DOI: 10.36108/ujees/5202.70.0150
UNIOSUN Journal of Engineering and Environmental Sciences. Vol. 7. No. 1, 2025

Synthesis of Biomass-Derived Sulphonated Heterogeneous Bifunctional Catalyst-Ce-OrP-SO_3H for Optimization of Biodiesel Production from Waste Cooking Oil

Aderibigbe, F. A., Harvis, B. S., Mustapha, S. I., Mohammed, I. A., Ochapa, S. O. and Adeyemo, A. A.

Abstract This study uses a bifunctional catalyst made from orange peel-derived porous activated carbon enriched with SO_3H and impregnated with calcined eggshell to optimise biodiesel production utilising waste cooking oil. The catalyst was characterised using SEM/EDX, XRD, BET, and FTIR techniques. The optimisation of biodiesel production was assessed through response surface methodology based on central composite design (RSM-CCD), considering factors such as temperature, catalyst loading, reaction time, and methanol-to-oil ratio. The optimal conditions were 2% catalyst loading, a 6:1 methanol-to-oil ratio, 60 °C reaction temperature, and 60 min reaction time, resulting in an 87.5% FAME (fatty acid methyl ester) conversion. Gas chromatography-mass spectrometry (GCMS) analysis showed both saturated and unsaturated fatty acids in the biodiesel.

Keywords: Biodiesel, Bifunctional catalyst, Optimization, Transesterification, Waste Cooking Oil

I. Introduction

Energy is essential to a nation's economic and social development, with demand rising significantly due to global population growth. Currently, fossil fuels account for 57.7% of transportation energy and up to 88% of overall energy consumption [1]. However, the combustion of fossil fuels releases greenhouse gases, contributing to environmental pollution and global warming. Renewable and sustainable energy sources, such as wind, solar, and biofuels, are being explored to address these challenges.

Biofuels, derived from biomass, offer an affordable, eco-friendly, and biodegradable alternative to fossil fuels, promoting sustainability while reducing environmental impact [2]. They can exist in solid (biocoal), liquid (biodiesel, bioethanol), or gaseous (biogas, biosyngas) forms [3]. Biodiesel is the second most commonly produced and widely utilised biofuel [4]. Composed of fatty acid methyl esters (FAME), biodiesel is renewable, biodegradable, sulphur-free, and emits a number of greenhouse gases than fossil fuels [5]. Its high oxygen content and flash point enhance engine efficiency, reducing air pollution [6].

Biodiesel production relies on methods such as pyrolysis, transesterification, direct vegetable oil blending, and micro-emulsion, with transesterification being the most efficient and widely used. This process converts triglycerides (TGs) from vegetable oil and other sources into biodiesel and glycerol, using alcohol as a reactant. Catalysts, either homogeneous (acidic or alkaline) or heterogeneous, accelerate this reaction. Homogeneous catalysts, though effective, are less desirable for industrial

Aderibigbe, F. A., Mustapha, S. I., Mohammed, I. A., Ochapa, S. O. and Adeyemo, A. A
(Department of Chemical Engineering, University of Ilorin. Ilorin, Kwara State)
Harvis, B.S
(Department of Chemical and Environmental Engineering, University of Arizona, Tucson, USA
Corresponding Author: aderibigbe.fa@unilorin.edu.ng
Phone: +2348033822123

applications due to their toxicity, corrosiveness, and challenges with separation and reuse. Heterogeneous catalysts, in contrast, are non-toxic, recyclable, and suitable for high-temperature operations [7].

Calcium oxide (CaO), a commonly used heterogeneous base catalyst, is preferred for its high activity and mild reaction conditions [8]. Additionally, bifunctional solid catalysts combine basic and Lewis acid sites, enabling simultaneous transesterification of TGs and esterification of free fatty acids (FFAs), even in feedstocks with high water and FFA content [9, 10]. Although enzyme catalysts are environmentally friendly, their high cost and slow reaction rates limit their practicality [11].

Biomass-derived heterogeneous carbon catalysts have emerged as a sustainable alternative in recent years. Non-toxic and cost-effective, these catalysts are often synthesised from waste materials like eggshells and fruit peels. For instance, calcined eggshells, primarily composed of calcium carbonate and sulphonic acid-grafted orange peel carbon, have demonstrated high catalytic efficiency and reusability, aligning with "green" chemistry principles [12].

The high cost of feedstock, comprising 60–70% of biodiesel production expenses, remains a significant challenge. Edible oils like palm and sunflower oil are expensive, compete with food resources, and may cause social issues [13]. To address this, less costly alternatives such as waste cooking oil (WCO) and non-edible oils like Jatropha and Karanja are being explored. WCO, a byproduct of frying in households and the food industry is 60% cheaper than fresh vegetable oils and offers an environmentally friendly solution for biodiesel production when properly utilised [14].

