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# Optimization of biodiesel produced from waste sunflower cooking oil over bi-functional catalyst

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ABSTRACT

In the current global climate emergency and with the interesting environmental advantages of biodiesel, a look into the commercialisation of such greener fuel is essential. While raw materials account for the most in the production cost, time and energy can be economised using statistical models. The optimisation of free methyl esters (FAME) synthesised from waste sunflower oil over a novel $CaO/Al_2O_3$, and methanol was carried out at the alcohol and oil ratio of 12:1. The aim was to investigate the effect of operation parameters on the yield of the produced sunflower biodiesel, with the use of low cost and time efficient central composite response surface methodology. The chosen variables were catalyst loading, temperature, and time while the response was the yield. The catalyst loading was the most consequential parameter on yield. The linear regression model was obtained to predict responses given by these variables, with 95% confidence. The predicted and experimental yield was comparable with 92.773% and 95.665% respectively. A significant yield of 98.23% was obtained at optimal operating conditions of catalyst loading (2.5 wt%), time (5 h) and temperature (60 °C). The properties of optimised FAME were within international standard limits set for biodiesel except for the high concentrations of Ca and Mg.

## 1. Introduction

Since the petroleum resource crisis in 1970 [1], there is a 1.6% annual expectation growth in primary energy demand worldwide, as energy consumption mainly originates from fossil fuel (88%), while nuclear and renewable energy make 7% and 5% respectively [2]. The global fossil fuels production is about 934 million tonnes of diesel annually [3] and the transportation sector makes about 97.6% use of oil resources [4]. All these contribute to the potential exhaustion of petroleum reserves [5], increase in fuel prices [6] and global warming [7]. More focus has been given to renewable energy studies which are capable of environmental preservation, economic and social sustainability.

According to the Kyoto protocol, the clean energy development mechanism is driven by energy security and environmental sustainability, with biodiesel, a potential replacement of fossil fuel in the future gaining huge research interest since the 1990s. This alternative fuel with appreciable reduction of greenhouse gases or extender of petrodiesel for combustion in diesel engine [8,9]. It is not economically feasible when the high-quality feedstock is used [10] since 70–95% of production cost is due to the raw material used [11]. With the increasing use of non-edible feedstocks such as waste cooking oils, there is a reduction in production costs [12] and a need for subsidy [13].

The American Society for Testing and Materials (ASTM) has defined this fuel as mono-alkyl esters produced from either vegetable oils or animal fats [14–16]. Different oil sources such as corn, and grapeseed can be used in its production, however, sunflower oil has proved to have better fuel quality as compared to other oil sources [17,18]. Furthermore, Simbi et al. [19], reported enhanced fuel quality of biodiesel produced from waste sunflower oil as compared to waste palm oil.

As a result of the availability of edible oils such as sunflower oil in certain regions like Europe and the USA, there is more advancement of this type of renewable energy development [20]. Although edible oils can be used, their availability [10,21], price and food vs fuel dilemma cause them to be less economical [22]. Therefore, the use of low-grade oils i.e. non-edible and waste oils are much more valuable due to potentially reduced production cost, with a slight issue regarding their high free fatty acids (FFA) within the feedstocks [23,24]. Therefore,

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waste oils or high FFA feedstocks would require acid-catalysis for esterification before transesterification [25], or a two-step reaction consisting of an acid-base process [26]. Bi-functional catalysts have been shown to mediate the conversion of high FFA feedstocks to fatty acids methyl esters (FAME) due to their possession of Lewis or Brønsted basic functionality and hydrogen bond donor [27–29]. Additionally, they can enhance biodiesel production [30].

The process of transesterification is commonly used in the conversion of oils to biodiesel using an alcohol and catalyst yielding methyl or ethyl esters [31]. This process has shown impressive results in decreasing the viscosity of the oils [32]. Factors influencing the yield can be varied from feedstock compositions, alcohol type to the operation parameters such as time, temperature, and catalyst weight [23,32,33]. To save time and energy as well as complex processes, a statistical experimental design can be performed. All relevant factors necessary can be evaluated through response surface methodology (RSM), in finding optimum reaction conditions [34–37].

Such a robust mathematical modelling tool has been reliable in finding the optimum reaction conditions for biodiesel production. RSM optimisation model is preferably used when a response is dependent on a variety of independent variables. It uses a statistical experimental design central composite design (CCD) to optimize responses, minimizing the number of experiments [38,39]. This method is used to avoid the limitations caused by conventional methods where one factor is studied at the time while other variables are kept constant, which results in a large number of unnecessary experiments and waste of resources [40,41].

In this study, the production of FAME from sunflower waste cooking oil over the enhanced bifunctional catalyst was studied, to investigate the relationships between selected conditions of time, temperature and catalyst loading in obtaining a maximum yield, and optimum reaction conditions for the transesterification. Response surface methodology composed of the central composite design was employed, in the design of experiments that provided empirical equations for biodiesel conversion prediction. Finally, the produced biodiesel was tested for fuel quality (viscosity, flash point, density, oxidation stability, acid value, water content, distillation, and contaminations).

## 2. Material and methods

### 2.1. Materials

Sunflower waste cooking oil was supplied by Suppa Oils (Cape Town, South Africa), while the catalysis synthesis was performed using CaO (>68%, Sigma-Aldrich, MO, USA), and $Al_2O_3$ (99.95% Labchem, Johannesburg, South Africa). Methanol (99.5% Sigma-Aldrich, Johannesburg, South Africa) was used as the alcohol for transesterification. All chemicals used in this study were of analytical grade.

### 2.2. Synthesis of catalyst

The wet impregnation method with a modified precursor salt was used in the preparation of the $CaO/Al_2O_3$ catalyst at room temperature [19]. 75% CaO was dissolved in 100 mL deionised water and 25% $Al_2O_3$ was added under continuously stirred by an overhead stirrer for 4 h (h). To remove excess water from the synthesised catalyst, it was filtered through a grade one Whatman filter paper and the resulting slurry was dried in a static oven at 120 °C for 18 h. Thereafter the dried precursor of $CaO/Al_2O_3$ was calcined at a temperature of 475 °C for 5 h in a muffle furnace.

### 2.3. Characterisation of catalyst

Fourier Transform Infrared spectroscopy (FTIR) was used to characterise the skeletal structure and functional groups actively present on the catalyst using the TWO LITA FTIR instrument (PerkinElmer, Inc., Walthan, MA, USA) with lithium tantalate detector (LiTaO3). FTIR spectra were recorded at room temperature for 10 scans over a wavenumber region of 400–4000 $cm^{-1}$ with a resolution of 4 $cm^{-1}$. Field-Emission Scanning Electron Microscope-(FESEM) (Nova NanoSEM 230, Hillsboro, OR, USA) operating at an accelerating voltage of 5 kV was employed to determine the morphology of the catalyst and the FESEM images were recorded at a magnification of 10,000×. A multipurpose X-ray diffractometer (XRD), D8-advanced (BRUKER AXS, Karlsruhe, Germany) was used to determine the crystalline phases of the synthesised catalyst using Cu-Kα X-ray as a radiation source, (wavelength $\lambda = 1.540593$ Å) in a 2θ range of 10°–80° at a scanning speed of 0.5 s/step. To determine the surface area, pore volume and pore size distribution of the synthesised catalyst, the nitrogen adsorption-desorption method at a low temperature was employed using the Brunauer-Emmett-Teller (BET) (TriStar II 3020 Analyser version 2.00, Micromeritics, Instruments Corporation, GA, USA).

