

OPTIMIZATION OF BIODIESEL PRODUCTION FROM RUBBER SEED OIL USING A BIFUNCTIONAL CATALYST DERIVED FROM CARBIDE SLAG AND PIG BONES

Kessington Obahiagbon, Chisom Nwafor and David Ohimai Ahonkhai

Abstract

This research explores the utilization of carbide slag from welder's waste as a crucial source of CaO for the development of a bi-functional heterogeneous catalyst, incorporating welder's waste and pig bones, in the simultaneous esterification and transesterification of Rubber seed oil for biodiesel production. Comprehensive characterization of the catalyst and its precursors assessed their structural, compositional, morphological, and thermal attributes. Employing a one-step transesterification method with response surface methodology (RSM) optimization, the bi-functional catalyst demonstrated bi-functionality, featuring a substantial surface area ($393 \text{ m}^2/\text{g}$) and pore volume ($0.203 \text{ cm}^3/\text{g}$). This catalyst facilitated a maximum biodiesel yield of 92.6%, achieved under optimized conditions: a reaction temperature of 60°C , catalyst loading of 1 wt.%, reaction time of 75 minutes, and a methanol-to-oil ratio of 6:1. The RSM model exhibited high adequacy ($R^2 = 0.9577$), and the biodiesel produced adhered to established standards. The synthesized catalyst presents advantages, including reusability, straightforward synthesis, stability, substantial surface area, and accessibility of precursor materials, positioning it as a promising alternative to conventional catalysts.

Keywords: Rubber seed oil, Biodiesel, Carbide slag, Heterogeneous catalyst, Transesterification

Introduction

The search for sustainable alternatives to fossil fuels has become increasingly important in recent years. Biodiesel, an environmentally friendly and economically viable alternative fuel, has garnered significant attention. Despite the emergence of cleaner fuels like liquefied petroleum gas (LPG) and compressed natural gas (CNG), their widespread adoption as replacements for traditional fuels such as gasoline and diesel remain challenging¹. Many researchers advocate for sustainable and biodegradable biofuels as a promising solution to the fossil fuel dilemma². Biofuels, including biodiesel, bioethanol, and biogas, are derived from organic matter or biomass³.

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¹ Kolakoti, A., Setiyo, M., & Latifur, M. (2022). A Green Heterogeneous Catalyst Production and Characterization for Biodiesel Production using RSM and ANN Approach. 11(3), 703–712.

² Bharadwaj, S., Venkata, A., Lakshmi, S., & Subramania, N. (2020). Biodiesel production from rubber seed oil using calcined eggshells impregnated with $\gamma\text{-Al}_2\text{O}_3$ as heterogeneous catalyst: A comparative study of RSM and ANN optimization. Brazilian Journal of Chemical Engineering, 37(2), 351–368. <https://doi.org/10.1007/s43153-020-00027-9>

³ Sharma, Y. C., Singh, B., & Upadhyay, S. N. (2008). Advancements in development and characterization of biodiesel: A review. Fuel, 87(12), 2355–2373. <https://doi.org/10.1016/J.FUEL.2008.01.014>

Biodiesel is typically produced through transesterification, a chemical reaction between triglycerides in oils or fats and alcohol in the presence of a catalyst. This process generates fatty acid alkyl esters, also called biodiesel and glycerol as a byproduct⁴.

The use of non-edible feedstock, like rubber seed oil, also offers environmental benefits by diversifying biofuel sources and enhancing sustainability, particularly in rural areas^{5,6}.

Heterogeneous catalysis is a key principle in biodiesel production, involving solid catalysts and liquid reactants. This approach allows for efficient catalytic reactions with easier separation and reuse of the catalysts^{7,8}. Rubber seed oil is suitable for biodiesel production due to its triglyceride content and relatively high oil content⁹.

Carbide slag and pig bones offer potential for catalyzing biodiesel production. They contain metal oxides and may function as heterogeneous catalyst due to their porous structure and metal content¹⁰. However, the precise catalytic mechanisms and efficiency of these unconventional catalysts requires further study.

The use of waste materials as catalysts for biodiesel production has gained attention due to their eco-friendliness and cost-effectiveness. Waste materials rich in calcium, such as calcium oxide (CaO), have shown promising catalytic activity in the transesterification of oils, making them attractive for biodiesel synthesis¹¹. Utilizing waste materials as catalysts aligns with the global trend toward renewable energy sources and sustainability. It reduces reliance on fossil fuels, minimizes environmental impacts, and promotes a circular economy approach to waste management¹².

To optimize biodiesel production, response surface methodology (RSM) is a valuable tool for reducing costs. RSM, widely accepted in mathematics, helps evaluate the impact of factors and

⁴ Amenaghawon, A. N., Obahiagbon, K., Isesele, V., & Usman, F. (2022). Optimized biodiesel production from waste cooking oil using a functionalized bio-based heterogeneous catalyst. *Cleaner Engineering and Technology*, 8, 100501. <https://doi.org/10.1016/J.CLET.2022.100501>

⁵ Kalam, A., Islam, M. A., Primandari, R. P., & Yaakob, Z. (2018). Non-Edible Vegetable Oils as Renewable Resources for Biodiesel Production: South-East Asia Perspective. *Advances in Biofuels and Bioenergy*. <https://doi.org/10.5772/INTECHOPEN.73304>

⁶ Kurowska, K., Marks-Bielska, R., Bielski, S., Kryszk, H., & Jasinskas, A. (2020). Food Security in the Context of Liquid Biofuels Production. *Energies* 2020, Vol. 13, Page 6247, 13(23), 6247. <https://doi.org/10.3390/EN13236247>