This study employs WCO and solid bifunctional catalysts derived from orange peel and eggshell to optimise biodiesel production, showcasing a sustainable and cost-effective approach to addressing energy challenges.

II. Materials and Methods

A. Materials and equipment

Chicken eggshells (Ce), orange peels (OrP), and waste cooking oil (WCO) were sourced from Ilorin, Kwara State, Nigeria. The University of Ilorin Chemical Engineering Laboratory provided analytical-grade chemicals (Sigma-Aldrich) such as concentrated sulphuric acid, hydrochloric acid, sodium hydroxide, potassium hydroxide, and barium chloride, as well as equipment like an electric oven, magnetic stirrer, and muffle furnace.

B. Pre-treatment and characterisation of WCO

The WCO was filtered to remove impurities, then preheated at 80 °C for 30 min to eliminate moisture. Its physicochemical properties were evaluated per ASTM D5555-95 (2011) standards.

C. Preparation of catalyst and characterisation

The chicken eggshell was washed, air-dried, crushed, and ground into a fine powder, then calcined at 900 °C for 2 h to convert $CaCO_3$ to CaO. The resulting chicken eggshell catalyst (CeC) was stored in a desiccator.

The Orange peel (OrP) solid acid catalyst was prepared with slight modifications to a method by Nagasundaram *et al.* [15]. The OrP was washed, sun-dried to constant weight, and carbonised at 400 °C for 2 h to form biochar. This biochar was ground and sifted, then 5 g of it sulfonated with 10 mL concentrated sulphuric

acid in a 250 mL beaker and placed in an orbital shaker at 50 °C for 24 h. After cooling, the mixture was washed with distilled water until no sulphate ions were detected using barium chloride. The catalyst was dried at 105 °C overnight to obtain the final sulfonated carbonised OrP catalyst.

The acid-base bifunctional catalyst of CeC and OrP was prepared via wet impregnation similar method described by Wang *et al.* [16]. The synthesised catalyst was characterised using FTIR to detect the presence of various functional groups, SEM-EDX to examine its surface morphology and chemical composition, BET for surface analysis, and XRD for crystallinity and elemental identification.

D. Optimization of biodiesel production

This study used response surface methodology with a central composite design (CCD) to optimise biodiesel synthesis conditions. Four input factors—methanol/WCO molar ratio, temperature, catalyst amount, and reaction time—were analysed for their impact on biodiesel yield. Design Expert USA software conducted 26 runs following Saidi *et al.* [17]. A quadratic polynomial model evaluated the output response, with Equation (1) calculating the biodiesel production rate.

$$\text{Yield } (\%) = \frac{\text{Weight of biodiesel}}{\text{Weight of oil}} * 100 \qquad (1)$$

Table 1: Independent Variable Quantities and Levels used for the Experimental Design

Factors	Symbols	(-1)	(+1)
Catalyst amount (wt %)	F1	2	4
Methanol to WCO ratio	F2	6:1	10:1
Reaction duration (min)	F3	60	120
Temperature (°C)	F4	60	70

III. Results and Discussion

A. Characterization of Waste Cooking Oil and Catalyst

The results in Table 2 show the biodiesel's WCO properties compared with the used cooking oil. The characteristics of the biodiesel produced in this study are within the acceptable EN14214 standard for biodiesel. WCO's qualities and suitability for biodiesel production are determined mainly by its characteristics.

Scanning Electron Microscopy (SEM) examined the bi-functional catalyst's morphology before and after optimisation, as shown in Figures 1(a) and (b). Before use, at x3000 magnification (10 kV), the catalyst displayed a rough, porous surface typical of calcined materials, indicating a high surface area for catalytic reactions [18]. The roughness likely stems from calcite crystals in eggshells or calcination. Similar effects were reported by Kumar *et al.* [19] on alumina-supported catalysts. After use, at x2000 magnification (15 kV), the catalyst surface appeared smoother with micro-cracks, indicating sintering and reduced surface area. Gupta *et al.* [20] observed similar degradation in metal oxide catalysts due to prolonged high-temperature exposure, leading to surface cracks and efficiency loss. Pore blockage from reaction by-products or structural collapse was evident.