### 2.4. Optimisation of biodiesel

Transesterification reaction was carried out in 250 mL round glass flasks suspended in a controlled water bath. 30 g of sunflower waste cooking oil was mixed with methanol in a 12:1 ratio for each run, with a total of 20 optimisation runs carried out. Varying catalyst loading percentages were measured according to the set conditions which were in the range of 2.5–5.5%. The reaction was carried out at calculated temperatures (60–70 °*C*), time (3–5 h) and a constant speed of 1300 rpm. After each reaction, samples were withdrawn using a syringe and subsequently centrifuged at 2200 rpm for 10 min to separate liquids from solids within each product sample. The liquid was decanted out into separating funnels while suspended catalyst residues were removed. Under the separating funnel, two liquid layers were formed with the upper layer presenting biodiesel with methanol while the bottom layer was glycerol. Glycerol was exited out through the bottom funnel, while trace methanol was removed by washing with warm deionised water (50 °C). The resultant biodiesel was dried using hot plates and to quicken the drying of the biodiesel, a drop of drying agent ($Na_2SO_4$) was added. The biodiesel was then left to cool down and store in an appropriate container for further use.

### 2.5. Reusability of catalyst

The stability of the $CaO/Al_2O_3$ catalyst synthesised by the wet impregnation method was examined for 5 cycles under the optimum conditions, with oil to-methanol molar ratio of 12:1, 2.5 wt% catalysts (based on oil weight), a reaction temperature of 60 °C, and a reaction time of 5 h. After each cycle, the used catalyst was separated from the reaction mixture by centrifugation and washed with methanol to remove any impurities of oil and/or glycerol. Before reusing in a new reaction cycle, the used catalyst was dried in an oven at 100 °C for 12 h and followed by recalcination at 475 °C for reutilization.

## 3. Results and discussion

### 3.1. Catalyst characterisation

The nitrogen adsorption-desorption isotherms recorded for $CaO/Al_2O_3$ shown in Fig. 1 revealed a type IV isotherm with an H1 desorption hysteresis loop conforming to a mesoporous material containing relatively wide cylindrical pores [42,43]. The surface area, pore volume and diameter for the synthesised catalyst were 13.001 $m^2/g$, 0.080 $cm^3/g$ and 24.037 nm respectively. As observed in Table 1, there was a significant enhancement in texture properties of the synthesised catalyst from 0.624 $m^2/g$ to 13.001 $m^2/g$, 0.001 $cm^3/g$ to 0.080 $cm^3/g$, and 5.915 nm–24.0377 nm with the impregnation CaO into $Al_2O_3$, calcinated at high temperatures ($75\%CaO/25\%Al_2O_3$).

Fig. 2 (a, b, and c) displays the XRD patterns of CaO, $Al_2O_3$ materials before calcination and after the $75\%CaO/25\%Al_2O_3$ catalyst was

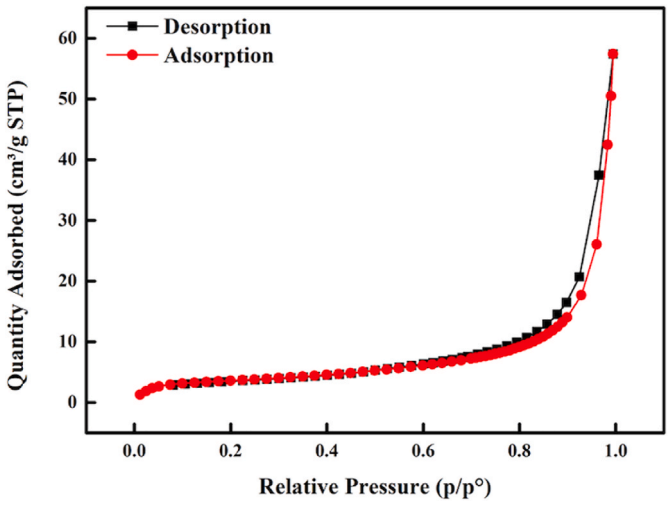


**Fig. 1.** Nitrogen Adsorption-desorption isotherm of synthesised 75%CaO/25%$Al_2O_3$.

**Table 1**
Textural parameters for $Al_2O_3$ and 75%CaO/25%$Al_2O_3$ catalyst.

| Catalyst | BET Surface Area ($m^2$/g) | Pore Volume ($cm^3$/g) | Pore Diameter (nm) |
|---|---|---|---|
| $Al_2O_3$ | 0.624 | 0.001 | 5.915 |
| 75%CaO/25% $Al_2O_3$ | 13.001 | 0.080 | 24.037 |

synthesised. The peaks of CaO (Fig. 2a) can be indexed to 32.20 °, 37.35 °, 54 ° and 64.15 ° representing face-centred cubic shape [44,45]. While rhombohedra $Al_2O_3$ support (Fig. 2b) appeared at intensified peaks of 25.55 °, 35.11 °, 43.30 °, 52.49 °, 57.43 ° and 68.13 °. The CaO/$Al_2O_3$ pattern (Fig. 2c) also indicated small peaks of rhombohedral $CaCO_3$, hexagonal $Ca(OH)_2$ and $(H_3O)_2Al_{22}O_{34}$, which were spread through with intense peaks of Ca(OH), CaO and $Al_2O_3$ in that order [19].

The FESEM images illustrating the external morphological characteristics of $Al_2O_3$ and synthesised CaO/$Al_2O_3$ are shown in Fig. 3. The FESEM micrograph of $Al_2O_3$ shows a corundum crystal particle, generally found to encourage densification of corundum shape-like composites. While the coexistence of CaO and $Al_2O_3$ was found to affect the morphology of $Al_2O_3$, a modification of $Al_2O_3$ into irregularly shaped clusters owing to the breakage of huge particles into smaller pieces is evident.

The presence of active functional groups has been confirmed by FTIR spectroscopy in Fig. 4, with absorption bands in the range of 400–4000 $cm^{-1}$. Fig. 4a illustrates CaO characteristics with carbonates species stretching at 874 $cm^{-1}$ and 1409.32 $cm^{-1}$ [46]. Before catalyst thermal treatment, the catalyst had some molecules of water which was indicated by a sturdy hydroxyl (H–O) bond stretching at 3640.79 $cm^{-1}$ vibrations [47,48]. The H-bonded hydroxyl group appeared due to moisture and the presence of $CO_2$ [43]. Fig. 4b illustrates a series of low wavenumber regions from 1000 to 400 $cm^{-1}$, which were characteristics peaks for Al–O (636.06 $cm^{-1}$, 554.55 $cm^{-1}$ and 485.48 $cm^{-1}$) [49,50]. The co-existence of Ca–O and Al–O within synthesised CaO/$Al_2O_3$ catalyst was confirmed in Fig. 4c, by the presence of CaO absorption bands at 875 $cm^{-1}$ and 713 $cm^{-1}$ corresponding to C–O and Ca–O bonding. Also, a larger $CaCO_3$ band was observed at 1469.80 $cm^{-1}$ [51].

