Research Article

Production, optimization, and characterization of biodiesel from almond seed oil using a bifunctional catalyst derived from waste animal bones and almond shell

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ARTICLE INFO	ABSTRACT
	The quest for eco-friendly alternatives to conventional fossil fuels intensifies amid the global transition to sustainable energy sources. With petroleum-based products dominating over 95.00% of the fuel market, concerns about their limited biodegradability and high eco-toxicity escalate. Addressing this, there's a rising demand for biobased solutions to mitigate pollution and cut greenhouse gas emissions. This study focuses on synthesizing biodiesel from waste almond seed oil (WCO) using an innovative bifunctional catalyst derived from waste animal bones and almond shells. Characterization via scanning electron microscopy, X-ray diffraction, X-ray fluorescence, Fourier transform infrared spectroscopy, and Brunauer, Emmett, and Teller analysis confirms the efficacy of the catalyst. Physicochemical properties of WCO and the resulting biodiesel align with ASTM D6751 and EN 14214 standards. Employing Box-Behnken design, we optimized the catalytic process by exploring key parameters, resulting in an impressive biodiesel yield of 86.20%. The optimal parameters were a methanol:oil ratio of 6.026, catalyst loading of 1.49917 wt%, reaction time of 66.8179 minutes, and temperature of 59.9806°C. Our findings underscore the potential of utilizing waste materials for sustainable biodiesel production, with the developed bifunctional catalyst offering a cost-effective and environmentally friendly alternative, contributing to cleaner fuel production methods. **Keywords:** almond oil, biodiesel, bifunctional catalyst, transesterification, waster animal bone, optimization

INTRODUCTION

The longstanding dependence on fossil fuels as the primary engine of economic growth has led to significant environmental concerns, including the rise in greenhouse gas emissions and the acceleration of climate change (Patel et al., 2020). This situation necessitates a shift towards alternative and renewable energy sources to decrease reliance on fossil fuels and lessen their adverse environmental effects (Gayen et

al., 2024; Hassan et al., 2024; Kandpal et al., 2024). Biodiesel, a form of biofuel, represents a promising solution by offering a cleaner and more sustainable form of energy, particularly for the transportation sector, which is responsible for a notable fraction of global energy consumption (Ifeanyi-Nze et al., 2023). Produced through the process of transesterification, biodiesel converts various organic feedstocks, such as vegetable oils, animal fats, and waste oils, into a biodegradable and non-toxic fuel (Mahlia et al., 2020; Topi, 2020; Vitoriano Julio et al., 2019). This reaction involves the combination of triglycerides with an alcohol, commonly methanol, in the presence of a catalyst, resulting in the formation of biodiesel and glycerol (Mohd Nor et al., 2021). Biodiesel boasts several environmental benefits over traditional fossil diesel, including reduced emissions of carbon dioxide, carbon monoxide, sulfur dioxide, and hydrocarbons, alongside a higher cetane number, improved lubricity, and greater biodegradability (Das et al., 2023). Additionally, the use of biodiesel can contribute to a nation's energy security and diversification by tapping into local and renewable resources (Rial, 2024).

The choice of catalyst is a key factor that determines the efficiency and cost of biodiesel production (Bharathiraja et al., 2022). The most common catalysts used for transesterification are homogeneous catalysts, such as sulfuric acid, sodium hydroxide, hydrochloric acid, and potassium hydroxide (Farouk et al., 2024; Wang et al., 2023). These catalysts, while commonly used, have notable disadvantages: they are energy-intensive, pose separation and recovery challenges, generate undesirable byproducts, can corrode processing equipment, and have negative environmental impacts (Gupta et al., 2023). Additionally, their effectiveness is compromised when processing feedstocks with high free fatty acid content, leading to reduced biodiesel yields (Al Mawaali et al., 2023). In light of these drawbacks, the focus has shifted to heterogeneous catalysts, which present a more efficient and environmentally friendly alternative (Alaei et al., 2018). These catalysts are solid substances that can be easily separated from the reaction mixture and reused, offering a solution to the issue of waste generation (Al Hatrooshi et al., 2020). They are also capable of processing feedstocks with higher levels of free fatty acids without the risk of saponification (Ahmed et al., 2023). Heterogeneous catalysts are categorized into base and acid types. Base catalysts, which include metal oxides, hydroxides, and carbonates, are known for their high activity and selectivity but necessitate elevated reaction temperatures and pressures and are susceptible to water and impurities (Amruth Maroju et al., 2023). On the other hand, acid catalysts, such as sulfonic acids, phosphoric acids, and metal sulfates, are less active and selective but can operate under milder conditions and are more tolerant of water and impurities (Abukhadra et al., 2019). This distinction is essential for selecting the most suitable catalyst for a particular biodiesel production process (Abdel-Hamid et al., 2023).

The advancement of biodiesel technology hinges on the development of efficient and cost-effective catalysts (Farouk et al., 2024). The latest innovations in this field have spotlighted biomass-derived heterogeneous catalysts as a sustainable and promising avenue. Biomass, a renewable resource, can be processed into a range of by-products, including biochar and bio-oil, through thermochemical

methods like pyrolysis (Ghazali, 2022). These catalysts, sourced from materials such as agricultural waste or animal bones, undergo various treatments to enhance their catalytic properties, by physical or chemical modifications, such as calcination, sulfonation, impregnation, and doping (Abdulsalam, 2023; Farouk et al., 2024). The benefits of biomass-derived catalysts are significant, offering low cost, high availability, extensive surface area, substantial porosity, and strong acidity or basicity, as well as remarkable stability (Abdulrahman, 2017). Their application in biodiesel production has yielded promising results across various feedstocks, under a spectrum of reaction conditions, showcasing their versatility and potential in renewable energy technology (Abdel-Hamid et al., 2023).