⁷ Melero, J. A., Iglesias, J., & Morales, G. (2009). Heterogeneous acid catalysts for biodiesel production: current status and future challenges. *Green Chemistry*, 11(9), 1285–1308. <https://doi.org/10.1039/B902086A>

⁸ Radu, D. R., & Kraus, G. A. (2015). Heterogeneous Catalysts for Biodiesel Production. 117–130. <https://doi.org/10.1039/9781849737494-00117>

⁹ Khazaai, S. N. M., Bhuyar, P., Strezov, V., Govindan, N., Rahim, M. H. A., & Maniam, G. P. (2023). Optimization of Rubber Seed Oil Extraction: Adaptive Neuro-Fuzzy Inference-Based Yield Prediction Model by Studying Polarity and Moisture Content. *BioEnergy Research* 2023, 1–11. <https://doi.org/10.1007/S12155-023-10635-1>

¹⁰ Galadima, A., & Muraza, O. (2020). Waste materials for production of biodiesel catalysts: Technological status and prospects. *Journal of Cleaner Production*, 263, 121358. <https://doi.org/10.1016/j.jclepro.2020.121358>

¹¹ Akhabue, C. E., Ukponahiusi, U. J., Osa-Benedict, E. O., Otoikhian, S. K., Inetianbor, O. C., & Oyedoh, E. A. (2022). Simultaneous Esterification and Transesterification of Neem Seed Oil Using Ferric Sulphate Doped With Poultry Droppings as a Bifunctional Catalyst. *Frontiers in Energy Research*, 10(July), 1–11. <https://doi.org/10.3389/fenrg.2022.927467>

¹² Hamza, M., Ayoub, M., Shamsuddin, R. Bin, Mukhtar, A., Saqib, S., Zahid, I., Ameen, M., Ullah, S., Al-Sehemi, A. G., & Ibrahim, M. (2021). A review on the waste biomass derived catalysts for biodiesel production. *Environmental Technology & Innovation*, 21, 101200. <https://doi.org/10.1016/J.ETI.2020.101200>

their interactions with fewer experiments, making it a cost-effective approach. It can create empirical models using linear regressions and has proven highly effective in modeling various transesterification processes for biodiesel synthesis^{13,14}.

Materials and Methods

Feedstock Collection and Preparation

The rubber seeds were gathered from a rubber plantation at Rubber Research Institute of Nigeria, Iyanomo (Edo State, Nigeria), and the pig bones were obtained from a local abattoir at New Benin market (Edo State, Nigeria), while the carbide slag was obtained from a local welder at Ewa Road (Edo state, Nigeria).

Oil Extraction

In this study, the solvent extraction method was employed¹⁵. First, seeds were manually separated from the husk and dried for one week to reduce moisture. They were then oven-dried for two hours at 80°C and blended to 0.5mm particle size. 400g of these blended seeds were placed in a thimble within a Soxhlet extractor. 750 ml of hexane was added to a round bottom flask, heated to 70°C, and each run took around 1 hour and 20 minutes. When the liquid in the siphon tube became clear, the heating was turned off, the thimble removed, and hexane recovery initiated. After recovery, the flask was placed in a water bath to evaporate residual hexane. The extracted oil still contained trace hexane, which dissipated upon exposure to air, reducing the oil's volume^{16,17}. The oil was then purified for biodiesel production.

Catalyst Preparation

The pig bones were washed to remove impurities and then sun-dried for 5 days, the bones were pulverized using a special-purpose milling machine and sieved to obtain 300µm particles. Afterwards, it was crushed and calcined in a muffle furnace at 800°C for 4 hours¹⁸. The material was then allowed to in a desiccator to prevent contamination and subsequently stored in an airtight container. The catalysts derived from the carbide slag were produced by subjecting the

¹³ Betiku, E., Odude, V. O., Ishola, N. B., Bamimore, A., Osunleke, A. S., & Okeleye, A. A. (2016). Predictive capability evaluation of RSM, ANFIS and ANN: A case of reduction of high free fatty acid of palm kernel oil via esterification process. *Energy Conversion and Management*, 124, 219–230.

<https://doi.org/10.1016/J.ENCONMAN.2016.07.030>

¹⁴ Obahiagbon, K., & Ahonkhai, D. O. (2023). Optimized Biodiesel Production from Waste Cooking Oil Using Poultry Droppings Catalyst: A Comparison of RSM and ANN. *Petroleum Technology Development Journal*, 13(2), 1-19.

¹⁵ Mohd-Setapar, S. H., Nian-Yian, L., & Mohd-Sharif, N. S. (2014). Extraction of rubber (hevea brasiliensis) seed oil using soxhlet method. *Malaysian Journal of Fundamental and Applied Sciences*, 10(1).

<https://doi.org/10.11113/mjfas.v10n1.61>

¹⁶ Pikula, K., Zakharenko, A., Stratidakis, A., Razgonova, M., Nosyrev, A., Mezhuev, Y., Tsatsakis, A., & Golokhvast, K. (2020). The advances and limitations in biodiesel production: feedstocks, oil extraction methods, production, and environmental life cycle assessment. <http://Mc.Manuscriptcentral.Com/Tgcl>, 13(4), 11–30.

<https://doi.org/10.1080/17518253.2020.1829099>

¹⁷ Zulqarnain, Ayoub, M., Yusoff, M. H. M., Nazir, M. H., Zahid, I., Ameen, M., Sher, F., Floresyona, D., & Budi Nursanto, E. (2021). A Comprehensive Review on Oil Extraction and Biodiesel Production Technologies. *Sustainability* 2021, Vol. 13, Page 788, 13(2), 788. <https://doi.org/10.3390/SU13020788>

¹⁸ Suraj, C. K., Anand, K., & Sundararajan, T. (2020). Investigation of biodiesel production methods by altering free fatty acid content in vegetable oils. *Biofuels*, 11(5), 587–595. <https://doi.org/10.1080/17597269.2017.1378993>

initial carbide slag to a calcination process within a temperature range of 700°C¹⁹. The method includes grinding carbide slag, sieving to 0.3mm, drying at 100°C, calcination in a muffle furnace for 4 hours, resulting in high CaO content material stored in an air-tight container.

