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Biodiesel Production from Used Cooking Oil over Nickel-modified Calcium Phosphate Scum (Ni-CaPs) Catalyst from the Sugar Refining Industry

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ABSTRACT: The increasing global energy demand has sparked a search for sustainable fuel sources. Biodiesel from organic waste offers a promising solution to reduce carbon emissions. Hence, the objective of this paper was to synthesize biodiesel production from used cooking oil using nickel-modified calcium phosphate scum (Ni-CaPs) from sugar refining industry as a catalyst. X ray diffraction analysis revealed the crystalline structure of CaO, NiO, and SiO_2. X-ray fluorescence showed a composition of 50.316 % CaO, 4.61 % NiO, and 18.60 % SiO_2. Fourier Transform Infrared spectroscopy identified functional groups associated with C-N, C-Cl, and C-H stretching bonds. Scanning Electron Microscopy and Energy Dispersive X-ray analysis confirmed the catalyst's morphological and compositional properties. Response Surface Methodology (RSM) optimized the reaction conditions: 55°C, 90 mins, 1 wt. % catalyst loading, and 12:1 methanol-to oil molar ratio. This yielded 93.2 % biodiesel, with an R^2 value of 0.9886. The Ni-CaPs catalyst offers cost-effectiveness, simple synthesis process, stability, and widespread availability of raw materials. This study demonstrates the potential of Ni-CaPs as a sustainable, efficient catalyst for biodiesel production from waste materials, contributing to a more environmentally friendly energy solution.

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The advancement of society has been significantly influenced by diverse energy sources. However, there is a growing need to replace fossil fuels with sustainable alternatives due to the adverse societal effects of their overexploitation, such as climate change, biodiversity loss, and greenhouse gas (GHG) emissions *(*Grönman *et al., 2019)*. Consequently, sustainable biofuels like bioethanol and biodiesel are garnering research interest as alternatives to traditional energy sources. Renewable energy sources are deemed capable of satisfying global energy demands without inflicting environmental harm associated with fossil fuel usage *(*Ang *et al., 2022)*. Production of biodiesel commercially is rooted in the elevated production expenses relative to fossil diesel, notwithstanding its diverse advantages. A crucial aspect in achieving cost-competitive biodiesel production involves the selection of an economical feedstock (triglyceride origin), the use of cost-effective reaction enhancers (catalyst and acyl-acceptor), and optimization of entire production process to increase efficiency. Sources of triglycerides that are affordable and useful for biodiesel synthesis have been researched for a range

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of substitute feedstock. For example, the utilization of used loquat seed oil has been scrutinized within this framework *(*Al-Muhtaseb *et al., 2021),* used cooking oils (UCO) *(*Catarino *et al., 2020),* waste date seed oil *(*Al-Mawali *et al., 2021),* etc. More specifically, UCO are discarded in the soil, drainage system, or trash can *(*Lopes *et al., 2019).* This sewage contributes to several environmental issues. (Kanagawa 2019). The utilization of UCO as feedstock to produce biodiesel has the potential to make the process extremely economical. Unlike edible oils, used cooking oil (UCO) is very attainable, does not pose an ecological risk, and eliminates the fuel and food competition. The primary setback associated with the utilization of UCO results from the difficulty in the transesterification process, as a result of the free fatty acid (FFA) resulting in exceedingly difficult response *(*Bardhan *et al., 2022).* Therefore, UCO requires pre-treatment by esterification with an acid (Van der Bruggen 2010) *(*Talebian-Kiakalaieh *et al., 2013)* before it can be employed for the transesterification reaction process to product biodiesel *(*Sindhu *et al., 2015).* The production of biodiesel involves the generation of fatty acid alkyl esters through transesterification of triglycerides obtained from animal fats or based oils. This chemical transformation takes place by introducing a short-chain alcohol and various catalysts *(*Boey *et al., 2011a;* Kouzu and Hidaka 2012*).* Catalysts, both homogeneous and heterogeneous, are engaged in a crucial role in facilitating the transesterification process *(*Pasae *et al., 2020).* Nonetheless, severe disadvantages are attached to using homogeneous catalysts for producing biodiesel, including issues with catalyst recovery and significant waste and water effluent generation *(*Zhang *et al., 2022)* . Utilizing heterogeneous catalysts can help to lessen these challenges with metal oxides like calcium oxide (Kouzu and Hidaka 2012) being extensively studied. Although, heterogeneous catalysts resolve several technological and environmental concerns, their commercial viability is hindered by high costs and complexity in production (Chouhan and Sarma 2011). Extensive research has been conducted over the past few years to ascertain the high-performance heterogeneous catalyst that not only demonstrates cost-effectiveness but also aligns with environmental sustainability principles. Using waste products as possible heterogeneous catalysts in the context of advancing sustainable practices represents a comparatively novel advancement in the energy and catalysis field *(*Nurfitri *et al., 2013).* Other mixed oxides have been employed as catalysts for the esterification and transesterification of oils and fats. For instance, sulphate-treated metal oxides, such as SO_4^{2-}/SnO_2 *(*Furuta *et al., 2004),* SO_4^{2-}/TiO_2 (Alaya and Rabah 2017) and SO_4^{2-}/ZrO_2 *(*Laosiripojana *et al., 2010)* have been utilized for the esterification of high-acid oils and FFAs. Consequently, there is growing interest in transition metal oxides like titanium, zinc, and zirconium oxides within the scientific community. Common solid acid catalysts such as sulfurated and tungstate-zirconia are employed for converting triglycerides into fatty acid alkyl esters (Clark 2003). Limited research exists on the utilization of calcium oxide (CaO) catalyst derived from waste materials for biodiesel production. Nevertheless, a few research on the extraction of CaO from different sources exist, they include CaO from waste capiz shells (Amusium cristatum) *(*Suryaputra *et al., 2013),* waste cockle shells (Anadara granosa) *(*Boey *et al., 2011b),* Mereterix mereterix *(*Nair *et al., 2012),* chicken eggshells *(*Khemthong *et al., 2012),* waste shells of Turbonilla striatula *(*Boro *et al., 2011),* oyster shells *(*Jairam *et al., 2012),* concrete waste *(*Osazuwa *et al., 2024)* and snails *(*Birla *et al., 2012).* The sugar refining industry generates industrial residues like calcium phosphate scum, which can serve as catalysts in biodiesel synthesis. The industry also produces considerable waste, including calcium phosphate scum. The high moisture content, foul smell, and attractiveness to insects make it difficult to handle *(*George *et al., 2010),* and there is also a risk of severe water contamination.