The innovative use of waste animal bones (WAB) as a catalyst for biodiesel production has been increasingly acknowledged in scientific research. Studies by Shankar et al.(2017) and Vogt et al. (2022) have recognized its potential. Abukhadra et al. (2019) and Nisar et al. (2017) conducted a seminal experiment that optimized the transesterification process of Jatropha oil, achieving a remarkable 96.10% biodiesel yield under meticulously calibrated conditions. This catalyst's reusability was further evidenced by its sustained activity over multiple cycles.

Complementing these findings, Nisar et al. (2017) and Obadiah et al. (2012) successfully synthesized biodiesel from palm oil, attaining a 96.78% yield, thereby affirming the efficacy of calcined WAB as a catalyst when juxtaposed with conventional calcium oxide (CaO). Li et al. (2022) extended this research by employing K-doped hydroxyapatite catalysts derived from WAB, culminating in a 96.40% yield under optimal conditions, with the catalyst demonstrating resilience through numerous reuse cycles.

These experiments echo the effectiveness of bifunctional catalysts, as illustrated by Akhabue et al. (2022), who achieved a 97.21% biodiesel yield using a catalyst formulated from ferric acid and poultry droppings. Similarly, Akhabue et al. (2020) reported a 92.89% yield utilizing a novel catalyst synthesized from sulfonated calcined corncobs and poultry droppings.

This investigation probed the catalytic efficacy of a novel bifunctional catalyst formulated from WAB and almond shells (AS), marking a stride towards cost-effective biodiesel catalyst production. The study leveraged response surface methodology (RSM) coupled with Box-Behnken design (BBD) to meticulously refine variables such as the methanol-to-oil ratio, catalyst dosage, reaction temperature, and time. The optimization process facilitated by BBD provided valuable insights into the operational parameters crucial for enhancing the biodiesel synthesis process.

The study's focus on developing a novel bifunctional catalyst from WAB and AS represents a significant advancement in biodiesel catalyst production. By leveraging RSM and BBD to optimize the transesterification process, particularly in the context of simultaneous esterification and transesterification reactions using almond oil as the feedstock, the research addresses a notable knowledge gap. This innovative approach not only contributes to waste resource management but also pushes the boundaries of sustainable biodiesel production methodologies. By explicitly delineating

these unique contributions in the introduction, readers can better grasp the originality and significance of the research in advancing the state of the art.

The research further aimed to validate the robustness of RSM as an optimization tool in the transesterification process, particularly focusing on its application in the simultaneous esterification and transesterification reactions using almond oil as the feedstock. Emphasis was placed on the utilization of a pioneering bifunctional catalyst derived from WAB and AS, which was subjected to rigorous testing for its dual catalytic capabilities. The study's comprehensive analysis of RSM's predictive modeling prowess helped in pinpointing the most favorable reaction conditions. Additionally, the biodiesel produced was rigorously evaluated against established standards to ascertain its commercial and industrial viability. This research contributes significantly to the discourse on process optimization, waste resource management, and the advancement of sustainable biodiesel production methodologies.

MATERIALS & METHODS

Materials

This research utilized a variety of materials and equipment to ensure the accuracy and reliability of experimental outcomes. Distilled water of analytical grade purity was employed as a solvent throughout the study. Carbon monoxide was sourced from a high-purity gas cylinder. Methanol, sulfuric acid, acetic acid, chloroform, benzene, and ethanol, all of analytical grade purity, were utilized as reagents in biodiesel synthesis and catalyst preparation. Phenolphthalein and starch indicators, certified to ACS reagent grade, were employed for titration purposes. Lithium carbonate of analytical grade purity was utilized as a reactant in catalyst synthesis. AS and WAB from dog, carefully selected for their purity and structural integrity, served as raw materials for catalyst preparation. Accurate weighing of materials was ensured using a laboratory weighing balance of precision grade. Sieves of appropriate mesh sizes were utilized for sample preparation and an oven was used to facilitate the drying process. Furthermore, advanced analytical instruments including Brunauer, Emmett, and Teller (BET) analyzer produced by autosorb, thermo fisher scientific Fourier transform infrared (FTIR) spectroscopy equipment, thermo fisher scientific scanning electron microscope (SEM), and Shimadzu X-ray diffraction (XRD) analyzer were employed for characterizing catalysts and analyzing the physicochemical properties of biodiesel products.

Catalyst Preparation

Preparation of precursor from waste animal bones

In accordance with the methodology outlined by Volli et al. (2019), the process commenced with the meticulous cleansing of exhumed WAB (dog bones) to eliminate extraneous substances. The initial step involved the removal of adherent meat remnants using a knife, followed by a thorough rinse with warm distilled water. Subsequently, WAB were fragmented into smaller segments via hammering, and any internal bone marrow was extracted.

Post-cleaning, the WAB underwent a drying phase, initially under direct sunlight for a duration of three days, and subsequently in an oven set at 110 °C for two hours. The dried bones were then pulverized into a fine powder, which was sifted through a 0.3 mm mesh to discard larger particles.

The subsequent phase entailed the chemical treatment of the sieved WAB powder with sodium hydroxide in a stoichiometric ratio of 1:1. This mixture was left to react for a period of 24 hours before being separated. The final step in the catalyst preparation involved the calcination of the treated WAB at a temperature of 900 °C for four hours within a muffle furnace. To prevent any atmospheric reactions, the calcined WAB were promptly transferred to a desiccator post-calcination. Once cooled, the resultant CaO catalyst was stored in an airtight container for future application and analysis.

