

# Optimization of Biodiesel Production from Used Vegetable Oil using Functionalized Catalyst derived from Anthill



E. O. Babatunde<sup>1,2\*</sup> and L. Mekuto<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering Technology, Faculty of Engineering and Built Environment, Doornfontein Campus, University of Johannesburg, South Africa.

<sup>2</sup>Department of Chemical Engineering, University of Ilorin, Nigeria.



**ABSTRACT:** In this research, silica-supported catalyst was developed from Anthill and zirconia for biodiesel production using used vegetable oil (UVO) in a transesterification process. The catalyst, which was made up of 80 wt% silica from Anthill and 20 wt% zirconia, was prepared by wet impregnation method and calcined at 800°C for 4 h in a muffle furnace. The developed catalyst was characterized by powder X-ray diffraction (XRD), Fourier Transform Infrared Ray (FTIR), Scanning Electron Microscopy (SEM), Brunauer–Emmett–Teller (BET), and Energy Dispersive X-ray (EDX). The characterisation showed that the product has good catalytic activity for the transesterification reaction. Optimisation of the process parameters; reaction temperature, time, catalyst loading, and methanol to oil ratio were investigated using central composite design (CCD). The optimum conditions for optimal yield (97.88%) were 1 h reaction time, 65 °C temperature, 0.5 wt.% catalyst loading, and 9:1 methanol to oil ratio. The experimental biodiesel yield was validated in triplicate at the optimal conditions and an average biodiesel yield of 97.78% was obtained which falls within the range predicted by the model. The quality of biodiesel produced was within the specification limits of biodiesel standard. The experimental study confirmed that the silica-supported catalyst developed from anthill is capable of transesterification of UVO into biodiesel under optimized conditions. Hence, the study recommends that other naturally occurring materials could be used as catalyst support to avoid low yield of biodiesel production.

**KEYWORDS:** Biodiesel; Silica; Transesterification; Functionalised catalyst; Optimization, Anthill

[Received Feb. 6, 2025; Revised Feb 20, 2025; Accepted Mar 2, 2025]

Print ISSN: 0189-9546 | Online ISSN: 2437-2110

## I. INTRODUCTION

Over-dependence on fossil fuels for domestic and industrial consumption has made its demand to outset its production (Adepoju et al., 2023; Nasar et al., 2017). Fossil fuels such as petroleum, coal, and natural gas have been the major sources of energy used all over the world for domestic, industrial, and transportation purposes (Yusuff et al., 2023b). However, these energy sources have some challenges, such as being non-renewable, generating large amounts of greenhouse gases, environmental degradation, and fuel crisis. Therefore, there is an urgent need to source alternative energy. Among the alternative energy sources, biodiesel as a fuel has shown appealing results because it provides solutions to environmental depletion and degradation (Babatunde et al., 2025) Biodiesel is a green and non-toxic fuel derived from plant oils (edible and non-edible oil) or animal fat using homogeneous or solid catalysts through transesterification (Babatunde et al., 2020). The chemical process that involves the reaction between one mole of triglyceride present in oil and three moles of primary alcohol (methanol) to produce three moles of methyl esters and one mole of glycerol is called transesterification reaction. This reaction occurs in three consecutive reversible stages, namely triglyceride to

diglyceride, diglyceride to monoglyceride, and finally monoglyceride to fatty acid alkyl ester and glycerol, and it occurs in the presence of a suitable catalyst. The fatty acid alkyl ester is referred to as biodiesel, which can be used as a replacement for fossil fuel (Ajala et al., 2024; Yusuff et al. 2020).

In past decades, feedstock such as soya bean oil, jatropha oil, castor oil, rubber oil, neem oil, palm oil, micro-algae, animal fats, vegetable oils, and coconut oil have been used in the synthesis of biodiesel (Dhawane et al., 2018; Dhawane et al., 2017; Zou and Lei, 2012; Berchmans and Hirata, 2012; Goyal et al., 2012; Halder et al., 2015a; Betiku et al., 2014). Derivation of biodiesel from edible oils may fail as an option because their usage brings about competition with food. This work is therefore aimed at addressing this problem through the recycle of used vegetable oils as feedstock for biofuel production.

Used vegetable oil (UVO) normally undergoes repetitive mixing with unspent oil for non-stop use in local restaurants or shops prior to discarding. In our homes, it is not often set aside for mixing but, released into local drainage systems. UVO generated by eateries, hotels, restaurants, and domestic use needs to be properly discharged, which usually incurs an additional cost. Safe disposal of this household waste is a cause for concern due to its environmental effects. Meanwhile,

\*Corresponding author: babatunde.eo@unilorin.edu.ng

doi: <http://dx.doi.org/10.4314/njtd.v22i1.3377>

the utilization as a biodiesel feedstock could contribute to the circular economy by converting waste to green fuel and lowering biodiesel production costs (Yusuff *et al.*, 2023b). In addition, UVO is bountifully accessible and can be obtained at a low cost. Hence, this mitigates the cost of biodiesel production by 65 – 70 % (Dhawane *et al.*, 2018; Chaveanghong *et al.*, 2018). UVO is a more economically viable source and is a promising substitution for virgin oils in biodiesel production (Ali *et al.*, 2018; Babatunde *et al.*, 2022a).

For the purpose of large-scale biodiesel production and favourable speed during the production process, homogeneous catalysts over the years have been employed by various industries. However, it is accompanied by several problems, such as the formation of saponified products, interference of water, difficulties in separating glycerol, and the repeated washing of biodiesel to achieve high purification and quality (AlSharifi and Znad, 2019). The drawback has made biodiesel expensive as well as posing a major barrier to its large-scale commercialization (Chaveanghong *et al.*, 2018). In view of the highlighted problems, further research into the use of solid catalyst that can be effortlessly separated from resulting products (Ramachandra *et al.*, 2013; Adepoju *et al.*, 2023; Ozioko *et al.*, 2024) was carried out in this study

To synthesize efficient alternatives to fossil fuels through cost-effective and environmentally benign processes, the development of a novel renewable heterogeneous green catalyst support can either be prepared from naturally occurring materials or waste generated from households. Anthill can meet the desirable properties as it is readily available, possesses zero cost, high surface area, and impressive mesopore volume (Babatunde *et al.*, 2020a; Yusuff *et al.*, 2018). Anthill is a clay deposited by termites that serves as waste and is found everywhere in almost all states in Nigeria. Thus, this clay can be used as a precursor to develop activated clay (silica) catalysts with high surface area (Babatunde *et al.*, 2020).