This research investigates the synthesis of a bi-functional catalyst from calcium phosphate scum and nickel nitrate for enhanced transesterification of used cooking oil to biodiesel, aiming to mitigate carbon footprint. Hence, the objective of this paper was to produce biodiesel from used cooking oil using nickel-modified calcium phosphate scum (Ni-CaPs) from sugar refining industry as a catalyst.

MATERIALS AND METHODS

Pre-treatment of UCO: The used cooking oil (UCO) sourced from local cafeteria was utilized in this research. The collected UCO had a high-water content and some food remnants. To eliminate solid particles, soluble salts, and moisture, the UCO was pre-treated and filtered using the procedure as adopted from literature *(*Amenaghawon *et al., 2021).*

Catalyst Preparation: The Calcium Phosphate Scum (CaPs) utilized as a catalyst precursor was gathered from within a sugar refining industry in Lagos State, Nigeria. Subsequently, the sample was dried for approximately 72 h, crushed, and sieved to obtain a 100 μm particle size distribution (Aghabarari and Martinez-Huerta 2016). The crushed powder precursor was calcined at 900 ℃ for 2 h, before then

transferred to a desiccator. The heat treatment was carried out to prevent the transformation of CaO into $CaCO_3$ (Aghabarari and Martinez-Huerta 2016). Adopting the wet impregnation technique, the bifunctional catalysts containing a 10 wt.% Ni on CaO were formulated *(*Weldeslase *et al., 2023)*. 400 mL of distilled water was utilized for dissolving the calcined calcium phosphate scum (now CaO composite), which was subsequently homogenized by the use of a magnetic stirrer. After a period of 10 mins, the precise quantity of Nickel (II) nitrate $(NiNO_3)_2$ was integrated into the mixture. Once a viscous fluid was generated, the resultant mixture was oven dried for 1 h, calcined at 900℃ for 1 h and then transferred to a desiccator for storage *(*Teo *et al., 2018)*.

Catalyst Characterization: The physicochemical properties of the synthesized catalyst were analysed using various known conventional techniques. The utilization of energy-dispersive X-ray technology and scanning electron microscopy (SEM-EDX) was employed to closely monitor the surface structure and element composition of the synthesized catalyst. X-ray fluorescence (XRF) was carried out to evaluate the composition of oxides in the catalyst. Brunauer, Emmett, and Teller (BET) investigations were utilized to gather data on surface area and pore characteristics. X-ray diffraction (XRD) examination ascertained the crystallite structure while fourier transform infrared (FTIR) spectroscopy was used to examine the configuration of chemical bonds and molecular interactions.

Biodiesel production and characterization: Considering the low acid value of the oil and the heterogeneous catalyst bifunctionality, a single-step transesterification procedure was implemented to produce biodiesel. A reflux condenser was integrated into a three-necked 250 mL glass reactor to introduce a precisely measured amount of UCO. The setup was heated to a specific temperature and placed on a hot plate with a magnetic stirrer. Upon the incorporation of methanol into the oil, accompanied by a stirring period of about 5 mins, the catalyst was subsequently introduced to commence the reaction for the specified period. The experimental framework dictated the fixed catalyst concentration, reaction temperature, methanol-to-oil molar ratio, and reaction duration (El-Gendy *et al., 2014)*. A filter was utilized to separate the catalyst and liquid post-completion of the reaction. Subsequently, the liquid underwent separation in a separating funnel and was allowed to settle overnight. The superior layer, comprising biodiesel and residual methanol, was introduced to a hot water wash to evaporate the excess methanol, whereas the lower stratum, which held glycerol, was poured off. Following this, the biodiesel was preserved for further examination. The biodiesel yield was obtained utilizing Eq. (**Error! Reference source not found.**) *(*Amenaghawon *et al., 2022)*. The physicochemical properties (density, viscosity, moisture content, acid value) and fuel characteristics (flash point, cetane number, and pour point) of the produced biodiesel were evaluated using established methodologies (Helrich 1990). Via gas chromatography-mass spectroscopy (GC-MS) examination, the fatty acid composition of the biodiesel was ascertained. The biodiesel yield was calculate by equation 1.

$$\text{Biodiesel Yield} = \frac{\text{Mass of biodiesel produced}}{\text{mass of UCO}} \times 100 \quad (1)$$

Design of experiment and RSM modelling: In the transesterification procedure, a Box-Behnken design (BBD) consisting of four different parameter ranges were employed as follows, reaction temperature (X1): (-1: 40, 0: 55, 1: 70) ℃, reaction time (X2): (-1: 60, 0: 75, 1: 90) mins, catalyst loading (X3): (1: 1, 0: 3, 1: 5) wt.%, and methanol-to-oil molar ratio (X4): (1: 6, 0: 12, 1: 18). The specified ranges for these input parameters were determined through preliminary experiments and relevant literature (Balajii and Niju 2019). Given the prevalence of quadratic responses in chemical engineering processes, this design was chosen due to its appropriateness for this application *(*Chitsaz *et al., 2018)*. A quadratic regression model, denoted by Eq. (**Error! Reference source not found.**), matched the data obtained from 29 experimental runs generated through BBD. Model term calculation was carried out through several regression analyses, with analysis of variance (ANOVA) utilized to ascertain the usefulness of the model terms.