Preparation of precursor from almond shell

To ensure the complete removal of moisture, AS were subjected to a sun-drying process extending over a period of 14 days (Soriano et al., 2021). Post-drying, AS were pulverized into a fine consistency and subsequently passed through a sieve with a mesh size of 0.3 mm to ensure uniformity.

The next phase involved the chemical treatment of the sieved AS using an equimolar solution of sulfuric acid (H_2SO_4). This mixture was then subjected to a controlled heating process at 70 °C for approximately two hours, with continuous agitation provided by a magnetic stirrer. Following this, the mixture was set aside to cool naturally over a 24-hour period.

Once cooled, the mixture underwent a thorough cleaning process, followed by an additional brief sun-drying phase. The final step in the preparation involved carbonization, where the treated AS were heated in a muffle furnace at 500 °C for three hours, resulting in the formation of ash. To prevent any oxidative reactions, the carbonized AS were promptly placed in a desiccator upon removal from the furnace. After cooling, the ash was stored in an airtight container for subsequent use and analytical purposes.

Synthesis of heterogeneous composite catalyst

To synthesize the biobased composite catalyst, the incipient wetness impregnation method was utilized (Jayakumar et al., 2021). Initially, a homogeneous mixture was created by combining 60 grams of WAB powder with 90 grams of almond seed shell (AS) powder in a 2:3 ratio with an adequate volume of water to form a slurry. This mixture was then subjected to continuous stirring on a magnetic stirrer set at 80°C to facilitate the complete evaporation of water over a span of 3 hours. Following the evaporation, the resultant solid mass was subjected to a drying process at 700 °C for two hours. The final step involved calcining the dried composite catalyst at 900 °C for three hours to activate it for subsequent use.

Transesterification Process

In the methodology delineated by Lani et al. (2017), the efficacy of a heterogeneous catalyst was assessed for its capacity to conduct esterification and transesterification concurrently within a batch reactor setup. Sweet almond oil served as the substrate in this dual reaction process, which

Table 1. Properties of ASO

Properties	Value
Acid value (mgKOH/g)	0.280500
Free fatty acid content (%)	0.140250
Peroxide value (mEqO$_2$/g)	0.500000
Iodine value (mgL$_2$/100g)	105.000000
Saponification value (mgKOH/g)	185.130000
Density of oil (g/ml)	0.820000
Average molecular weight of ASO (g/mol)	669.763486

took place in a 250 ml conical flask positioned on a magnetic stirrer that maintained a steady temperature. A predetermined amount of heterogeneous composite catalyst was combined with an equivalent volume of methanol in a separate beaker, under continuous agitation. This catalyst-methanol solution was then introduced to the conical flask containing 50 grams of pre-warmed sweet almond oil. To preserve the integrity of the reaction and prevent the evaporation of methanol, the stirring speed was regulated, and the flask was insulated.

Upon completion of the reaction, the catalyst was separated from the reaction mixture through filtration using a cloth filter, as per the method described by Akhabue et al. (2020). The filtrate was then placed into a separating funnel to facilitate phase separation. Three distinct layers were identified: the upper layer consisting of surplus methanol, the intermediate layer rich in biodiesel, and the bottom layer comprising glycerol.

The biodiesel layer underwent a purification process using warm distilled water to eliminate any residual methanol, glycerol, and unreacted lipid components until the wash water ran clear. Post-washing, the biodiesel was dried. The yield of biodiesel produced was quantified using the formula provided in Eq. (1) by Lani et al. (2017).

$$Biodiesel\ Yield = \frac{Mass\ of\ biodiesel\ (g)}{Mass\ of\ sweet\ almond\ oil\ (g)} * 100. \qquad (1)$$

RESULTS & DISCUSSION

Properties of Almond Seed Oil

The properties of almond seed oil (ASO) were investigated, and the results are presented in **Table 1**.

Catalyst Characterization

These characterization analysis techniques were used to analyze the catalyst.

Scanning electron microscope analysis

SEM analysis revealed the structural characteristics of the catalyst, as illustrated in **Figure 1** and **Figure 2** show images captured by SEM showcased a heterogeneous pore distribution. A comparative assessment of SEM images, taken before and after the impregnation process, indicates an increase in pore availability within the doped catalyst relative to its undoped counterparts. This enhancement in porosity can be attributed to the impregnation process involving agricultural waste, which is predominantly composed of CaO, resulting in a catalyst that exhibits not only increased porosity but also augmented catalytic activity.
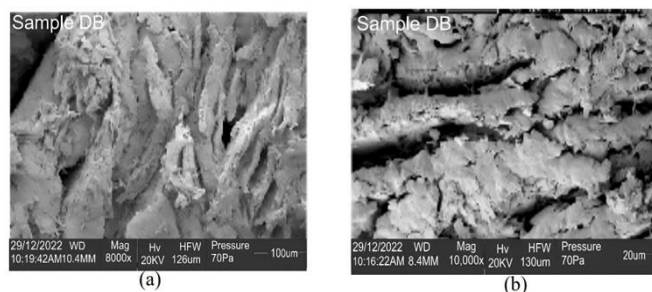