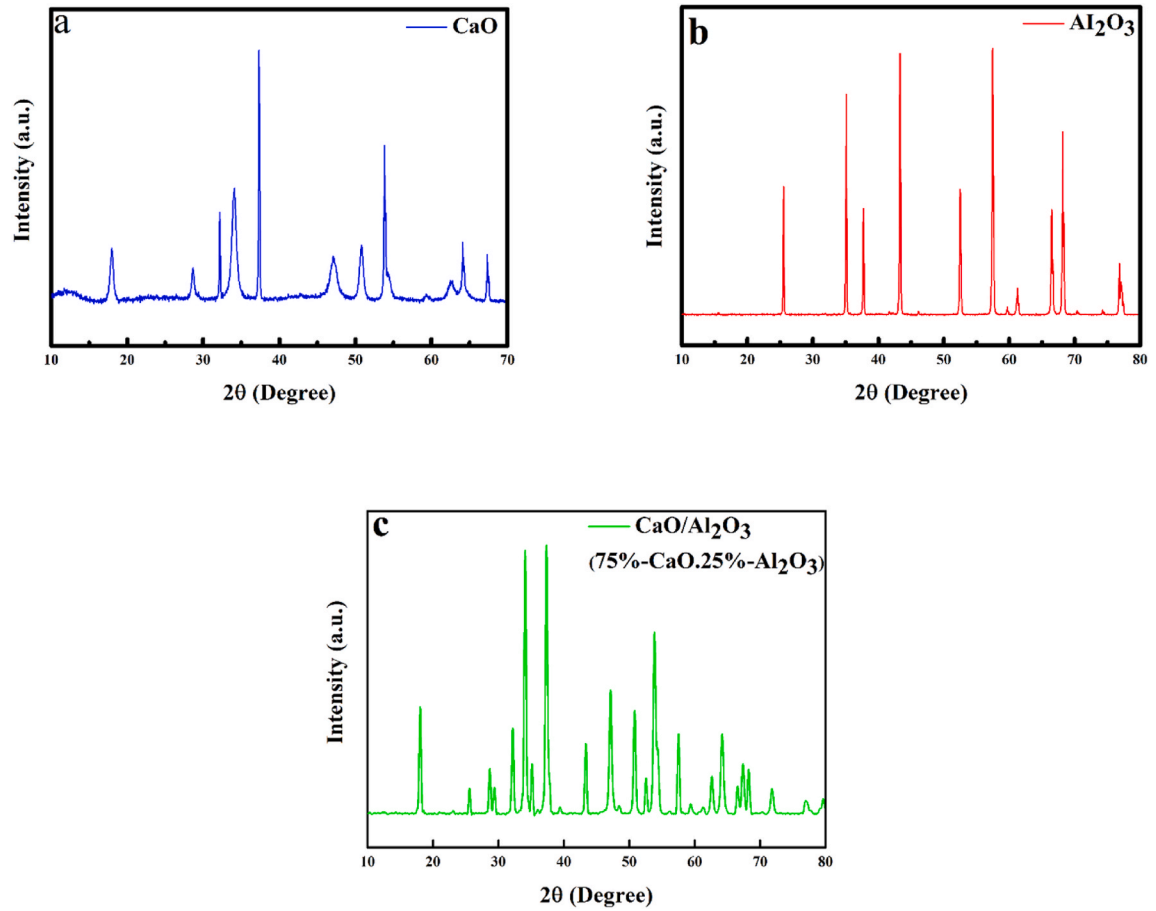


**Fig. 2.** XRD patterns of (a) CaO, (b) $Al_2O_3$ and (c) 75%CaO/25%$Al_2O_3$ catalyst.

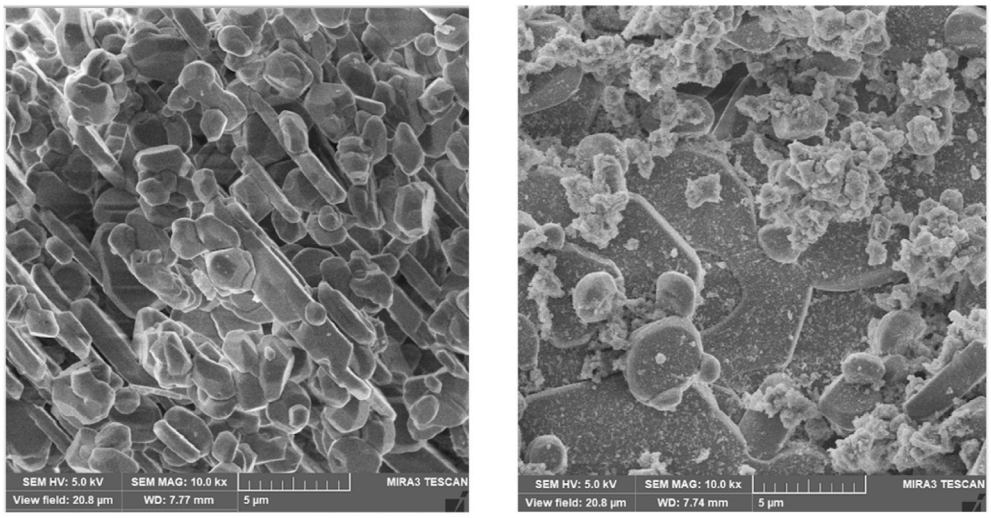


**Fig. 3.** SEM images for (a) $Al_2O_3$ and (b) 75%CaO/25%$Al_2O_3$ bifunctional catalyst.

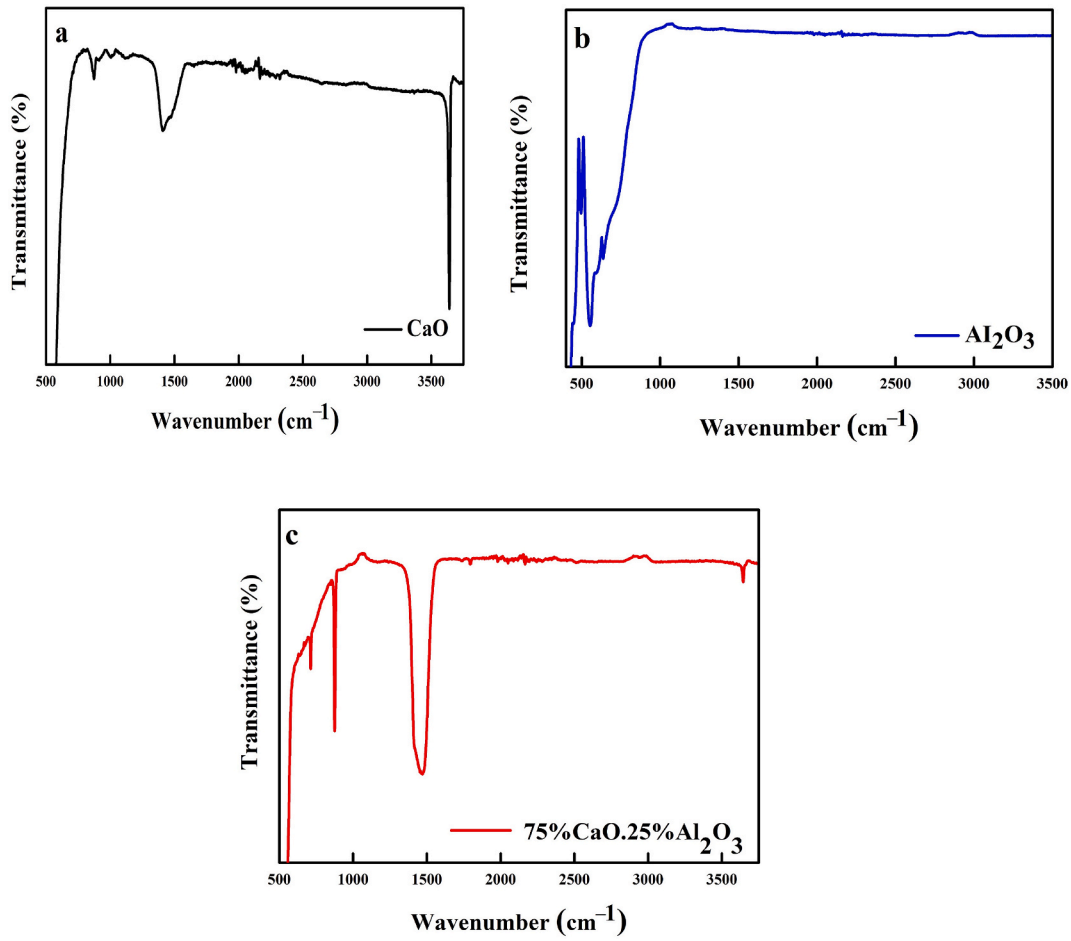


**Fig. 4.** FTIR spectra of (a) CaO (b), $Al_2O_3$ and (c) 75%CaO/25%$Al_2O_3$ bifunctional catalyst.

### *3.2. Statistical analysis using response surface methodology*

This study used applications of central composite design (CCD) and response surface methodology (RSM) techniques in the optimisation of sunflower biodiesel since these methods are conventionally used for environmental and chemical processes i.e. the transesterification of FAME [52]. This has the capability of generating a model equation and calculating the optimum conditions [34].

The experimental design applied was $2^3$ factorial response surface methodology using Design-Expert Software version 12.0.9.0 (STAT-EASE Inc., Minneapolis, USA). Regression and analysis of experimental data were employed in investigating the impact of time (A), temperature (B) and catalyst loading (C) on the yield of biodiesel. These variables had ranges of time 3–5 h, temperature 60–70 °C and catalyst loading 2.5–5.5 wt%. A randomised order was followed with a combination of each variable at either its lowest (−1) or highest (1) level in 20 experimental runs. Analysis of variance (ANOVA) was used in the statistical analysis of the model and check for adequacy of the empirical model; the model fit was evaluated using coefficients determination ($R^2$) and a linear polynomial equation from regression analysis was developed to plot response surface. Table 2 lists the experimental design layout of ranges and levels of those independent variables in the study with the response obtained. The conversion of waste sunflower oil to FAME ranged from 87.567% to 98.23% in yield with design points 2 and 4 respectively, at minimum operation condition at 65.95 °C, with 3.75673 wt% for 3.07 h and maximum conditions of 64.5 °C, with 4.15 wt% for 4.96 h.