Design Expert software was used to carry out the experimental design and the corresponding statistical analysis.

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i X_i + \sum b_{ii} X_i^2 + e_i \quad (1)$$

Where; The dependent variable (biodiesel yield) is represented by Y, while X_i and X_j denote the independent variables. The offset term is b_o, the single and interaction effect coefficients are bi and b_{ij}, and the experimental error term is e_i; this methodology was adapted from *(*Shegun *et al., 2022)*.

RESULTS AND DISCUSSION

Characterization of waste cooking oil: The characteristics of the UCO was pre-determined and all values obtained as: 2.5950 mg $KOHg^{-1}$ oil for acid value, FFA of 1.2975 %, moisture content of 0.0200 %, 29.5000 mPa.S for dynamic viscosity @ 40℃, saponification value of 300.1350 mg KOH g^{-1} oil, 903.0000 kg m^{-3} for density @ 40 ℃, and specific gravity of 0.9127. Using the Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration and Standard Test Method for Saponification Number of Petroleum Products (American Society for Testing and Materials (ASTM) D664 and (ASTM) D94), the acid value and saponification value were calculated and used to derive the relative molecular mass (M) 565.638 g mol^{-1}, which was comparable to literature *(*Abubakar *et al., 2016).* These values represent the physicochemical characteristics of the UCO employed prior to the experimental reaction.

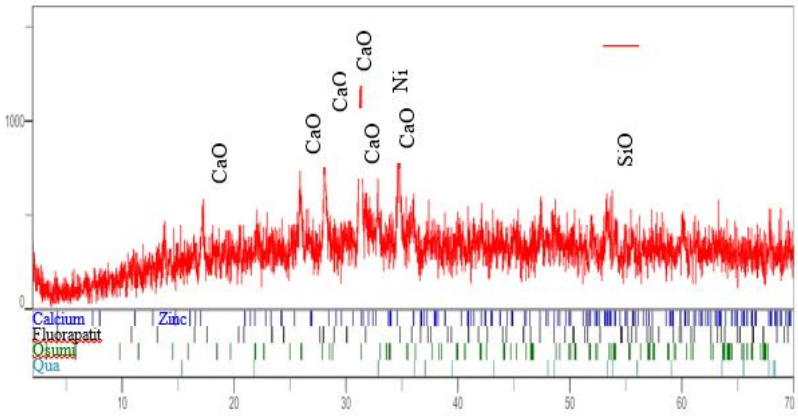

Fig. 1: XRD pattern of the Ni-modified calcium phosphate scum (Ni-CaPs) catalyst

Characterization of the Ni-modified calcium phosphate scum (Ni-CaPs) catalyst X-ray Diffraction (XRD) Analysis: **Error! Reference source not found.** represents the crystalline structure and phase transition of the synthesized Ni-modified calcium phosphate scum (Ni-CaPs) catalyst analysed using the XRD analyser. The crystalline structure of the active component, calcium oxide (CaO), displays distinct peaks at 2θ of 17.20°, 25.90°, 28.10°, 31.29°, 32.05°, and 32.83° representing the presence of CaO, while 34.73° and 53.31° represent the presence of Ni and SiO respectively.

X-ray Fluorescence (XRF) Analysis: XRF analysis was carried out to determine the chemical composition of the Ni-modified calcium phosphate scum (Ni-CaPs) catalyst and the result is tabulated in **Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.**

Table **1**. Oxides like calcium oxide (CaO), nickel oxide (NiO), silica (SiO_2), and alumina (Al_2O_3), each having distinct catalytic properties essential for biodiesel production were present. As evident, the basic nature of CaO and the acidic attributes of NiO play vital roles in the catalytic process *(*Moradi *et al., 2014).* The presence of NiO can be attributed to the doping procedure employed during the preparation, thereby enhancing the catalyst's acidic strength. Nickel (Ni) doping was intended to increase the catalyst activity by augmenting catalytic sites, thereby promoting esterification and transesterification reactions *(*Teo *et al., 2014).* Specifically, NiO promotes the esterification reaction, while CaO facilitated the transesterification reaction (Kouz and Hidaka 2012).

Table 1: XRF analysis of synthesized catalyst

Component	Concentration (%)
SiO_2	18.60
V_2O_5	0.251
Cr_2O_3	0.038
MnO	0.046
Fe_2O_3	1.481
Co_3O_4	0.008
NiO	4.610
CuO	0.039
Nb_2O_3	0.016
WO_3	0.002
P_2O_5	0.000
SO_3	0.255
CaO	50.316
MgO	0.000
K_2O	0.010
BaO	0.174
Al_2O_3	18.406
Ta_2O_5	0.032
TiO_2	4.760
ZnO	0.005