Figure 1. Waste animal bones at (a) 8,000x & (b) 10,000x (Source: Authors' own elaboration)
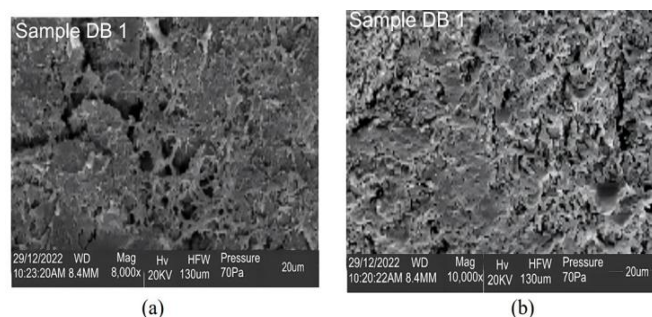
Figure 2. Doped waste animal bones at different magnifications (a) 8,000x & (b) 10,000x (Source: Authors' own elaboration)
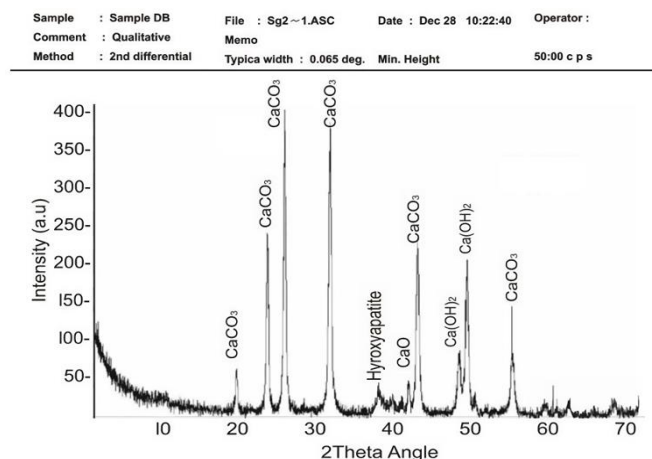
Figure 3. XRD analysis of pure catalyst (Source: Authors' own elaboration)

X-ray diffraction analysis

XRD patterns for the calcined WAB catalyst, presented in **Figure 3**, exhibit pronounced peaks indicative of calcium carbonate (CaCO$_3$). CaCO$_3$ is a widely recognized inorganic material that serves as a catalyst in various chemical transformations. It is particularly noted for its role as a solid acid catalyst, facilitating the conversion of alcohols to alkyl halides and esters to acids, as well as catalyzing the dehydration of alcohols into alkenes and the decarboxylation of carboxylic acids. The catalytic efficiency of CaCO$_3$ is influenced by specific reaction parameters, including temperature and pH levels. To augment the catalytic performance of CaCO$_3$, it may be beneficial to introduce a promoter or activator. In this context, agricultural waste, exemplified by AS in this study, can serve as an effective promoter/activator.

Figure 4. XRD analysis of doped catalyst (Source: Authors' own elaboration)

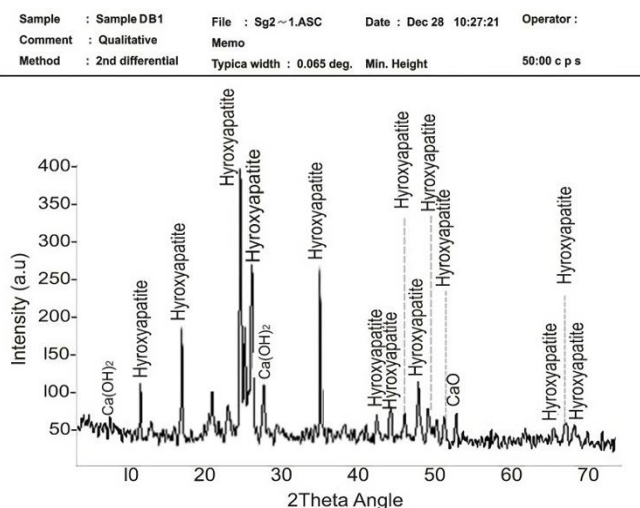Furthermore, XRD patterns of the WAB-AS calcined catalyst, depicted in **Figure 4**, display distinct peaks corresponding to hydroxyapatite, underscoring the catalyst's multifaceted nature. The catalyst exhibits essential attributes of an effective catalyst and support material, such as minimal water solubility, enhanced porosity, controlled basicity/acidity, and thermal stability at elevated temperatures. These characteristics were achieved by incorporating AS as a promoter, which significantly improved the activity and porosity of the base catalyst.

Fourier transform infrared radiation spectroscopy

FTIR analysis conducted on the samples provided invaluable insights into the molecular composition of the catalysts under study. Each peak in FTIR spectrum corresponds to specific functional groups within the compounds, offering a detailed map of their chemical structure.

In the first sample (**Figure 5**), the presence of a broad initial peak at 3,767 cm^1 suggests a strong indication of O-H stretching vibrations, characteristic of hydroxyl groups commonly found in alcohols and phenols. This observation is crucial as it underscores the potential involvement of these hydroxyl moieties in the catalytic activity. Furthermore, the subsequent peaks at 3,472 cm^1 and 2,529 cm^1 hint at the presence of N-H stretching and C≡C stretching, respectively, indicating the potential presence of amine and alkyne functional groups.

Moving forward through the spectrum, peaks in 1,703 cm^1 and 1,462 cm^1 are attributed to C=O stretching and C-H bending, respectively, suggesting the presence of carbonyl and alkane groups. These findings showed the molecular landscape of the catalyst, indicating a diverse array of functional groups that could play pivotal roles in catalytic activity.

