was carried out using the procedure of Falowo, et al. [14]. Basically, a two-neck round bottom flask of 500 mL was used in a modified microwave reactor. According to the process condition specified by the design matrix, a known volume of MeOH/oil blend molar ratio and a certain amount of the developed catalyst were charged into the reactor. The microwave (Severin MW 7820) timer was set to the designated duration and the reaction mixture was performed at 450 W irradiation power. After the reaction, the mixture was poured into a centrifuge bottle and spun at 5000 rpm for 10 min to achieve phase separation. The process effectively separated the glycerol (by-product), methyl esters, and the solid catalyst. The recovered methyl esters was washed with warm distilled water for purification and dried with sodium sulfate on a hot-plate. The amount of methyl esters produced was measured gravimetrically according to Eq. (1).

$$\text{Methyl esters yield (\%)} = \frac{\text{Weight of biodiesel (methyl esters)}}{\text{Weight of oil blend used}} \times 100 \quad (1)$$

2.7. Modeling and optimization of the oil blend one-pot process

A three-factor, four-level CCRD of RSM was utilized to investigate the impact of key process parameters (MeOH/oil blend molar ratio, catalyst amount, and reaction time) on the conversion of the oil blend into methyl esters. A total of 15 experiments were generated, divided into 5 full-factorial, 6 partial-factorial, and 4 replicated center points. The relationship between the independent variables (MeOH/oil blend molar ratio of 5:1–15:1; reaction time of 5–15 min; catalyst amount of 1–3 wt%) and the dependent variable (methyl esters yield) was modeled using a second-order polynomial equation according to Eq. (2).

$$Y = \alpha_0 + \sum_{j=1}^k \alpha_j x_j + \sum_{j=1}^k \alpha_{jj} x_j^2 + \sum_{i=1}^k \sum_{j=2}^k \alpha_{ij} x_i x_j + e_i \quad (2)$$

where Y represents the dependent variable; x_i and x_j are the independent variables (ranging from 1 to k); α_0 is the model intercept; α_j , α_{jj} , and α_{ij}

are the interaction coefficients for linear, quadratic, and second-order terms, respectively; k is the number of independent variables ($k = 3$ in this scenario); and e_i denotes the error term [31]. Design of the experiment, analysis of the methyl esters yields from the experiment, and statistical optimization of the process were performed using statistical software (Design Expert 13.0.5.0, Stat-Ease, USA).

2.8. Energy consumption and CO₂ emissions analysis

The specific energy consumption in a production system serves as a measure of both process efficiency and economic feasibility. The energy consumption and specific energy requirements for producing a unit kilogram of biodiesel were calculated according to Oladipo, et al. [32]. Similarly, the CO₂ emission and specific CO₂ emission associated with the production of a unit kilogram of biodiesel were evaluated using the expression in Oladipo, et al. [32].

2.9. Qualities of synthesized methyl esters

The physicochemical properties of the methyl esters produced in this study were determined using AOAC standard methods [10,39]. The measured parameters are compared to the American Society for Testing and Materials (ASTM D6751) and European (EN 14214) standards.

3. Results and discussion

3.1. Bifunctional catalyst characterization

Fig. 2 shows the particle size distribution plot. There is no large variation in particle size since the sample between D10–D90 contains 0.85 to 15.10 μm . The catalyst particle size obtained in the region of D10 has a high tendency to form an emulsion with the reaction mixture. The broadness of the size distribution in a sample is undesirable since it causes difficulty in ascertaining a true representative size of the sample [40]. The value of the median particle size (D50) indicates that the majority of the particles in the sample are $\leq 3.08 \mu\text{m}$. The catalytic performance of most powder-based materials is often closely related to both the particle size and the concentration of fine particles. Smaller particle sizes are advantageous in biodiesel production as they enhance the specific surface area and increase surface energy, thereby promoting better contact between the catalyst and the reactants [41].

The textural properties revealed the specific surface area, pore diameter, and pore volume of the catalyst as 52.38 m^2/g , 8.34 nm, and 0.11 cm^3/g , respectively. Ala'a, et al. [42] reported BET surface area, pore volume, and average pore size of 15 wt% CaO-CeO₂ catalyst as

39.65 m^2/g , 0.51 cm^3/g , and 7.87 nm, respectively. The increment in surface area of the catalyst was adjudged to be due to increased interaction between the metallic oxides, resulting in the opening of new pores on the external surface of the catalyst. A typical triglyceride molecule was reported to be $\sim 5.8 \text{ nm}$ in pore diameter [43]. The pore diameter of the synthesized bifunctional catalyst in our study is larger than that of triglyceride molecules, indicating that the reactant molecules would easily diffuse into the interior of the acid-base active sites with no limitation. The specific pore volume which can be defined as the total internal volume per unit is greater than several bifunctional catalysts reported in Omar and Amin [43]. The developed bifunctional catalyst in this current study has sufficient pore volume to facilitate biodiesel conversion by amplifying the reaction surface. The N₂ adsorption–desorption isotherm (at 77 K) of the synthesized bifunctional catalyst is shown in Fig. 3 and the inset represents its BJH pore size distribution. The isotherm of the catalyst steadily increases at lower pressure regions and has major adsorption at relative pressure P/P_0 higher than 0.8 as the value approaches 1.

The observed isotherm was Type IV adsorption, characteristic of samples dominated by mesoporous particles. The characteristic H3 hysteresis loop confirmed the presence of mesoporosity, attributed to the metastable fluid state of nitrogen during adsorption as it transforms from monolayer to multilayer adsorbate formation on the surface of the catalyst [44]. It should be noted that porosity of material plays a vital role in anchoring other functional groups, and a material having a high specific surface area with connected mesopores and micropores could facilitate high incorporation [45]. Mesoporous material has a uniform pore structure and high surface area which could promote the adsorption of large organic molecules [46]. From the pore size distribution analysis, the synthesized catalyst has an appreciable high pore diameter $> 2 \text{ nm}$. Based on IUPAC classification, pore size distribution in the range of 2–50 nm exhibited by the sample in this study is mesoporous material [14].