Ag_2O	0.008
Cl	0.837
ZrO_2	0.104
SnO_2	0.000

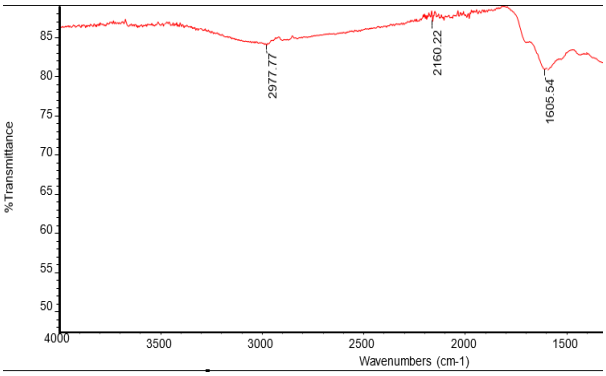

Fig. 2, revealed several absorption peaks depicting different functional groups on the catalyst surface. Significantly, peaks at 2160.22 cm^{-1}, 1057.90 cm^{-1}, and 792.72 cm^{-1} were found to be associated with C-N, C-Cl, and C-H stretching bond, respectively, and

Fourier Transform Infrared (FTIR) Analysis: The catalyst surface was subjected to Fourier transform infrared (FTIR) analysis to determine its functional groups. The results, shown in **Error! Reference source not found.Error! Reference source not found.**

the principal peak was observed at 2977.77 cm^{-1}, which was related with O-H stretching bonds previously reported in literature and synthesized from catalysts made from animal bones *(*Chingakham *et al., 2019).*

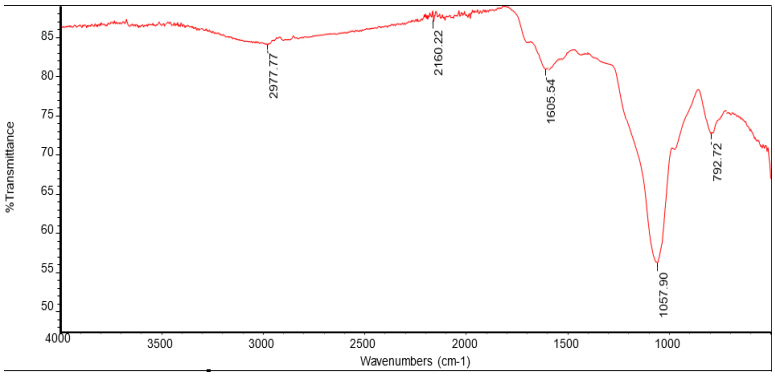

Fig. 2: FTIR spectra of the prepared catalyst

Scanning Electron Microscopy (SEM) Analysis: The morphological properties of the synthesized Ni-modified calcium phosphate scum (Ni-CaPs) catalyst utilized during the transesterification process is shown in

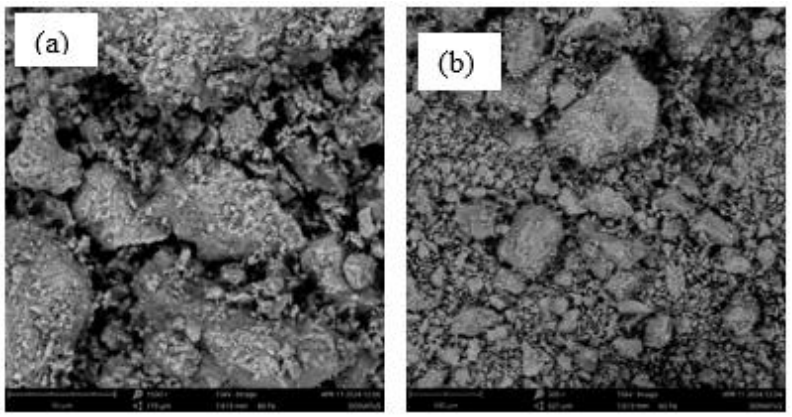

Fig. 3**Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.**. The SEM image demonstrates the presence of non-uniform voids within the composite material. The heterogeneous nature of the catalyst material characterized by varying composition and surface properties can be attributed to the uneven distribution of catalytic pores *(*Okoduwa *et al., 2024)*.

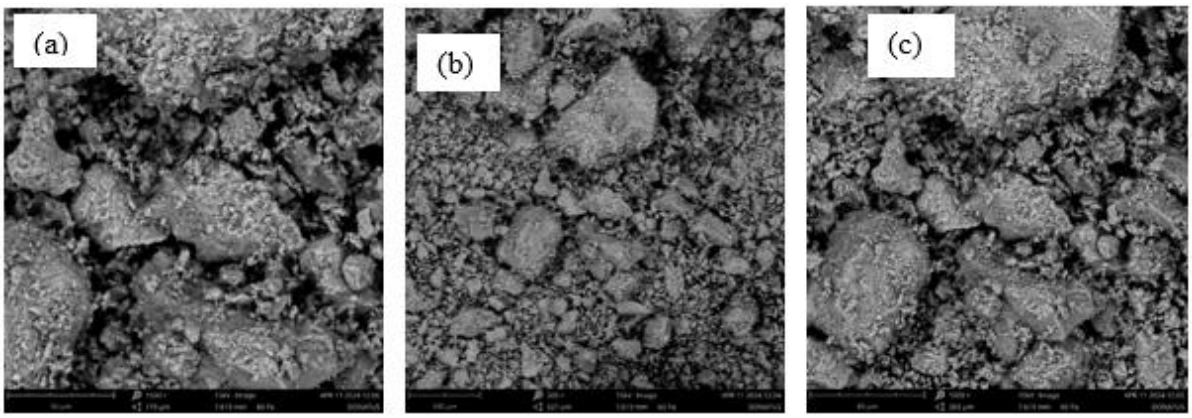

Fig. 3: SEM analysis of the synthesized Ni-modified calcium phosphate scum (Ni-CaPs) catalyst (a) ×500 (b) ×1000 (c) ×1500

Energy Dispersive X-ray (EDX): The Energy Dispersive X-ray (EDX) provided details of the compositions of the Ni-modified calcium phosphate scum (Ni-CaPs) catalyst. Substantial amounts of calcium (62.67%), phosphorus (25.99%), iron (5.23%), and silicon (3.00%) were detected in the catalyst. Due to their high reactivity, these metals likely contribute to the enhanced catalytic performance of the Ni-modified calcium phosphate scum (Ni-CaPs) catalyst *(*Yusuff *et al., 2017)*.