Similarly, in the second sample (**Figure 6**), the broad peak at 3767 cm^1 again suggests significant O-H stretching vibrations, reinforcing the presence of hydroxyl groups. This consistency across samples strengthens the reliability of the FTIR results. Furthermore, peaks at 3,784 cm^1 and 3,695 cm^1 may correspond to C-H stretching, while the peak at 3,410 cm^1
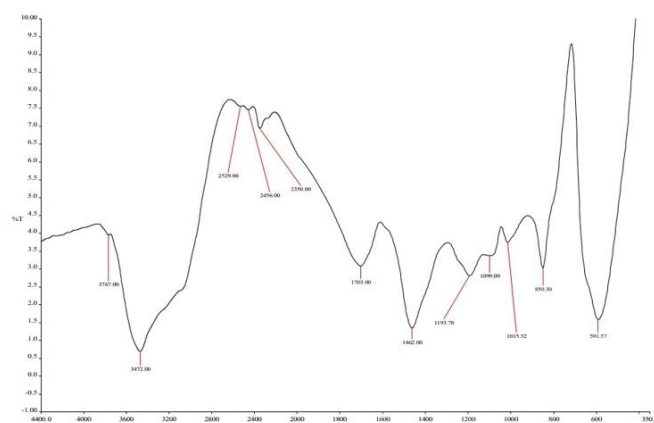
Figure 5. FTIR spectrum of pure waste animal bones (Source: Authors' own elaboration)
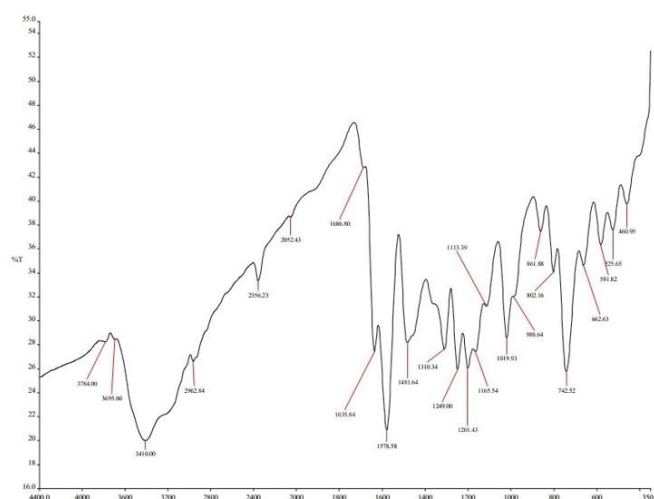
Figure 6. FTIR spectrum of waste animal bones (Source: Authors' own elaboration)

indicates N-H stretching, all pointing towards a complex molecular architecture rich in diverse functional groups.

The peaks at higher wavenumbers in both samples suggest the presence of additional functional groups such as C=O stretching, C-N stretching, and C=C stretching, further enriching our understanding of the molecular complexity of the catalysts.

Understanding the impact of these functional groups on catalytic activity is paramount. Functional groups like hydroxyl, carbonyl, and amino groups are known to actively participate in adsorption, reactant activation, and intermediate formation during catalytic reactions. Moreover, the presence of conjugated systems (e.g., C=C) can facilitate electron delocalization, potentially enhancing catalytic activity.

Conversely, bulky or electron-withdrawing groups may pose steric hindrance or alter the electronic environment around active sites, potentially influencing catalytic performance.

By thoroughly analyzing the FTIR spectra and correlating specific functional groups with catalytic activity, researchers can confidently decipher the intricate relationship between molecular structure and catalytic function. These findings

Figure 7. BET surface plot for pure catalyst (Source: Authors' own elaboration)

Figure 8. BET surface plot for doped catalyst (Source: Authors' own elaboration)

pave the way for informed catalyst design strategies aimed at optimizing performance and efficiency in various industrial applications.

Brunaer, Emmett, & Teller analysis

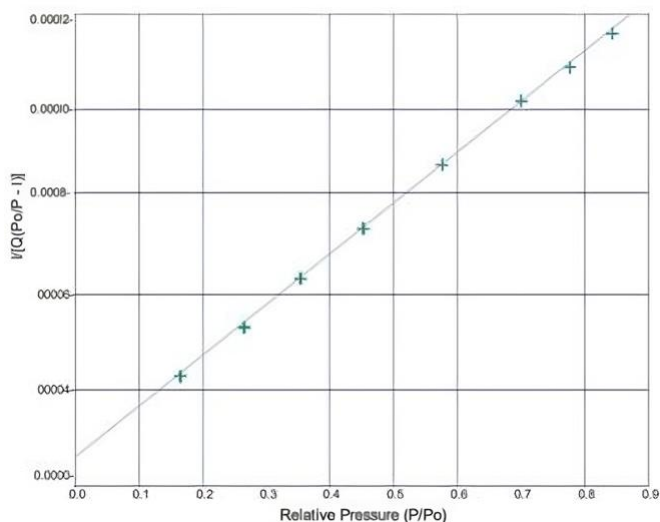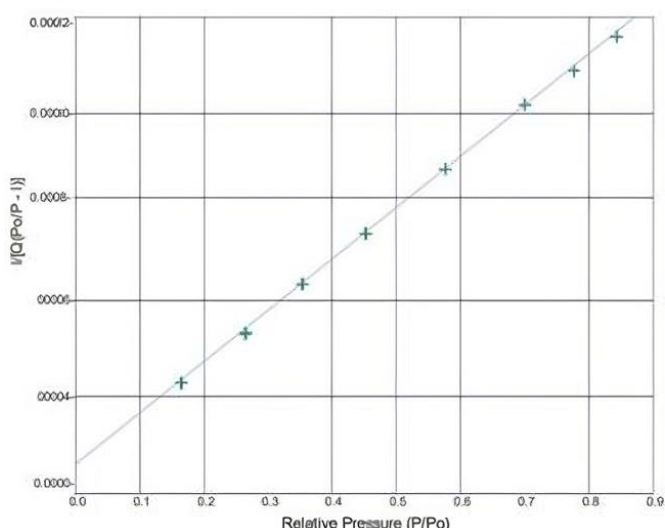BET study analysis plot is shown in **Figure 7** and **Figure 8**. The analysis done reveals that the pore volume and size have modified by the doping of the pure catalyst with agricultural waste. The pure catalyst's surface area and that of the doped catalyst sample were 272.350 m^2/g and 279.220 m^2/g, respectively. This basically implies that the doped catalyst is more porous than the pure catalyst. The micropore area of the doped catalyst was 22.220 m^2/g while that of the pure catalyst was 22.200 m^2/g, which implies that there is an increase in easy accessibility to the active site of the catalyst.