### 3.3. Validating the mathematical model

The accuracy of the model was checked with residual analysis plots [36], in Figs. 5–7, where good conformity was seen in Fig. 5 since the line was linear. While the graphical collation of experimental and predicted values of the response variable is illustrated in Fig. 6, there is a reasonable data fit along the line of unit slope [52]. Colour indicators starting from dark blue to red on the graph indicate the lowest to highest yield. An adequate model is shown in Fig. 7, indicated by the random patterns of residuals, where all points were within limits which are good [53]. To find optimum conditions in the synthesis of biodiesel, a numerical optimisation was conducted by minimizing all 3 independent variables to maximize yield, and responses given by the software were reaction time of 3 h with catalyst loading of 2.5 wt% at a reaction temperature of 60 °C having a conversion of 95.129% and highest desirability of 0.918, while high conversion of 97.014% was achieved when all variances were kept in range to maximize the yield. However, the desirability was 0.886, the conditions given were temperature of 60 °C, 2.5 wt% catalyst loading for 5 h. Different variable ranges were assessed for good yield and optimisation. It was concluded for this study that for the transesterification of waste sunflower oil, with 12:1 methanol to oil ratio at speed of 1100 rpm, optimum reaction parameters chosen for this model were 2.5 wt%, 60 °C for 5 h which was desirable in comparison to the previous study reported by Kesić et al. [54].

**Table 2**
Experimental design layout of 3 parameters with results of the response.

| Run | Factor 1 A: Time (hrs) | Factor 2 B: Temperature (°C) | Factor 3 C: Catalyst loading (wt %) | Response 1 Yield (%) |
|---|---|---|---|---|
| **1** | 4.9 | 69.5 | 4 | 97.5 |
| **2** | 3.07 | 65.95 | 3.75673 | 87.567 |
| **3** | 3 | 60 | 3.61 | 93.5 |
| **4** | 4.96 | 64.5 | 4.15 | 98.23 |
| **5** | 4.25 | 60 | 5.5 | 89.267 |
| **6** | 5 | 60 | 2.5 | 95.667 |
| **7** | 3 | 60.0299 | 5.49306 | 95 |
| **8** | 3 | 70 | 2.5 | 95.83 |
| **9** | 3.9 | 64.5 | 2.56 | 94.93 |
| **10** | 3.9 | 64.5 | 2.56 | 95.567 |
| **11** | 4.96 | 64.5 | 4.15 | 93.93 |
| **12** | 3 | 66.3 | 5.5 | 91.167 |
| **13** | 5 | 70 | 5.5 | 89.23 |
| **14** | 4.96 | 64.5 | 4.15 | 95.4 |
| **15** | 3.9 | 64.5 | 2.56 | 95.73 |
| **16** | 3.9 | 69.85 | 4.15 | 94.63 |
| **17** | 5 | 70 | 2.5 | 96 |
| **18** | 4.17 | 65.85 | 5.485 | 89.93 |
| **19** | 4.17 | 60.25 | 3.745 | 95.8 |
| **20** | 3.9 | 69.85 | 4.15 | 95.167 |

