

Optimization and kinetic study of biodiesel production from beef tallow using calcium oxide as a heterogeneous and recyclable catalyst

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ABSTRACT

Production of biodiesel from beef tallow animal fat has largely remained unexplored. Beef tallow is a low-cost and abundant animal fat, while calcium oxide catalyst is a renewable and highly catalytic material obtained from limestone. Therefore, this study reports on the optimization and kinetic study of biodiesel production using calcium oxide solid catalyst. Several characteristics, were determined by SEM (scanning electron microscopy), XRD (X-ray diffraction spectrometry), XRF (X-ray fluorescence), TGA (Thermo-gravimetric analyses), BET (Brunnauer, emmitt and teller analysis) and FTIR (Fourier Transform Infrared) analysis. Process variables optimization for biodiesel production were studied using RSM-CCD approach. The R^2 values were found to be 0.9592 and 0.9595, which show that the model was significantly fit with the experimental data. Maximum FAME conversion was 72% for the synthesized catalyst under optimum process conditions (the four parameters studied in the acid catalyzed esterification of beef tallow resulted in an optimum FFA of 0.60 at operating conditions of acid catalyst amount of 7.1%, methanol to oil ratio of 9:1, reaction temperature of 60 °C and a reaction time of 96 min. The obtained FFA from the actual experimental data showed a close correlation with the predicted FFA result where a predicted FFA of 0.61 was obtained. Components of FAME present in biodiesel was shown by the GCMS analysis. More research is needed on the effect of agitation speed, pressure of reacting mixtures and effect of alcohol and catalyst on process optimization.

Introduction

There is need to reduce fossil fuel resources and the consequent environmental challenges arising from their utilization as energy sources [1]. This is because, the continuous use of common fossil fuels (such as coal, oil, and gas) have increased atmospheric toxic emissions, leading to global warming [2,3]. Besides, the need for more energy supply due to the increased energy consumption, have only left us to face an energy crisis [4]. Based on recent studies, we can now say many thanks to biodiesel for its abundant and renewable nature [5].

Biodiesel is a good alternative source of energy that reduces the problems associated with conventional fossil fuels. This is because it is renewable, non-toxic, and biodegradable with desirable lubricant functions [6]. More so, utilizing biodiesel does not require much engine refinement and cost demands [7], since they possess less aromatic compounds than the fossils, with high oxygen content, and octane

number, as well as low cold – filter plugging point [8]. Overall, these findings show that biodiesel, which is the product of transesterified fatty acid glycerides, can be of close similarity to petrochemical diesel, in combustion and lubrication performance [9]. While biodiesel has been produced from several common sources including oils [3], and algae [10], it is commonly reported that total production cost of biodiesel depends upon cost of feedstock (Haas et al 2006). Moreover, the use of plant products for biodiesel production endangers the environment, even when they are non-edible. This is because, the delicate balance of carbon cycle for photosynthesis and global-warming is upset.

Alternatively, solid-base catalysts such as carbon oxide brings about heterogeneous and highly efficient transesterification reaction. When compared to homogeneous acid catalysts, homogeneous base catalysts have faster reaction rates, catalyzes reaction at low temperatures and pressures, less corrosive and are readily available [11]. Also, heterogeneous catalysts allow simultaneous esterification and transesterification

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reactions to occur, eliminates the extra washing step for biodiesel purity, and can be hydrophobic and are tolerant to presence of water in feedstock. That is, they allow for reduced cost of biodiesel production. Utilizing calcium oxide for the catalytic transesterification reaction of biodiesel production has been much reported [12,13,14]. However, the use of bio-based catalysts has also been reported from eggshell wastes [10], palm oil [15], waste cooking oil [16], soybean oil [17], Mesua ferrea oil [6], Calophyllum inophyllum oil [18], almond [19] and sunflower oils [20].

Over the years, researchers have focused on biodiesel production from these plant sources. Nonetheless, only fewer have presented kinetic descriptions and determined optimal conditions at which maximum FAME (fatty acid methyl ester) content could be obtained. Specifically, several of these studies have produced biodiesel from tannery waste [21], waste cotton-seed cooking oil [22], *bombax ceiba* oil [23], kusum oil [24], wild radish oil [25], *ceiba pentandra* oil [26], *Hydnocarpus wightiana* oil [27] and diary waste scum [27].

Furthermore, there is need for feedstock that are easy to access, and that presents no conflict between food and fuel. Also, we have to consider feedstock that can produce high quality biofuels with highly saturated fatty acids than oil. Consequently, none other feedstock could be more considered than animal fats [28]. Recently, Roman et al. [29] reported the optimization and kinetic study of biodiesel production through esterification of oleic acid applying ionic liquids as catalysts. They found that 90% FAME content was obtained at optima conditions of 8 h reaction time, $110 \pm 2^\circ\text{C}$ reaction temperature, molar ratio of 14:1 and 14 wt% catalyst dosage. More recently, Jambulingam et al examined process optimization of biodiesel production from waste beef tallow. This was with the use of co-solvent based transesterification, that is, methanol-ethanol, and KOH catalyst. A maximum yield of $97.2 \pm 1.08\%$ was obtained at optimal reaction conditions of 1:6 oil to alcohol molar ratio, catalyst concentration of 0.55% KOH, 70°C reaction temperature and 35 min reaction time.

Building on the work of Jambulingam et al, we have examined for the first time, biodiesel production from beef tallow oil using calcium oxide catalyst. The catalyst was synthesized from limestone (CaCO_3) using calcination, and characterized for its morphology, size and surface area. Also, oil has been extracted from beef tallow, and characterized for their moisture content, specific gravity, kinematic viscosity, pH value, acid value and free fatty acid. The biodiesel was produced through a 2-step transesterification process. The objectives of this study are to synthesize calcium oxide catalyst from limestone using calcination and characterization for morphology, size and surface area properties. Also, the beef tallow was characterized for their free fatty acid content, moisture, viscosity and saponification value. Then, production and characterization of biodiesel from beef tallow by two-step transesterification technique, as well as optimization and study of the reaction kinetics of the two-step transesterification. Finally, determination of the reusability of calcium oxide catalyst.

Experimental

Materials

The major feedstock used in this research work was beef tallow, a hard fat rendered from the fatty tissues of cattle that is removed during processing of beef. Tallow was purchased from Kure Market in Minna, Niger State, Nigeria. Limestone used as source of calcium oxide catalyst was obtained from Obajana in Kogi State, Nigeria.

Collection, preparation and synthesis of CaO from CaCO_3

Lumps of limestone were collected by hand picking randomly from limestone site in Obajana, Kogi state. It was washed with water to remove surface impurities. These samples were oven dried for 6 h at temperature of 150°C after thorough rinsing with distilled water for

further cleansing. Crushing of dried limestone lumps into smaller pieces was done with a jaw crusher. Then grinding and sieving of samples into mesh size of $100\ \mu\text{m}$ (200 - mesh) was done. Pulverized limestone sample was stored in an air tight container prior to analysis and further treatment. Highly active calcium oxide catalyst was synthesized by calcination. Pulverized limestone sample was weighed in batches of 50 g, each placed in a crucible and calcined at temperatures of 600°C , 700°C , 800°C and 900°C in a muffle furnace for 4 h. Each batch of highly active calcium oxide catalyst were labeled C-600, C-700, C-800, and C-900 respectively and placed in an air tight container.

Catalyst characterization

The chemical, physical and morphological properties of calcium oxide sample obtained before and after calcination were characterized and evaluated using Thermo-gravimetric analyses (TGA), Scanning Electronic Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray fluorescence (XRF) spectrometry, and X-ray diffraction (XRD) respectively.

Thermo-gravimetric analyses (TGA)

The thermal transition and decomposition of catalyst sample was done via TGA analysis using PerkinElmer TGA 4000 instrument. 50 mg each of catalyst samples was placed into the instrument via the top loading pan and covered. Nitrogen gas supply to the instrument was adjusted and purge rate was set to 50 ml/min before analysis was conducted. Samples were analyzed at stepwise temperature ranges of 50°C to 1000°C and data captured by Pyris software.