Elemental constituents of the synthesized catalyst were C: 4.1 %, O: 20.13 %, S: 6.43 %, Ca: 45.37 %, Fe: 23.42 %, and Al: 0.54 %. As expected, the result has an approximation value of the composition reported in Falowo, et al. [26], except with the inclusion of Al. The percentage composition of calcinated chicken eggshells at 800 and 900 °C showed that the sample was dominated by Ca, O, and C [47]. Meanwhile, the incorporation of Fe species over CaO particles generated from the calcination of eggshell waste was observed. The EDX spectrum (Fig. 4) depicted that Ca, Fe, and O were the concentrated elements on the catalyst. Likewise, the presence of S indicates that the impregnation

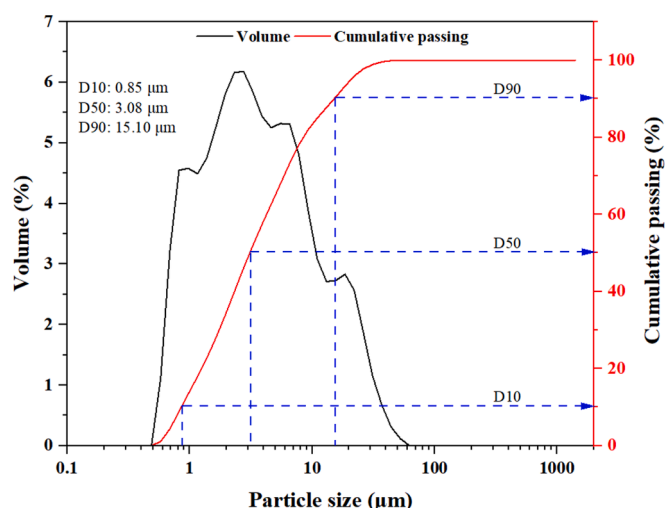


Fig. 2. Particle size distribution of the bifunctional catalyst.

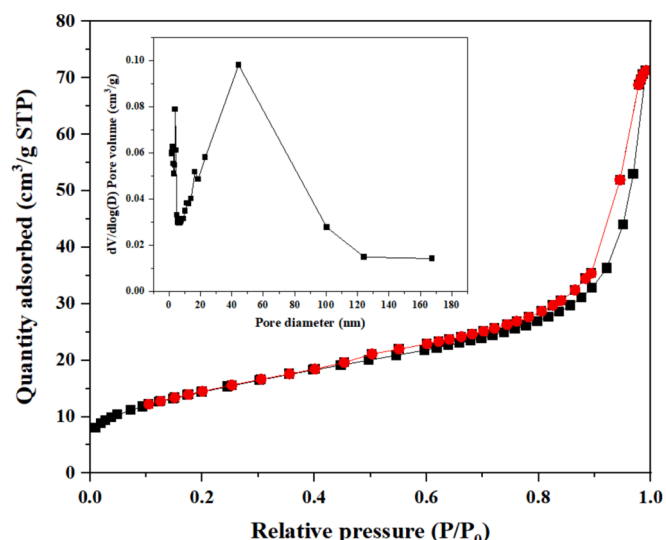


Fig. 3. N₂ adsorption–desorption curves and BJH pore size distribution (inset).

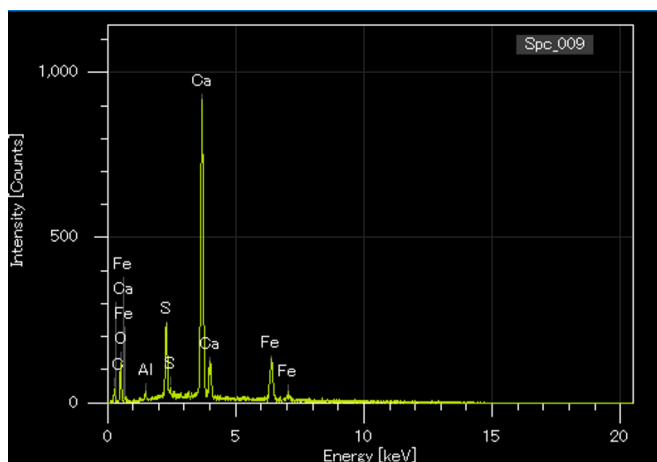


Fig. 4. EDX spectra of the synthesized catalyst.

method employed was effective. There is a considerable amount of Lewis acidic sites (Fe^{2+}) on the catalyst, where the carbonyl oxygen of the fatty acid interacts, facilitating the formation of a carbocation [24].

SEM images of the synthesized bifunctional catalyst are presented in Fig. 5 to understand the morphology at different magnifications. Fig. 5a portrayed rod-like growth of crystal aggregate made of dense particles. It can be observed that the surface of the catalyst has whitish grains that are heterogeneously distributed, indicating an active phase probably imprinted during the incorporation stage [26,48]. However, at higher magnification (Fig. 5b), the interspersed large particle size and small grains throughout the catalyst surface are a testament to its porosity. Heterogeneous catalysts having this feature mostly possess higher specific surface area [11].