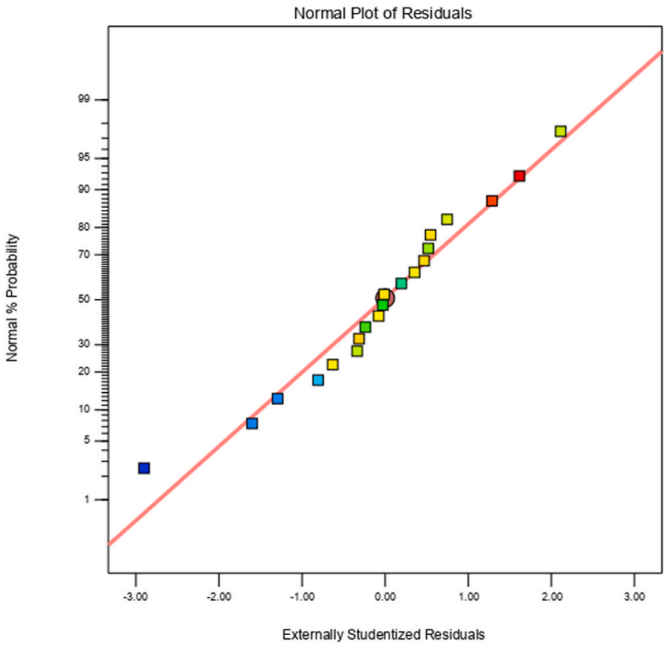


**Fig. 5.** Normal distribution of Residuals.

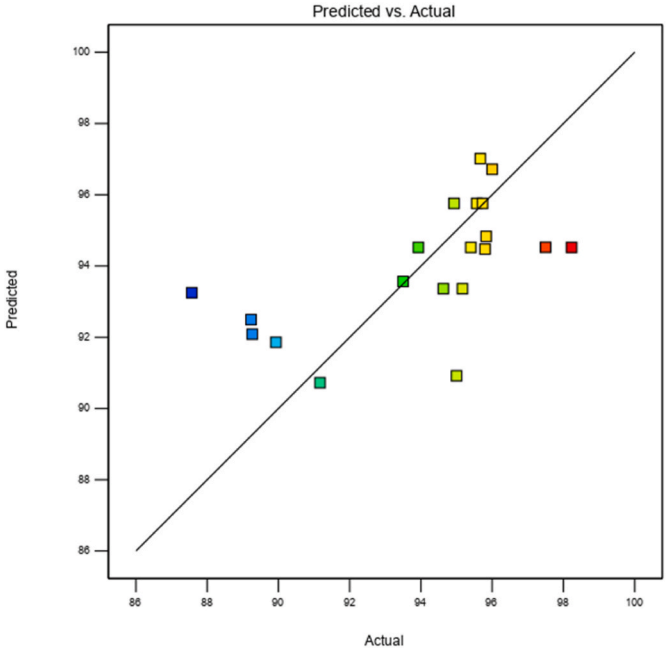


**Fig. 6.** Predicted vs actual plot of the response variable.

### 3.4. Interaction effects of parameters on yield

#### 3.4.1. Interaction of reaction time and temperature on yield

An increase in the temperature of the reaction will increase the reaction rate by decreasing the viscosity of oils and reducing reaction time [55]. In Fig. 8, the influence of temperature and time on the yield of FAME when catalyst loading was kept at optimum (2.5 wt%), a high yield was found as compared to using 5.5 wt%. Increased catalyst weight from 2.5 to 5.5 wt% reduced yield significantly from 96 to 89.23%. An increased catalyst loading resulted in the mass transfer challenge, which reduces the accessibility of reactants to the active sites. When the

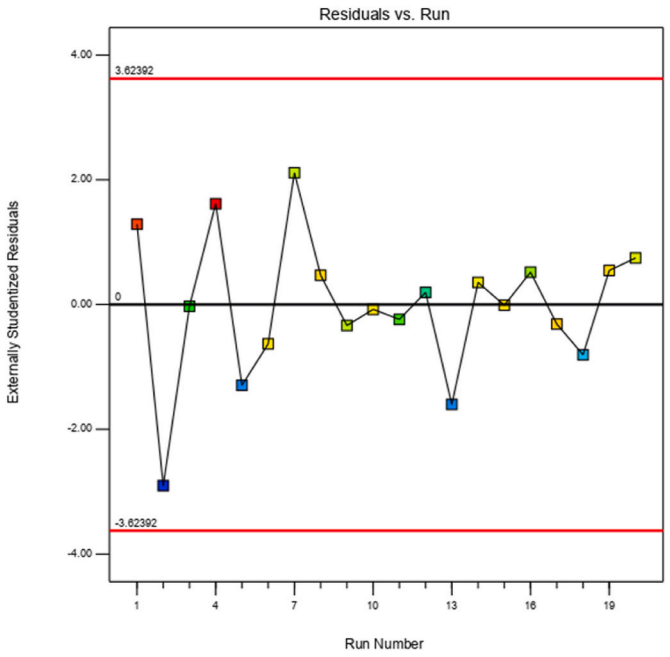


**Fig. 7.** Residuals vs run orders.

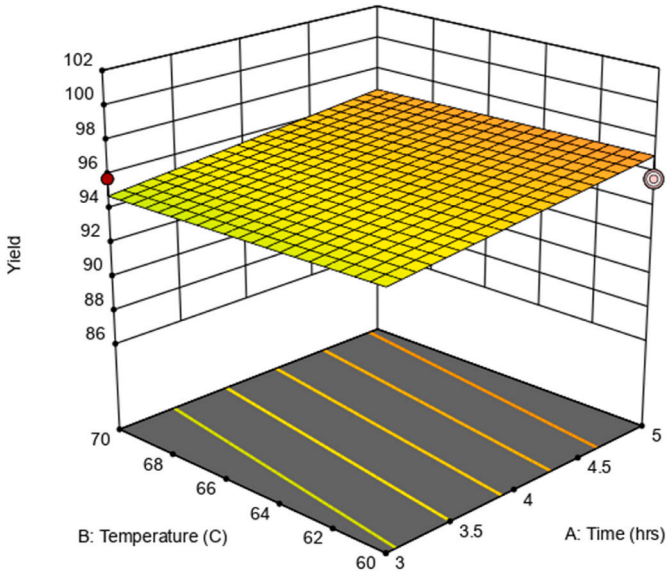


**Fig. 8.** Interaction of reaction temperature and time on biodiesel yield.

temperature was kept at 60 °C and time was maximized to 5 h, a 95.667% yield was found, while 95.830% yield was obtained when the maximum temperature of 70 °C was applied and minimum time of 3 h. However, this appeared above the surface design, and consequently in maximizing both time and temperature to 5 h and 70 °C, a 96% yield was found which was below the surface design. This was supported by the literature [36], that at low catalyst loading, elevating temperatures increased the yield. While keeping the temperature constant at a maximum of 70 °C and increasing the time from 3 to 5 h resulted in an increased yield from 95.83 to 96%, as the bulk of waste cooking oil (WCO) was converted to FAME over a longer reaction time. This observation was supported by a previous study by Kesserwan et al. [56].

On the other hand, keeping time constant at 5 h and having an increase in temperature from 60 to 70 °C resulted in a yield of 95.667–96% which is in agreement with a previous report by Phan & Phan, [57]. An increase in temperature of the reaction from 30 to 50 °C increased yield from 88 to 99%, while a high increase in temperature up to 70 °C reduced the conversion of WCO. This was in contrast with the results obtained for the current study. Additionally, there is a need to obtain a reaction temperature that consumes less energy while giving a high yield and therefore reducing the cost of production [12]. Leung et al. [58], found optimum reaction temperatures to be between 50 °C and 60 °C, while Knothe [59], found that a typical temperature of 60–65 °C should be used in transesterification in presence of methanol. Therefore, from the results obtained, employing a temperature of 60 °C for 5 h was considered as ideal to save more energy as opposed to using 70 °C for 5 h.

### 3.4.2. *Interaction of reaction time and catalyst loading on yield*

The interaction between time and catalyst loading is illustrated in Fig. 9. This is more significant than other interactions since all the design points appeared within the surface. A decrease in catalyst loading with elevating the reaction time increased the yield, therefore a maximum of 5 h reaction time with catalyst loading of 2.5 wt% is expected to have the highest desirability and yield which was 95.83%. This was also true when the reaction was kept at 60 °C, while in increasing the temperature there was a significant decrease in the design points. Moreover, when the time was decreased to 3 h and catalyst loading was increased from 2.5 to 5.5 wt%, a 93.5% yield was observed for reaction of 3 h and 3.61 wt% while elevating time and catalyst loading to 4.25 h and 5.5 wt%, the yield was reduced to 89.296%. The significance of catalyst loading and time is supported by p-values in Table 3. which shows that catalyst loading was the most significant factor having the lowest value, then time and lastly temperature.