Energy dispersive analysis (EDX) in Figures 2(a) and (b) confirmed sulphur (57%) as the dominant element in fresh catalysts due to sulphonation of orange peel, along with calcium and oxygen from eggshell-based calcium oxide [21]. In recovered catalysts, calcium predominated, with oxygen, phosphorus, and trace elements such as aluminium and magnesium the basic components (CaO) derived

Table 2: Characteristics of WCO

Properties (Units)	WCO	WCO Biodiesel	EN 14214
Acid Value (mg KOH/g)	1.0659	0.512	≤ 0.8
Saponification Value (mg KOH/g)	185.13	174	-
Iodine Value **(**g Iodine/100g**)**	87.5	88	≤ 120
Density (g/cm^3)	0.94	0.876	0.86 – 0.9
Free Fatty Acid Content	**%**	0.5	< 0.5

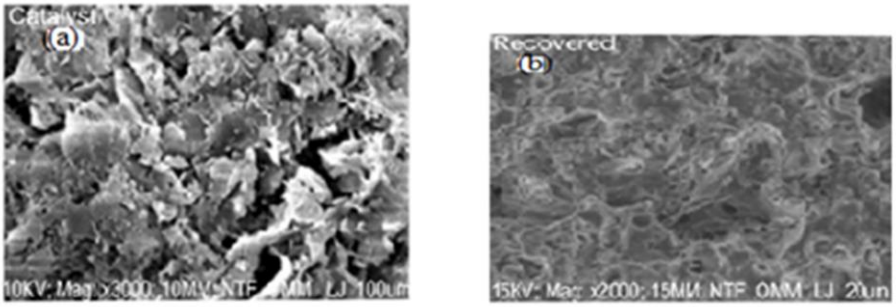

Figure 1: SEM image of the catalyst (a) before and (b) after use (recovered)

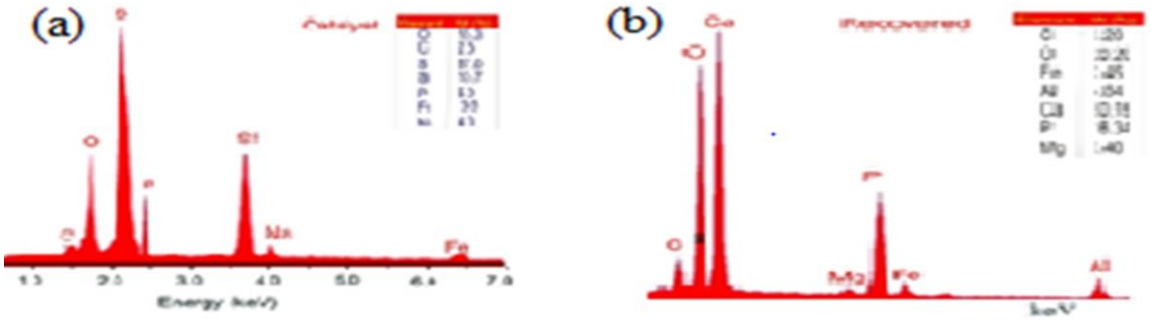

Figure 2: EDX pattern of the catalyst (a) before and (b) after use (recovered)

orange peel. A strong peak at 2516 cm^{-1} suggests C≡C or C≡N stretching, while a sharp prominent spike at 1796 cm^{-1} corresponds to C=O stretching from carbonyl compounds. The S=O bond peak at 874 cm^{-1} confirms sulphonate groups from orange peel sulphonation [23]. Peaks at ~485 and 435 cm^{-1} represent M-O or M-S bonds, indicating inorganic components like calcium from eggshells. These findings confirm the presence of both organic and inorganic components.

For the recovered catalyst [Figure 3(b)], peaks at 3600–2929 cm^{-1} indicate O-H stretching, attributed to hydroxyl groups from sulfonated orange peel. The peak at 1612 cm^{-1} signifies C=O stretching, indicating carbonyl groups [24]. Sulphate groups are confirmed by strong S=O

peaks at 1099 and 1441 cm^{-1}, while peaks at ~550 and 460 cm^{-1} represent M-O or M-S bonds, suggesting calcium or metal oxide-sulphonate interactions. These findings indicate the retention of organic components after the transesterification reaction.