In our previous study (Babatunde *et al.*, 2020), the anthill was used without modification, which resulted in a low yield of biodiesel with high methanol concentration (12:1 to oil molar ratio) and reaction temperature (68 °C). In another research (Yusuff *et al.*, 2018), activated anthill was mixed with calcined eggshells and the resulting catalyst was inefficient in the transesterification, resulting in only 70.7 %w/w biodiesel yield with high methanol concentration and reaction time (3h) when the anthill and calcined eggshell were mixed in 80-20 ratio. It was seen that catalysts prepared when low anthill was used produce a low yield of product. Therefore, it was reasoned that metal oxide doped on the activated anthill can be a very effective catalyst in the transesterification of UVO for high biodiesel yield. Also, the presence of zirconia makes the anthill support hard and resistant to sintering during calcination.

In the industry where sustainability and large output are required, the development of heterogeneous catalysts from low-cost material with high reactivity for biodiesel synthesis is beneficial to the entire process (Lee *et al.*, 2014; Mardhiah *et al.*, 2017; Odetoye *et al.*, 2021). Although, the use of ZrO, K<sub>2</sub>O, MgO and ZnO alone from their various compounds as catalyst in biodiesel production comes with limitations such as low production yield and leaching (Olutoye and Hameed, 2011;

Takase *et al.*, 2014; Wang *et al.*, 2012; Olutoye and Hameed, 2013), most metal oxides were found to be suitable to this effect due to their basic nature (Refaat, 2011; Babatunde *et al.*, 2022b). The combinations of the metal oxides (ZrO) with silica support as catalysts to study the effect and interaction on the production of biodiesel from UVO have not, in most cases, been documented. Also, the use of the CCD via RSM in this work could be viewed as a novel approach to fill the research gaps in waste utilization for energy generation. Hence, this report provides relevant information on the synthesis and the use of metal oxide on silica support for biodiesel production through a transesterification process to overcome the challenge of leaching, which leads to biodiesel yield reduction.

For optimization of the transesterification process, a software approach can be used, and to reduce the number of experiments, response surface methodology (RSM) via central composite design was employed in designing the experimental matrix, given that the number of runs required is far less than one variable at a time (OVAT) method. Using experimental data, the software analyses the association among the various input parameters and one or more responses with a reduced number of experiments. RSM has been widely used in optimizing various industrial processes. For example, Adepoju *et al.* (2021) used the RSM approach to optimize the biodiesel production from a quaternary blend of Carica papaya - citrus sinensis - hibiscus sabdariffa - waste used oil catalysed by CaO based catalyst. The analysis of variance (ANOVA) was also used to validate the model revealed (Halder *et al.*, 2015a).

The objective of the current study is to synthesize a silica-based catalyst from naturally occurring anthill material functionalized with metal (Zr) oxides through impregnation and thermal activation. The prepared catalyst was analysed using XRD, EDX, SEM, FTIR, and BET techniques and utilised to produce fatty acid methyl ester (FAME) from used vegetable oil (UVO). The influences of various parameters such as reaction temperature, methanol/oil molar ratio, reaction time, and catalyst loading on catalytic reaction were studied, as well as the physicochemical properties of the produced fuel. Hence, anthill could be an efficient precursor for the development of catalyst support to be used in the transesterification of UVO into biodiesel to meet the growing energy demand.

## II. MATERIALS AND METHODS

### A. Materials

The Anthill clay was collected from Share, Kwara State, Nigeria. The UVO was obtained from the students' cafeteria, Doorfontein campus, University of Johannesburg, South Africa; the reagents used in this research were methanol (analytical grade, 99.5%), potassium hydroxide, and zirconium oxide. The methanol and zirconium oxide were procured from Rochelle Chemicals (South Africa). All the experimental work was executed using analytical/research-grade chemicals.

## B. Methods

### 1) 1) Characterization of Used Vegetable Oil

The used vegetable oil was initially filtered and thereafter preheated at 110°C for 60 min to eliminate moisture. Analysis of the UVO was done using procedure in the literature (Adepoju *et al.*, 2021). Determination of the acid value of UVO was done by titrimetric assay (ASTM Method D974). Ideally, for biodiesel production, the FFA content should be less than 2%. For determining the acid value and initial FFA content, a solution of 0.1 M KOH was carried out to be used as a standard solution. 1 ml of UVO was put in a conical flask, and 50 ml of methanol (used as solvent) was added alongside two drops of phenolphthalein solution (as an indicator). Titration of the mixture against 0.1 M KOH, which was added drop-wise with continuous shaking until there was a change in colour, preferably pink colour. The titrations were carried out in triplicates to ensure reproducibility. Hence, both acid value (AV) and free fatty acid content (FFA %) were calculated as given by Equation (1) and (2):

$$AV = \frac{56.1 \times N \times t}{m} \quad (1)$$

$$FFA(\%) = \frac{28.2 \times N \times t}{m} \quad (2)$$

Where t is the titre value, N is the molarity of KOH, and m is the mass of the oil sample.

56.1 is the molar mass of KOH, and 28.2 is the mass of oleic acid present in the oil sample.

### 2) Preparation of Catalyst

Anthill sample was collected, ground, and pretreated to remove dirt, oven-dried at 110°C for 24 h, and later screened using 125 µm to obtain a fine powder. The treated fine powder was denoted SS, which acts as a support in this study. The modified method of calcination and activation described in the literature was followed to develop the catalyst (Dhawane *et al.*, 2017). Treated silica was impregnated with pure zirconium oxide by mixing 40 g of SS in 10 g of ZrO<sub>2</sub>/150 ml of deionised water. SS with ZrO solution was agitated in an orbital shaker at 200 rpm at a constant temperature of 30°C for 24 h. Separated solid catalyst from the solution was dried at 105°C overnight and thereafter thermally treated by calcination in a muffle furnace (CSMF136Z, N.R. Enterprise, Kolkata, India) at 800°C for 4 h. The calcined silica functionalized with zirconium oxide was stored in a desiccator and labelled as SZ-80 prior to use.