X-ray fluorescence (XRF) spectrometry

X-rays fluorescent (XRF) analysis was conducted using PAN-analytical XRF spectrometer (MiniPal 4). X-RF analysis was carried out by placing 2 g of $100\ \mu\text{m}$ size of the sample on a clean stainless steel lid which was placed in the cubicle of the spectrometer to determine its elemental composition. When the sample was irradiated by X-rays, the system software measures the individual component wavelengths of the fluorescent emission produced by atoms in the sample and compares to standard wavelengths of atoms of known elements.

Scanning electron microscope (SEM) analysis

The physical surface morphology of catalyst sample obtained was examined using LEO S-440 Scanning Electron Microscope. A thin layer of calcium oxide catalyst sample was mounted on an aluminum holder by a double-sided tape. To avoid poor image resolution and discharge of electrostatics, the catalyst sample was coated with gold (Au) to thickness of 1.5 to 3 nm. The test was conducted at different magnifications and data generated was recorded.

Fourier transform infra-red (FT-IR) spectroscopy

The infra-red spectrometer analysis of calcium oxide catalyst was performed using Bruker Alpha II infra-red spectrometer. In carrying out the analysis, the spectrometer was powered and allowed to warm up for 5 min. For a reliable analysis, the spectrometer sample press tip and the diamond sampling window were cleaned and made clear of any residue from previous sample which was confirmed by the system software. The sample was then placed on the cleaned crystal window and the overhead press tip adjusted until it exerted the desired pressure on the introduced sample. Transmission spectra of composite films were recorded at ambient temperature. Sample was scanned from 4000 to $400\ \text{cm}^{-1}$ with resolution of $0.4\ \text{cm}^{-1}$.

X-ray diffraction (XRD) spectrometry

First, 2 g sample of size $100\ \mu\text{m}$ was pressed in stainless steel holder and then identification of the crystalline phase was conducted by X-ray diffractor (X'Pert MPD – PAN analytical X-ray B.V.) using Cu-K α radiation operated at 45 kV, 35 mA in which the incidence angle spanned

from 5° to 85°2 θ at 0.02°2 θ step size with a scan speed of 0.5 s/step. This method was used to obtain a high-quality diffraction data of the sample.

Brunnauer, emmitt and teller (BET) analysis

The BET analysis gives the surface area, pore size and pore volume of the sample. The Quantachrome Instruments Nova 3200e surface area analyzer was used to analyze the sample.



Plate V: Melting of beef tallow



Plate VI: Tallow cut in bits



Plate VII: Obtained beef oil

Physical and chemical characterization of beef tallow

Before the production of biodiesel, beef tallow was characterized for color, odor, fatty acid content, moisture, viscosity and saponification value to ascertain its physical and chemical properties. The physical properties determined for the beef tallow include moisture content, density, specific gravity, kinematic viscosity, while the chemical properties tested for include pH value, acid value/free fatty acid (FFA), and ester value.

Extraction of oil from beef tallow

2 kg of beef tallow purchased from the abattoir was thoroughly rinsed with distilled water to remove blood stains and impurities. Thereafter, beef tallow was rendered into smaller pieces and placed in a pan which was heated to a temperature of 400 °C for 10 min. This led to the melting of beef tallow, suspension of solid particles and evaporation

of residual water contained in the tallow [30]. The hot mixture was then filtrated using a cotton sieve to obtain oil.

Two-step transesterification of beef tallow

Two-step transesterification experiment was conducted for synthesis of biodiesel. Acid catalyzed esterification was carried out on the extracted oil from beef tallow in order to reduce the free fatty acid (FFA) and moisture which leads to saponification and poor-quality biodiesel

yield [31]. Then, transesterification was conducted using the refined oil obtained.

Acid catalyzed esterification

The pre-treatment of oil sample was done by esterification with sulfuric acid. Esterification was conducted in a 250 ml three-neck round-bottom flask. A thermometer was inserted into the first neck to measure the temperature. And to the second neck, a water cooled condenser was connected on top of the reactor to reduce evaporative loss of methanol. The third neck was used for chemical addition and taking samples. The

Table 1
Independent Factors used for Kinetics Study.

Parameters	Unit	Values		
Temperature	(°C)	40	50	60
Time	(min)	10, 20, 30, 40, 50, 60	10, 20, 30, 40, 50, 60	10, 20, 30, 40, 50, 60

batch reactor was placed in a water bath and heated on a hotplate. Methanol and 1 M solution of H_2SO_4 were mixed before the reaction. 50 ml of oil sample was heated to the desired temperature before the addition of methanol and H_2SO_4 mixture. 12 ml of methanol was added to each 2 ml of oil to get the methanol to oil ratio of 6:1. The methanol and oil are immiscible so the use of mixer was employed to ensure efficient mixing. At the end of esterification reaction, the mixture was allowed to cool for 24 h before decanting the refined oil from other by products.

Heterogeneous catalyzed transesterification

Transesterification reaction was carried out in a 250 ml three-neck round-bottom flask equipped with a condenser and a magnetic stirrer. For all reactions which took place in a water bath, the reaction mixture consisted of 50 ml of refined oil, percentage weight of catalyst, molar ratio of methanol to oil, at desired temperature and time according to the design of experiment. Once the reaction was completed, the excess catalyst and other by products like glycerin, methanol, and water were separated from the mixture by allowing the reaction mixture to settle for 24 h. Biodiesel obtained after separation by decantation from mixture was washed by passing the esters through warm water at temperature of 45 °C to remove impurities. After washing, biodiesel was dried by gradually heating to a temperature of 100 °C to obtain a clean biodiesel. The conversion of biodiesel was calculated [32].

Catalyst reusability test

Reusability test was conducted to investigate the efficiency of calcium oxide catalyst. The catalyst that gave the highest biodiesel conversion using the same reaction condition as given by design of experiment was used. After the first reaction was done, the catalyst was separated from the reaction product. The catalyst was then washed with acetone for three times to remove the non-polar compounds attached on the catalyst. The catalyst was dried in oven for 24 h and further used in the next transesterification reaction. The procedures were repeated until no conversion can be recorded [33].

Collection of kinetics data

For the purpose of kinetics study of esterification and transesterification of beef tallow, the effect of reaction temperature and reaction time were investigated. 10 ml of the reaction mixture was taken with a syringe at varying values of factors investigated as given in Table 1. The reaction mixture was cooled by placing in ice bath to stop reaction after which titration method was used to determine the end point of the reaction from which effect of the parameters were evaluated.

Experimental design

Response surface methodology (RSM) with five-level-four-factor central composite design (CCD) was applied to optimize free fatty acid (FFA) reduction during esterification reaction and to maximize production of biodiesel from beef tallow respectively using DESIGN EXPERT (Version 7.0.0, Stat Ease, Inc., USA) software. Four factors evaluated in this study are methanol to oil ratio, catalyst loading, reaction time and reaction temperature. A total of 30 experiments (24

Table 3

Independent Factors used for CCD in Transesterification of Beef Tallow.

Variables	Low	High
Methanol to Oil ratio (v/v)	6:1	10:1
Catalyst Loading (%vol)	4	10
Reaction Temperature (°C)	42	60
Reaction Time (minutes)	60	120

axial points and 6 center points) were conducted separately to obtain experimental responses for percentage reduction in FFA and biodiesel yield. The independent factors used in this study for esterification and transesterification of beef tallow are given in Tables 2 and 3.

Characterization of biodiesel produced

As a way of quality control, biodiesel produced was characterized using American Society for Testing and Materials (ASTM).

Kinematic viscosity

A viscometer was inserted into a water bath with a set temperature and left for 30 min. The biodiesel sample was added to the viscometer and allowed to remain in the bath as long as it reaches the test thermometer. The sample was allowed to flow freely and the time required for the meniscus to pass from the first to the second timing mark was taken using a stop watch. The procedure was conducted according to ASTM D445 and was repeated a number of times and the average value were taken which was then multiplied with the viscometer calibration to give the kinematic viscosity.