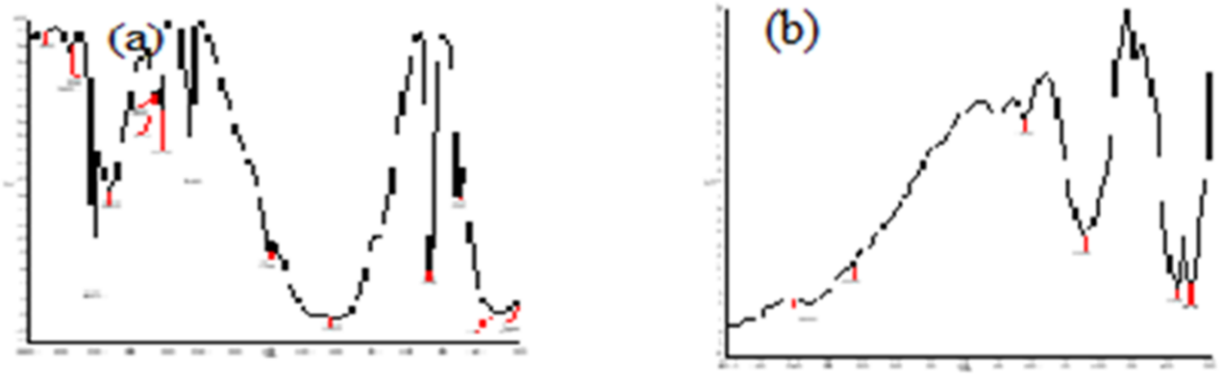

Figure 3: FTIR spectrum of the catalyst (a) before and (b) after use (recovered)

The crystalline phases of the synthesized catalyst were identified using XRD analysis, as shown in Figure 4(a). Peaks at 2θ angles of 20°, 26.2°, and 37° confirmed the presence of SiO_2 crystalline phases, while the peak at 19° indicates sulphate presence and suggests partial crystallinity with possible amorphous phases. Additional smaller peaks at 30° and 40° also correspond to SiO_2 and sulphate-related phases. Comparatively, Lathiya *et al.* [25] identified peaks at 27.4° as quartz SiO_2 and at 52.38°, 53.7°, and 55.8° as SO_3H groups, confirming the successful conversion of orange peel biomass into an amorphous sulphonated acid catalyst.

The XRD pattern of the recovered catalyst (Figure 4(b)) shows peaks at 2θ angles of 20°, 24°, 28°, 19°, and 36°, corresponding to calcium, potassium, phosphorus, iron, and manganese, respectively. Additional peaks labeled "Si" (at 8°, 14°, and 26°) indicated silicon in various crystalline forms. The sharpness of these peaks suggests the presence of well-defined crystalline structures for these elements.

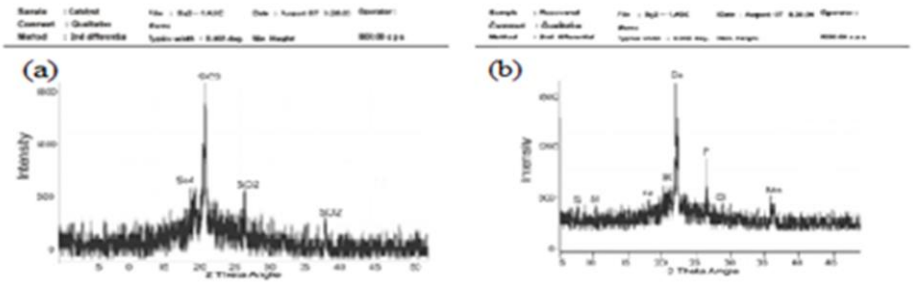

Figure 4: XRD pattern of the Catalyst (a) before and (b) after use (recovered)

Table 3 shows the BET analysis results for the catalyst's surface area, pore volume, and pore size before and after use. The exact surface area of the fresh catalyst (980.5 m^2/g) is suggestively higher than that of the recovered catalyst (365 m^2/g), indicating higher catalytic activity in the fresh catalyst, as surface area strongly influenced catalytic performance. However, the drastic reduction in the surface area of the catalyst might be due to deactivation or poisoning. The pore volume showed minimal change between the two. Similarly, Fatimah *et al.* [26] observed a rise in the exterior area from 60.2 to 82.8 m^2/g for a $ZnO\text{-}SiO_2$ impregnated catalyst.

Table 3: BET Surface Area, Pore Volume, and Size.

Sample	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
Catalyst	980.5	0.6035	3.034
Recovered Catalyst	365.2	0.6054	2.854

B. Optimization of Biodiesel Production

The optimization study employed central composite design (CCD), a response surface methodology (RSM), with four independent factors: catalyst loading (F1) methanol-to-oil ratio (F2), time (F3), and temperature (F4) [27]. Biodiesel yields for each experimental run are presented in Table 4.

i. Statistical analysis of transesterification of WCO

The model was validated through analysis of variance (ANOVA) and assessed individual parameter contributions in the quadratic response surface model. Statistical analysis, conducted with Design Expert (Version 13.0.0, Stat Ease, Inc., USA) based on RSM CCD, is shown in Tables 5 and 6. The variation coefficient (C.V% = 2.05) indicates high experimental precision and reliability. The predicted R^2 (0.7555) aligns well with the adjusted R^2 (0.9264), with a difference below 0.2, confirming model reliability. Adequate precision, at 17.1344, reflects a strong signal, making the model suitable for exploring the design space.