The XRD pattern of the bifunctional catalyst is presented in Fig. 6. Three crystalline phases present as mixed crystals in the catalyst were observed: CaSO_4 (JCPDS: 00-41-0224) at $2\theta = 12.0^\circ, 20.8^\circ, 23.7^\circ, 32.2^\circ$, and 26.5° ; CaO (JCPDS: 00-37-1497) at $2\theta = 27.3^\circ, 29.2^\circ, 34.7^\circ, 38.6^\circ, 43.5^\circ$, and 47.9° ; and Fe_2O_3 (JCPDS: 00-33-0664) at $2\theta = 31.2^\circ, 33.4^\circ, 36.8^\circ, 40.8^\circ, 46.0^\circ, 48.5^\circ$, and 50.4° . The formation of these crystalline compounds results from the thermal and chemical transformations of the materials during calcination and synthesis. Ammonium molybdate was included in the synthesis of the bifunctional catalyst to enhance its acidic strength. However, the absence of Mo-related compounds in the XRD analysis suggests that Mo likely exists in an amorphous or highly dispersed state, attributable to its low molar concentration relative to other precursors. This indicates that Mo played a functional role in improving the accessibility of other active catalytic sites. The presence of CaO primarily provides the sites for basic activity while CaSO_4 and Fe_2O_3 provide the sites for acidic activity. It is also important to mention that CaSO_4 also contributes to stabilizing the structure of the catalyst

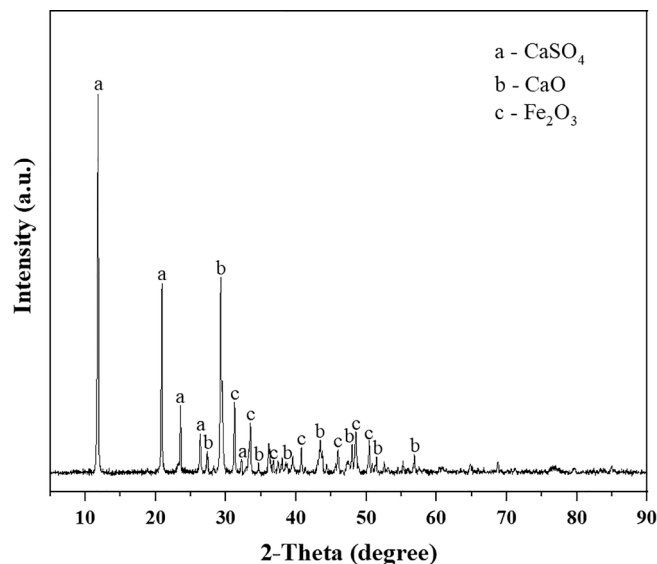


Fig. 6. Diffraction pattern of synthesized bifunctional catalyst.

and also assists in the adsorption of intermediate products. The findings support the dual catalytic functions necessary for simultaneous esterification and transesterification for biodiesel production. The observations on the XRD result are consistent with the elemental constituents identified using EDX.

TPD analysis provides essential information on the distribution of basic and acidic sites. The thermograms of the CO_2 -TPD and NH_3 -TPD of the synthesized bifunctional catalyst are shown in Fig. 7. The observed similarities in the TPD profiles could indicate the presence of overlapping acidic and basic sites with comparable strengths. The CO_2 -TPD profile reveals desorption peaks detected between 60 and 800 $^\circ\text{C}$ (Fig. 7a). A medium basic site appears at 318 $^\circ\text{C}$. This site stabilizes reaction intermediates and helps control reaction rates, thus minimizing undesired side reactions. The peaks at 636 and 742 $^\circ\text{C}$ correspond to strong basic sites, predominantly from CaO species derived from calcined eggshells. These sites provide high-energy O^{2-} ions [49,50] for deprotonating methanol, thereby generating methoxide ions for transesterification. The NH_3 -TPD profile, showing desorption from 100 and 800 $^\circ\text{C}$ (Fig. 7b), reveals a medium acidic site at 314 $^\circ\text{C}$. This site initiates early esterification reactions by providing moderate protonation capacity that enhances the reactivity of free fatty acids. The strong acidic sites at 627 and 735 $^\circ\text{C}$ are associated with Fe species, introduced via ferric sulfate impregnation. These sites generate protons (H^+), which catalyze the protonation of free fatty acids, facilitating their conversion to esters and simultaneously minimizing soap formation through neutralization reactions with basic sites. The total basicity of 50.76 $\mu\text{mol CO}_2/\text{g}$ and acidity of 51.48 $\mu\text{mol NH}_3/\text{g}$ obtained for the bifunctional

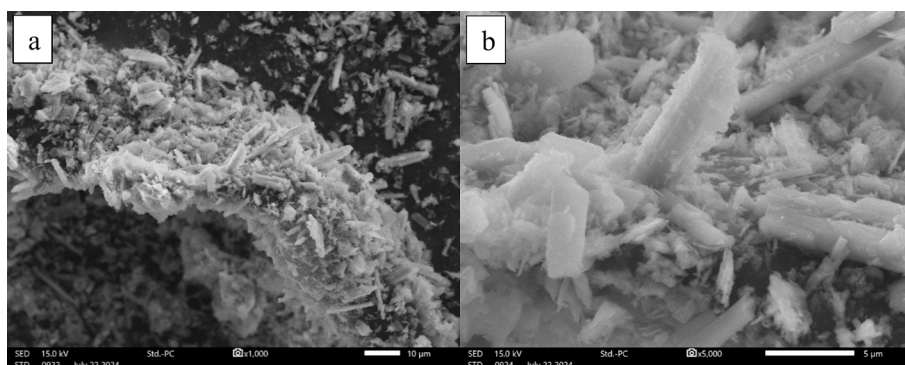


Fig. 5. SEM images of the synthesized bifunctional catalyst at different magnifications.