BET Analysis: The textural properties of the synthesized catalyst displayed surface area, pore diameter, and pore volume were 235.505 m^2 g^{-1}, 2.920 nm and 0.132 cc g^{-1}, respectively which correlates with existing literature *(*Zhang *et al., 2023)*. These results possibly account for the enhanced surface properties of the composite catalyst. Moreover, some studies have noted that catalysts for biodiesel production require high surface areas *(*Madai *et al., 2020)*. For instance, a mixed metal oxide functionalized with banana peel ash (Li–$CaO/Fe_2(SO_4)_3$) showed a pore volume of 0.628 cm^3 g^{-1}, a pore size of 3.01 nm, and a surface area of 411.2 m^2 g^{-1}.

Modelling of Biodiesel Production: Response surface methodology (RSM) utilized a core composite design with four key parameters: methanol-oil ratio, catalyst loading, reaction temperature, and reaction time. The relationship among the response and independent variables was elucidated through multiple regression analysis, resulting in the biodiesel yield model represented in Eq. (**Error! Reference source not found.**). A comparison of the actual biodiesel yield with the model's prediction revealed a strong correlation, indicating the RSM model's efficacy in forecasting biodiesel yield using the biodiesel yield model as presented in equation 1.

$$\text{Yield} = +80.84 + 1.47A + 6.17B - 4.55C + 6.82D + 2.67AD - 2.10BC + 2.02CD - 9.98A^2 - 1.69C^2 - 6.69D^2 \quad (2)$$

The quadratic model was selected based on p-values, lack of fit tests, and R-square (R^2) metrics among linear, 2F1, quadratic, and cubic alternatives. The model's significance is underscored by a P-value ($P < 0.0001$) and a lack of fit ($P > 0.05$) that enhance its reliability. The R_2 value indicates the ratio of explained variance to total variation *(*Elkelawy *et al., 2020)*. With an R^2 of 0.9886, the quadratic model demonstrates a superior fit. This finding suggests that the system's behavior is accurately represented by the expected 2nd order polynomial model. Additionally, the high modified R^2 value of 0.9773 further substantiates the model's reliability. Employing actual versus predicted data is a crucial method for assessing the proposed model's significance. The empirical model correlates strongly with observed values within the operational variable range, aligning with expected outcomes. Noteworthy correlations exist with prior research findings *(*Elkelawy *et al., 2020)*. To ascertain the model's suitability in predicting biodiesel yield, various goodness-of-fit criteria were employed. Parameters such as coefficient of variation, standard deviation,

acceptable accuracy, predicted R^2, adjusted R^2, and R^2 were utilized. The outcomes are presented in

Effect *of reaction parameters Effect of Catalyst Loading and the Reaction Time:*

Experimental *validation:* The RSM model achieved a biodiesel yield of 93.2% under optimal conditions: 55°C, 1 wt.% catalyst, 90 mins, and a 12:1 methanol-oil ratio. This result was obtained through numerical optimization utilizing a genetic algorithm alongside the RSM model. The optimal biodiesel production conditions identified in this study corresponded closely with findings from previous research. Specifically, the 93.2% yield exceeded the prior results of 89.3% and 80% reported by Farooq and Ramli (2015) and Naveenkumar & Baskar (2019), respectively.

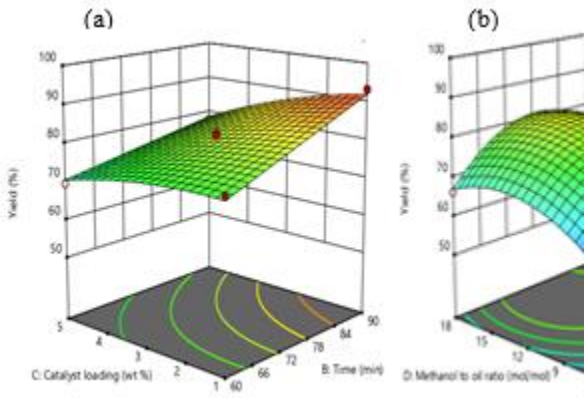

Fig. 4a depicts how catalyst loading and reaction duration influence biodiesel yield. The conversion rate of fatty acid esters increases with extended reaction time. Initially gradual, the reaction rate accelerates upon mixing alcohol and oil, leading to higher yields. The optimal yield was achieved after 90 mins with a constant catalyst dosage of 1 wt.%, with a subsequent decline in yield consistent with prior findings *(*Weldeslase *et al., 2023)*.

Table 2, where a high R^2 value close to unity is desirable. The biodiesel model's R^2 value of 0.9877 confirms a strong alignment between predictions and experimental data, as shown in

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Characterization of the produced Biodiesel: Standard testing: The produced biodiesel was assessed against the Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, and European Standard for Fatty Acid Methyl Esters (FAME) for Use in Diesel Engines and Heating Appliances (ASTM D6571 and EN 14214 standards), as tabulated in Table 3. The evaluation indicated an acid value of 0.23 mg KOH g^{-1} oil, suggesting minimal risk of corrosion in the fuel system during engine operation *(*Alves *et al., 2019)*. Additionally, the biodiesel exhibited favorable fuel properties, notably a cetane number of 52.17. With an iodine value of 106 g/100g, the fuel demonstrated excellent oxidative stability, enhancing its storage potential without significant quality deterioration *(*Huang *et al., 2022)*. In summary, the biodiesel generated under optimized conditions exhibited numerous desirable characteristics that met the requirements of EN 14214 and ASTM D6571.