The model F-value of 23.49 indicates statistical significance, with only a 0.01% chance of occurring by random noise, as shown in Table 6. The F-value of 0.52 for Lack of Fit suggests non-significance relative to pure error, meaning an 80.40% chance it could result from noise, which is favourable. The coded values A, B, C, and D correspond to catalyst concentration, methanol-to-oil ratio, reaction time, and temperature [28]. P-values less than 0.05 indicate significant terms, with A, C, AC, BC, A^2, B^2, C^2, and D^2 being substantial. ANOVA confirmed the significance of the quadratic polynomial Equation (2).

$$\text{Yield} = 818.51660 + 5.71290A + 14.92431B - 1.51183C - 22.63388D + 0.239769AB - 0.082225AC + 0.184166AD + 0.03945BC + 0.042691BD + 0.001397CD - 2.7444A^2 - 1.39610B^2 + 0.007118C^2 + 0.167182D^2 \quad (2)$$

The equations can predict the response for given factor levels. Table 4 shows the experimental data and predicted values from the CCD, with an optimal yield of 87.5% in experimental run 2

Table 4: CCD for the Experimental Runs

Run	Catalyst (wt %)	Methanol: Oil	Time (min)	Temp (°C)	(Yield %)	Predicted Yield (%)
1	2	8	90	65	76.4	77.49
2	2	6	60	60	87.5	86.7
3	3	8	60	65	83.44	84.5
4	4	8	90	65	69.68	68.96
5	2	10	120	60	85	83.67
6	4	6	60	60	80.49	80.3
7	3	8	90	70	79.89	80.75
8	4	10	120	60	68.61	69.32
9	3	8	90	60	79.26	79.55
10	4	10	60	60	75.64	74.2
11	2	10	120	70	83.2	84.29
12	3	10	90	65	69.2	69.65
13	4	6	120	70	69.7	68.56
14	4	10	60	70	76.71	77.67
15	3	8	90	65	77.9	75.97
16	2	6	120	60	82.47	82.22
17	2	10	60	70	80.3	78.46
18	2	6	60	70	84.78	84.78
19	3	8	120	65	81.2	80.25
20	2	10	60	60	76.89	78.68
21	3	6	90	65	71.2	71.12
22	2.5	9	90	70	81.1	80.06
23	4	6	120	60	64.73	65.96
24	3	8	90	65	74.9	75.97
25	2	6	120	70	80.5	81.14
26	4	6	60	70	81.6	82.06

Table 5: Statistical Fit

Std Dev	Mean	C.V %	R^2	Adjusted R^2	Predicted R^2	Adequate Precision
1.59	77.78	2.05	0.9676	0.9264	0.7555	17.1344

Table 6: Analysis of variance (ANOVA)

Source	Sum of Squares	Degree of Freedom	Mean Square	F-value	p-value	
Model	835.06	14	59.65	23.49	< 0.0001	Significant
A-Catalyst	282.58	1	282.58	111.27	< 0.0001	
B- Methanol: Oil	8.53	1	8.53	3.36	0.0940	
C- Rxn time	70.16	1	70.16	27.63	0.0003	
D- Temp	5.78	1	5.78	2.28	0.1595	
AB	3.11	1	3.11	1.22	0.2921	
AC	82.35	1	82.35	32.43	0.0001	
AD	11.51	1	11.51	4.53	0.0567	
BC	75.82	1	75.82	29.86	0.0002	
BD	2.5	1	2.5	0.9857	0.3421	
CD	0.5939	1	0.5939	0.2339	0.6381	
A^2	38.67	1	38.67	1.40	0.2638	
B^2	135.98	1	135.98	4.93	0.0507	
C^2	234.75	1	234.75	8.51	0.0154	
Residual	27.93	11	2.54			
Lack of Fit	23.43	10	2.34	0.5208	0.8040	Not significant
Pure Error	4.50	1	4.5			
Cor Total	862.99	25				

at 60 °C, 2 wt% catalyst loading, 60 min response time, and a 6:1 methanol to oil ratio. In their work, Aderibigbe *et al.* [29] reported 98.98 % conversion at time 6 h, temperature 65 °C, catalyst loading 6% wt/wt of WCO, and methanol to oil ratio of 11.75:1. Ngige *et al.* [30] in their work reported a similar result, while Ajala *et al.* [31] reported 98.28% at 6:1 MeOH: oil molar ratio, 3 h reaction time, 55 °C temperature, and 2% (w/w) catalyst quantity in transesterification of palm kernel oil to biodiesel. Figure 5(a) confirmed the minimal difference between predicted and actual values, validating the quadratic model's suitability for this study.