### 3) Characterization of Catalyst

Brunauer-Emmett-Teller (BET) was used to study the pore volume and total surface area of the samples by Micrometrics NOVA 2000 (USA) apparatus at 77K using nitrogen as the adsorption gas. FTIR was used to reveal the functional groups in the designed catalyst. The FTIR spectra was obtained using a pectin Elmer system 2000 Spectrometer via the standard KBr disk method. Wide-angle XRD patterns were obtained using a diffractometer to observe the crystalline structure and unit cell parameters of the synthesized catalysts. Furthermore, a High-Resolution Scanning Electron microscopy (HRSEM) was used

by means of Quanta FEG 450 to examine the surface morphology while EDX allowed calculation of the elemental composition of the sample.

### 4) Experimental Design

For optimization purposes, the experimental matrix was statistically designed by RSM via central composite design (CCD) using Design Expert 10.0 software (Stat-Ease, USA). The reaction temperature, catalyst loading, reaction time, and methanol/oil molar ratio were the selected independent parameters while the dependent variable is the yield of FAME. CCD is a very efficient approach for fitting experimental data in the second-order model (Halder *et al.*, 2015b). Variables were coded at three equally spaced levels -1, 0, and +1 for low, intermediate, and high values, respectively, as shown in Table 1. Prior to the selection of the actual values of the lower (-1) and upper (+1) limit of each of the parameters in Table 1, a preliminary one-way optimization study was carried out to determine the boundary at which each of the process variables has a significant effect on the yield.

**Table 1: Experimental Design Matrix by CCD for Three-Level Four-Factors Response**

Independent variables	Coded levels		
	-1	0	+1
A: Methanol to oil ratio	6:1	7.5:1	9:1
B: Temperature (°C)	55	62.5	70
C: Reaction time (h)	1	2	3
D: Catalyst amount (wt %)	0.5	1.25	2.0

### 5) Transesterification of UVO with methanol

The production of biodiesel from UVO was carried out in a 500 mL three-neck round bottom flask with a thermometer attached to one neck, stirrer and reflux condenser was attached to the other necks to maintain the amount of methanol to oil ratio by preventing loss through evaporation. For every run, 50 mL of UVO was measured into the three-neck flask according to the suggested values by the CCD. The required amount of methanol was measured and poured into a beaker alongside the catalyst was also weighed and poured into the same beaker. The mixture of catalyst with methanol were introduced into the oil in the reactor, and the mixture was stirred at 550 revolutions per minute (rpm). The process parameters viz: reaction temperature, catalyst loading, reaction time, methanol to oil ratio, were varied based on the designed experiment (Betiku, 2014).

Catalyst recovery was carried out by transferring the reaction mixture into a funnel equipped with filter paper, while the filtrate was then transferred into a separating funnel. Two distinct layers were obtained; the bottom layer was glycerol, while the upper layer was the biodiesel. The biodiesel was washed with water and dried to remove impurities and spent water (Chuah, 2016). The biodiesel yield also called fatty acid methyl ester (FAME) produced was calculated using Equation 3.

\*Corresponding author: babatunde.co@unilorin.edu.ng

$$\text{FAME yield (\%)} = \frac{\text{weight of Product obtained}}{\text{weight of UVO}} \times 100 \quad (3)$$

### 6) Characterization of biodiesel produced

Physico-chemical properties of the FAME produced were estimated according to ASTM standards. Kinematic viscosity was measured using a Redwood viscometer. Flashpoint and fire point are critical features of fuel that help us guesstimate the smallest temperature at which a fuel forms vapours and an ignitable mix with air. The flash point and fire point of the fuel were determined by using a closed cup Penskey Martens apparatus.

## III RESULTS AND DISCUSSION

### A. Properties of the Used Vegetable Oil

The values obtained after the analysis of UVO are summarized in Table 2. It was observed that the FFA content of UVO was less than 2%, which indicated that the collected oil could be used directly for transesterification without any chemical pretreatment. The used oil was expected to have high FFA because it has been used for frying severally, as reported by Adepoju *et al.* (2020). The low FFA may be due to the type of oil and the geographical location where the seed oil was grown; this is corroborated with the work of Yusuff *et al.* (2023), who studied the optimization of waste cooking oil obtained in Nigeria. The kinematic viscosity was high, hence, the oil was not fit for direct blending with fossil diesel. The energy content of the oil may be very high because of the calorific value of 39.55 MJ/kg. The moisture content of 2.2% shows the need for heating the oil to prevent hydrolysis during the process of transesterification.

**Table 2: Physicochemical Properties of UVO**

Properties	Values
Acid value (mg KOH/g)	3.366
Moisture content (%)	2.2
Free fatty acid (%)	1.683
Density (g/cm <sup>3</sup> )	0.873
Viscosity @ 40 °C/(mm <sup>2</sup> /s)	8.360
Calorific value (MJ/kg)	39.55

### B. Catalyst Characterization

The BET analysis and basicity of the catalyst sample are presented in Table 3. From the table, the surface area, total pore volume, and average pore diameter of silica are 668.5 m<sup>2</sup>/g, 0.658 cm<sup>3</sup>/g, and 21.45 Å, respectively. These properties showed that the prepared support possesses enough surface area and pore volume for the dispersion of the zirconium oxide on its surface (Yusuff *et al.*, 2019).

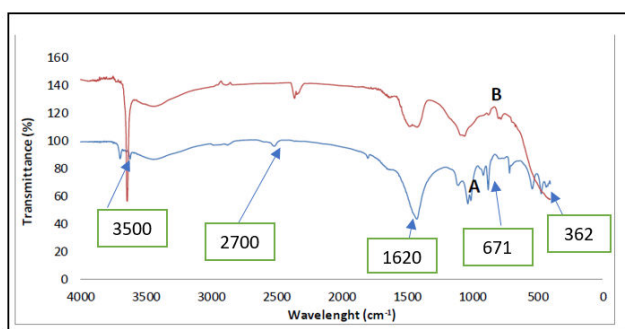
Furthermore, this property of silica signifies that a large number of active sites are available for transesterification reaction, which increases methyl ester yield. Therefore, these properties are proofs of catalyst support to function efficiently (Sharma *et al.*, 2010). The surface area, pore volume, and pore diameter observed for the synthesized SZ-80 catalyst

(Functionalised catalyst) are 150.4 m<sup>2</sup>/g, 0.056 cm<sup>3</sup>/g, and 20.35 Å, respectively. The loading of zirconia brought about a decrease in the silica sample textural features; this shows that there was an increase in the active sites on the catalyst surface. In other words, this decrease in surface area is an indication that the adsorption of metal oxide was successfully done. The catalyst possessed high catalytic ability and performed better. The decrease in pore volume after impregnation is an indication of better confinement effects, increasing the interaction between reactants and catalytic sites, which may improve selectivity and efficiency in biodiesel production (Babatunde *et al.*, 2025). The pore sizes of both the silica and SZ-80 implied that they are mesoporous materials (> 2 Å). The basicity of the catalyst shows that it is basic in nature, as reported by Yusuff and Owolabi (2019). The effects of the basicity of the catalyst and basic strength on activity are correlated; for transesterification, the base sites over the SZ-80 catalyst are active centres (Refaat, 2011; Yusuff and Owolabi, 2019). The high biodiesel yield obtained was attributed to strong basic strength, which was greater than the value (15.0) reported by AlSharifi and Znad (2019) for lithium-supported chicken bone.