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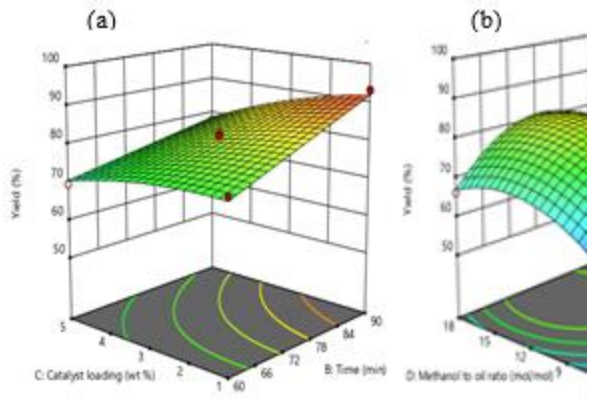

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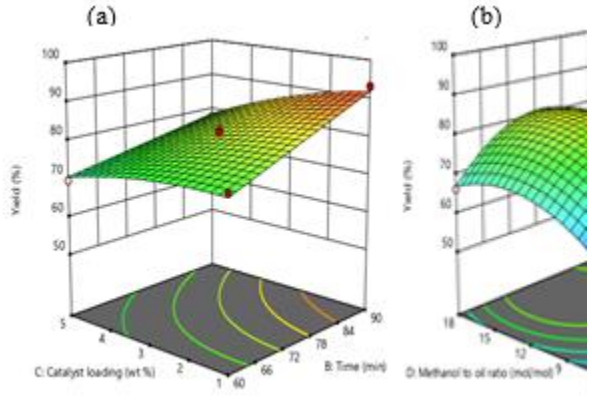
Table 2. Specifically, the R^2 of 0.9877 indicates that 98.77% of variability is explained by the model. Furthermore, a modified R^2 value of 0.9771 reflects a commendable fit between models. A comparison of the standard deviation (1.36) with the mean observation (73.23) reveals minimal variation, supporting the model's fit with a coefficient of variation (CV) of 1.85%. The reliability of experimental runs is validated when expressed as a percentage of the mean. Consistent with literature, the model's precision is affirmed by a signal-to-noise ratio exceeding 4, recorded at 37.9748 *(*Abuhassna *et al., 2020)*.



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Effect of reaction parameters Effect of Catalyst Loading and the Reaction Time:

Experimental *validation:* The RSM model achieved a biodiesel yield of 93.2% under optimal conditions: 55°C, 1 wt.% catalyst, 90 mins, and a 12:1 methanol-oil ratio. This result was obtained through numerical optimization utilizing a genetic algorithm alongside the RSM model. The optimal biodiesel production conditions identified in this study corresponded closely with findings from previous research. Specifically, the 93.2% yield exceeded the prior results of 89.3% and 80% reported by Farooq and Ramli (2015) and Naveenkumar & Baskar (2019), respectively.

Characterization of the produced Biodiesel: Standard testing: The produced biodiesel was assessed against the Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, and European Standard for Fatty Acid Methyl Esters (FAME) for Use in Diesel Engines and Heating Appliances (ASTM D6571 and EN 14214 standards), as tabulated in Table 3. The evaluation indicated an acid value of 0.23 mg KOH g^{-1} oil, suggesting minimal risk of corrosion in the fuel system during engine operation *(*Alves *et al., 2019)*. Additionally, the biodiesel exhibited favorable fuel properties, notably a cetane number of 52.17. With an iodine value of 106 g/100g, the fuel demonstrated excellent oxidative stability, enhancing its storage potential without significant quality deterioration *(*Huang *et al., 2022)*. In summary, the biodiesel generated under optimized conditions exhibited numerous desirable characteristics that met the requirements of EN 14214 and ASTM D6571.

higher yields. The optimal yield was achieved after 90 mins with a constant catalyst dosage of 1 wt.%, with a subsequent decline in yield consistent with prior findings *(*Weldeslase *et al., 2023)*.

Table 2: Goodness of fit statistics for RSM model representing biodiesel yield.

Parameter	value
R^2	0.9877
Adjusted R^2	0.9771
Predicted R^2	0.9457
Mean	73.23
Standard deviation	1.36
C.V. %	1.85
Adequate Precision	37.9748

Effect of Methanol to Oil Molar Ratio and Reaction Temperature:

Experimental *validation:* The RSM model achieved a biodiesel yield of 93.2% under optimal conditions: 55°C, 1 wt.% catalyst, 90 mins, and a 12:1 methanol-oil ratio. This result was obtained through numerical optimization utilizing a genetic algorithm alongside the RSM model. The optimal biodiesel production conditions identified in this study corresponded closely with findings from previous research. Specifically, the 93.2% yield exceeded the prior results of 89.3% and 80% reported by Farooq and Ramli (2015) and Naveenkumar & Baskar (2019), respectively.