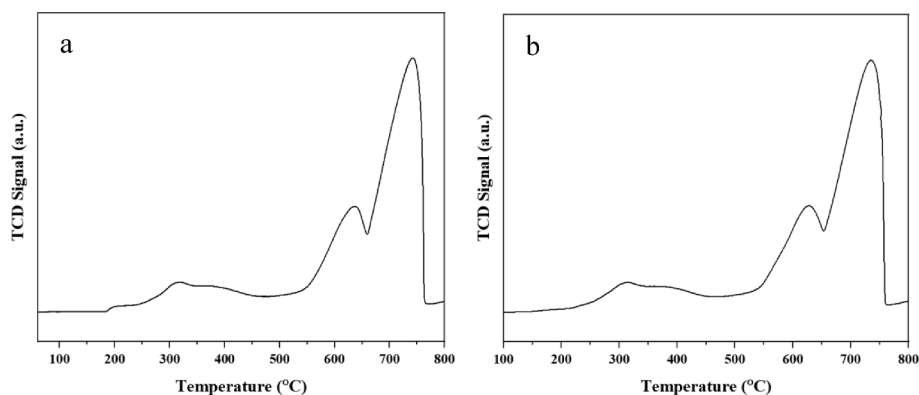


Fig. 7. (a) CO₂-TPD and (b) NH₃-TPD of the bifunctional catalyst.

catalyst indicate a well-balanced distribution of active sites, enabling a synergistic catalytic mechanism, conducive to biodiesel production from high-FFA feedstocks.

The FTIR spectrum of the synthesized bifunctional catalyst is presented in Fig. 8. The peaks located at 418, 599, and 664 cm⁻¹ are typically associated with metal–oxygen stretching likely indicating Ca–O or Fe–O vibrations due to the presence of Ca and Fe in the catalyst [29,45]. The out-of-plane bending of CO₃²⁻ group is identified at 709 cm⁻¹. Meanwhile, the peaks at 853, 873, 1446, and 1473 cm⁻¹ correspond to the stretching vibration of CO₃²⁻ group. This band becomes increasingly strong as the percentage weight of carbonates in the support increases [42]. The interaction between the CaO from the calcined sample and CO₂ led to the formation of carbonate. The absorption peak at 1114 cm⁻¹ is assigned to the chelating double ligand S₂O₈ which indicates a symmetric stretching vibration of the O–S–O bond [51,52]. The peaks located at 1617 and 1682 cm⁻¹ are ascribed to the O–H bending of adsorbed water molecules. Furthermore, the absorption bands at 3398 and 3522 cm⁻¹ are attributed to the O–H stretching vibration, likely from water or hydroxyl groups on the surface [52], an indication of an increased hydrophilicity nature of the bifunctional catalyst.

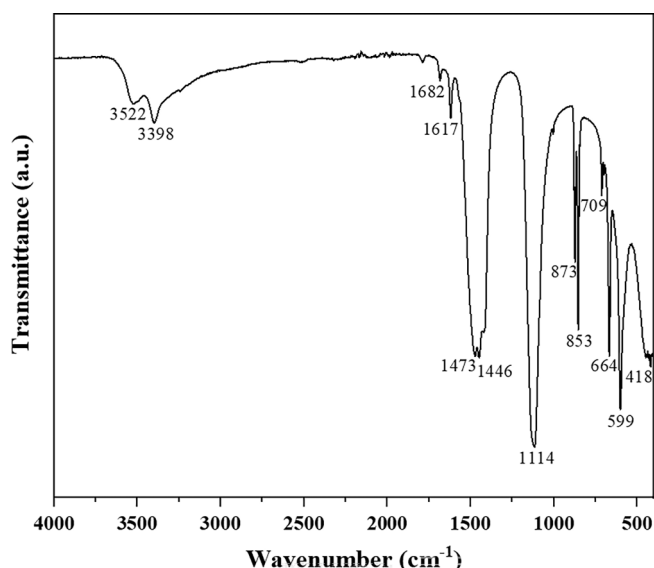


Fig. 8. FT-IR spectrum of the synthesized catalyst.

3.2. Methyl esters production from DRSO-WCO blend using developed bifunctional catalyst

The developed catalyst was subsequently assessed for methyl esters synthesis from a blend of DRSO and WCO. The process parameters such as MeOH/oil blend molar ratio, catalyst amount, reaction time, and the methyl esters yield are presented in Table 1. The yields recorded were between 73.76 and 98.52 %. There is an improvement in biodiesel yield compared to previous works that produced biodiesel from a single feedstock [18,19]. For example, using DRSO, our previous work established an optimal biodiesel yield of 89.45 % using a sulfated bifunctional catalyst of 1.5 wt% and a reaction time of 60 min [19]. Miriam, et al. [18] reported an optimized biodiesel yield of 97 % at 95 min using 4 wt % catalyst loading developed from a bamboo stem. Likewise, biodiesel yield of 89.33 % using 5 g catalyst and 4 h reaction time [53], 91.1 % at 10 wt% catalyst for 6 h [54], 93 % at 5 wt% catalyst loading for 150 min [55] were produced from WCO. A few minutes into the reaction is sufficient to produce methyl ester as high as 98.52 %, ascertaining the superiority of the microwave-aided process over the conventional heating process.

The regression model was fitted to the experimentally obtained responses (methyl esters yield) through multiple regression analysis to estimate the coefficients of the model generated. The model equation in terms of coded process factors is presented in Eq. (3).

$$\text{Methyl esters yield (\%)} = +86.21 + 0.0495A - 6.87B + 2.11C + 6.11BC \quad (3)$$

where A, B, and C represent MeOH/oil blend molar ratio, catalyst

Table 1
CCRD experimental matrix and methyl esters yield.