**Table 3: BET analysis and basicity of synthesized catalyst**

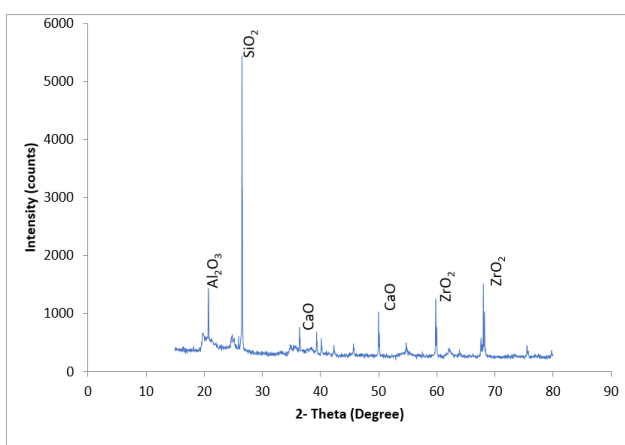
Sample	Basicity (mmol/gcat)	Surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Pore size (Å)
Silica (support)	-	668.5	0.658	21.45
SZ-80	19.6	150.4	0.056	20.35

Figure 1(A) and (B) present the FTIR spectra of the support and SZ-80 catalyst, respectively, at a wavenumber range of 4000–0 cm<sup>-1</sup> with an interval of 500 cm<sup>-1</sup>. The spectra of both samples showed sharp bands in the 3600-3448 cm<sup>-1</sup> range due to the stretching vibrations of the surface-free hydroxyl groups. The bands observed in the region 1620-1465 cm<sup>-1</sup> are attributed to carbon molecules bonded to hydroxyl ions and are characteristic of Si-O stretching of the silica oxide. The observed band at 671 cm<sup>-1</sup> could be traced to the presence of Al-OH stretching vibration. Also, the vibrational bandwidth at 450-362 cm<sup>-1</sup> suggests the presence of zirconia compounds. The presence of these functional groups contributed to the effective activity of a catalyst and was similar to what was observed in the work of Yusuff *et al.* (2018).



**Figure 1: FTIR spectra of (A) catalyst support and (B) SZ-80 catalyst**

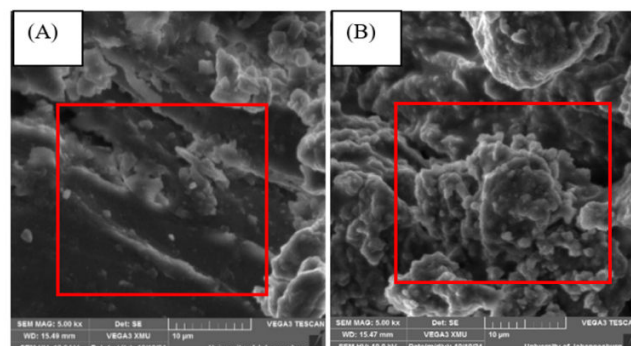
Figure 2 shows the XRD pattern of the synthesized catalyst, which provides information about the catalyst's phase. The XRD pattern of the synthesized catalyst showed basically characteristic peaks of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CaO}$ , and  $\text{ZrO}_2$ . These components of the catalyst tend to crystallize at  $2\theta = 21^\circ$ ,  $27^\circ$ ,  $37^\circ$ ,  $50.9^\circ$ ,  $60.1^\circ$  and  $68.9^\circ$ . This observation was confirmed by the EDX, further indicating the homogeneity of the synthesized catalyst sample. It also affirmed that the zirconium metal was well incorporated onto the surface of the catalyst. The different peaks obtained showed that the catalyst was crystalline in nature, which is a good characteristic of an efficient catalyst (Dhawane *et al.*, 2018).



**Figure 2: XRD pattern of synthesized catalyst (SZ-80)**

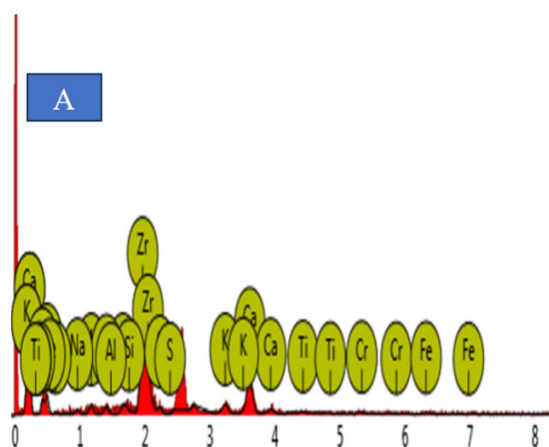
The SEM analysis shows the surface topography of the catalyst support (Figure 3A) and that of the functionalized silica catalyst (Figure 3B). It can be observed from the highlighted part that Figure 3(A) contains a smooth and flat structure; this brought about pores on the surface, while the SZ-80 catalyst shows large agglomerates and few pores due to the dispersion of  $\text{ZrO}_2$  on the surface to form a stable heterogeneous catalyst. Figure 3 (B) further revealed that the particles of SZ-80 are well-agglomerated and clustered. A reduction in pores often corresponds to a higher concentration of active catalytic sites on the surface, which can enhance the

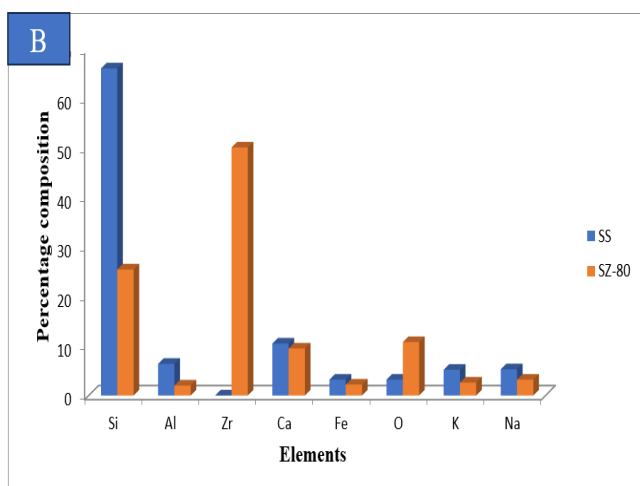
reaction rate by providing more accessible active sites for the transesterification process. This is similar to what was observed by (Sumit *et al.*, 2016; Yusuff and Owolabi, 2019).