To create the bi-functional catalyst, calcined carbide slag, calcined pig bone, Iron (III) chloride, and Strontium nitrate were combined in deionized water (30%, 30%, 25%, and 15% respectively). The mixture was stirred for 1 hour, dried at 110°C for 6 hours, calcined at 900°C for 4 hours, cooled in a desiccator, and stored in an airtight container for future use.

Catalysts Characterization

Various analyses were conducted to evaluate the characteristics and compositions of the catalyst and its precursors. XRF determined the chemical composition, SEM and EDX detected morphological features and elemental spectra, XRD examined crystalline structure, BET analysis assessed surface area, pore diameter, and pore volume, FTIR identified functional groups, and TGA and DTA evaluated thermal stability.

Biodiesel Production and Optimization

The method employed simultaneous esterification and transesterification, and the performance of the heterogeneous catalyst was assessed by conducting batch-wise simultaneous esterification and transesterification of RSO. This simultaneous esterification and transesterification of RSO took place within a 250 ml conical flask positioned on a constant-temperature magnetic stirrer²⁰.

In brief, a specific amount of the catalyst was dissolved in methanol in a conical flask while gently warming the mixture. This mixture was then added to preheated 50 g of RSO in another conical flask, placed on a temperature-controlled magnetic stirrer. The stirring rate was kept constant, and the flask was well insulated to prevent methanol evaporation during the reaction.

After the reaction, the catalyst was filtered out, and the mixture was separated into two layers: the top layer with biodiesel, and the bottom layer containing glycerol in a separating funnel. To remove any remaining traces of methanol, glycerol, unreacted triglycerides, diglycerides, monoglycerides, and acids, the biodiesel underwent a washing process with warm distilled water until the rinse water became clear. Finally, the purified biodiesel was dried in an oven.

The biodiesel yield was calculated using the Equation;

$$\text{Biodiesel yield (wt \%)} = \frac{\text{amount of biodiesel produced (g)}}{\text{amount of rubber seed oil (g)}} \times 100 \quad \dots (1)$$

Experiment Design

The study utilized Response Surface Methodology (RSM) with Box-Behnken Design (BBD) in Design Expert 13 to examine the effects of four process variables (methanol/oil ratio, catalyst loading, reaction temperature, and reaction time) on biodiesel yield. Table 1 shows the coded and

¹⁹ Li, F. J., Li, H. Q., Wang, L. G., & Cao, Y. (2015). Waste carbide slag as a solid base catalyst for effective synthesis of biodiesel via transesterification of soybean oil with methanol. *Fuel Processing Technology*, 131, 421–429. <https://doi.org/10.1016/j.fuproc.2014.12.018>

²⁰ Obahiagbon, K., & Ahonkhai, D. O. (2023). Optimized Biodiesel Production from Waste Cooking Oil Using Nickel (II) Nitrate Doped Chicken Manure as Catalyst. *European Journal of Applied Sciences*, 11(3), 812–824. <https://doi.org/10.14738/AIVP.113.14891>

actual levels of these variables, along with their ranges. Equation (2) represents a quadratic regression model fitted to data from 29 experimental runs in the BBD analysis.

The model terms were determined through multiple regression analysis, and their significance was assessed using analysis of variance (ANOVA);

$$Y = \beta_0 + \sum_{i=1}^p \beta_i X_i + \sum_{i=1}^p \sum_{j=1}^p \beta_{ij} X_i X_j + \sum_{i=1}^p \beta_{ii} X_i^2 + e_i \quad \dots (2)$$

Where Y is the dependent variable (Biodiesel yield),

X_i and X_j represent the independent variables.

β_0 is the offset term,

β_i and β_{ij} are the single and interaction effect coefficients and

e_i is the experimental error term²¹.

Table 1 shows the range of input factors for Box-Behnken design.

Table 1: Range of Input factors for Box-Behnken design.

Process variables	Units	Factor	Coded Low	Mean	Coded High
Methanol/oil ratio	Mol/mol	A	6	12	18
Reaction time	min	B	60	75	90
Reaction temperature	°C	C	50	60	70
Catalysts loading	wt. %	D	1	3	5

Results and Discussion

Physical Properties of Extracted RSO

The physical properties of the extracted RSO determined using the AOAC procedure are shown in Table 2

Table 2: Physical properties of extracted RSO

Property	Value
Saponification value (mg/KOH/g)	184
Acid Value	22.8
FFA value (%)	11.4
Density @ 30°C (g/cm ³)	0.83
Specific gravity @ 30°C	0.83
Viscosity @ 40°C (mm ² /s)	38.2

²¹ Amenaghawon, A. N., Evbarunegbe, N. I., & Obahiagbon, K. (2021). Optimum biodiesel production from waste vegetable oil using functionalized cow horn catalyst: A comparative evaluation of some expert systems. *Cleaner Engineering and Technology*, 4, 100184. <https://doi.org/10.1016/J.CLET.2021.100184>

Catalysts Characterization

X-Ray Fluorescence (XRF) Analysis

Table 3 shows XRF analysis results for precursors and the doped catalyst, revealing the metallic oxides in these materials. CaO was the major constituent in all three. The doped catalyst had a higher concentration of active agents (CaO, Fe₂O₃, and NiO) for transesterification, while silicon oxide and other acidic oxides like phosphorous oxide (P₂O₅) offered active sites for esterification, making it a bi-functional catalyst for biodiesel production²².