Table 2. Experimental & predicted biodiesel production results

Actual & coded factor values				Biodiesel yield (%)	
Run	X_1 (-)	X_2 (wt%)	X_3 (min)	X_4 (C)	Yield	Prediction
1	6	1.0	60	50	80.9	80.32
2	18	0.5	75	50	78.6	79.00
3	12	1.0	75	50	80.2	80.48
4	6	1.0	90	50	79.8	80.55
5	18	1.0	60	50	81.8	81.05
6	6	1.0	75	40	70.4	69.51
7	12	0.5	60	50	79.0	79.15
8	12	1.0	60	60	85.4	85.65
9	18	1.5	75	50	80.2	80.30
10	12	1.0	90	40	68.6	69.07
11	6	1.0	75	60	84.8	84.58
12	12	1.0	75	50	85.0	80.48
13	12	1.0	75	50	79.0	80.48
14	12	1.5	60	50	82.0	82.25
15	6	0.5	75	50	77.4	78.02
16	12	0.5	75	40	67.8	67.82
17	12	1.5	75	60	86.2	86.18
18	12	1.5	75	40	70.0	70.22
19	18	1.0	75	40	69.0	68.50
20	12	1.0	75	50	80.2	80.48
21	12	1.5	90	50	81.8	80.93
22	12	0.5	90	50	80.0	79.03
23	6	1.5	75	50	81.4	81.72
24	12	1.0	75	50	78.0	80.48
25	12	1.0	90	60	85.2	85.24
26	18	1.0	75	60	85.0	85.16
27	18	1.0	90	50	78.8	79.38
28	12	1.0	60	40	69.4	70.09
29	12	0.5	75	60	83.8	83.58

Note. X_1: Methanol:oil ratio; X_2: Catalyst wt/loading; X_3: Reaction time; & X_4: Reaction temperature

Modelling & Optimization of Biodiesel Production

Response surface methodology analysis

The data presented in **Table 2** shows the outcome from 29 experimental runs in the production of biodiesel. An initial model using RSM was developed to streamline the optimization of the process. The experimental data were subjected to a multiple regression analysis to fit them into a quadratic regression model, resulting in Eq. (2), which represents the model terms:

$$R_1 = 252.93 - 4.163X_1 - 16.69X_2 - 1.56X_3 - 0.37X_4 - 0.053X_1X_2 + 0.0020X_1X_3 - 0.0068X_1X_4 + 0.067X_3 + 0.16X_2X_4 + 0.0064X_3X_4 + 0.28X_1^2 - 0.098X_2^2 + 0.0039X_3^2 - 0.013X_4^2, \quad (2)$$

where R_1 is for biodiesel yield, X_1, X_2, X_3, and X_4 stand for methanol:oil ratio, catalyst wt/loading, time (min), and temperature (°C), respectively, the direct linear impacts of the independent process variables are represented by the coefficients X_1, X_2, X_3, and X_4.

In contrast, the linear interaction effects between mole ratio/catalyst loading, mole ratio/time, and mole ratio/temperature, catalyst loading/temperature and time/temperature are represented by X_1X_2, X_1X_3, X_1X_4, X_2X_4, and X_3X_4, respectively. The quadratic impacts of the related process variables are X_1^2 X_2^2 X_3^2 and X_4^2.
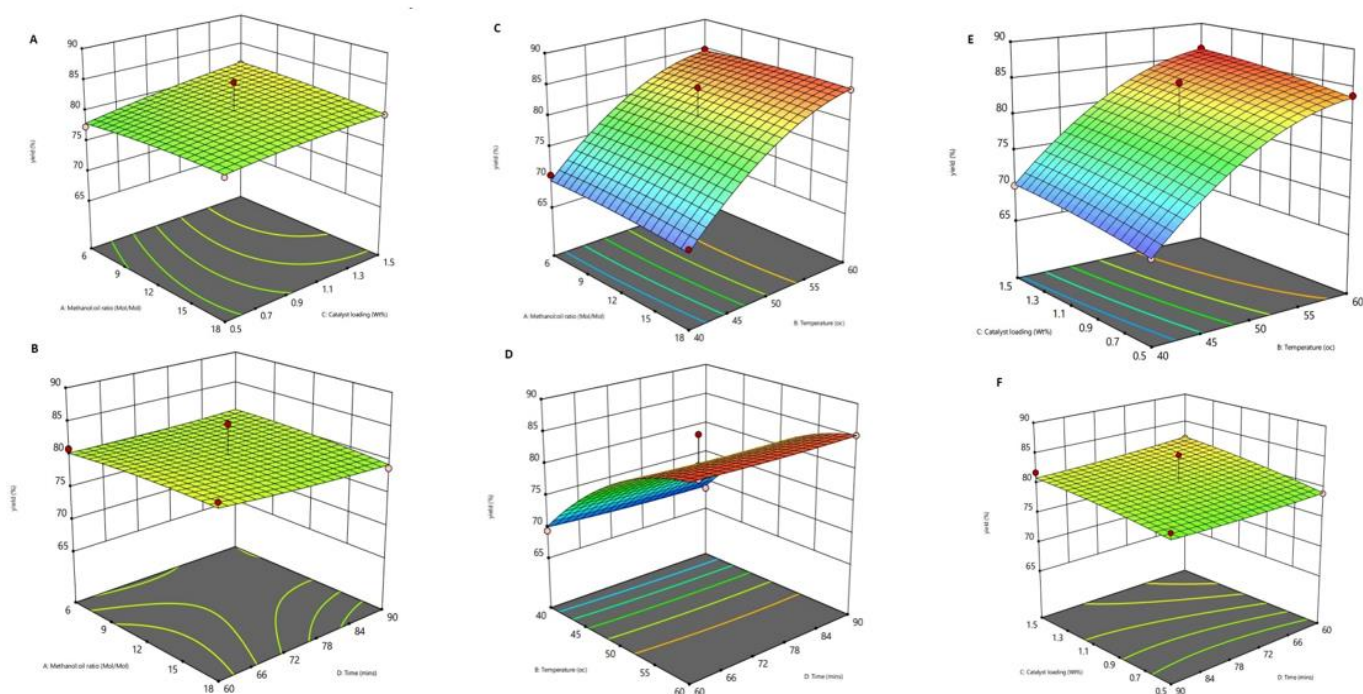
Figure 9. Response surface plot: (A) simultaneous effect of methanol-oil ratio & catalyst concentration on yield, (B) simultaneous effect of methanol-oil ratio & reaction time on yield, (C) simultaneous effect of methanol-oil ratio & temperature on yield, (D) simultaneous effect of reaction temperature & time on yield, (E) simultaneous effect of catalyst loading & temperature on yield, & (F) simultaneous effect of catalyst loading & reaction time on yield (Source: Authors' own elaboration)