### 3.4.3. *Interaction of reaction temperature and catalyst loading on yield*

Fig. 10 illustrated the interaction between temperature and catalyst loading, with reaction time kept constant at 5 h. When the reaction time was decreased, the desirability and most of the design points were above the surface, only one point was below the surface design, which had a yield of 93.5% using reaction conditions of temperature and time of 60 °C and 3 h respectively. In the figure, when conducted at a temperature of 70 °C, and with catalyst loading of 2.5–5.5 wt%, the yield obtained was 96–89.23%. However, a 95.667% yield was achieved when the temperature was decreased to 60 °C and catalyst loading of 2.5 wt%. It is noticeable from the results, that low catalyst loading with either low or high temperatures should be considered. However, according to the interaction between temperature and time as well as catalyst loading,

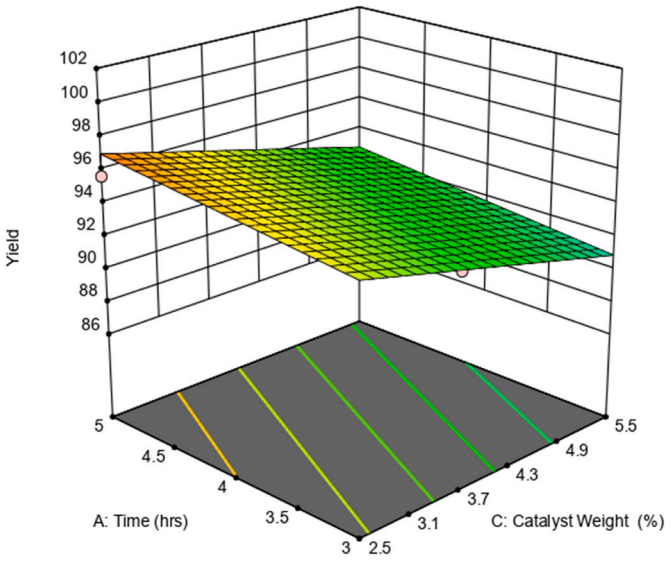


**Fig. 9.** Interaction between time and catalyst loading.

**Table 3**
ANOVA for the linear model.

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|---|---|---|---|---|---|---|
| Model | 60.04 | 3 | 20.01 | 3.02 | 0.0603 | Not significant |
| A-Time | 9.95 | 1 | 9.95 | 1.50 | 0.2378 | Not significant |
| B-Temperature | 0.2328 | 1 | 0.2328 | 0.0352 | 0.8536 | Not significant |
| C-Catalyst Weight | 48.05 | 1 | 48.05 | 7.26 | 0.0159 | Significant |
| Residual | 105.89 | 16 | 6.62 | | | |
| Lack of Fit | 95.84 | 11 | 8.71 | 4.33 | 0.0589 | Not significant |
| Pure Error | 10.05 | 5 | 2.01 | | | |
| Cor Total | 165.93 | 19 | | | | |

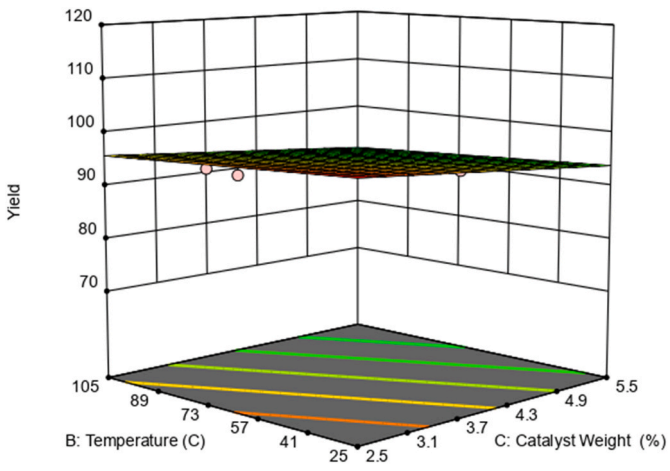


**Fig. 10.** Interaction of reaction temperature and catalyst loading on yield of biodiesel.

there is a clear observation that high temperature is not desirable. The use of low temperature, low catalyst loading, and high reaction time should be used for experiments to obtain optimum yield with high desirability.

Tables 4–6, show the summary of the analysis of different models, the possibility of their significance in evaluating the most effective parameters on the yield of biodiesel. While a detailed summary of the suggested model, with a significant of 95% confidence intervals is shown in Table 3. Normally, insignificant models appear when p-values of parameters are greater >0.05 [60]. Hence, the list of variables that were significant at < 0.05 of each catalyst loading was 0.0159, with the highest F-value of 7.26 among the other variables, while time and temperature had 0.2378, 0.8536 and 1.50, 0.0352 of p-values and F-values respectively. This confirmed that catalyst loading was the most important variable in biodiesel produced from WCO [36]. Therefore, time and temperature could not be disregarded since they were necessary for the support of the model hierarchy.

The selected model had an insignificant lack of fit since its p-value was 0.0589 which was slightly higher than 0.05 [61]. This was better compared to 0.0258 for the quadratic model and 0.0432 for the two-factor interaction (2FI) model as seen in Table 5. The p-value > 0.05 implies that there was no significance relating to pure error, which is good as it specifies that the model is fitted to all data [34]. F-value found for the suggested model was 3.02, implying that there is a 6.03% (0.0603 p-value) possibility that such occurrence was due to noise, which is in agreement with Worapun et al., [35]. The adequate precision which measures signal to noise ratio was found to be 5.468, which indicated adequate signal since it was above 4 [34]. Based on actual parameters, a linear regression model equation shown below can be used to make predictions about the response for given levels of each factor:

$$Y = 97.60355 + 0.942336A - 0.029759B - 1.40628C \quad (1)$$

Here, Y is the response variable which is the yield of FAME. A, B, and C are actual values of predictors, namely time, temperature and catalyst loading respectively. The positive sign in front of a term is pro linearity while the negative sign shows an antagonistic effect on Y [51]. This shows that an increase in reaction time will have a positive effect on yield while a decrease in temperature and catalyst loading will increase the yield, this is further supported by the interaction of parameters shown in Figs. 8–10. The quality of the model fit was evaluated using R-squared ($R^2$), where predicted $R^2$ measures how good the model predicts values for response (Table 4) [34]. The $R^2$ value is always between 0 and 1 and according to Worapun et al. [35], a good statistical model should be closer to 1. The linear model had an $R^2$ value of 0.3618 and negative predicted $R^2$ (−0.0352) while the cubic model had better $R^2$ and adjusted $R^2$ results of 0.9394 and 0.7697 respectively. Even though the cubic model had good $R^2$ values as compared to other models, the predicted $R^2$ was not calculated due to some missing data which is evident in Tables 4–6, therefore, making it aliased. Negative predicted $R^2$ implies that the overall mean, which was 94 for the suggested model might be a better predictor. Nevertheless, the adjusted $R^2$ for the suggested model was 0.2422 (24.22%), which was within 0.2, confirming no issue with experimental data or the model [34]. Therefore, since the sum of squares was 60.04 for linear vs mean, a polynomial order was suggested where other terms are significant and not aliased.