**Figure 3: SEM images of (A) catalyst support (B) SZ-80 Catalyst**

The elemental analysis (EDX) results are shown in Figures 4A and B. In Figure 4A (SZ-80), the zirconia has the highest percentage, which confirms that  $\text{ZrO}_2$  was significantly adsorbed onto the catalyst support; this made the heterogeneous catalyst efficient for methyl ester production. Also, in Figure 4B, the bar chart represents the percentage of each element in the synthesized catalyst and silica support. The amount of all the possible elements on the surface was determined and observed on the SZ-80 catalyst as zirconium (55.24 %), silicon (24.17%), aluminium (3.45 %), calcium (6.93 %) and oxygen 10.26 %. This shows that the impregnation of the metal oxide on the support surface was successful with the result of the elemental composition of the SZ-80 catalyst. This data obtained by the EDX for the SZ-80 sample is in close agreement with the report in the literature for anthill clay (Babatunde *et al.*, 2020). Hence, the heterogeneous catalyst could be used for the transesterification process.





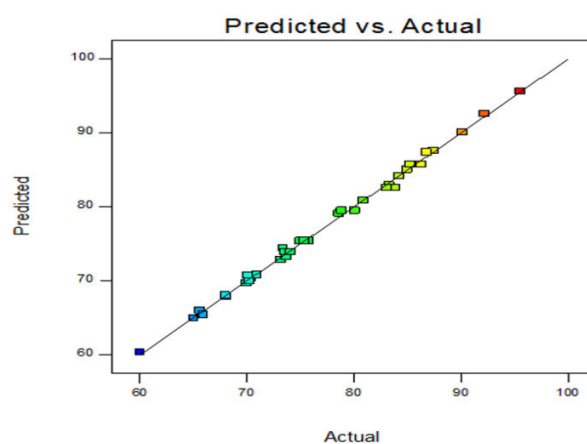
**Figure 4:(A) EDX Spectra of SZ-80 and (B) are EDX showing percentage composition of each element present in the catalyst support (SS) and SZ-80 Catalyst.**

### C. Statistical Analysis by Response Surface Methodology

The biodiesel yield represents the experimental design response. The quadratic model obtained as equation (4) with 0.9959 coefficient of determination was used to predict the corresponding response of each experimental result based on each set of process variables. The predicted yields are much closer to the experimental response data, with a predicted  $R^2$  value of 0.9765 and  $R^2$  value of 0.9959, respectively (Table 4). This shows that the model equation is sufficient in describing the relationship between independent and dependent (biodiesel yield) variables. The plot predicted against actual biodiesel yield shows a linear relationship (Figure 5).

To carry out the Analysis of variance (ANOVA), the developed second-order response surface model equation was tested using F-value. A 95 % confidence level, with an F-value of 13.05 (Table 5), was achieved; this shows that the model is statistically significant. Model terms with a probability less than 0.05 are significant, while those above 0.05 are insignificant. Therefore, A, B, C, D, AC, BC, BD, CD,  $A^2$ ,  $B^2$ ,  $C^2$ , and  $D^2$  are significant model terms, and only AB is insignificant (Table 5). The F-value of 13.05 is very small, which accounts for why only one model term is insignificant, and this shows that the lack of fits is not significant. Hence, model reduction is not necessary to improve the model.

$$Y = 97.88 + 0.74A + 1.49B + 3.47C + 2.87D - 0.068AB - 1.4AC - 0.56AD + 0.87BC - 1.05BD + 0.89CD - 6.57A^2 - 3.34B^2 - 5.53C^2 - 6.61D^2 \quad (4)$$



**Figure 5: Predicted biodiesel yield vs. Actual biodiesel yield (%)**

**Table 4: The four-factor central composite design matrix and the FAME yield**

Run	A: Methanol/ Oil ratio	B: Temp. (°C)	C: Time (h)	D: Catalyst amount (wt. %)	FAME Actual Yield (%)	FAME Predicted Yield
1	9.00	60.00	2.00	1.25	69.22	66.40
2	8.00	65.00	3.00	0.50	72.40	84.10
3	7.00	60.00	3.00	1.25	74.31	71.23
4	8.00	55.00	1.00	2.00	68.78	63.60
5	8.00	55.00	3.00	0.50	74.10	78.39
6	6.00	55.00	3.00	2.00	80.48	82.70
7	6.00	55.00	3.00	0.50	70.19	74.41
8	8.00	65.00	1.00	0.50	71.26	76.22
9	7.00	60.00	2.00	1.25	94.94	94.88
10	7.00	60.00	0.00	1.25	61.99	63.20
11	9.00	65.00	2.00	1.50	97.88	96.65
12	7.00	60.00	2.00	2.00	80.09	79.82
13	6.00	55.00	1.00	2.00	69.97	68.29
14	7.00	60.00	2.00	1.25	94.94	94.88
15	6.00	55.00	1.00	0.50	62.62	66.92
16	8.00	55.00	1.00	0.50	70.49	69.87
17	6.00	65.00	3.00	2.00	81.47	83.12
18	7.00	50.00	2.00	1.25	77.50	77.09
19	7.00	60.00	2.00	1.25	94.94	94.88
20	6.00	65.00	1.00	0.50	67.25	74.31
21	7.00	60.00	2.00	1.25	94.94	94.88
22	7.00	60.00	2.00	1.25	94.94	94.88
23	7.00	60.00	2.00	1.25	94.94	94.88
24	8.00	55.00	3.00	2.00	79.58	81.05
25	8.00	65.00	3.00	2.00	80.57	81.23
26	6.00	65.00	1.00	2.00	75.58	75.35
27	7.00	70.00	2.00	1.25	84.97	82.31
28	6.00	60.00	2.00	1.25	67.43	67.35
29	7.00	60.00	2.00	1.25	64.82	63.54
30	8.00	65.00	1.00	2.00	76.55	74.35