Cetane number

Cetane Number is a measure of the fuel's ignition delay. Higher cetane numbers indicate shorter times between the injection of the fuel and its ignition. Higher numbers have been associated with reduced engine roughness and with lower starting temperatures for engines.

Flash point

The flash point of biodiesel was tested in accordance to ASTM D93. Sample of biodiesel was heated in a close vessel and ignited. When the sample burns, the temperature was recorded; the pensky-martens cup tester measures the lowest temperature at which application of the test flame causes the vapor above the sample to ignite. The biodiesel was placed in a cup in such quantity as to just touch the prescribed mark on the interior of the cup. The cover was then fitted onto the position on the cup and Bunsen burner was used to supply heat to the apparatus at a rate of about 5 °C per minute. During heating, the biodiesel was constantly stirred. As the biodiesel approaches its flashing, the injector burner is lighted and injected into the oil container after every 12 s intervals until a distinct flash is observed within the container. The temperature at which the flash occurred was recorded. The above step was repeated three times and the average taken.

Acid value/free fatty acid

Both values were determined using the procedure reported in ASTM D5555 – 95 (2011) standards. 10 g of biodiesel was poured into a 250 ml conical flask and a few drops of phenolphthalein added. 25 ml of ethanol and 25 ml of diethyl ether were mixed in a separate beaker to which 0.2 ml of phenolphthalein solution was also added and then poured into the conical flask. The mixture was agitated continuously and titrated with the solution of potassium hydroxide until a pink color is noticed which lasts for at least 10 s, the titration is stopped.

Table 2

Independent Factors used for CCD in Esterification of Beef Tallow.

Variables	Low	High
Catalyst (H_2SO_4) Amount (%)	4	10
Methanol ratio (w/v)	1:9	1:12
Reaction Temperature (°C)	45	60
Reaction Time (minutes)	50	120

$$\text{Acid Value} = \frac{V_{\text{KOH}} \times \text{NofKOH} \times W_{\text{KOH}}}{W}$$

where N = normality (concentration) of KOH, W = weight of biodiesel; V = volume of KOH used in titration; W_{KOH} = molecular weight of KOH.

$$\% \text{ Free Fatty Acid (FFA)} = AV \times 0.503$$

Sulphur content

ASTM D5453 was used to quantify the sulphur content in the biodiesel produced. The sulphur content was determined by the energy dispersive X-ray fluorescence spectroscopy technique. Biodiesel sample was placed in disposable plate covered with male and female cells; the sample was placed in oil in sulphur test equipment and left for 10 min. The equipment measured the sulphur content of the biodiesel three consecutive times and the average was recorded as the sulphur content.

Pour point

Sample of biodiesel produced was kept in the freezer to a temperature of 50 °C then placed in a heating mantle to melt. The temperature at the bottom of the test jar was the temperature at which the biodiesel starts to pour and was taken as the pour point.

pH value

The pH value of the sample was determined in accordance with ASTM E70 – 07 standards. The pH meter was used to measure the pH of the biodiesel sample simply by inserting its probe into the sample and for about 3 min so that the readings stabilize. The value was then recorded.

Cloud point

This was carried out by filling a test-tube to about one third of its capacity with the biodiesel sample. A thermometer was then inserted through the test tubes cork until its bulb was immersed in the biodiesel sample. The setup was kept in a refrigeration unit. The setup was checked at regular intervals until a cloudy mist began to form on the test tubes neck. This marked the cloud point and the temperature was read off.

Iodine value

Iodine value (IV) determination in the biodiesel sample was carried out based on the standard accepted procedure by ASTM D5768 – 02 (2010). 2 g of the oil was weighed and poured into a glass-stopper. 10 ml of carbon tetra chloride was added to the biodiesel sample to dissolve it. 20 ml of Wijs solution was added and the mixture was left to stay in the dark for about 30 min. 15 ml of potassium iodide solution (10%) and 100 ml of water was then added and the mixture was thoroughly mixed and titrated with 0.1 M sodium thiosulphate solution using starch as an indicator. A blank was also carried out using the same procedure. The iodine value was determined using the expression below:

$$IV = \frac{0.1269 \times (B - A) \times N \times 100}{W_{\text{OIL}}}$$

where:

B = volume of sodium thiosulphate used in blank titration; A = volume of sodium thiosulphate used in titration with oil; N = normality of sodium thiosulphate; W_{oil} = weight of oil used.

Table 4

Chemical Characterization of Raw Limestone (CaCO_3).

Composition	Weight (%)
CaO	52.01
K ₂ O	0.06
Fe ₂ O ₃	0.15
MnO	0.01
TiO ₂	0.23
Na ₂ O	0.15
Al ₂ O ₃	0.24
MgO	1.06
SiO ₂	2.04
P ₂ O ₅	0.03
SO ₃	0.12
V ₂ O ₅	0.80
LOI	43.01
Total	99.91

Saponification value

Saponification value was determined in accordance with the ATSM 5558–95(2011) standard. 2 g of the biodiesel was weighed into a conical flask, 25 ml of 0.1 N ethanolic potassium hydroxide was then added. A reflux condenser was placed over the flask. The setup was then placed over a heating mantle and allowed to boil gently with continuous stirring for 60 min. The flask was allowed to cool and few drops of phenolphthalein indicator added. It was then titrated with 0.5 M HCl to the end point (i.e. when a pink color appears). A blank test was also carried out.

$$S.V = \frac{56.1N(V_0 - V_1)}{M}$$

V_0 = ml of HCl used in blank, V_1 = ml of HCl used in titrating sample, M = weight of sample, N = normality of HCl.

Ester value

This is simply the number of mg of potassium hydroxide required to saponify the esters in 1.0 g of the sample expressed as.

$$\text{Ester value} = \text{saponification value} - \text{acid value}$$

GC–MS analysis

A QP- 2010 model GC–MS machine was used for the characterization of biodiesel. In the conduct of the analysis, 2 µl (micro liters) of the biodiesel sample was injected into the gas chromatograph with its oven temperature programmed between 60 °C and 280 °C at 5 °C/min holding time. The injected sample in the gas chromatograph was separated on a column. Helium gas was used as a carrier gas and mass selective detector was used for the analyses. The analyses were done in scan mode and the components identified based on software matching with standard mass spectra.

Table 5

BET Analysis Result for Limestone at Different Temperatures.

Samples	Surface area (m ² /g)	Pore volume (cc/g)	Pore size (nm)
Raw Limestone	418.33	0.2201	2.128
C-600 °C	479.558	0.2878	2.115
C-700 °C	507.004	0.1919	1.777
C-800 °C	545.472	0.3066	2.124
C-900 °C	586.272	0.2936	2.125

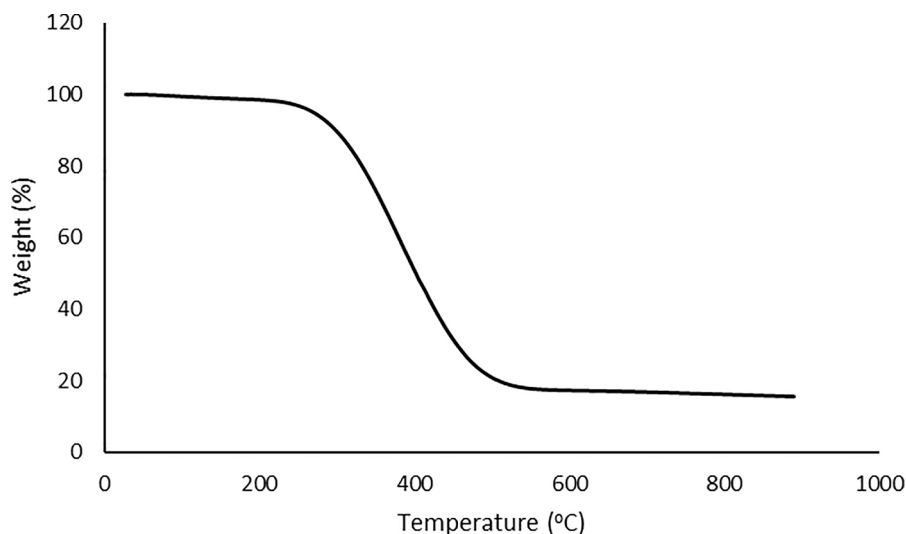


Fig. 1. TGA curve for the limestone sample.