Run	A: Methanol/ oil blend ratio (v/v)	B: Catalyst amount (wt%)	C: Time (min)	Actual methyl esters yield (wt %)	Predicted methyl esters yield (wt%)
1	10	3.41	10	74.76	76.50
2	15	3	5	73.76	72.20
3	10	2	10	86.73	86.20
4	10	2	2.93	81.23	83.24
5	5	1	5	98.52	97.64
6	17.07	2	10	84.35	83.24
7	10	2	10	86.39	86.28
8	10	0.59	10	95.76	95.93
9	10	2	10	87.37	86.21
10	10	2	10	86.45	86.21
11	15	1	15	89.04	89.13
12	2.93	2	10	84.21	86.14
13	5	3	15	88.54	87.52
14	10	2	10	86.71	86.21
15	10	2	17.07	89.40	89.19

amount, and reaction time, respectively.

Analysis of variance (ANOVA) plays a critical role in validating the statistical significance and reliability of the experimental results, as it helps determine the effect and interaction of process variables on the response. ANOVA for this study is presented in Table 2. At a 95 % confidence level, the model was significant with a p -value ≤ 0.0001 . Other model terms such as catalyst amount (B), reaction time (C), and interactive term of BC were significant, indicating that a unit change in the value of this term influenced the methyl esters yield significantly.

Fit statistics from Stat-Ease software provide insight into the performance and precision of the regression model. The average response of the methyl esters yield in this study is 86.21 with a lower standard deviation, S.D. of 1.63, which suggests lower variability in the prediction of the model [20]. The relative variability of the model is measured by the coefficient of variation (C.V.). A low C.V. (1.89 %) obtained indicates that the variation in the biodiesel response is small relative to the mean, suggesting a stable and reliable model [55]. The R^2 of the model is a measure of how well the independent variables explain the variation in the response. An R^2 value of 0.9549 means that 95.49 % of the variability in the methyl esters yield is explained by the model [12,56]. A close observation revealed that the adjusted R^2 is close to unity. A value of 93.68 % obtained suggests that the regression model still explains a large proportion of the variability, but without overfitting due to unnecessary variables. The predicted R^2 value of 0.8122 demonstrates that the model can predict new data sufficiently since 81.22 % of the variability in the new data can be accounted for [10,57]. Likewise, the difference between the adjusted R^2 and predicted R^2 is less than 0.2, which means there is reasonable agreement between the two parameters, suggesting that the model has good predictive performance. Adequate precision of 27.54 compares the range of predicted biodiesel responses to the average prediction error. Having a value > 4 is sufficient for the model, however, a high signal-to-noise ratio of the magnitude in this study suggests that the model is reliable for forecasting and has a high level of precision for optimization [25,37]. The plot of the predicted against the actual methyl esters yield is shown in Fig. 9. As observed, there is a close agreement of the data to the line of fitness.

The plot of methyl esters yield against reaction time and catalyst amount is depicted in Fig. 10. It can be observed that maximum methyl esters yield was produced at low reaction time and catalyst loading than at a higher unit of the variables. Increasing the amount of catalyst in the reaction mixture with time negatively impacts the methyl esters yield. A significant reduction in esters yield suggests that mass-transport limitation has taken over the process. At a longer reaction time and MeOH/oil blend molar ratio of 10:1, there was a serious diffusion limitation of triglyceride molecules in the reaction mixture [52]. Sufficient time is

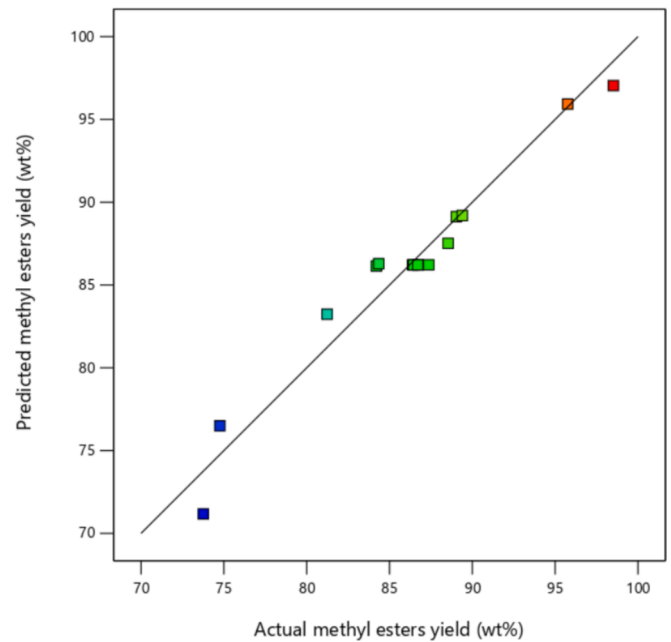


Fig. 9. Plot of predicted versus actual methyl esters yield.

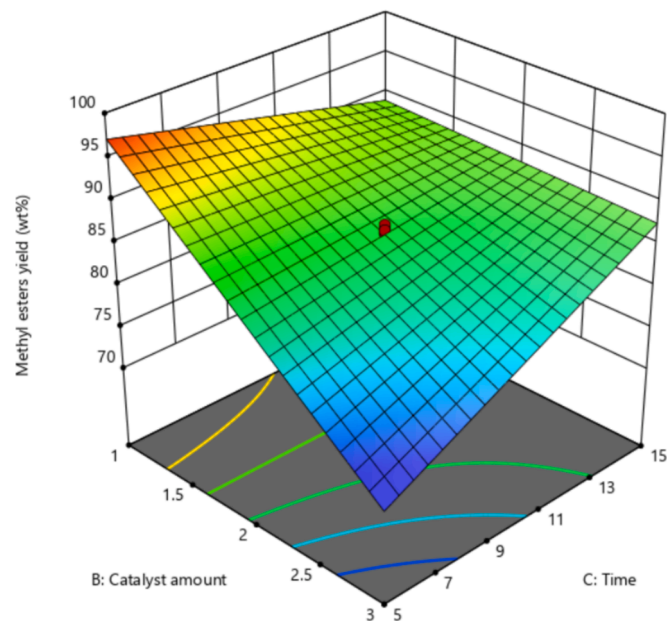


Fig. 10. Plot of methyl esters yield against time and catalyst amount.