C. Biodiesel characterization

The biodiesel was analysed using GC-MS to identify its chemical composition, particularly fatty acid methyl esters (FAME) [32]. Figure 5(b) revealed various FAMEs, including octanoic acid methyl ester (RT 4.106 min), decanoic acid methyl ester (RT 5.279 min), and dodecanoic acid methyl ester (RT 6.309 min) similar to the findings of [33]. Both saturated and unsaturated FAMEs, like linoleic acid methyl ester (RT 8.334 min), contribute to the biodiesel's stability, melting points, fluidity, and cold flow characteristics, influencing its performance [34, 35].

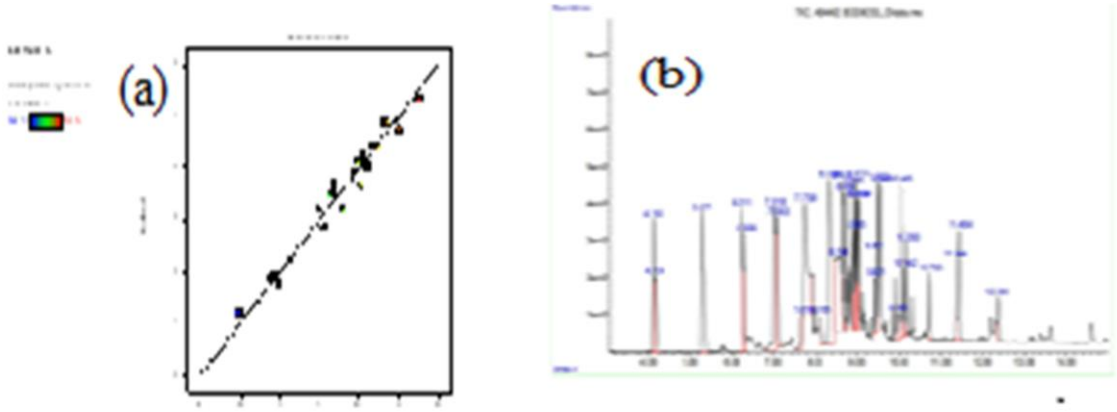

Figure 5: (a) Predicted Versus Actual Values of Biodiesel Yield; (b) GC-MS Profile Analysis

III. Conclusion

The current study gives insight into the preparation and the use of orange peel-derived porous activated carbon enriched with SO_3H impregnated with calcined chicken eggshell as a bifunctional catalyst for optimizing biodiesel production from waste cooking oil (WCO). Characterizations of Ce-Orp-SO_3H were carried out before and after use to include SEM-EDX, FTIR, XRD, and BET, and the optimum FAME conversion of 87.5% was obtained with a 2% wt catalyst loading, a methanol-to-oil ratio of 6:1, a reaction temperature of 60 °C, and a reaction time of 60 min. GCMS study shows FAME components found in biodiesel to include saturated and unsaturated fatty acids.

References

[1] Naji, S. Z., & Tye, C. T. "A review of the synthesis of activated carbon for biodiesel production: Precursor,

preparation, and modification", *Energy Conversion and Management: X, 13,* 100152, 2022, pp. 1-15.

[2] Kam, Y.L., Agutaya,J.K.C.N., Quitain,A.T., Ogasawara,Y., Sasaki, M., Lam, M.K., Yusup, S., Assabumrungrat, S. & Kida, T. "In-situ transesterification of microalgae using carbon-based catalyst under pulsed microwave irradiation" Biomass and Bioenergy, 168, 2023, 106662.

[3] Demirbas, A. "Biodiesel for future transportation energy needs", *Energy Sources, Part A: Recovery, Utilization, and Environmental Effect*, *32*, 2010, pp. 1490-1508.

[4] Raducanu, C. E., Gavrila, A. I., & Dobre, T., & Chipurici, P. "Study on alumina supported heterogeneous catalysts for biodiesel production", *Revista de Chimie, 69*(8), 2018, pp. 2138–2143.

[5] Thangaraj, B., Solomon, P. R., Muniyandi, B., Ranganathan, S., & Lin, L. "Catalysis in biodiesel production—A review". *Clean Energy,* 3(1), 2019, pp. 2-23.

[6] Jayakumar, M., Karamegam, N., Gundapalli, M. P., Gebeyehu, K. B., Asfaw, B. T., Chang, S. W., Ravindran, B., & Awasthi, M. K. "Heterogeneous base catalysts: Synthesis and application for biodiesel production—A review" *Bioresource Technology, 331*, 125054, 2021.