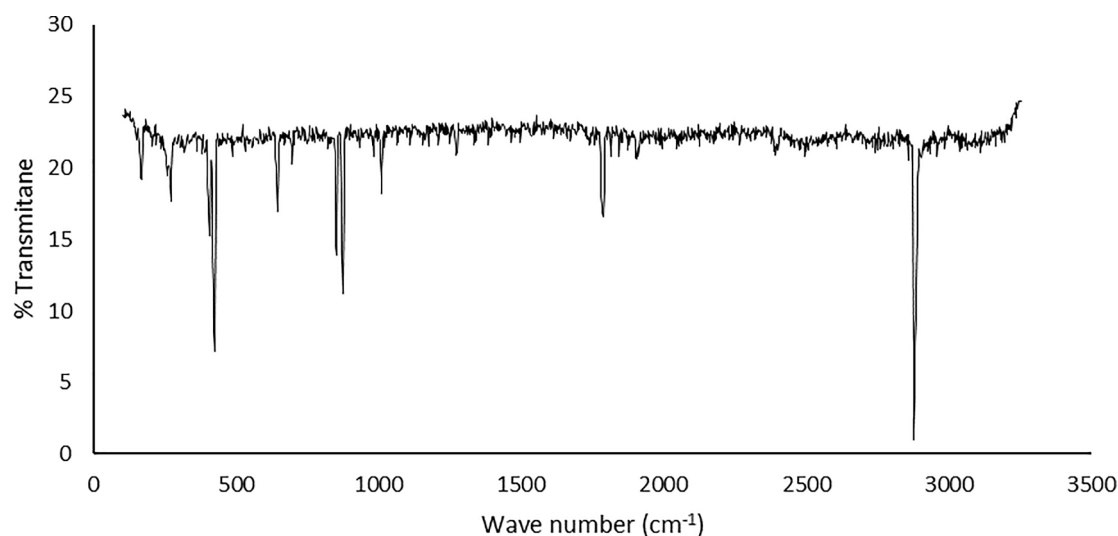


Fig. 2. FTIR spectra of the synthesized CaO catalyst.

Results and discussion

Characterization studies of catalyst

X-ray fluorescence (XRF) spectrometry

Table 4 shows the XRF elemental analysis of limestone (CaCO₃) obtained from Obajana in Kogi State. This was carried out to determine the chemical composition of the limestone sample. Result obtained revealed that limestone from Obajana mainly contains calcium oxide (52.01%), as a major component. Also present in varying proportions are oxides of silica, aluminum, manganese, magnesium, sodium, iron, phosphorus and titanium. The loss on ignition (LOI) value of limestone from Obajana is 43.01%. According to Elueze et al. [34], the theoretical LOI value of pure calcium carbonate to weight of carbon dioxide is equal to 44%. Therefore, the nearness of the LOI value (43.01%) of Obajana limestone to the theoretical value indicates its purity.

Brunauer emmet teller (BET) analysis

The BET analysis of limestone samples calcined at different

temperatures shows the pore sizes and the surface area of the different samples and aids in selection of catalyst to be used for biodiesel production. It was observed that surface area of limestone sample increases as temperature increases. Pore size of limestone sample decreased from 600 °C to 700 °C which may be due to high shrinkage. As temperature increases from 800 °C to 900 °C, pore size was observed to increase. According to Itodo et al. [35], a low shrinkage and high porous lime (CaO) is produced at temperatures between 800 °C and 900 °C which represent the most probable temperature for optimum reactivity. Table 5 shows the surface area and pore sizes of the different samples.

Thermo-gravimetric analysis (TGA)

The TGA analysis shows the thermal transition and decomposition of the limestone sample.

From Fig. 1, the dissociation of limestone (CaCO₃) increases as calcination temperature increases. At temperature range of 31.54 °C to 228.8 °C, heat was absorbed by limestone sample to break internal bonding forces as such no visible weight loss was observed. However, as dissociation progresses, a drastic loss of weight from 98 % wt. to 17 %

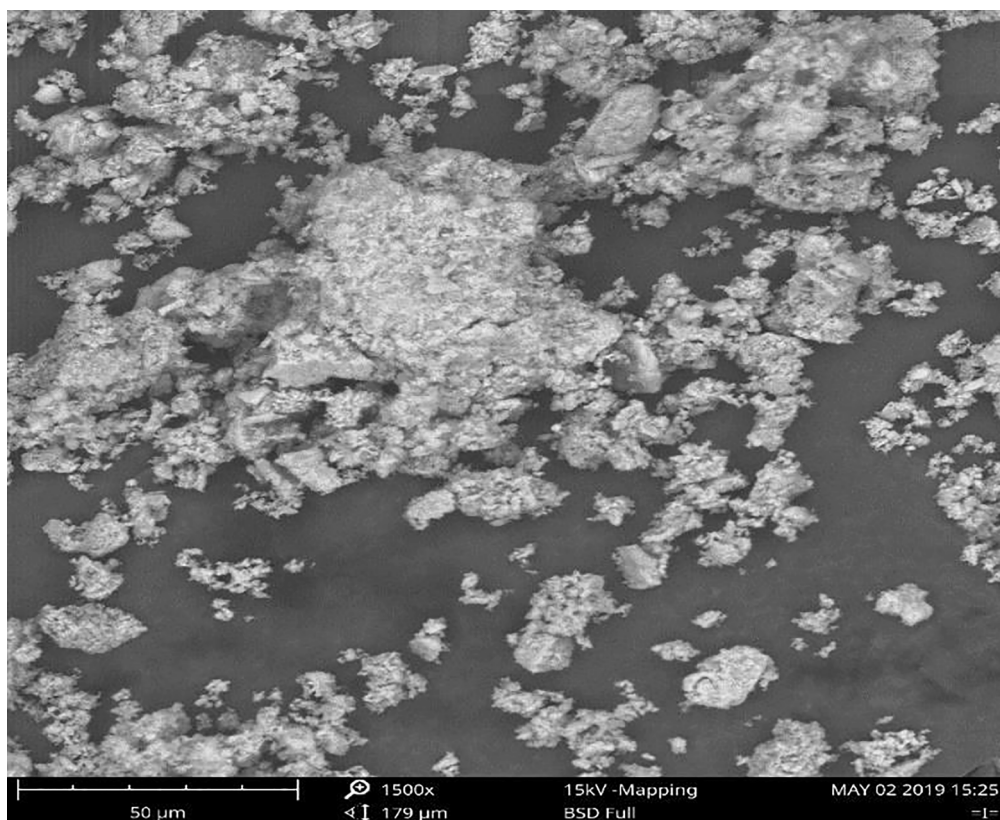


Fig. 3. SEM micrograph of CaO catalyst calcined at 900 °C at magnifications of (1500X).

wt. was observed at temperature of 300 °C. Complete dissociation of calcium carbonate was observed at temperature of 550 °C as shown by the steady state in weight loss of limestone sample as temperature increases above 550 °C. According to researchers, lime (CaO) of higher purity is usually obtained at temperature above that which complete dissociation took place.

Fourier transform infrared spectra (FT-IR) analysis

FTIR spectra in Fig. 2 shows characteristic absorption peak of synthesized calcium oxide calcined at 900 °C at 2890 cm^{-1} , 877 cm^{-1} , and 491 cm^{-1} . The characteristic absorption peak at 491 cm^{-1} corresponds to strong broad band of CaO crystal lattice which is similar to the absorption peak of CaO for Obajana limestone as reported by Itodo et al. [35]. The absorption peak at 877 cm^{-1} corresponds to planar bending of the C—O as a result of breaking of carbonate bond during formation of CaO. While C=O of oxide of carbonate was observed at absorption bands of 2890 cm^{-1} .