The predicted biodiesel yields, as calculated using the above regression equation, are compared within **Table 2**. The close alignment between the experimental results and the model's predictions serves to validate the model's accuracy, with the predicted yields ranging from 67.82% to 86.18%.

RSM was further employed to visually depict the influence of the independent variables and their interactions on the biodiesel yield. This was achieved through three-dimensional response surface plots, as illustrated in **Figure 9**, in accordance with the regression model.

Impact of methanol:oil ratio & catalyst loading interaction

Part A in **Figure 9** demonstrates the effect of the methanol-to-oil ratio and catalyst loading on biodiesel production, with the experiment conducted at a stable temperature of 60 °C and a reaction time of 90 minutes.

The graph indicates that an increase in both the methanol-to-oil ratio and the weight percentage of the catalyst leads to a higher yield of biodiesel. This enhancement in yield is likely due to the greater availability of active sites on the catalyst, which is a direct result of increased catalyst loading.

Similarly, elevating the methanol-to-oil ratio, while keeping the catalyst loading constant, also contributes to an uptick in biodiesel production. These observations suggest that optimizing both the methanol-to-oil ratio and catalyst loading is crucial for maximizing biodiesel yield.

Impact of methanol:oil ratio & reaction time interaction

Part B in **Figure 9** depicts the relationship between the methanol-to-oil ratio and reaction time on biodiesel yield, with the experiment maintaining a constant temperature of 60 °C and a catalyst weight percentage of 1.50%. The data indicates that an increase in the methanol-to-oil ratio, while keeping the reaction time unchanged, leads to an enhancement in biodiesel production.

Conversely, extending the reaction time, without altering the methanol-to-oil ratio, does not significantly influence the yield of biodiesel. This suggests that the methanol-to-oil ratio is a more critical factor than reaction time in optimizing biodiesel production under the specified conditions.

Impact of methanol:oil ratio & temperature interaction

Part C in **Figure 9** illustrates the effects of varying the methanol-to-oil ratio and the reaction temperature on the yield of biodiesel, while maintaining a constant catalyst loading of 1.5 wt% and a reaction time of 90 minutes. The graph indicates that an increase in temperature from 40 °C to 60 °C, at a fixed methanol-to-oil ratio, leads to an enhanced yield of biodiesel. This is consistent with the general understanding that reaction rates tend to increase with temperature. But it is crucial to ensure that the reaction temperature does not exceed the boiling point of methanol, which would result in its evaporation.

Also, the data shows that increasing both the methanol-to-oil ratio and the reaction temperature concurrently results in a higher biodiesel yield.

Impact of reaction temperature & time interaction

Part D in **Figure 9** presents the effects of varying reaction temperature and duration on biodiesel yield, while keeping the catalyst loading and methanol-to-oil ratio constant. Observations over a minimum period of 60 minutes indicated that an elevation in reaction temperature correlates with an increase in biodiesel yield.

However, as the reaction duration approached 90 minutes, a decrease in yield was observed with higher temperatures. This trend suggests that prolonged reaction times at elevated temperatures may lead to a reversal of the transesterification process, thereby reducing the overall yield of biodiesel.

Impact of catalyst loading & temperature interaction

Part E in **Figure 9** show cases correlation between catalyst loading and reaction temperature, and their collective influence on yield of biodiesel. Data indicates that a concurrent rise in both the temperature and the amount of catalyst leads to an enhancement in biodiesel production. This observed increase is likely due to the higher number of active sites available for the reaction, which is a result of increased catalyst weight percentage. Also, a higher reaction temperature accelerates the reaction rate, further contributing to the improved yield.

Impact of catalyst loading & reaction time interaction

As shown in part E in **Figure 9**, we examine concurrent influence of catalyst concentration (expressed as weight percentage) and the duration of the reaction on the production yield of biodiesel. The data indicated a marginal enhancement in yield correlating with the simultaneous augmentation of both the catalyst weight percentage and the reaction period.

Optimal conditions for biodiesel production

The optimum parameters for this process of waste almond oil transesterification with prepared catalyst were determined using design expert 13 software to solve the quadratic model equation to obtain values of methanol:oil ratio $(X_1)=6.03$, catalyst loading $(X_2)=1.50$ wt%, reaction time $(X_3)=66.82$ min, and temperature $(X_4)=59.98$ °C. For a biodiesel yield (Y) is 86.20%

Table 3 shows ANOVA outcomes for RSM. **Table 4** shows Evaluation of RSM.