**Table 4**
Model summary statistics.

| Source | Std. Dev. | $R^2$ | Adjusted $R^2$ | Predicted $R^2$ | PRESS | |
|---|---|---|---|---|---|---|
| Linear | 2.57 | 0.3618 | 0.2422 | −0.0352 | 171.77 | Suggested |
| 2FI | 2.68 | 0.4368 | 0.1768 | −1.2950 | 380.79 | |
| Quadratic | 2.84 | 0.5132 | 0.0750 | −4.7170 | 948.60 | |
| Cubic | 1.42 | 0.9394 | 0.7697 | | * | Aliased |

### 3.5. Properties of optimised sunflower biodiesel

Table 7 shows the properties of optimised biodiesel from sunflower waste cooking oil. Almost all results obtained were within the limits specified by the International standard for biodiesel ASTM or EN.

#### 3.5.1. Viscosity

The viscosity is a property that has a major role in biodiesel having a great contribution in the atomization of the fuel as reported by Borugadda et al. [6], and there is a need for the lowering of viscosity in the vegetable oil [62]. Through the process of transesterification, reduction of the viscosity in oils is achievable [63]. The process transforms triglycerides which are highly unsaturated fatty acids and very susceptible to oxidation [64], into mixtures of long-chained fatty acid esters, which are more saturated [65]. The decrease of the viscosity in biodiesel is observed in an order of magnitude than that of its source oil [66]. The viscosity of the produced biodiesel was 5.33 $mm^2/s$ (Table 7), from 29.8 $mm^2/s$ of sunflower waste cooking oil. In studies conducted by Knothe [67], and Gopinath et al. [66], viscosity was reported to increase according to molecular structure, chain length of hydrocarbons and degree of saturation. Produced FAME from waste sunflower cooking oil, in this

**Table 5**
Sequential model sum of squares.

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|---|---|---|---|---|---|---|
| Mean vs Total | 1.767E+05 | 1 | 1.767E+05 | | | |
| Linear vs Mean | 60.04 | 3 | 20.01 | 3.02 | 0.0603 | Suggested |
| 2FI vs Linear | 12.43 | 3 | 4.14 | 0.5765 | 0.6406 | |
| Quadratic vs 2FI | 12.68 | 3 | 4.23 | 0.5231 | 0.6761 | |
| Cubic vs Quadratic | 70.73 | 5 | 14.15 | 7.03 | 0.0258 | Aliased |
| Residual | 10.05 | 5 | 2.01 | | | |
| Total | 1.769E+05 | 20 | 8844.69 | | | |

**Table 6**
Lack of fit tests.

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|---|---|---|---|---|---|---|
| Linear | 95.84 | 11 | 8.71 | 4.33 | 0.0589 | Suggested |
| 2FI | 83.40 | 8 | 10.43 | 5.18 | 0.0432 | |
| Quadratic | 70.73 | 5 | 14.15 | 7.03 | 0.0258 | |
| Cubic | 0.0000 | 0 | | | | Aliased |
| Pure Error | 10.05 | 5 | 2.01 | | | |

**Table 7**
Physico-chemical properties of optimised sunflower biodiesel.

| Biodiesel Properties | Sunflower biodiesel | ASTM D6751 | EN 14214 | Unit |
|---|---|---|---|---|
| Kinematic Viscosity @40 °C | 5.33 | 1.9–6 | 3.5–5 | $mm^2/s$ |
| Density @15 °C | 0.8811 | 0.80–0.90 | 0.875–0.90 | $g/cm^3$ |
| TAN | 0.2 | <0.5 | <0.5 | mg KOH/g |
| Oxidation Stability @110 °C | 4.20 | 3 | >6 | hrs |
| Water Content (ppm) | 0.03 | Max 0.08 | <0.05 | wt% |
| Flash Point | 170 | >130 | >120 | °C |
| Distillation 90% | 335.59 (@80%) | <360 | | °C |
| 10%dist. Residue | 24 | – | | % mass |
| Ca, Mg by ICP-OES | 27.559 | Max 5 | | mg/L |
| Na, K by ICP-OES | 0.333 | Max 5 | | mg/L |
| Phosphorus | 8.239 | Max 10 | Max 10 | mg/L |
| Sulfur | 4 | - | Max 10 | mg/L |
| Nitrates | 10 | | | |
| Sulphates | 111 | | | |
| Glycol | 0 | | | |
| Sool | 1 | | | |
| Total contaminant | >40 | - | <20 | mg/L |

study was found to have a good viscosity which meets the ASTM standardisation, as compared to those found by Hossain and Boyce, [68]. For neat sunflower cooking oil and waste sunflower cooking oil the determined viscosity of their biodiesels were 5.8 $mm^2/s$ and 9.5 $mm^2/s$ respectively.

### 3.5.2. Density

The density of the fuel quality affects its performance, engine emissions, production, transportation and distributions [69]. The produced biodiesel had a density of 0.8811 $g/cm^3$ as shown in Table 6, The density will improve from the oil to the biodiesel, a reduction was reported by Samanta and Sahoo [70], since density increases with decreasing chain length and increasing number of double bonds [61]. However, the decrease in density from oils to biodiesel is usually not much as previously reported by Simbi et al. [19], due to the similarity within feedstocks. In this study, methanol (0.792 $g/cm^3$) which was used in the process of converting waste sunflower oil (0.9225 $g/cm^3$) into biodiesel, have very close values to the actual alkyl methyl esters. The high density resulted in the increased mass of injected fuel, causing elevated heat and carbon, and consequently increasing power in diesel engines [71]. The density of biodiesel is usually between 0.86 $g/cm^3$ and 0.90 $g/cm^3$ which is higher than that of diesel fuel [72,73].

### 3.5.3. Oxidation

As shown in Table 6, the oxidation stability was measured by induction periods of methyl esters produced from waste sunflower using the Rancimat method as described in Ref. [74]. According to a report by Yaşar [18], if feedstocks have more polyunsaturated fatty acids, they will oxidize more than those with saturated fatty acids. Therefore, resulting in low oxidation stability as reported by Moser [75], waste sunflower oil possess high linoleic acid causing low stability as compared to other biodiesel i.e. palm biodiesel [19]. The studies conducted by Can [76], and Cursaru et al. [77], found the oxidation stability of biodiesel produced from waste sunflower oil to be extremely low with 0.43 h and 1.81 h. However, this study recorded improved oxidation stability of 4.2 h [19].

### 3.5.4. Flashpoint

This is an important measure that determines the handling and transportation safety [78], indicating the flammability of the fuel as it considers the lowest temperature at which heated vapor and the air above the fuel will ignite [79]. This guides against contamination of highly volatile impurities [7]. In this study flashpoint for sunflower biodiesel was 170 °C as seen in Table 6 which according to Yasin et al. [73], was found safe. The flashpoint of biodiesel is different to mineral petrodiesel by 85% according to Senthil and Silambarasan [80], adding that normally it is above 150 °C. Similarly, in a study by Sirisomboonchai et al. [23], in biodiesel produced from waste cooking oil (WCO), the flashpoint of 179 °C was reported. Therefore, in this study sunflower biodiesel produced is regarded as safe.