Scanning electron microscopy (SEM) analysis

The SEM micrograph in Fig. 3 shows the honey comb surface morphology of CaO catalyst calcined at 900 °C. From the SEM micrograph generated, some crystalline compact particles were observed. Due to the presence of smaller particles with larger surface as observed, the adsorptive capacity of CaO synthesized is high (Figs. 4 and 5).

Electron dispersive spectroscopy (EDS)

This is an add-on function of SEM used to identify chemical elements distributed on the surface of the sample. The EDS analysis shows that calcium and Oxygen are the 2 main components present on the catalyst surface. The summary of the elements present in the catalyst are listed in Table 6. Tables 7 and 8.

X-ray diffraction (XRD) spectrometry

According to Minaria and Risfidian, (2016) standard peaks for CaO occur at 2θ : 32.3° , 37.5° , 47.1° , 64.3° , 67.5° . The XRD patterns observed in the X-ray Diffraction Spectrometry of the synthesized CaO catalyst bear a close resemblance to already establish standard CaO peaks. The synthesized CaO catalyst 2θ peaks occurred at 30.3° , 37.5° , 47.5° , 64.3° and 66.7° .

Feedstock quality characterization

The suitability of a feed stock for biodiesel production relies heavily on its properties. The following results were obtained based on the characterization of the feed stock (beef tallow).

Optimization of acid catalyzed esterification

The optimization of the acid catalyzed esterification process of beef tallow was conducted using the DESIGN EXPERT (Version 7.0.0, Stat Ease, Inc., USA) software. The parameters evaluated include acid

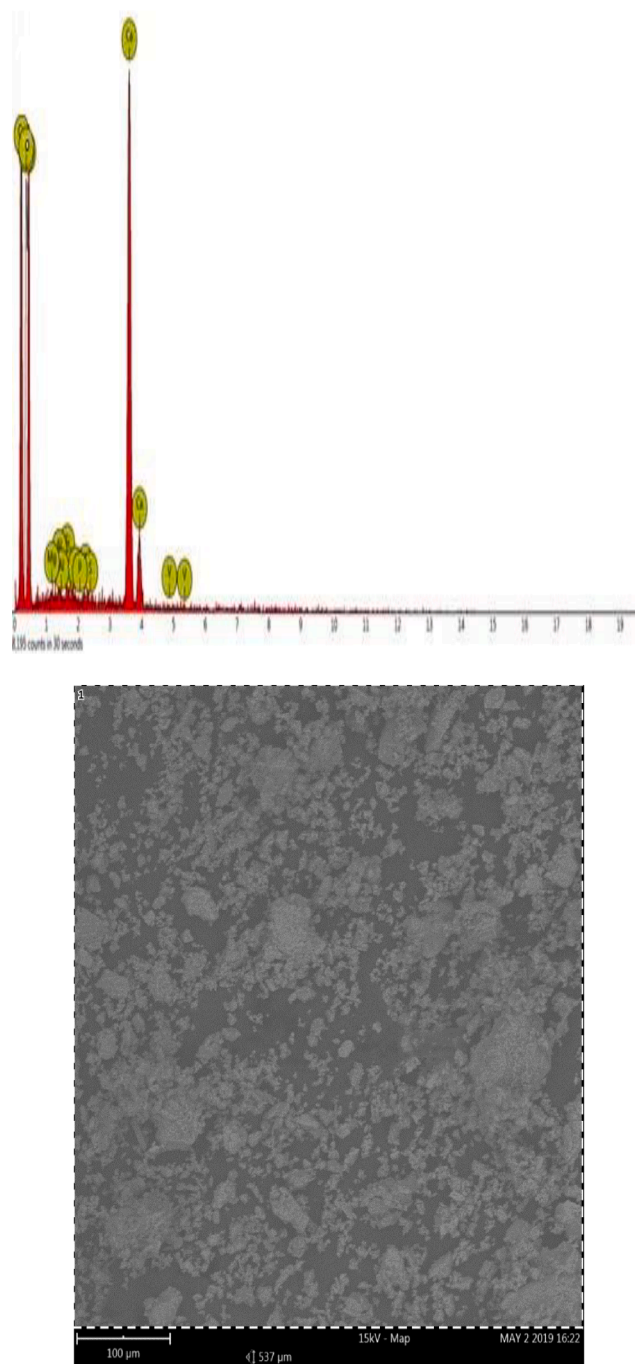


Fig. 4. EDS spectroscopy of the synthesized catalyst.

catalyst dosage (A), methanol to oil ratio (B), reaction temperature (C) and reaction time (D) as shown in appendix B.

Statistical analysis of acid catalyzed esterification of beef tallow

The variance and regression analyses were carried out using DESIGN EXPERT (Version 7.0.0, Stat Ease, Inc., USA). The experiments were conducted based on the Response Surface Method (RSM) Central Composite Design (CCD).

Analysis of variance for esterification

The analysis of the variance (ANOVA) for the response surface quadratic model is shown in Table 9. The model expression developed that relates the FFA and the four reaction parameters considered (A, B, C, D), was considered suitable because its p-value is less than 0.05. The

model F-value of 25.21 implies the model is significant. The F-value is the ratio of the model SS / residual SS and shows the relative contribution of the model variance to the residual variance. A large number indicates more of the variance being explained by the model; a small number says the variance may be more due to noise. The model fit is also checked with the correlation factor R^2 , which equals to 95.92%. This indicates that the sample variation of 95.92 % is attributed to independent variables and 4.08 % of the total variation is not explained by the model. The value of the coefficient of variation ($CV\% = 13.12$) gives the precision and reliability of the experiment carried out where a lower value of $CV\%$ indicates a better precision and reliability of the experiments carried out. The predicted R^2 of 0.7903 is in reasonable agreement with the adjusted R^2 of 0.9212 as in Table 10 with the difference less than 0.2. Adequate (Adeq) precision measures the signal to noise

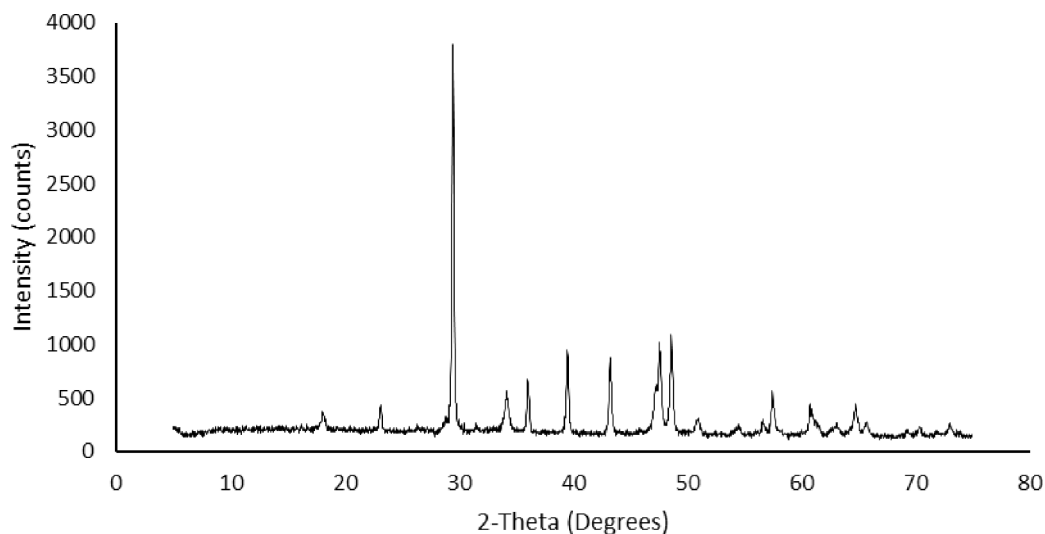


Fig. 5. X-ray diffraction (XRD) spectrometry of catalyst.