Table 3: XRF analysis results

Constituents	Concentration (%)		
	Pig bones	Carbide slag	Doped catalyst
Silicon oxide (SiO ₂)	0.093	3.760	1.723
Vanadium pentoxide (V ₂ O ₅)	0.026	0.017	0.002
Chromium oxide (Cr ₂ O ₃)	0.000	0.031	0.005
Manganese oxide (MnO)	0.032	0.013	0.006
Iron (iii) oxide (Fe ₂ O ₃)	0.262	0.205	11.476
Cobalt tetraoxide (Co ₃ O ₄)	0.070	0.072	0.070
Nickel oxide (NiO)	0.004	0.017	0.004
Copper oxide (CuO)	0.030	0.033	0.040
Niobium pentoxide (Nb ₂ O ₃)	0.005	0.000	0.011
Molybdenum trioxide (MoO ₃)	0.023	0.018	0.000
Tungsten oxide (WO ₃)	0.010	0.000	0.015
Phosphorus oxide (P ₂ O ₅)	31.638	0.000	10.826
Trioxosulphate (SO ₃)	0.300	0.376	2.841
Calcium oxide (CaO)	63.797	84.140	61.736
Magnesium oxide (MgO)	0.498	3.868	0.000
Potassium oxide (K ₂ O)	0.254	0.000	1.806
Barium oxide (BaO)	0.027	0.036	0.145
Aluminum oxide (Al ₂ O ₃)	1.779	6.570	1.700
Tantalum pentoxide (Ta ₂ O ₅)	0.018	0.017	0.032
Titanium oxide (TiO ₂)	0.000	0.041	0.090
Zinc oxide (ZnO)	0.027	0.005	0.006
Chlorine (Cl)	0.759	0.462	0.321
Zirconium oxide (ZrO ₂)	0.021	0.008	0.985

²² Weldehlase, M. G., Benti, N. E., Desta, M. A., & Mekonnen, Y. S. (2023). Maximizing biodiesel production from waste cooking oil with lime-based zinc-doped CaO using response surface methodology. *Scientific Reports*, 13(1), 4430. <https://doi.org/10.1038/s41598-023-30961>

Scanning Electron Microscope (SEM) Analysis

The SEM analysis of the precursors and doped catalyst's structure is illustrated in Figures 1(a), 1(b), and 1(c). The pore configuration displayed irregularities, as observed in the SEM images. A noticeable difference can be discerned when comparing the SEM images before and after impregnation. Specifically, the doped catalyst exhibits a greater amount of accessible pore space compared to the pure catalysts. This phenomenon can be attributed to the use of promoters such as strontium nitrate and iron (III) chloride during the impregnation process.

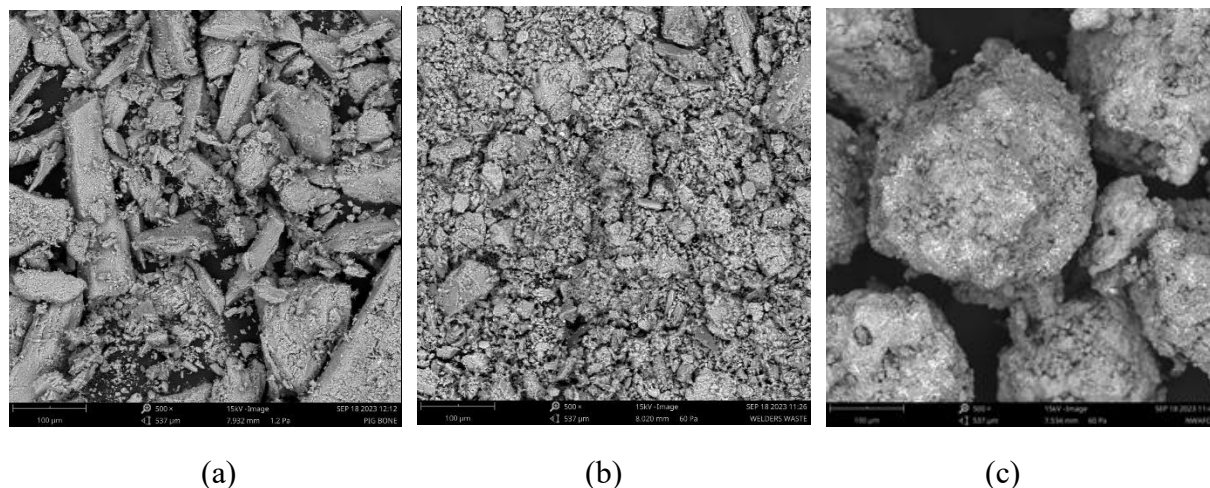
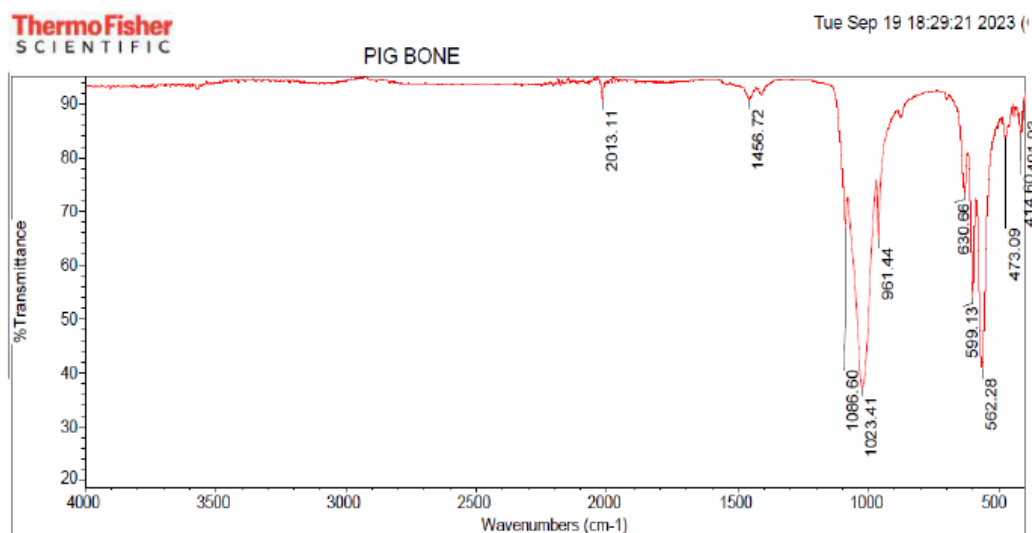