[7] Makepa, D. C., Chihobo, C. H., Manhongo, T. T., & Musademba, D. "Life-cycle assessment of microwave-assisted pyrolysis of pine sawdust as an emerging technology for biodiesel production", *Results in Engineering,* 20, 101480, 2023.

[8] Aqliliriana, C. M., Ernee, N. M., & Irmawati, R. "Preparation and characterization of modified calcium oxide from natural sources and their application in the transesterification of palm oil", *International Journal of Scientific and Technology Research, 4*(11), 2015, pp. 168-175.

[9] Fattah, I. M. R., Ong, H. C., Mahila, T. M. I., Mofjur, M., Silitonga, A. S., Rahman, S. M., & Ahmad, A. "State of the art of catalysts for biodiesel production", *Frontiers in Energy Research, 8*(1), 2020, pp.1–17.

[10] Mansir, N., Teo, S. H., Rashid, U., Saiman, M. I., Tan, Y. P., Alsultan, G. A., & Taufiq-Yap, Y. H. "Modified waste eggshell derived bifunctional catalyst for biodiesel production from high FFA waste cooking oil: A review", *Renewable and Sustainable Energy Reviews, 82*(10), 2018, pp. 3645–3655.

[11] Helmi, M., Tahvildari, K., Hemmati, A., & Safekordi, A. "Phosphomolybdic acid/graphene oxide as a novel green catalyst for biodiesel production from waste cooking oil via electrolysis method: Optimization using response surface methodology (RSM)", *Fuel, 287*, 119528, 2021.

[12] Wei, Z., Xu, C., & Li, B. "Application of waste eggshell as low-cost solid catalyst for biodiesel production", *Bioresource Technology, 100*(11), 2009, pp. 2883–2885.

[13] Foroutan, R., Peighambardoust, S. J., Mohammadi, R., Peighambardoust, S.

H., & Ramavandi, B. "Application of walnut shell ash/ZnO/K2CO3 as a new composite catalyst for biodiesel generation from Moringa oleifera oil", *Fuel, 311*, 122624, 2022.

[14] Talebian-Kiakalaieh, A., Amin, N. A. S., & Mazaheri, H. "A review on novel processes of biodiesel production from waste cooking oil", *Applied Energy, 104*, 2013, pp. 683-710.

[15] Nagasundaram, N., Kokila, M., Sivaguru, P., Santhosh, R & Lalitha, A. "SO3H@carbon powder derived from waste orange peel: An efficient, nano-sized greener catalyst for the synthesis of dihydropyrano[2,3-c]pyrazole derivatives. *Advanced Powder Technology*, 31(4), 2020, pp. 1516-1528

[16] Wang, S., Shan, R., Wang, Y., Lu, L., & Yuan, H. "Synthesis of calcium materials in biochar matrix as a highly stable catalyst for biodiesel production", *Renewable Energy, 130*, 2019, pp. 41–49.

[17] Saidi, M., Safaripour, M., Ameri, F. & Jomeh,M. "Application of sulfonated

biochar-based magnetic catalyst for biodiesel production: Sensitivity analysis and process optimization." *Chemical Engineering and Processing-Process Intensification* 190**,** 109419, 2023.

[18] Zhang, B., Gao, M., Geng, J., Cheng, Y., Wang, X., Wu, C., Wang, Q., Liu, S., & Cheung, S. M. "Catalytic performance and deactivation mechanism of a one-step sulfonated carbon-based solid-acid catalyst in an esterification reaction", *Renewable Energy, 164,* 2021, pp. 824-832.

[19] Kumar, S., Agrawal, A., Pradhan, A., Singh, A., Verma, A., & Rao, G. K. "Thermal treatment effects on the morphology and performance of alumina-supported catalysts", *Catalysis Today, 342*, 2020, pp. 29-38

[20] Gupta, R., Sharma, D., Jha, R., & Tandon, A. "Surface cracking and roughness in metal oxide catalysts: Implications for catalytic efficiency", *Catalysis Today, 323*, 2019, pp. 45-54.

[21] Sangar, S. K., Syazwani, O. N., Farabi, M. S. A., Razali, S. M., Shobhana, G., Teo, S. H. & Taufiq-Yap, Y. H. "Effective biodiesel synthesis from palm fatty acid distillate (PFAD) using carbon-based solid acid catalyst derived from glycerol" *Renewable Energy, 142*, 2019, pp. 658–667.