Table 2

ANOVA obtained for the methyl esters synthesis.

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value
Model	560.21	4	140.05	52.92	< 0.0001
A–MeOH/oil blend molar ratio	0.0098	1	0.0098	0.0037	0.9527
B–Catalyst amount	377.55	1	377.55	142.66	< 0.0001
C–Reaction time	35.51	1	35.51	13.42	0.0044
BC	74.77	1	74.77	28.25	0.0003
Residual	26.46	10	2.65		
Lack of Fit	25.86	6	4.31	28.54	0.0030
Pure Error	0.6040	4	0.1510		
Cor Total	586.67	14			

Model accuracy indicators: $R^2 = 0.9549$, Adj $R^2 = 0.9368$, Pred $R^2 = 0.8122$, Adeq precision = 27.54, C.V. = 1.89 %, S.D. = 1.63, Mean = 86.21.

required for the complete conversion of triglyceride molecules to biodiesel, on the contrary, excessively long reaction time can result in the degradation of methyl esters, thereby reducing its quality and yield [58].

The influence of the three process parameters applied in the methyl esters yield affects the response in different ways (Fig. 11). Two (catalyst amount and reaction time) out of the three process parameters considered were significant. As revealed by ANOVA, catalyst amount had the highest influence on esters yield while the influence of MeOH/oil blend molar ratio could not be quantified statistically. However, increasing the catalyst amount in the reaction mixture led to a reduction in the yield of esters in this study. Contrary to the popular position, increasing the catalyst amount increases the active sites concentration and reactants in the reaction mixture, and consequently increases methyl esters yield

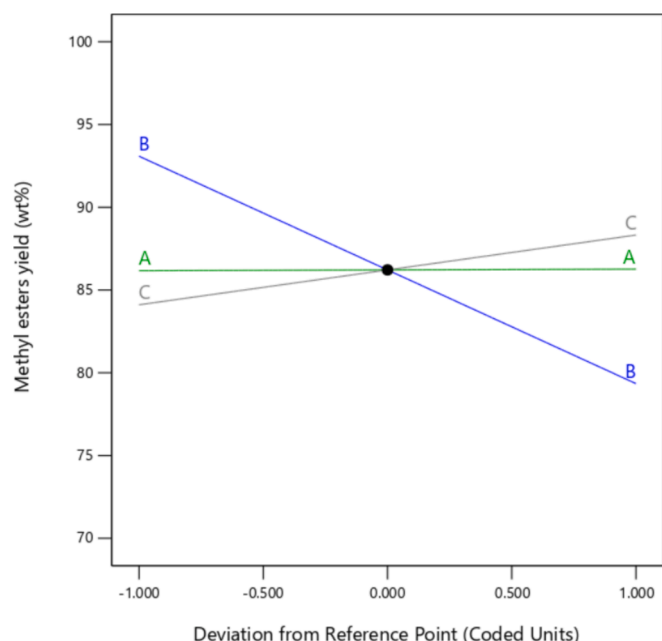


Fig. 11. Perturbation effect of process factors on methyl esters yield.

[51]. Only reaction time marginally had a synergistic effect on methyl esters yield.

3.3. Process optimization and model validation

In this work, the transesterification process was optimized through the numerical capabilities of RSM, aiming to achieve maximum biodiesel yield while maintaining all factors within specified boundaries. As RSM serves as a local optimization technique, its optimal solutions are inherently constrained to the defined parameter space [32]. To aid in this procedure, the quadratic polynomial model, as expressed in Eq. (7), was utilized. At a microwave power of 450 W, the optimal conditions predicted by RSM-CCRD were a MeOH/oil blend molar ratio of 15:1, a catalyst amount of 1.00 wt%, and a reaction time of 5 min, with a corresponding methyl esters yield of 98.82 %. The accuracy of the proposed model was validated by carrying out methyl esters production in a single-step in the presence of the developed bifunctional catalyst. Three experiments were conducted under the RSM-CCRD optimal predicted process conditions, and the resulting methyl esters yield was averaged. The experimentally obtained esters yield at the optimal condition was 98.52 ± 0.26 %. The observed yield was reasonably close to the predicted value calculated from the regression model. This further validates the precision and suitability of the model in optimizing the single-step methyl esters production from the DRSO-WCO mixture under the process conditions. Esters yield obtained at optimal conditions was compared to other bifunctional catalysts (Table 3). The value from this study is higher than some biodiesel yields produced from modified solid catalysts. This is due to the heating method of microwave-irradiation employed in this study, which energized polar molecules and enhanced fast molecular collisions, leading to consistent catalyst activation and reaction efficiency.

3.4. Proposed reaction mechanism for simultaneous esterification-transesterification process

A combined esterification and transesterification process is believed to have occurred in this study, as there is clear evidence of both acidic and basic functional groups, each with varying degrees of reactivity, available from the profiles of NH_3 -TPD and CO_2 -TPD. The catalyst support, calcined eggshell plays a dual role, accommodating both the

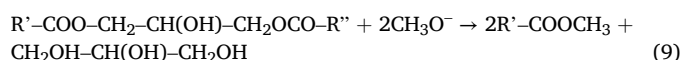
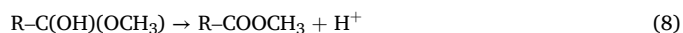
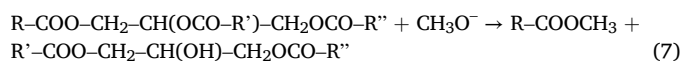
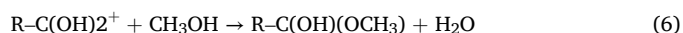
Table 3

Comparison of different bifunctional catalysts from various waste shell precursor.