**Table 5: Analysis of variance (ANOVA)**

Source	Sum of Squares	Df	Mean Square	F Values	p-value Prob>F	
Model	3189.75	14	227.84	261.96	<0.0001	Significant
A-Methanol: Oil	13.31	1	13.31	15.30	0.0014	✓
B-Temperature	53.07	1	53.07	61.02	<0.0001	✓
C-Time	197.28	1	197.28	226.83	<0.0001	✓
D-Catalyst Loading	289.33	1	289.33	332.65	<0.0001	✓
AB	0.074	1	0.074	0.085	0.7741	Not significant
AC	31.16	1	31.16	35.83	< 0.0001	Significant
AD	5.10	1	5.10	5.86	0.0286	✓
BC	12.20	1	12.20	14.02	0.0020	✓
BD	17.66	1	17.66	20.31	0.0004	✓
CD	12.73	1	12.73	14.63	0.0017	✓
A <sup>2</sup>	1182.19	1	1182.19	1359.22	< 0.0001	✓
B <sup>2</sup>	305.54	1	305.54	351.30	< 0.0001	✓
C <sup>2</sup>	839.58	1	839.58	965.31	< 0.0001	✓
D <sup>2</sup>	1198.00	1	1198.00	1377.39	< 0.0001	✓

Residual	13.05	15	0.87	
Lack of Fit	13.05	10	1.30	not significant
Pure Error	0.000	5		
Cor Total	3202.79	29		

Adjusted  $R^2 = 0.9921$ , Predicted  $R^2 = 0.9765$ ,  $R^2 = 0.9959$ , Standard deviation = 0.9, PRESS = 5.15, Adequate Precision = 48.782, Mean = 77.30, C.V (%) = 1.21

#### D. Model Validation by Experiment

Sequel to the statistical analysis of the biodiesel yield and optimization of the production process, the predicted optimum yield and process conditions at a reaction time of 1 h, reaction catalyst loading of 0.5 wt%, temperature of 65°C, and methanol to oil ratio of 9:1 were subjected to triplicate experimental runs according to biodiesel production procedure stated in the methodology. This was done in order to ascertain and also establish the replication of the predicted yield. The result of the experimental validation in Table 6 shows that the

three validated yields are very close to the optimum predicted yield (98.23 %) by Design Expert 10.0 software. Hence, the optimization result is accurate as well as valid. The result in Table 6 also shows a significant achievement in terms of yield when compared with the 87.80% biodiesel yield reported for used frying oil by Ismail and Ali (2015) and the 93.20 % biodiesel yield from used frying oil by Yusuff and Owolabi (2019). The high yield of biodiesel may be associated with the effectiveness of the catalyst used. The leaching was minimal, which increased the conversion of oil to biodiesel.

**Table 6: Model validation by confirmatory experiments**

Run	Catalyst loading (wt %)	Reaction temperature (°C)	Methanol to oil ratio	Reaction time (h)	Biodiesel Yield (%)	
					Predicted	Actual
1	0.5	65	9:1	1.0	98.23	97.68
2	0.5	65	9:1	1.0	98.23	97.88
3	0.5	65	9:1	1.0	98.23	97.79

#### E. Characterization of biodiesel produced

The saponification values, acid value, free fatty acid, specific gravity, flash point, fire point, cetane number, viscosity, pour, and cloud point were determined and presented in Table 7. All the values agree with ASTM standards, which showed that the biodiesel produced is energy efficient and high quality. The higher values of the fire point and flash point show that the storage and transportation of the fuel are safe. The cloud property determines the storage and usefulness of the fuel in winter and cold environments. Acid value is an important property in determining biodiesel quality (Babatunde et al., 2025). This study's acid value of 0.1 mg KOH/g is within the maximum acceptable ASTM limit of 0.8 mg KOH/g. A high FFA content of biodiesel, oil, and fat can indicate that it has gone bad.

The 0.05 % FFA in this study is acceptable, being below the 2% threshold of ASTM. It can be inferred that the low acid value in this study is an indication that the purification process of UVO biodiesel produced was efficient. Ismail and Ali (2015) reported that biodiesel with an FFA value of more than 2% would be associated with the difficulty of post-production purification and soap separation problems. The saponification value gives information about the molecular weight of oil, which is measured with respect to milligrams of Potassium hydroxide (KOH/g oil) (Okwonna et al., 2023). The saponification value of 120.7 KOH/g recorded in this study is below the 194 KOH/g reported by used frying oil biodiesel by

Ismail and Ali (2015). The specific gravity of biodiesel is a very important property of the fuel as it affects the pump and injection system, which determines the delivery of the amount needed for complete combustion. There is not much difference between the 0.9102 specific gravity in this study and the ASTM standard of 0.872 -0.9; this shows that the biodiesel produced in this study meets the specific gravity requirement for use as biodiesel fuel. The viscosity of fluid determines the extent of resistance to the flow of the fluid; its value is temperature dependent. A more viscous fluid has a higher viscosity value and a lower flow tendency. In this study, the viscosity of 4.68 mm/s<sup>2</sup> at 40°C falls within the acceptable limit of 5-6 mm/s<sup>2</sup> at 40°C set by ASTM. However, it is slightly below 4.71 mm/s<sup>2</sup> at 40 °C for used frying oil biodiesel reported by Yusuff and Owolabi (2019).



Table 7: Characterization of UVO and biodiesel produced

Properties	ASTM Limit	Biodiesel produced
Saponification value (mg KOH/g)	-	120.7
Acid value (mg KOH/g)	0.80	0.10
FFA (wt.%)	< 2	0.05
Specific gravity at 30 °C	0.875-0.900	0.9102
Flash point (°C)	>130 (ASTM D93)	170
Fire point (°C)	-	185
Cetane number	>47 (ASTM D613)	53
Viscosity (mm <sup>2</sup> /s) @ 40°C	5-6 (ASTM D445)	4.68
Pour point (°C)	-	-22
Cloud point (°C)	-3 to 12 (ASTM D6751)	12

#### IV. CONCLUSION

Fatty acid methyl ester produced from UVO using functionalised silica-supported solid catalyst derived from anthill clay was investigated and proven to be highly effective. The reaction was optimised by four process variables, namely reaction time, temperature, catalyst loading, and methanol to oil ratio, using response surface methodology (RSM). The experimental optimum process conditions obtained with RSM were time of reaction at 1 h, catalyst loading at 0.5 wt%, temperature of reaction at 65 °C, and methanol to oil ratio at 9:1 with 97.88% yield. The developed second-order regression model equation was validated at optimum conditions. The properties of the biodiesel produced in this study are within the acceptable limit of the ASTM standards. Hence, UVO-based biodiesel could be energy efficient and a replacement for fossil fuel, thereby reducing environmental pollution and energy crises. Further studies on catalyst reusability, kinetics and economic feasibility are recommended.