Figure 1: SEM Images of (a) Pig bone, (b) Carbide slag, and (c) Doped catalyst

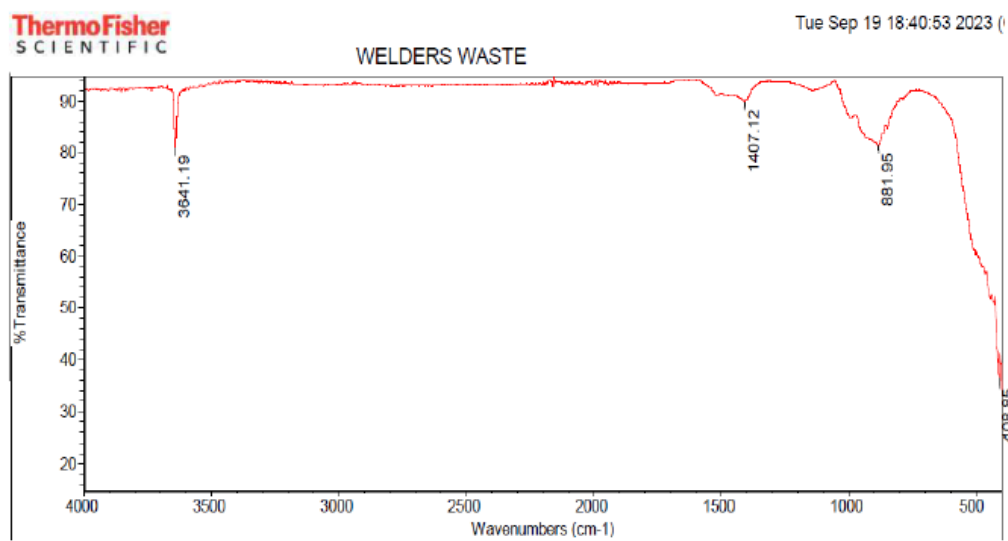
Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectra of the doped catalyst spectrum as shown in Figure 2, a distinctive peak at 558.85 cm^{-1} corresponds to the presence of metallic oxide (CaO). Peak at 674.31 cm^{-1} is typically associated with rocking vibrations of methylene (CH_2) groups in aliphatic compounds, it suggests the presence of saturated hydrocarbons or aliphatic chains, and peak at 1027.95 cm^{-1} is related to C-O stretching vibrations. It indicates the presence of ether (C-O-C) groups or ester (C-O) groups.

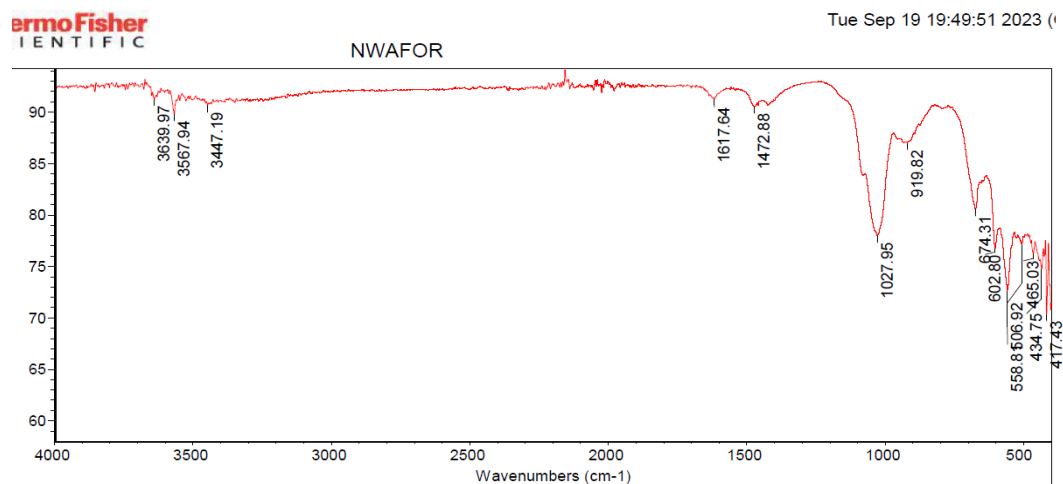
OPTIMIZATION OF BIODIESEL PRODUCTION FROM RUBBER SEED OIL USING A BIFUNCTIONAL CATALYST DERIVED FROM CARBIDE SLAG AND PIG BONES



(a)



(b)



(c)