Design-Expert® Software
FFA

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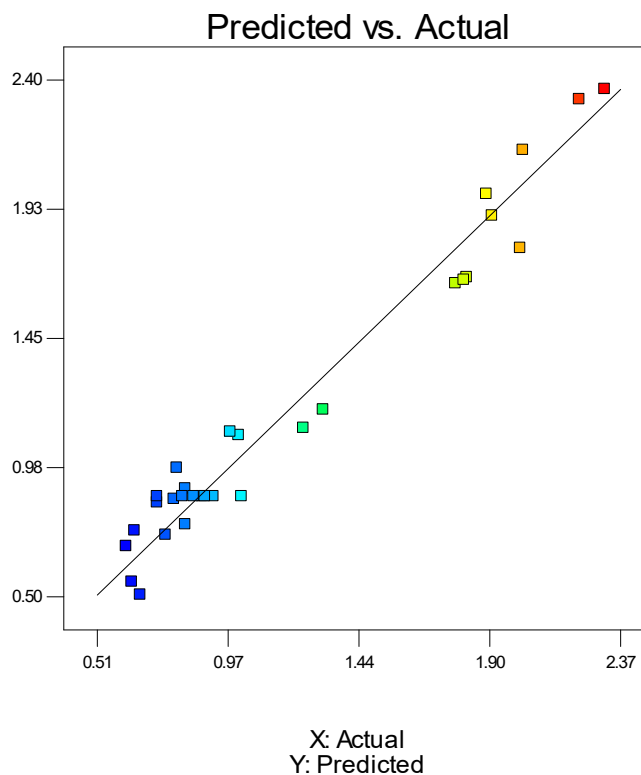


Fig. 6. Graph of predicted values vs. actual values obtained from the acid catalysed esterification of beef tallow.

Table 6
Elemental weight composition of synthesized catalyst.

Element Name	Atomic Conc.	Weight Conc.
Calcium	78.33	80.68
Oxygen	15.01	14.16
Aluminium	2.77	1.92
Vanadium	0.75	0.98
Magnesium	1.52	0.94
Sulfur	1.08	0.89
Phosphorus	0.54	0.42

ratio. A ratio greater than 4 is desirable. The ratio of 16.882 indicates an adequate signal. Therefore, this model can be used to navigate the design space.

The significant factors from ANOVA analysis are the acid catalyst amount with a p-value of 0.0001 which is less than 0.05. Another significant factor is the temperature and time factors with p values of 0.0001 respectively. The other significant factors are the interaction effect of the acid catalyst amount and reaction temperature and acid catalyst amount and reaction time with p-values of 0.0128 and 0.0023. The quadratic effects of the acid catalyst amount, the reaction temperature and also the reaction time are also significant factors with p-values of 0.0002, 0.0010 and 0.0005. The other factors of the model have no

Table 7

Characteristics of Beef Tallow.

S/N	Property	Unit	Present study	EN14214
1.	% Moisture Content	wt. %	14.6	–
2.	Density	g/cm ³	0.943	0.86–0.9
3.	Specific Gravity at 40 °C	–	0.93	–
4.	Kinematic Viscosity at 40 °C	mm ² /s	24.6	35–50
5.	pH Value	–	6.4	–
6.	Saponification Value	mgKOH/g	261.65	–
7.	Acid Value	mgKOH/g	4.82	<5
8.	Ester value	wt. %	256.85	–
9.	Iodine Value	mgI/100 g	62.3	<120
10.	Peroxide Value	mmol peroxide/kg sample	5.3	–
11.	Flash Point	°C	168	>120 °C
12.	Free Fatty Acid (FFA)	wt. %	2.41	>96.5

statistically significant effect. The regression analysis produced the following coded equation:

$$\text{FFA} = 0.87 - 0.34A - 0.0025B - 0.31C - 0.25D - 0.026AB + 0.11AC + 0.14AD - 0.015BC + 0.020BD - 0.081CD + 0.15A^2 - 0.00125B^2 + 0.12C^2 + 0.13D^2.$$

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings. When the factors are orthogonal the VIFs are 1; VIFs greater than 1 indicate multi-collinearity, the higher the VIF the more severe the correlation of factors. As a rough rule, VIFs less than 10 are tolerable. The linear effect of A and C, the interaction effect of AC and AD and the quadratic effect of C² and D² are the general determining factors of acid catalysed esterification of beef tallow as they have the larger coefficients.

In this statistical analysis the acid catalyst amount (factor A) has the highest coefficient among the four independent variables. This implies that the FFA of the acid catalysed esterification of beef tallow relies greatly on this factor. Fig. 11 shows the graph of the predicted value vs the actual values obtained in the acid catalysed esterification of beef tallow. It is observed that the actual data is in agreement with the predicted data by the model. From Fig. 6 the minimum predicted value of the FFA obtained from the acid catalysed esterification of beef tallow is 0.55 while the actual experimental value is 0.61. Therefore the most suitable conditions for the process are obtained at experiment number 8.

The optimization solution obtained shows that an FFA of 0.61 at operating conditions of acid catalyst amount of 10.0%, methanol to oil ratio of 9:1, reaction temperature of 60 °C and a reaction time of 120 min respectively.

From Fig. 6 the actual values obtained from the study lie close to the regression line as such they correlated with the predicted values generated by design expert. This shows that there is no much disparity between the actual and predicted results and this quadratic model is suitable model for this study.

Regression analysis for esterification

The effects of each of the parameters and how they affect the acid catalyzed esterification of beef tallow are studied. These parameters which include the methanol: oil ratio, the catalyst concentration, the reaction time and the reaction temperature.

Fig. 7 shows the regression graph of the effect of acid catalyst amount on FFA of beef tallow. From the plot it was observed that increase in acid catalyst amount from 1% to 4% resulted in an increase in FFA because catalyst amount was not sufficient to drive reaction. Further increment above 6 % caused a sharp decline in FFA indicating the presence of sufficient catalyst amount to favour reaction. These findings agree with similar findings reported by Goyal *et al.* 2012. The R² value of 0.9553 indicates the closeness of the predicted and actual experimental data.

Fig. 8 shows the regression graph of the effect of methanol to oil ratio on FFA of beef tallow. From the plot it was observed that FFA was lowest at methanol to oil ratio of 13.5:5 because acid catalyzed esterification

Table 8

Analysis of Variance of Acid Catalyzed Esterification of Beef Tallow.

Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	p-value
					Prob > F
Model	8.56	14	0.61	25.21	0.0001
A- Acid Catalyst amount	2.84	1	2.84	117.20	0.0001
B- Methanol to Oil ratio	1.5E-4	1	1.5E-4	6.184E-3	0.9384
C-Reaction Temperature	2.36	1	2.36	97.14	0.0001
D- Reaction Time	1.51	1	1.51	62.25	0.0001
AB	0.011	1	0.011	0.45	0.5105
AC	0.19	1	0.19	7.98	0.0128
AD	0.32	1	0.32	13.39	0.0023
BC	3.6E-3	1	3.6E-3	0.15	0.7055
BD	6.4E-3	1	6.4E-3	0.26	0.6150
CD	0.11	1	0.11	4.35	0.0544
A ²	0.59	1	0.59	24.19	0.0002
B ²	4.286E-5	1	4.286E-5	1.767E-3	0.9670
C ²	0.40	1	0.40	16.62	0.0010
D ²	0.48	1	0.48	19.85	0.0005
Residual	0.36	15	0.024		
Lack of Fit	0.31	10	0.031	3.01	0.1180
Pure Error	0.052	5	0.010		
Cor Total	8.93	29			

Table 9
Fit Statistics.

Std. Dev.	Mean	C.V. %	R ²	Adjusted R ²	Predicted R ²	Adeq Precision
0.1557	1.19	13.12	0.9592	0.9212	0.7903	16.8820

reaction is favoured by high ratio of methanol to oil. This finding agrees with similar findings reported by Sukjit and Punsuvon, (2013). The R² value of 0.8829 indicates the closeness of predicted versus experimental values.

Fig. 9 shows the regression graph of the effect of reaction temperature on FFA of beef tallow. From the plot it was observed that there was increase in FFA as the reaction temperature proceeded from 37.5 °C to 45 °C. Further increment in reaction temperature above 60 °C led to corresponding decline in FFA because at higher reaction temperature FFA reacts more rapidly with alcohol to form esters. The R² value of 0.9668 indicates the closeness between actual and predicted experimental values.