#### AUTHOR CONTRIBUTIONS

**E. O. Babatunde:** Conceptualization, Data curation, Formal analysis, Validation, Writing - original draft, Methodology. Writing - review and editing

**L. Mekuto:** Funding acquisition, Project administration, Software, Investigation, Resources, Supervision,

#### DECLARATION OF COMPETING INTEREST

Authors declare no competing interest or conflicts of interest whatsoever.

#### ACKNOWLEDGMENTS

The authors would like to thank the University of Johannesburg, South Africa, for providing research facilities and the technical staff members in the Department of Chemical Engineering Technology, UJ, for their support.

#### REFERENCES

- Adepoju, T.F., Ibeh, M.A., Babatunde, E.O., Abegunde, G.S. and Asuquo, A.J. (2020):** Appraisal of CaO derived from waste fermented-unfermented kola nut pod for Fatty acid methyl ester (FAME) synthesis from *Butyrospermum parkii* (Shea butter) oil. *South African Journal of Chemical Engineering*, 33:160-171.
- Adepoju, T.F., Ibeh, M.A., Udoetuk, E.N and Babatunde E.O (2021):** Quaternary blend of *Carica papaya* - *Citrus sinensis* - *Hibiscus sabdariffa* – Waste used oil for biodiesel synthesis using CaO-based catalyst derived from binary mix of *Lattorina littorea* and *Maetra coralline* Shell. *Journal of Renewable Energy*, 171:22-33.
- Adepoju, T. F., Ukanwa, K. F., Eyibio, U. P., Etim, V., Amabogha, B., Eloka-Eboka, A. C., Balogun, T. A. (2023).** Biodiesel production from renewable biosources ternary oil blends and its kinetic-thermodynamic parameters using Eyring Polanyi and Gibb's-Duhem equations, *South Africa Journal, of Chemical Engineering*, 44, 103–112.
- Ajala, E. O., Ajala, M. A., Afolabi, F. D., Ajala, J. O., Opawoye, S. and Ariyoosu, D. A (2024).** Waste-ram-fat as a Feedstock for Biodiesel Production using Heterogeneous Catalyst of Kaolinite-clay Impregnated Calcium-oxide from Chicken Eggshell. *Nigeria Journal of Technological Development*. 21(4), 168-178.
- Ali, C. H., Asif, A. H., Iqbal, T., Sattar, A., Kazmi, M. A., Yasin, S., and Mu, B. (2018).** Improved transesterification of used cooking oil into biodiesel using calcined goat bone as a catalyst. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 40,(9), 1076-1083.
- Al-Sharifi, M. and Znad, H. (2019).** Development of a lithium-based chicken bone (Li-Cb) composite as an efficient catalyst for biodiesel production. *Renewable Energy*, 136, 856-864. <https://doi.org/10.1016/j.renene.2019.01.052>.
- Babatunde E. O., Saka H. B., Olutoye M. A., Akpan U.G. and M. Auta. (2020).** Synthesis of fatty acid methyl esters from used vegetable oil using activated anthill as catalyst. *Nigerian Journal of Technology (NIJOTECH)*, 39, (1), 140-147.
- Babatunde E. O., Saka H. B., Aderibigbe F. A., Yusuff A.S., Bisheswar K., Samuel L. R. and Gopinath H. (2022a).** Valorization of restaurant used oil and cow-bone doped siliceous termite hills towards biodiesel production: Kinetics and thermodynamics. *Journal of Sustainable Chemistry and Pharmacy*, 30:100895.
- Babatunde, E. O., Aderibigbe, F. A., Ebhodaghe, S. O. and Ogunjobi T. O (2022b):** Optimization and kinetic study of biodiesel production from beef tallow using calcium oxide as a heterogeneous and recyclable catalyst, *Journal of Energy Conversion and Management: X*, 4:100221