Figure 2: FTIR result for (a) Pig bone, (b) Carbide slag, and (c) Doped catalyst

Brunauer-Emmett-Teller (BET) Analysis

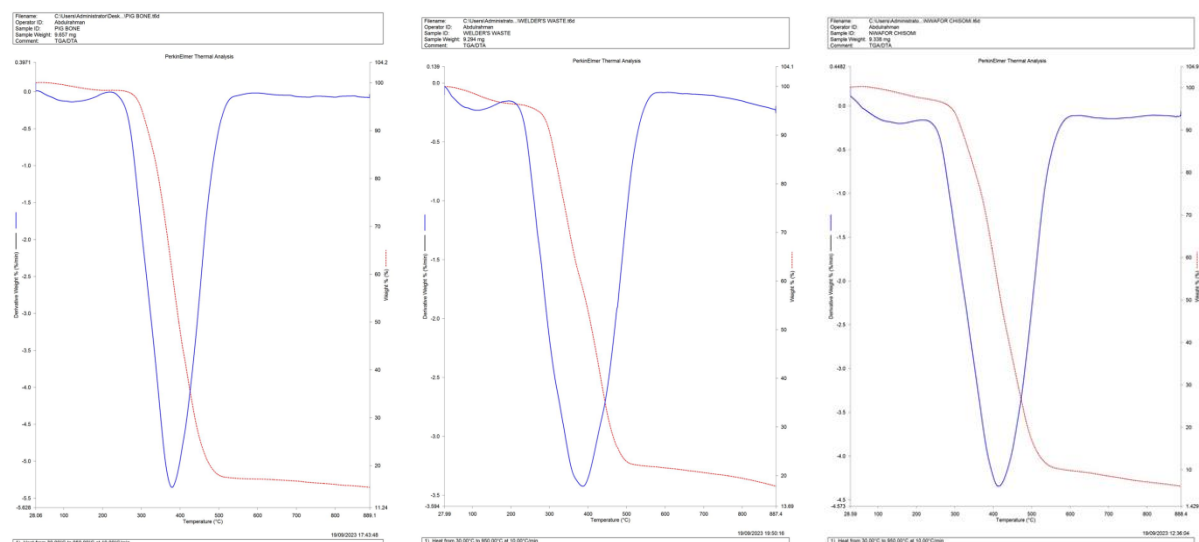
The surface area BET analysis of the doped catalyst reveals a multi-point BET analysis result of $393 \text{ m}^2/\text{g}$, indicating a substantial specific surface area. This suggests that the catalyst possesses a significant active surface available for catalytic reactions. Notably a comparison with the precursors (Pig bone and Carbide slag) reveals distinct surface characteristics, the surface areas of the precursors yield results of $239.1393 \text{ m}^2/\text{g}$ and $433.1393 \text{ m}^2/\text{g}$ respectively.

The variation in the surface area of the precursors highlights the transformation and restructuring occurring during the catalyst's synthesis process, influencing the final catalyst's surface area. The increase in surface area from precursor to catalyst suggests a successful doping process, potentially enhancing the catalyst's efficacy in catalyzing reactions.

Thermogravimetric Analysis (TGA)/ Differential Thermal Analysis (DTA)

The TGA/DTA analysis results for pig bone, carbide slag and the catalyst are shown in Figure 3. In Figure 3 (a), the pig bone exhibited a substantial weight decrease between 300°C and 500°C . Figure 3 (b) indicates significant weight loss for the carbide slag between 350°C and 550°C , while Figure 3 (c) shows the catalysts experiencing notable weight loss between 300°C and 550°C . These weight reductions may be attributed to the elimination of the organic materials during the drying and calcination process. The DTA curve peaks around 600°C for all samples, and beyond 600°C , the material's weight reduction is not substantial. The elevated temperature is crucial for activating constituents within the materials.

OPTIMIZATION OF BIODIESEL PRODUCTION FROM RUBBER SEED OIL USING A BIFUNCTIONAL CATALYST DERIVED FROM CARBIDE SLAG AND PIG BONES



(a)

(b)

(c)

Figure 3: TGA Analysis for (a) Pig bone, (b) Carbide slag, and (c) Doped catalyst

Modelling and Optimization of Biodiesel Yield

The actual values of the factors A (Methanol/oil ratio), B (Reaction time), C (Reaction temperature) and D (Catalyst loading) as designed by Box-Behnken design of Design expert 13 software and the corresponding response (predicted and actual values) are shown in Table 4.

Table 4: Transesterification experimental design and biodiesel yield

Run	Factor 1	Factor 2	Factor 3	Factor 4	Biodiesel Yield	Predicted Yield
	A: Methanol/oil ratio	B: Reaction time	C: Reaction temp.	D: Catalyst loading		
	mol/mol	mins	°C	wt. %	%	%
1	12	75	70	1	75.6	76.26
2	12	90	50	3	82.8	83.89
3	12	75	60	3	81.7	82.66
4	12	60	60	1	90.5	88.39
5	18	75	50	3	75.4	74.70
6	18	60	60	3	77.8	78.56
7	12	60	70	3	73.9	74.47
8	12	75	60	3	83.8	82.66
9	18	90	60	3	82	79.43
10	12	75	60	3	82.5	82.66
11	6	75	60	5	85.5	85.89
12	6	75	60	1	92.6	91.87
13	12	75	50	5	82.5	80.83
14	18	75	60	5	73.4	75.79
15	12	60	50	3	85.3	86.07

16	12	75	60	3	83.1	82.66
17	12	75	50	1	86.5	86.51
18	18	75	70	3	70.5	69.35
19	12	60	60	5	85	83.45
20	6	90	60	3	91.5	89.73
21	12	90	60	1	87.4	88.30
22	12	75	70	5	73.2	72.18
23	6	75	50	3	89.5	90.00
24	18	75	60	1	78.3	79.57
25	12	90	70	3	75.7	76.59
26	6	60	60	3	89.1	90.66
27	12	90	60	5	82	83.47
28	12	75	60	3	82.2	82.66
29	6	75	70	3	76.4	76.45