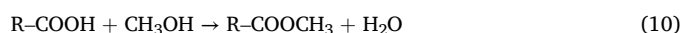
Feedstock	Catalyst source	Reaction conditions ^a	Biodiesel yield (%)	References
DRSO-WSO mixture	Waste eggshell modified by $\text{Fe}_2(\text{SO}_4)_3$ and ammonium molybdate	450 W, 15:1, 1 wt%, 5 min	98.52	This study
Canola oil	Waste eggshell treated with NaNO_3 and K_2SO_4	50 °C, 9:1, 3 wt%, 180 min	97.6	[59]
Waste cooking oil	Waste eggshell modified with $\text{Fe}_2(\text{SO}_4)_3$	70 °C, 5:1, 4 wt%, 45 min	89.94	[26]
Jatropha curcas oil	<i>Achantinoidea</i> shell modified with $\text{Fe}_2(\text{SO}_4)_3$	62.36 °C, 15:1, 8.9 wt %, 180 min	84.74	[25]
Waste cooking oil	Snail shell modified by TiO_2 and ZnO	65 °C, 6:1, 3 wt%, 180 min	95 and 90	[56]
Palm-derived waste oil	Waste eggshell modified with tungsten-zirconia	80 °C, 15:1, 2 wt%, 60 min	94.1	[48]

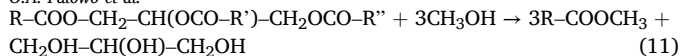
^a Temperature (°C)/heating power (W), MeOH/oil molar ratio, catalyst loading (wt%), reaction time (min).

acidic and basic functional groups for the catalyst. This study proposes a three-step mechanism of biodiesel production from the DRSO-WCO blend, involving both esterification and transesterification processes, with distinct active sites for each process. In the first step, the free fatty acid ($\text{R}-\text{COOH}$) is protonated by an acidic proton (H^+) from the bifunctional catalyst, forming a carbocation intermediate ($\text{R}-\text{C}(\text{OH})_2^+$) that makes the carbonyl carbon more electrophilic (Eq. 4). Simultaneously, the O^{2-} ions on the catalyst deprotonate methanol (CH_3OH), forming methoxide ions (CH_3O^-) on the basic site, which are highly reactive nucleophiles (Eq. 5). In the second step, CH_3OH attacks the $\text{R}-\text{C}(\text{OH})_2^+$, leading to the formation of an intermediate ester ($\text{R}-\text{C}(\text{OH})(\text{OCH}_3)$) and water (H_2O) molecule (Eq. 6). Concurrently, the CH_3O^- ion attacks the carbonyl carbon of the triglyceride ($\text{R}-\text{COO}-\text{CH}_2-\text{CH}(\text{OCO}-\text{R}')-\text{CH}_2-\text{OCO}-\text{R}''$), displacing one fatty acid chain to form an ester ($\text{R}-\text{COOCH}_3$) and a diglyceride intermediate ($\text{R}'-\text{COO}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{OCO}-\text{R}''$), remaining lipid structure (Eq. 7). In the final step, the intermediate ester undergoes dehydration to form the final ester product (biodiesel) and regenerates the acidic site (H^+) on the catalyst, for further catalysis (Eq. 8). Whereas the nucleophilic substitution reaction repeats two more times for the remaining fatty acid chains, ultimately producing three ester molecules and one molecule of glycerol ($\text{CH}_2\text{OH}-\text{CH}(\text{OH})-\text{CH}_2\text{OH}$), as by-product (Eq. 9).



The overall simultaneous esterification reaction for the FFA and the transesterification reaction for the triglyceride are summarized in Eqs. (10) and (11), respectively.





3.5. Evaluation of energy utilization and CO₂ emissions

Optimizing energy use is crucial in biodiesel production, as reducing specific energy consumption decreases the overall energy input required, thereby potentially increasing production efficiency. The specific energy consumption of 1.9 kWh/kg of biodiesel in this study is lower than some previously reported values, such as 5.4 kWh/kg obtained for waste palm oil biodiesel synthesis [60] and 2.32 kWh/kg estimated for olive oil biodiesel production [61]. This indicates that the microwave-assisted transesterification process in our study is more energy-efficient, likely due to better optimization of process parameters, requiring less energy to achieve a high biodiesel yield. The environmental impact of biodiesel production can be further assessed by examining CO₂ emissions. The microwave-assisted transesterification of DSRO-WCO to produce its methyl esters resulted in CO₂ emissions of 0.03 kg and a specific CO₂ emission of 1.52 kg/kg of biodiesel. For comparison, generating 1 kWh of energy from coal or fossil fuels emits ~ 800 g of CO₂ [62,63]. This indicates that the microwave-assisted biodiesel production process in this study results in significantly lower CO₂ emissions than traditional fossil fuel combustion, highlighting its potential environmental advantages.

3.6. Fuel and physicochemical properties of synthesized methyl esters

The properties of methyl esters produced were within the limits specified for biodiesel (Table 4). The most crucial biodiesel fuel properties directly related to engine performance and exhaust emission include kinematic viscosity, density, cetane number, and heating value [64]. The values obtained in this study comply with the stipulated limits. The density of biodiesel influences fuel characteristics such as combustion heat, fuel consumption, injection properties, and exhaust emissions [65]. A higher kinematic viscosity value is not desirable in biofuel since it results in poor fuel atomization and incomplete combustion [37]. This value was significantly reduced compared to the initial value of the oil mixture. Meanwhile high cetane number and rich oxygen content are part of the properties of biodiesel that enable it to act as a superior alternative fuel [66]. The biofuel synthesized has a reasonably high value in this regard. The cetane number describes the fuel ignitability behaviour. A low cetane number is not desirable as it may result in the delay of combustion of fuel in an engine at the required time [67]. The calorific or heating value of biodiesel significantly impacts brake-specific energy consumption. The biofuel produced in this study has

Table 4
Characterization of methyl esters produced.