- Babatunde, E.O., Enomah, S., Akwenuke, O. M., Adepoju, T. F., Okwelum, C. O., Mundu, M.M., Aiki, A., Oghenejabor, O.D (2025).** Novel-activated carbon from waste green coconut husks for the synthesis of biodiesel from pig fat oil blends with tallow seed oil. *Case Studies in Chemical and Environmental Engineering*, 11:101058.
- Berchmans H.J and Hirata, S. (2012)** Biodiesel production from crude *Jatropha curcas* L. seed oil with a high content of free fatty acids. *Bioresource. Technology*, 99, (6), 1716-1721.
- Betiku, E., Omilakin, O.R and Ajala, S.O. (2014).** Mathematical modelling and process parameters optimization studies by artificial neural network and response surface methodology: A case of non-edible neem (*Azadirachta indica*) seed oil biodiesel synthesis. *Energy*, 72, 266-273.
- Bisheswar K., Sucharita S. and Gopinath H. (2020).** Delonix regia heterogeneous catalyzed two- step biodiesel production from *Pongamia pinnata* oil using methanol and 2-propanol. *Journal of Cleaner Production*, 120313.
- Chuah, L.F., Bokhari, A., Suzana, Y., Klemes, J.J., Akbar, M.M and Saminathan, S. (2016).** Optimisation on pretreatment of rubber seed (*Hevea brasiliensis*) oil via esterification reaction in a hydrodynamic cavitation reactor. *Biomass conversion and biorefinery*, 7, (1), 91-99.
- Chaveanghong, S., Smith, S. M., Smith, C. B., Luengnaruemitchai, A., and Boonyuen, S. (2018).** Simultaneous transesterification and esterification of acidic oil feedstocks catalyzed by heterogeneous tungsten loaded bovine bone under mild conditions. *Renewable Energy*, 126, 156–162.
- Dhawane, S.H., Bora, A.P., Kumar, T and Halder, G. (2017).** Parametric optimization of biodiesel synthesis from rubber seed oil using iron doped carbon catalyst by Taguchi approach. *Renewable Energy*, 105, 616-624.
- Dhawane, S. H., Karmakar, B., Ghosh, S., and Halder, G. (2018).** Parametric optimisation of biodiesel synthesis from used cooking oil via Taguchi approach. *Journal of Environmental Chemical Engineering*, 6, (4), 3971–3980.
- Goyal, P., Sharma, M.P and Jain, S. (2012).** Optimization of esterification and transesterification of high FFA *Jatropha curcas* oil using response surface methodology. *Journal of Petroleum and Science Research*, 1, (3), 36-43.
- Halder, G., Dhawane, S., Barai, P and Das, A. (2015a).** Optimizing chromium (VI) adsorption onto superheated steam activated granular carbon through response surface methodology and artificial neural network. *Environment program sustainable energy*, 34, (3) 638-647.
- Halder, S., Dhawane, S.H., Kumar, T. and Halder, G. (2015b).** Acid-catalyzed esterification of castor (*Ricinus communis*) oil: optimization through a central composite design approach. *Biofuels*, 6, 191-201.
- Ismail S. A. A. and Ali R. F. M. (2015).** Physico-chemical properties of biodiesel manufactured from used frying oil using domestic adsorbents. *Science and Technology of Advanced Materials*,
- Lee, A.F., Bennett, J.A., Manayil, J.C and Wilson, K. (2014).** Heterogeneous Catalysis for sustainable biodiesel production via esterification and transesterification. *Chemical Society Review*, 43, 7887–7916.
- Mardhiah, H. H., Ong, H. C., Masjuki, H. H., Lim, S., and Lee, H. V. (2017).** A review on latest developments and future prospects of heterogeneous catalyst in biodiesel production from non-edible oils. *Renewable and Sustainable Energy Reviews*, 67, 1225–1236.
- Nisar, J., Razaq, R., Farooq, M., Iqbal, M., Khan, R. A., Sayed, M., and Rahman, I. (2017).** Enhanced biodiesel production from *Jatropha* oil using calcined used animal bones as catalyst. *Renewable Energy*, 101, 111–119.
- Odetoye, T. E., Agu, J. O., & Ajala, E. O. (2021).** Biodiesel production from poultry wastes: Waste chicken fat and eggshell. *Journal of Environmental Chemical Engineering*, May, 105654.
- Okwonna, O. O., Obuebite, A. A., and Otaraku, I. J. (2023).** Oil extraction from *Treculia africana* seeds: process conditions, kinetic and thermodynamic studies. *Nigerian Journal of Technological Development*, 20(3):54-62.
- Olutoye, M. A. and Hameed, B. H. (2011).** Synthesis of fatty acid methyl ester from used vegetable cooking oil by solid reusable  $Mg_{1-x}Zn_{1+x}O_2$  catalyst. *Bioresource Technology*, 102, 3819-3826.
- Olutoye, M. A. and Hameed, B.A. (2013).** A highly active clay-based catalyst for the synthesis of fatty acid methyl ester from used cooking palm oil. *Applied Catalysis A: General*, 450, 57-62.
- Ozioko, F.C, Onwuachi-Iheagwara, P. N., Cyril, A., Mabel, K., Nwadiolu, R., Oboreh, J.C., Adepoju, T. F., Oboreh, J.S.(2024)** Synthesis of biofuel from *Luffa cylindrica*-*Dennettia tripetala* oil blend (BT40) using catalytic sweet corn stock acidified with iron (III) sulfate ( $Fe_2(SO_4)_3$ ), *South Africa Journal, of Chemical Engineering*. 49, 200–209,
- Ramachandran, K., Suganya, T., Gandhi, N. N., and Renganathan, S. (2013).** Recent developments for biodiesel production by ultrasonic assist transesterification using different heterogeneous catalyst: a review. *Renewable and sustainable energy reviews*, 22, 410-418.
- Refaat, A.A. (2011).** Biodiesel production using solid metal oxide catalysts. *International Journal of Environmental Science and Technology*, 8(1), 203 – 221.
- Sharma, Y. C., Singh, B. and Korstad, J. (2010).** Application of an efficient nonconventional heterogeneous catalyst for biodiesel synthesis from pongamiapinnata oil. *Energy Fuels*, 24, 3223-3231
- Sumit H. D, Tarkeshwar K. and Gopinath H. (2016).** Biodiesel synthesis from hevea brasiliensis oil employing carbon supported heterogeneous catalyst: Optimization by Taguchi method. *Renewable Energy*, 89, 506-514.
- Takase M., Zhang M, Feng W., Chen Y., Zhao T and Cobbina, S. (2014)** Application of zirconia modified with KOH as heterogeneous solid base catalyst to new non-edible oil for biodiesel. *Energy Conversion Management*, 80, 117–25.
- Wang, Z., Qu, Z., Quan, X. and Wang, H. (2012).** Selective catalytic oxidation of ammonia to nitrogen over ceria–zirconia mixed oxides. *Applied Catalysis A: General*. 114, 131-138.
- Yusuff, A. S., Adeniyi, O. D., Olutoye, M. A., and Akpan, U. G. (2018).** Development and Characterization

of a Composite Anthill chicken Eggshell Catalyst for Biodiesel Production from Used Frying Oil. *International Journal of Technology*, 1, 1-11.

**Yusuff, A. S & Owolabi J.O. (2019).** Synthesis and characterization of alumina supported coconut chaff catalyst for biodiesel production from used frying oil. *South African Journal of Chemical Engineering*, 30, 42-49.

**Yusuff, A. S., Popoola L.T. and Babatunde E.O. (2019).** Adsorption of cadmium ion from aqueous solutions by copper-based metal organic framework: equilibrium modelling and kinetic studies. *Journal of applied water science* 9, 106.

**Yusuff, A. S., Aka, O. P., Igbafe, I. A. (2023a).** Optimization of Methanolysis of Used Cooking Oil by the Taguchi Experimental Design Approach. *Chemical Engineering Technology*. 47(3), 494–503.

**Yusuff, A.S., Dada, T., Olateju, I.I., Azeez, T.M., Azeez, S.O. (2023b):** Experimental investigation of influence of methyl, ethyl and methyl-ethyl ester blends of used cooking oil on engine performances and emissions. *Energy Conversion Management X* 17, 10034.

**Zou, H. and Lei, M. (2012).** Optimum process and kinetic study of *Jatropha curcas* oil pre-esterification in ultrasonical field. *Journal of the Taiwan Institute of Chemical Engineers*, 43, (5), 730-735.