Table 5: Analysis of variance (ANOVA) for a quadratic model of biodiesel yield

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	962.27	14	68.73	22.64	< 0.0001	significant
A-Methanol/oil ratio	376.32	1	376.32	123.96	< 0.0001	
B-Reaction time	0.0033	1	0.0033	0.0011	0.9740	
C-Reaction temp.	267.91	1	267.91	88.25	< 0.0001	
D-Catalyst loading	71.54	1	71.54	23.57	0.0003	
AB	0.8100	1	0.8100	0.2668	0.6135	
AC	16.81	1	16.81	5.54	0.0338	
AD	1.21	1	1.21	0.3986	0.5380	
BC	4.62	1	4.62	1.52	0.2375	
BD	0.0025	1	0.0025	0.0008	0.9775	
CD	0.6400	1	0.6400	0.2108	0.6532	
A²	0.7795	1	0.7795	0.2568	0.6202	
B²	33.67	1	33.67	11.09	0.0050	
C²	142.32	1	142.32	46.88	< 0.0001	
D²	6.05	1	6.05	1.99	0.1799	
Residual	42.50	14	3.04			
Lack of Fit	39.85	10	3.98	6.01	0.0493	significant
Pure Error	2.65	4	0.6630			
Cor Total	1004.77	28				

The obtained data were evaluated using analysis of variance (ANOVA) to fit a quadratic response surface model using the least squares method, assessing the model's quality. With a model F -value of 22.64 and a p -value < 0.0001, the fitted model proved highly significant, indicating reliability in predicting biodiesel yield percentage. The quality of model fit is assessed by the coefficient of determination (R^2). The fit statistics data showed that the R^2 and adjusted R^2 values were 0.9577 and 0.9157 respectively. The difference of less than 0.2 indicates that the

predicted R^2 and adjusted R^2 values corresponds. Therefore, this model could be used in the theoretical prediction of the biodiesel production process.

An empirical model showing the mathematical relationship between the independent variables considered and the biodiesel yield from the transesterification process of RSO is given by Equation (3) in terms of coded units.

$$\begin{aligned} \text{Yield}(\%) = & 82.66 - 5.60A - 0.0167B - 4.73C - 2.44D + 0.4500AB + 2.05AC \\ & + 0.5500AD + 1.07BC + 0.0250BD + 0.4000CD - 0.3467A^2 + 2.28B^2 \\ & - 4.68C^2 + 0.9658D^2 \dots (3) \end{aligned}$$

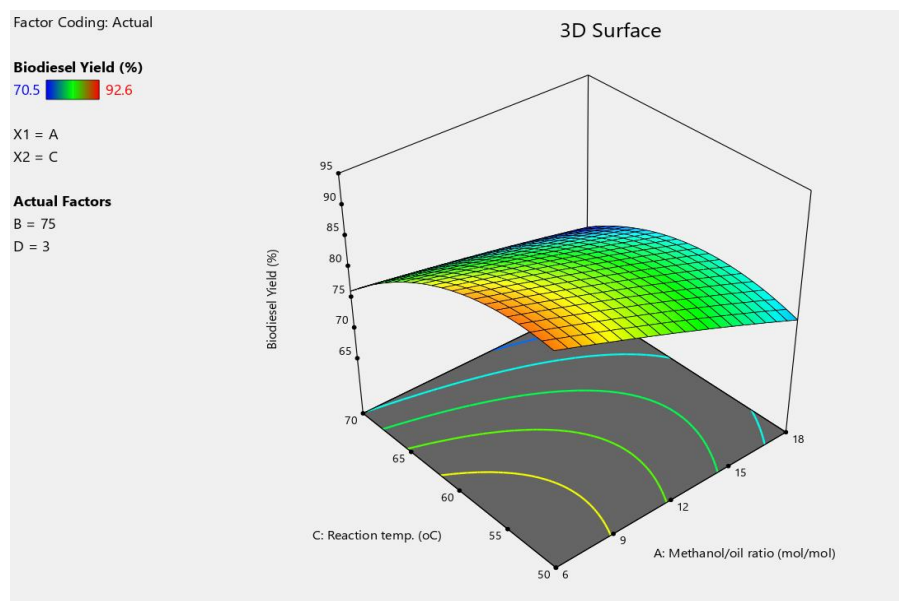
The positive sign of the coefficients in Equation (3) indicates the synergistic effect, whereas the negative sign suggests an antagonistic effect. It was observed from Equation (3) that all individual operating variables methanol/oil ratio (A), reaction time (B), reaction temperature (C), and catalyst loading (D) and some quadratic factors (A^2 and C^2) have negative effects on the percentage biodiesel yield, while all interaction factors (AB, AC, AD, BC, BD and CD) and some quadratic factors (B^2 and D^2) had positive effects on the percentage biodiesel yield from the transesterification of RSO.