Fig. 10 shows the regression graph of the effect of reaction time on FFA of the beef tallow. From the plot it was observed that there was an increase in the FFA as the reaction time proceeded from 15 min to 50 min. Further increment in the reaction time brought about a decline in the FFA with a slight FFA increment observed at a reaction time of 120 min. At reaction time above 120 min, there was a corresponding decrease in the FFA which shows that forward reaction is favoured with increase in reaction time. R² value of 0.9182 indicates the closeness between actual and predicted values.

The effect of interaction between process parameters for esterification

The Three-dimensional response surfaces are plotted on the basis of the generated model equation to investigate the interaction among the variables and to determine the optimum condition of each factor for minimum FFA.

Fig. 11 represents the 3D plot of the effect of methanol: oil ratio and acid catalyst amount on FFA at reaction time of 85 min and reaction temperature of 52.5 °C. From the plot, the plane was observed to be inclined along both z-axis (methanol: oil ratio) and x-axis (acid catalyst). This shows that increase both methanol to oil ratio and catalyst amount led to reduction in FFA. It was observed that a decline in the acid catalyst amount from 10 % to 4 % brought about an increase in the FFA. Similarly, an increment in the methanol to oil ratio from 9:1 to 12:1 had significant effect on FFA. In terms of the interaction of the methanol to oil ratio and the acid catalyst amount on the FFA, it was observed that an optimum FFA of 0.64 was obtained at a methanol to oil ratio of 12:1 and acid catalyst amount of 10% at a constant reaction temperature and time of 52.5 °C and 85 min respectively.

Fig. 12 represents the 3D plot of the effect of methanol: oil ratio and

reaction temperature on FFA at a reaction time of 85 min and acid catalyst amount of 7 %. From the plot it was observed that the plane was inclined towards the x-axis (methanol: oil ratio) and z-axis (temperature). Similarly, an increment in the methanol to oil ratio from 9:1 to 12:1 led to decrease in FFA. In terms of interaction effect of the methanol: oil ratio and reaction temperature on the FFA it was observed that optimum FFA of 0.66 was obtained at a methanol to oil ratio of 12:1 and a reaction temperature of 60 °C at a constant reaction time of 85 min and acid catalyst amount of 7%.

Fig. 13 represents the 3D plot of the effect of methanol: oil ratio and reaction time on FFA at a reaction temperature of 52.5 °C and acid catalyst amount of 7 %. The plot was inclined towards the z-axis (methanol: oil ratio) and x-axis (time) indicating interaction between both parameters. It was observed that as there was decrease in reaction time from 120 min to 50 min there was corresponding increase in the FFA. Similarly an increase in the methanol to oil ratio brought about appreciable decrease in the FFA. An optimum FFA of 0.73 was observed at methanol: oil ratio of 9:1 and a reaction time of 120 min with constant reaction temperature and acid catalyst amount of 52.5 °C and 7 % respectively.

Fig. 14 represents the 3D plot of the effect of acid catalyst amount and reaction temperature on FFA at a methanol to oil ratio of 10.5:1 and reaction time of 85 min. A steep inclination towards temperature and acid catalyst amount was observed. From the plot it was observed that a decrement in the acid catalyst amount resulted in an increment in the FFA while a similar decrement in the reaction temperature also saw an increase in the FFA. The interaction effect of acid catalyst amount and reaction temperature led to an optimum FFA of 0.59 at acid catalyst amount of 10 %, reaction temperature of 60 °C, methanol: oil of 10.5:1 and reaction time of 85 min.

Fig. 15 represents the 3D plot of the effect of acid catalyst amount and reaction time on FFA at methanol: oil ratio of 10.5:1 and reaction temperature of 52.5 °C. From the plot it was observed that an increment in the acid catalyst amount resulted in a decline in the FFA similarly an increase in the reaction time brought about a decline in the FFA. In terms of the interaction effect of acid catalyst amount and reaction time on the FFA, an optimum FFA of 0.69 was obtained at acid catalyst amount of 10% and reaction time of 120 min at a constant methanol: oil ratio of 10.5:1 and reaction temperature of 52.5 °C.

Fig. 16 represents the 3D plot of the effect of reaction temperature and reaction time on FFA at methanol: oil ratio of 10.5:1 and acid catalyst amount of 7%. From the plot it was observed that as the reaction temperature increased the FFA decrease progressively. Similarly, increase in reaction time led to decline in FFA. In terms of the interaction effect reaction temperature and reaction time on the FFA, an optimum FFA of 0.48 was obtained at a reaction temperature of 60 °C and reaction time of 120 min at a constant methanol to oil ratio of 10.5:1 and acid catalyst amount of 7%.

Table 10
Regression Coefficients of Predicted Quadratic Model.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	0.8683	1	0.0636	0.7328	1.00	
A-Acid Catalyst Amount	−0.3442	1	0.0318	−0.4119	−0.2764	1.0000
B-Methanol:Oil ratio	−0.0025	1	0.0318	−0.0703	0.0653	1.0000
C-Temperature	−0.3133	1	0.0318	−0.3811	−0.2456	1.0000
D-Time	−0.2508	1	0.0318	−0.3186	−0.1831	1.0000
AB	−0.0262	1	0.0389	−0.1092	0.0567	1.0000
AC	0.1100	1	0.0389	0.0270	0.1930	1.0000
AD	0.1425	1	0.0389	0.0595	0.2255	1.0000
BC	−0.0150	1	0.0389	−0.0980	0.0680	1.0000
BD	0.0200	1	0.0389	−0.0630	0.1030	1.0000
CD	−0.0812	1	0.0389	−0.1642	0.0017	1.0000
A ²	0.1462	1	0.0297	0.0829	0.2096	1.05
B ²	−0.0013	1	0.0297	−0.0646	0.0621	1.05
C ²	0.1212	1	0.0297	0.0579	0.1846	1.05
D ²	0.1325	1	0.0297	0.0691	0.1959	1.05

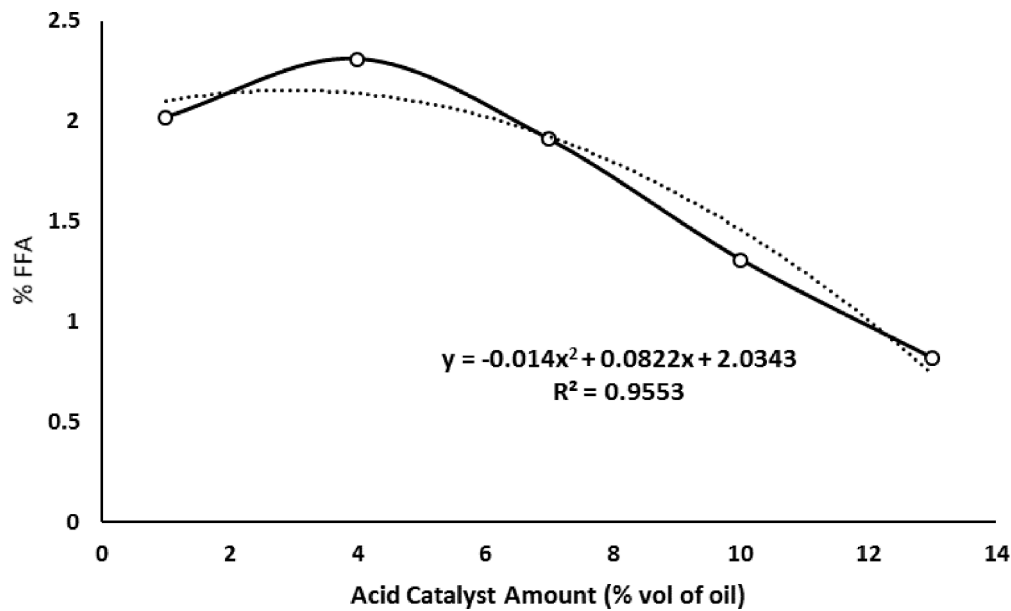


Fig. 7. Regression graph of the effect of acid catalyst amount on FFA.