### 3.5.5. Water content

The water content test was carried out using the European standards since the test was done separately from sediments [81]. The extremely hygroscopic nature of the biodiesel promotes biological growth within biodiesel storage which subsequently leads to further corrosion of metals such as copper (Cu), iron (Fe), chromium (Cr) and zinc (Zn) [82]. Additionally, the presence of water will cause low heating value in biodiesel [83], and together with the FFA within feedstock, the formation of soap will occur during transesterification as a result of the reduction in catalytic effectiveness, subsequently reducing the yield [2]. According to Table 6, the produced sunflower biodiesel had a water content of 0.03 wt% which was below the maximum limits allowed by international standards. This was lower than those found in literature for biodiesel produced from sunflower and waste cooking oils [36,77].

### 3.5.6. Acid number

The produced sunflower biodiesel had an acid number of 0.2 mg KOH/g which was below the standard limit as seen in Table 6. A similar value was found for biodiesel produced from clean sunflower oil [77]. This property indicates the presence of FA in the biodiesel, the increase in acid number is caused by organic acids and oxidation. High acid can result in severe corrosion of the fuel supply systems in petrodiesel engines [84]. From the study by Avila Orozco et al. [85], it was reported that various biodiesels produced from different sunflower oils and other

oils had acid values ranging from 0.3 to 0.6 mg KOH/g. The acid number value is important for controlling degradation during storage and needs to be kept low [73]. Therefore, there was an improvement with the produced biodiesel. The acid value of this study was lower than those found in literature, where an alkaline catalyst was used for the transesterification of both pure and waste sunflower oils to biodiesel [1,43].

### 3.5.7. Metal content

According to Table 6, sunflower biodiesel had 27.559 mg/L of calcium and magnesium (Ca + Mg), 0.333 mg/L of sodium and potassium (Na + K), 8.913 mg/L of phosphorus (P) and 4 mg/L of sulfur (S). Additionally, sulphates were extremely high while nitrates, soot and glycol were low. According to Lyra et al. [86], The presence of these metals could have been incorporated into the biodiesel during the cleaning and washing process, and the feedstock used [87], or left in by the catalyst used [19]. Contamination by soot, nitrates, sulphates and glycol indicate chances for incomplete combustion, engine failure and operating condition issues, therefore are undesirable, Furthermore, the presence of elemental compounds in the biodiesel is usually due to degradation or contamination, by harmful compounds in the engine [88]. According to standard requirements for the total contaminants in biodiesel, the produced sunflower biodiesel failed with Ca + Mg metals, and sulphates as they were higher than the standards limit. These compounds are responsible for emission hence, a reason for great concern.

### 3.5.8. Distillation

Distillation is crucial in terms of the safety and behavior of the fuel as it measures the percentage of vaporized fuel as temperature increases [89]. The presence of components in the fuel with high boiling points will have an influence on the formation grade solid deposit during combustion [90]. Therefore, the recommended temperature for biodiesel distillation is 360 °C maximum, at a temperature of 90% distilled volume (T90), as the sunflower biodiesel was completely evaporated at this point with its final boiling point being 335.59 °C at 80% distilled volume (T80). High boiling points at T90 indicates the presence of heavy compounds and therefore deposits build-up and engine problems [91]. However, the 10 vol% distillation residues were 24%. This was above the 0.3% standard limit set for biodiesel. High carbon residues indicate the presence of impurities and deposits in the biodiesel i.e. methanol, glycerol, catalyst residues, which will decrease the flashpoint and cetane number and subsequently lead to corrosion and blockage of nozzles [57,92,93].

## 3.6. Reusability test

The results of bifunctional $CaO/Al_2O_3$ catalyst's reusability in transesterification experiments of the waste sunflower oil and methanol were carried out with optimal conditions of 2.5 wt% catalyst weight at 60 °C for 5 h, to obtained optimum yield. Fig. 11 shows the reusability of the catalyst in sunflower biodiesel yield for five successive reuse cycles. It was observed that the biodiesel yield decreased as the catalyst was continuously used during each stage, from 95.402% to 76.379% after the fifth cycle. The 19.023% loss in the efficiency at the fifth cycle of the catalyst reuse was ascribed to the loss in active sites on the catalyst surface [94], and the agglomerations of the catalyst particle [95], or catalyst leaching [96,97]. Finding in this study was also supported by the reported in Zabeti et al. (2009) study [34], where CaO-based catalysts were reported to be deactivated due to CaO reacting with glycerol forming calcium diglyceroxide, hence resulting in reduced catalyst activity and subsequently lower yield of the biodiesel. The surface of CaO was also found to react with air or $CO_2$, hence leading to the poisoning of active sites, which resulted in inactive catalyst and a decrease in the yield of biodiesels produced [43].

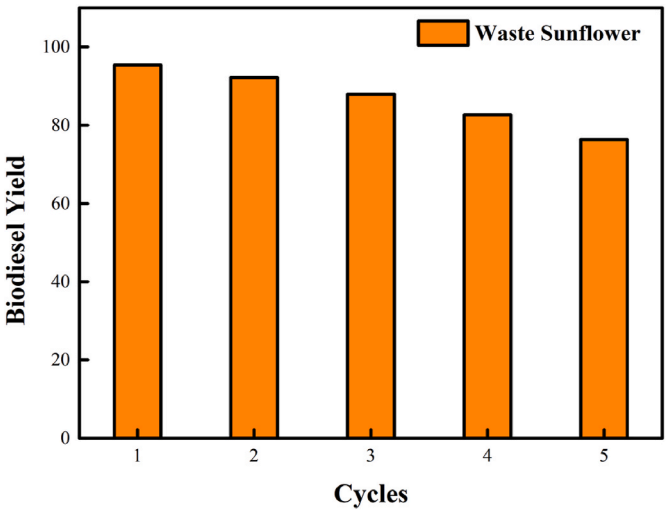


**Fig. 11.** $CaO/Al_2O_3$ catalysts reusability at ideal reaction conditions.

## 4. Conclusion

Response surface methodology was conducted in an investigation for the optimisation of biodiesel produced from waste sunflower oil, with the use of methanol to oil ratio of 12:1 and a bifunctional catalyst. The method studied the effect of time, temperature and catalyst loading for the transesterification of waste sunflower oil. As shown by the ANOVA results, catalyst loading was the most significant parameter having an impact on the yield and a linear model was used. In order to obtain the maximum yield of 98.23%, the optimised catalyst loading was 2.5 wt% with a reaction temperature of 60 °C and reaction time of 5 h. The predicted value of the yield using the linear regression model was 92.773% which was comparable with the experimental yield of 95.667%, showing a good relationship and an agreement with the data fit of the selected model. The model was statistically significant at 95% confidence, with catalyst affecting the yield the most, followed by time and then temperature. Additionally, sunflower biodiesel produced was characterised for the fuel quality and the properties were within the biodiesel standard specifications, except for the high Ca + Mg content and sulphates.

## Credit author statement

Ines Simbi: Resources, Methodology, Formal analysis, Writing – original draft, Conceptualisation, Writing – review & editing. **Uyiosa Osagie Aigbe:** Conceptualisation, Software validation, Writing – review & editing, Project administration, Supervision. **Oluwaseun Oyekola:** Conceptualisation, Software validation, Writing – review & editing, Project administration, Supervision, Funding acquisition. **Otolorin Adelaja Osibote:** Conceptualisation, Software validation, Writing – review & editing, Project administration, Supervision, Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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