3.3.1 Effects of interaction of process variables on biodiesel yield

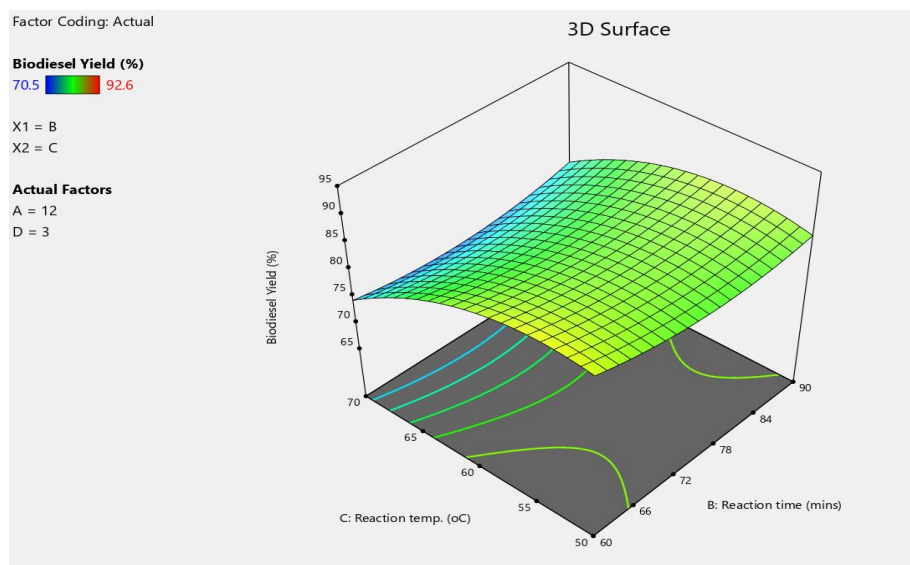
Response surface curves were utilized to assess the impact of various process variables on biodiesel yield and identify optimal variable levels. This involved creating 3D response surfaces using a regression model. Figure 4(a) illustrates the relationship between biodiesel yield, methanol/oil ratio, and reaction temperature. An increase in methanol/oil ratio led to reduced biodiesel yield, with the highest yield at 6:1. For reaction temperature, an initial increase improved yield up to 60°C, but further temperature rise reduced yield, possibly due to methanol evaporation.

Figure 4(b) shows the relationship between biodiesel yield, reaction time, and reaction temperature. Biodiesel yield increased with longer reaction times, but after 75 minutes, the increase became less significant.

In Figure 4(c), biodiesel yield, catalyst loading, and reaction temperature are considered. Lower catalyst loading favored the reaction, with only 1 wt.% catalyst needed for a maximum yield of 91.5%.

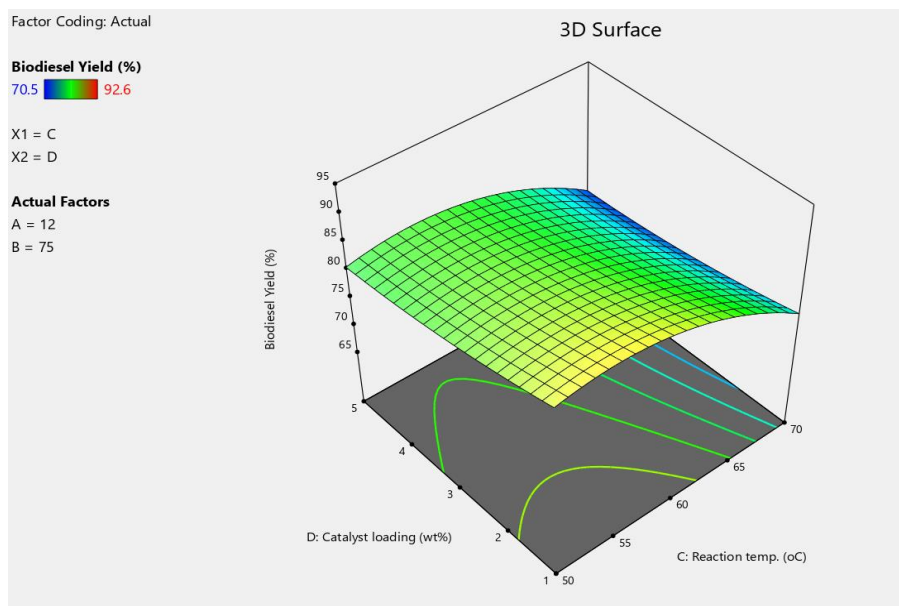


(a)



(b)

OPTIMIZATION OF BIODIESEL PRODUCTION FROM RUBBER SEED OIL USING A BIFUNCTIONAL CATALYST DERIVED FROM CARBIDE SLAG AND PIG BONES



(c)

Figure 4: 3D plots showing the interaction between (a) Reaction temperature and Methanol/oil ratio, (b) Reaction temperature and Reaction time and, (c) Catalyst loading and Reaction temperature

Analysis of Physicochemical Properties of Biodiesel

The properties of biodiesel produced at the optimized conditions were compared with ASTM D6751 and EN 14214 standards as given in Table 6.

Table 6: Physiochemical properties of biodiesel produced

Biodiesel Properties	ASTM D6751	EN 14214	Values obtained
Viscosity at 40°C (mm ² /s)	1.9 – 6.0	3.5 – 5.0	4.7
Density at 15°C (kg/m ³)	>880	860 – 900	876.5
Flashpoint (°C)	100 – 170	–	219
Acid number (mg KOH/g)	0.5 max	0.50 max	0.45

Conclusion

The successful synthesis of a heterogeneous bi-functional catalyst from welder's waste and pig bones enabled simultaneous esterification and transesterification of Rubber seed oil (RSO) for biodiesel production. This catalyst demonstrated remarkable activity in facilitating the transesterification of RSO-containing free fatty acids, resulting in a high biodiesel yield. Comprising essential metallic oxides like CaO, Fe₂O₃, P₂O₅, and SO₃, the catalyst exhibited enhanced catalytic performance. Notably, its tolerance to high free fatty acid levels positions it as a promising alternative to conventional catalysts. Utilizing response surface methodology (RSM), the study achieved a R^2 of 0.9577, underscoring RSM's effectiveness in optimizing the

biodiesel production process. The physical properties of the produced biodiesel adhered to American Standards for Test and Method (ASTM) specifications, confirming its suitability for various applications.

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