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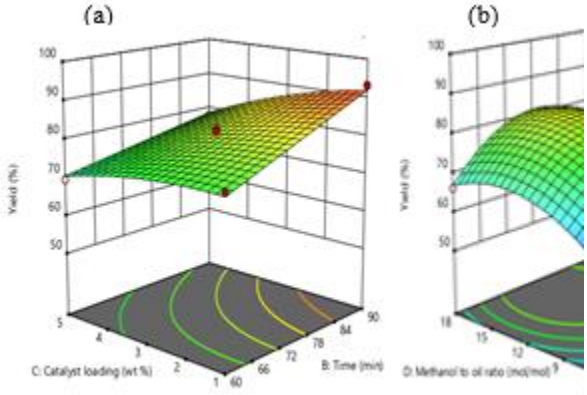

Fig. 4b demonstrates the relationship between reaction temperature, biodiesel yield, and methanol-to-oil ratio. Increased reaction temperatures facilitate greater biodiesel production. Higher temperatures improve catalyst dispersion, mass transfer, and interactions between catalyst and methanol molecules *(*Yusuff *et al., 2021)*. The peak biodiesel yield of 93.2% was recorded at 55℃, aligning with previous reports of a 93% yield at 57.5℃ using a chicken bone and soybean composite catalyst (Goli and Sahu 2018).

Effect of molar ratio and catalyst concentration on the biodiesel yield:

Experimental *validation:* The RSM model achieved a biodiesel yield of 93.2% under optimal conditions: 55°C, 1 wt.% catalyst, 90 mins, and a 12:1 methanol-oil ratio. This result was obtained through numerical optimization utilizing a genetic algorithm alongside the RSM model. The optimal biodiesel production conditions identified in this study corresponded closely with findings from previous research. Specifically, the 93.2% yield exceeded the prior results of 89.3% and 80% reported by Farooq and Ramli (2015) and Naveenkumar & Baskar (2019), respectively.

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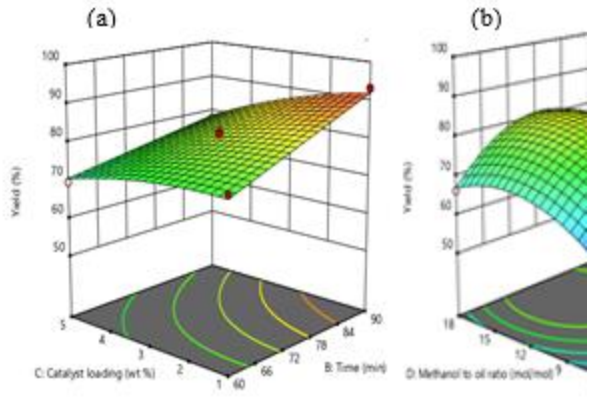

Fig. 4c illustrates the impact of catalyst loading and methanol-to-oil ratio on biodiesel production. Optimization of key variables is indicated by the increase in biodiesel yield when shifting from a lower to a higher methanol-to-oil ratio (1 wt. %, 6:1 to 1 wt. %, 12:1). Biodiesel output improved from 71.9% to 93.2% with the methanol-to-oil ratio change while maintaining a constant catalyst dosage of 1 wt.%. Previous research corroborates the relationship between methanol-oil ratio and catalyst concentration *(*Yahya *et al., 2020)*. A higher concentration of reactants typically enhances collision frequency between reactants and catalyst, affecting active site availability and consequently improving yield *(*Kanda *et al., 2017)* (Chumuang and Punsuvon 2017).

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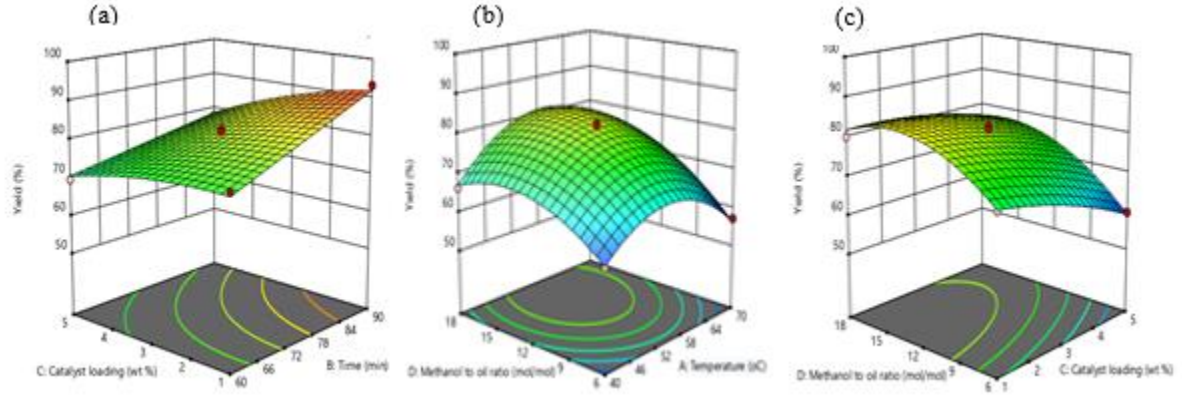

Fig. 4: 3D surface plots showing the effect of (a) catalyst loading and reaction time, (b) methanol/oil ratio and reaction temperature, (c) methanol/oil ratio and catalyst loading on biodiesel yield.

Table 3: Summary of biodiesel properties

Properties	**Biodiesel**	**ASTM D6751**	**EN 14214**
Acid value	0.23 mg KOH g^{-1} oil	< 0.5	< 0.5
FFA	0.115 %	Not specified	Not specified
Iodine value	106 mg L^{-1}g Oil	Not specified	< 120
Flash point	154 ◦C	> 130	> 130
Pour point	- 4℃	< 0	< 0
Cloud point	2℃	Not specified	Not specified

Cetane number	52.17	≥ 47	≥ 51

Table 4: GC-MS analysis showing the chemical composition of the biodiesel produced.