[22] Sutapa, I. W., Wahab, A. W., Taba, P., & Nafie, N. "Synthesis and structural profile analysis of MgO nanoparticles produced through the sol-gel method followed by annealing process", *Oriental Journal of Chemistry, 34*(2), 2018, pp. 1016-1025.

[23] Dawodu, F. A., Ayodele, O., Xin, J., Zhang, S., & Yan, D. "Effective conversion of non-edible oil with high free fatty acid into biodiesel by sulphonated carbon catalyst" *Applied Energy, 114,* 2014, pp. 819–826.

[24] Cheng, J., Qiu, Y., Zhang, J., Huang, R., Yang, W., & Fan, Z. "Conversion of lipids from wet microalgae into biodiesel using sulfonated graphene oxide catalysts", *Bioresource Technology,* 244*,* 2017, pp. 569–574.

[25] Lathiya, D. R., Bhatt, D. V., & Maheria, K. C. "Synthesis of sulfonated carbon catalyst from waste orange peel for cost-effective biodiesel production", *Bioresource Technology Reports,* 2, 2018, pp. 69-76.

[26] Fatimah, I., Purwiandono, G., Sahroni, I., Sagadevan, S., Chun-Oh, W., Ghazali, S. A. I. S. M., & Doong, R. "Recyclable catalyst of ZnO/SiO_2 prepared from salacca leaves ash for sustainable biodiesel conversion", *South African Journal of Chemical Engineering, 40,* 2022, pp. 134-143.

[27] Caglar, A., Sahan, T. Cogenli, M.S., Yurtcan, A.B., Aktas, N. & Kivrak, H, "A novel central composite design based response surface methodology optimization study for the synthesis of Pd/CNT direct formic acid fuel cell anode catalyst." *International Journal of Hydrogen Energy* **43**(24) 2018, pp. 11002-11011.

[28] Gonçalves, M.A., Santos, H.C. Lima, da Silva, M.A.R., da Cas Viegas, A., da Rocha Filho, G.N., G & da Conceição, L.R.V. "Biodiesel production from waste cooking oil using an innovative magnetic solid acid catalyst based on Ni–Fe ferrite: RSM-BBD optimization approach", *Journal of Industrial and Engineering Chemistry* Vol 135, 2024, pg 270-285.

[29]. Aderibigbe, F. A., Saka, H. B., Ajala, E. O., Mustapha, S. I., Mohammed, I. A., Amosa, M. K., & Solomon, B. O. "Development of Bi-functional heterogeneous catalyst for transesterification of waste cooking oil to biodiesel: optimization studies", *Advanced Materials Research*, *1163*, 2021, pp. 128-147.

[30] Ngige, G. A., Ovuoraye, P.E.,Igwegbe, C.A.,Fetahi, E.,Okeke, J.A., Yakubu, A.D.& Onyechi, P.C.

"RSM optimization and yield prediction for biodiesel produced from alkali-catalytic transesterification of pawpaw seed extract: Thermodynamics, kinetics, and Multiple Linear Regression analysis." *Digital Chemical Engineering* **6**: 100066, 2023..

[31] Ajala, E.O., Ajala,M.A., Agbeleoba, E.D., Odetoye, T.E., Eromonsele, O.P. and Ayanshola, A.M. "*Archachatina marginata* Snail-shell as a Feedstock for the Synthesis of Solid Catalysts for Methanolysis of Oil from Palm Kernel in an Optimisation Process" *UNIOSUN Journal of Engineering and Environmental Sciences Vol. 4, No. 1***,** 2022, pp. 9-30.

[32] Husár, J., Pecha, J.& Šánek, L. "Development and validation of a simple and reliable alternative method for process monitoring and final product quality control during fatty acid ethyl esters production." Talanta **235**: 122752, 2021.

[33] Tesfaye Tefera, N., Nallamothu, R.B., Alemayehu, G. & Kefale,, Y. "Optimization, characterization, and GC-MS analysis of CSOME produced using alkali catalyzed transesterification" *Energy Conversion and Management*: X 22, April 2024, 100549

[34] Gopinath, A., Sairam, K., Velraj, R. & Govindaraj, K. "Effects of the properties and the

structural configurations of fatty acid methyl esters on the properties of biodiesel fuel: a review." Proceedings of the institution of mechanical engineers, Part D: *journal of automobile engineering* **229**(3) 2015, pp. 357-390.

[35] Pradana, Y.S., Makertihartha, I.G.B.N., Indarto, A., Prakoso, T. & Soerawidjaja, T.H. "A Review of Biodiesel Cold Flow Properties and Its Improvement Methods: Towards Sustainable Biodiesel Application" *Energies*, 17(18), 2024, 4543.