Biodiesel characteristics

The properties of the produced biodiesel were determined as in **Table 5**.

Limitations of Study

In this section, we elucidate the limitations inherent in the production, optimization, and characterization of biodiesel derived from ASO, employing a bifunctional catalyst

Table 3. ANOVA outcomes for RSM

Source	SS	df	MS	F-value	p-value
Model	849.2000	14	60.6600	24.1600	<0.0001
X1	0.1408	1	0.1408	0.0561	0.8162
X2	755.2500	1	755.2500	300.81	<0.0001
X3	18.7500	1	18.7500	7.4700	0.0162
X4	1.5400	1	1.5400	0.6137	0.4465
AB	0.6400	1	0.6400	0.2549	0.6215
AC	1.4400	1	1.4400	0.5735	0.4614
AD	0.9025	1	0.9025	0.3595	0.5584
BC	0.0100	1	0.0100	0.0040	0.9506
BD	0.0900	1	0.0900	0.0358	0.8526
CD	0.3600	1	0.3600	0.1434	0.7106
A²	0.8642	1	0.8642	0.3442	0.5668
B²	65.4900	1	65.4900	26.0800	0.0002
C²	0.8060	1	0.8060	0.3210	0.5800
D²	0.2861	1	0.2861	0.1139	0.7407
Residual	35.1500	14	2.5100		
Lack of fit	6.2200	10	0.6223	0.0860	0.9991
Pure error	28.9300	4	7.2300		
Correlated total	884.3500	28			
CV	2.0100				
Adequate precision	16.1169				

Note. SS: Sum of squares & MS: Mean square

Table 4. Evaluation of RSM

Parameter	RSM
R	0.9821
R²	0.9603
Adjusted R²	0.9537
MSE	1.2117
RMSE	1.1008
SEP	1.3942
MAE	0.6579
AAD	0.8297

synthesized from WAB and AS. These limitations offer valuable insights into areas necessitating further investigation and consideration within the scope of our research.

One significant limitation concerns the availability and cost of raw materials. ASO, particularly waste almond seed oil (WCO), serves as the primary feedstock for biodiesel synthesis. However, its accessibility may be constrained in specific geographic regions. The cost-effectiveness and scalability of utilizing WCO hinge upon its widespread availability and economic feasibility. Secondly, our study introduces an innovative bifunctional catalyst derived from unconventional

Table 5. Result of biodiesel characterization

		ASTM D6751	EN 14214
Acid value (mgKOH/g)	0.190	0.5 max	0.5 max
Flash point (℃)	152.000	130	120
Peroxide value (mEqO₂/g)	2.700	-	-
Iodine value (mgL₂/100g)	75.000	-	120
Saponification value (mgKOH/g)	201.600	370 max	-
Pour point (℃)	-7.000	-	-
pH	6.900	-	-
Free fatty acid	0.095	-	-
Cetane number	49.300	47	51
Calorific value (MJ/kg)	35.930	-	-
Density at 30℃	0.910	-	-
Kinematic viscosity at 40℃	4.750	1.9-6.0	3.5-5.0
Cloud point	-4.000	-3 to -12	-

sources, namely WAB and AS. Nonetheless, the long-term stability and reusability of this catalyst demand meticulous scrutiny. Potential catalyst deactivation across successive reaction cycles could compromise the overall efficiency of the biodiesel production process. Furthermore, while the bifunctional catalyst demonstrates environmental superiority over conventional counterparts, the environmental ramifications associated with its synthesis warrant attention. A comprehensive assessment encompassing energy consumption, emissions, and waste generation during catalyst preparation is imperative.

Scaling up the process from laboratory to industrial scales presents formidable challenges. Considerations pertaining to reactor design, safety protocols, and economic viability are indispensable to ensure seamless transition and successful implementation. Moreover, while the physicochemical properties of the resultant biodiesel were evaluated against ASTM D6751 and EN 14214 standards, real-world applicability necessitates compatibility with existing diesel engines and infrastructure. Further investigations encompassing engine performance, emissions, and the long-term stability of the produced biodiesel are imperative. Additionally, our study accentuates the environmental benefits derived from the utilization of waste materials. However, a comprehensive life cycle assessment (LCA) is essential to provide holistic insights into the overall environmental footprint. LCA accounts for factors including energy consumption, land utilization, water usage, and emissions throughout the entire life cycle. Lastly, viability and adoption of methodology hinge upon market dynamics. While our study underscores impressive biodiesel yields under optimal conditions, considerations such as economic feasibility, policy support, and consumer preferences exert substantial influence on the practical realization of sustainable biodiesel production methodologies.

CONCLUSIONS

In this research, a heterogeneous catalyst (WAB-AS) was successfully produced and utilized for the synthesis of biodiesel by transesterifying ASO with methanol, an alcohol. BET study demonstrated that calcination had a favourable effect on the produced catalyst as its textural qualities were enhanced. XRD examination identified the presence of hydroxyapatite in the doped catalyst, which depicts an increase in porosity and thermal stability from that of the pure catalyst. SEM scans of the catalyst sample's surface revealed several voids, otherwise known as pores. Experimental data obtained showed that the prepared catalyst was sufficient enough to catalyze the transesterification reaction. RSM and adaptive neuro-fuzzy inference system (ANFIS) were employed to model and optimize the process parameters to obtain the optimal biodiesel yield. ANFIS model was proven to be superior as it gave a better fit, which is evident in the R^2 value of 0.9673 while that of RSM was 0.9603.

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