Peak	Retention time Rt (min)	Compounds identified	Chemical formula	Composition (%)
1	16.966	aniline	$C_6H_5NH_2$	8.81
2	17.477	Linoleic acid ethyl ester	$C_{20}H_{36}O$	6.92
3	21.563	Oleic Acid	$C_{18}H_{34}O_2$	6.9
4	26.984	Squalene	$C_{30}H_{50}$	0.72
5	27.597	Linoelaidic acid	$C_{18}H_{32}O_2$	6.81
6	29.317	gamma-Tocopherol	$C_{28}H_{48}O_2$	1.12
7	30.2	9-Octadecenoic acid (Elaidic acid)	$C_{18}H_{34}O_2$	11.92
8	30.622	6-Octadecenoic acid (Petroselinic acid)	$C_{18}H_{34}O_2$	7.03
9	31.543	gamma-Sitosterol	$C_{29}H_{50}O$	2.36
10	31.991	Z-4-Nonadecen-1-ol acetate	$C_{21}H_{40}O_2$	11.86
11	32.103	9-Octadecenoic acid (Elaidic acid)	$C_{18}H_{34}O_2$	7.46
12	32.865	9-Octadecenoic acid (Elaidic acid)	$C_{18}H_{34}O_2$	8.05
13	35.848	n-Propyl 11-octadecenoate	$C_{21}H_{40}O_2$	11.47
14	36.764	cis-9-Tetradecenoic acid (Myristoleic acid)	$C_{14}H_{26}O_2$	8.56

For further verification, the produced biodiesel was subjected to GC-MS analysis to confirm the formation of methyl esters and analyse other possible impurities present in the sample. Results of the retention time, and molecular formulas of identified components are presented in Table 4. The primary component detected was elaidic acid (27.43%), followed by Z-4-Nonadecen-1-ol acetate (11.86 %), n-Propyl 11-octadecenoate (11.47 %), aniline (8.81 %), and Myristoleic acid (8.56 %) as evident in similar study in literature for the production of biodiesel *(*Ibrahim *et al., 2023)*.

FTIR Analysis: Fig. 5 shows the FTIR spectra of the biodiesel produced from used cooking oil. The distinctions in chemical composition between the used vegetable oil and biodiesel are elucidated within the spectrum range of 1500 to 900 cm^{-1} *(*Nisar *et al., 2017)*. The peaks at 2922 and 2854 cm^{-1} signify the stretching vibrations of C-H in the CH_2 and CH_3 groups, respectively. The notable signal at 1166.67 cm^{-1} indicates the presence of the carbonyl groups' C=O stretching vibration in triglycerides and esters. The bending vibrations of CH_2 and CH_3 aliphatic groups are indicated by peaks in the 1600–1400 cm^{-1} region, while HCH bending is observed at 1372 cm^{-1} and CH_2 and scissoring at 1488 cm^{-1}. The stretching vibration of the C-O ester as depicted by peaks between 1263 and 1242 cm^{-1}. Additionally, the stretching vibration of C = O in the ester is confirmed by the peak at 11166.67 cm^{-1}, and C–O stretching vibrations are validated by peaks within the 1500 – 1300 cm^{-1} range *(*Tariq *et al., 2011)*.

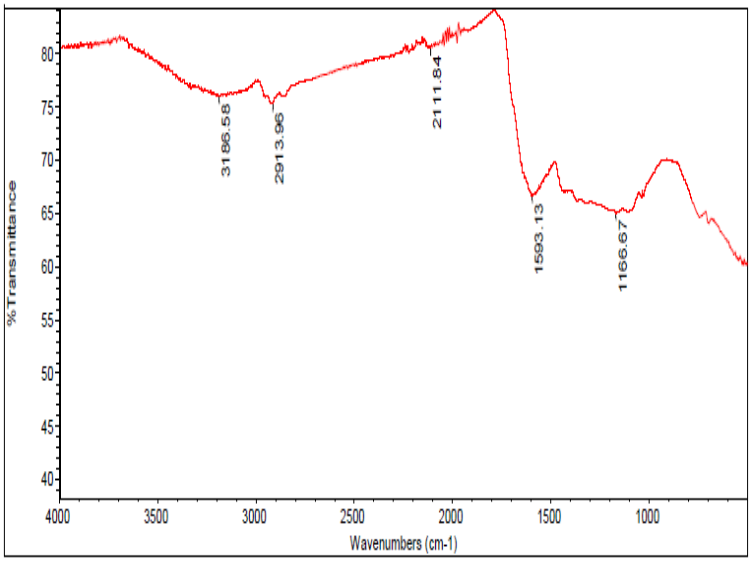

Fig. 5: FTIR spectrum of synthesized biodiesel

Conclusions: A novel heterogeneous catalyst, Ni-modified calcium phosphate scum (Ni-CaPs), was successfully developed and applied for biodiesel production from used cooking oil (UCO). The catalyst exhibited optimal surface area, pore volume, and balanced basic-acidic properties, enabling efficient transesterification and esterification reactions. Optimization studies revealed ideal conditions: 90°C temperature, 90-mins reaction time, 1 wt.% catalyst loading, and 12:1 methanol-to-oil ratio, yielding 93.2% biodiesel. The quadratic model showed an excellent fit (R^2 = 0.9886). The synthesized biodiesel met ASTM D6571 and EN 14214 standards, demonstrating suitable fuel properties and cold flow characteristics. The Ni-CaPs catalyst enables efficient conversion of used cooking oil into high-quality biodiesel, supporting a cleaner energy sector and offering scalability for industrial production.

Declaration of Conflict of Interest: The authors declare no conflict of interest.

Data Availability Statement: Data are available upon request from the first author or corresponding author or the co-author.

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