Property	DRSO-WCO mixture	Methyl esters produced	EN 14,214	ASTM D6751
Acid value (mg KOH/g)	5.78	0.42	<0.5	<0.5
Density (g/cm ³)	1.05	0.88	0.86–0.90	0.86–0.90
Kinematic viscosity (mm/s)	16.98	4.6	3.5–5	1.9–6
Saponification value (mg KOH/g)	280	261	–	–
Iodine value	48.49	54	<120	–
Cetane number	53	52.45	> 51	48–65
Calorific value (MJ/kg)	39.64	40.65	32.9	37.3
Specific gravity	0.92	0.867	–	–

sufficient energy to generate the same power output as diesel fuel. The oxidative stability of biodiesel is affected by the composition of fatty acid, acid number, and iodine content of the biofuel [68]. According to the result, the methyl ester in this study is well stable. A higher acid number could indicate that the biodiesel would easily undergo degradation during storage [68]. Biodiesel produced in this study has a lower oxidation tendency. Likewise, the maximum allowable iodine value for biodiesel according to EN 14214 standard is set at 120 [11].

3.7. Reusability result of bifunctional catalyst

A recoverable solid bifunctional catalyst is an attractive strategy to reduce the total biodiesel cost. Besides the reduction of net cost, wastewater generation and environmental contamination is reduced through a reusable catalyst [9,52]. Methyl esters synthesis from a DRSO-WCO blend using the bifunctional catalyst at optimal conditions was reasonably high and the recovered catalyst was reused without further purification. The recovered catalyst was reused in 6 successive runs under the optimal experimental conditions (Fig. 12). After each reaction, the recovered catalyst was dried at 105 °C for 30 min to regenerate the active sites and maintain the pore volume, which are essential for the performance of the catalyst. There is a significant loss in catalytic activity after the 4th cycle (5.18 % biodiesel loss) with respect to the amount of catalyst recovered from the reaction mixture. The loss in activity of the catalyst is likely due to the gradual deactivation of active acidic and basic sites. At the end of the 6th cycle, the catalyst exhibited a substantial decline in performance, as evidenced by a 10.04 % reduction in biodiesel yield. This reduction is likely attributed to structural deterioration and a gradual loss of crystallinity within the catalyst. However, considerable methyl esters yield (88.63 wt%) was still obtained from the process. The catalyst performed better than the bifunctional catalyst developed by Falowo, et al. [26], indicating that the bifunctional catalyst synthesized in this study showed better stability and catalytic properties.

4. Conclusion

The present study prepared an improved bifunctional catalyst of CaO from waste eggshell and ferric sulfate in ammonium molybdate solution. Initiating the wet impregnation process increases the strength of the developed catalyst by opening the pores and creating multiple moderate to strong active acidic and basic sites. The bifunctional catalyst has a high surface area and contains mesoporous particles with active crystalline phases of CaO, CaSO₄, and Fe₂O₃. Microwave-aided processing of

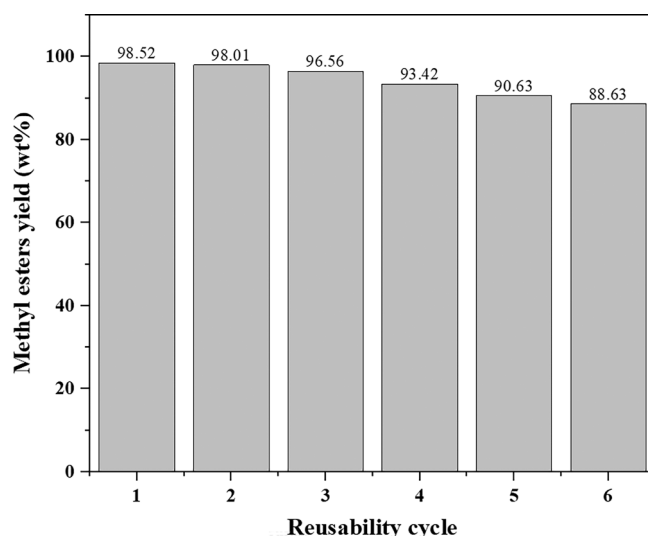


Fig. 12. Reusability of the synthesized bifunctional catalyst.

triglycerides showed that methyl esters can be produced at minimal processing time. The optimal conditions for esters yield (98.52 %) were: MeOH/oil blend molar ratio of 15:1, reaction time of 5 min, and catalyst amount of 1 wt% at 450 W microwave power. The catalyst demonstrated high activity during the reusability test, even up to 6 successive cycles. The physicochemical and fuel properties of the methyl esters met the stipulated standards in ASTM D6751 and EN 14214. Due to the high performance and reusability of this catalyst, it could be employed in industrial-scale biodiesel production along with an improved heating technology such as microwave energy.

Funding

This study did not receive funding from any organizations in the public, commercial, or not-for-profit sectors.

CRediT authorship contribution statement

Olayomi Abiodun Falowo: Writing – original draft, Visualization, Validation, Supervision, Project administration, Formal analysis, Data curation, Conceptualization. **Babatunde Oladipo:** Writing – review & editing, Writing – original draft, Visualization, Validation, Formal analysis, Data curation. **Siyeofori-Ogan Sofiri:** Validation, Methodology, Investigation. **Tunde V. Ojumu:** Resources, Software, Writing – review & editing.

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.

Acknowledgment

The authors appreciate the technical assistance offered by the Chemical Engineering laboratory staff, at Landmark University, Omu-Aran, Nigeria.

Data availability

The data supporting the current study are available within the article.

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