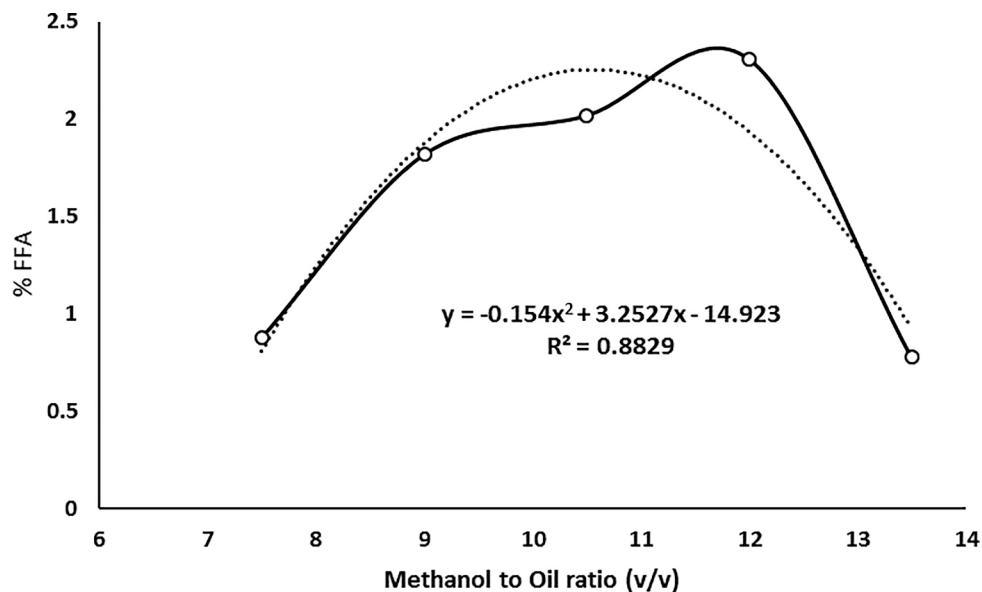


Fig. 8. Regression graph of the effect of methanol to oil ratio on FFA.

In summary, the effects of the process parameters studied in this work affect the FFA differently. As observed, FFA of 0.73 was obtained at a methanol: oil ratio of 9:1 and reaction time of 120 min with constant reaction temperature and acid catalyst amount of 52.5 °C and 7% respectively. Similarly, when the effect of reaction temperature and reaction time on FFA were considered an optimum FFA of 0.48 was obtained at a constant methanol: oil ratio of 10.5:1 and acid catalyst amount of 7%. This shows that combination of any of the factors would result in a minimum FFA of 0.48 and a maximum FFA of 0.73.

Optimization of biodiesel production from beef tallow

Optimization of the transesterification process from beef tallow was conducted using the DESIGN EXPERT (Version 7.0.0, Stat Ease, Inc., USA) software. The parameters considered include methanol to oil ratio (A), catalyst loading (B), reaction time (C) and reaction temperature (D) as in appendix B2.

Statistical analysis of transesterification reaction of beef tallow

The analysis of variance (ANOVA) was carried out using DESIGN EXPERT (Version 7.0.0, Stat Ease, Inc., USA). The experiments were conducted based on the Response Surface Method (RSM) Central Composite Design (CCD).

Analysis of variance for transesterification

The analysis of the variance (ANOVA) for the response surface quadratic model is shown in Table 11. The model expression developed that relates the biodiesel yield and the four reaction parameters considered (A, B, C, D), was suitable because its p-value is less than 0.05. The model F-value of 25.40 implies the model is significant. The F-value is the ratio of the model SS / residual SS and shows the relative contribution of the model variance to the residual variance. A large number indicates more of the variance being explained by the model; a small number says the variance may be more due to noise. The significant factors from ANOVA analysis are the methanol to oil ratio and the

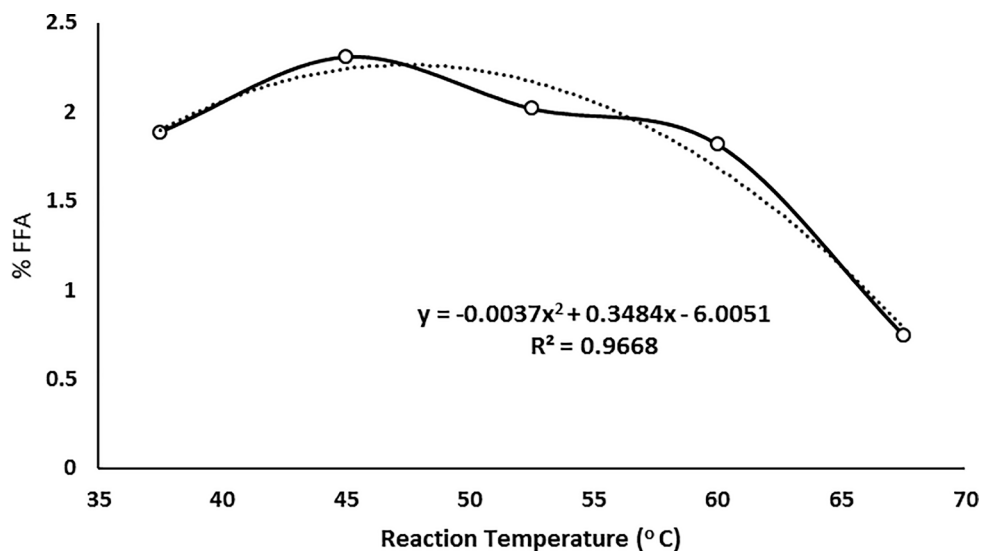


Fig. 9. Regression graph of the effect of reaction temperature on FFA.

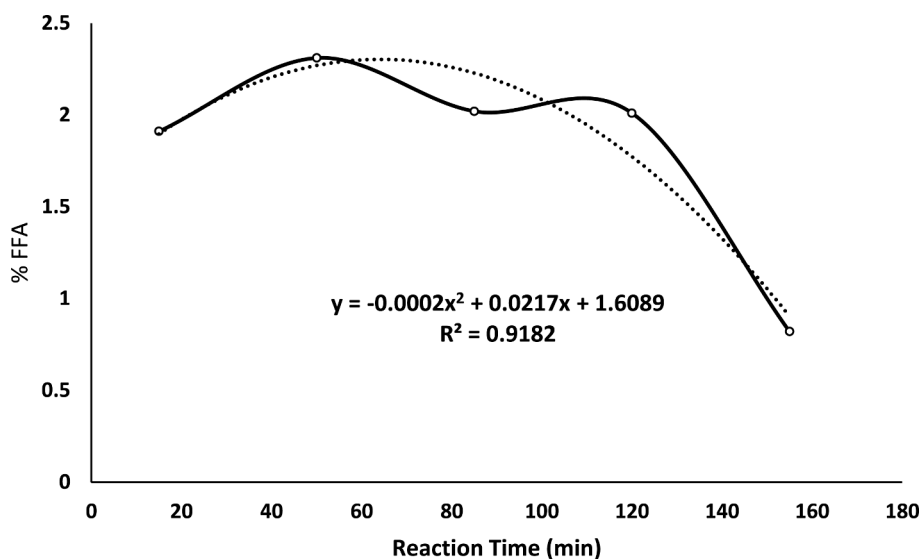


Fig. 10. Regression graph of the effect of reaction time on FFA.

reaction temperature with p-values of 0.0001 respectively which is less than 0.05. The other significant factors are the interaction effect of the methanol to oil ratio and catalyst loading and the interaction effect of methanol to oil ratio and reaction temperature with p-values of 0.0109 and 0.0001. Similarly, the quadratic effects of the reaction temperature and the quadratic effect of reaction time are also significant factors with p-values of 0.0214 respectively. The other factors of the model have no statistically significant effect (Tables 12–17).

In this study, the model fit is checked with the correlation factor R^2 , which equals to 95.95% indicating that the sample variation of 95.95% is attributed to independent variables and 4.05% of the total variation is not explained by the model. The value of the coefficient of variation (CV % = 5.98) gives the precision and reliability of the experiment carried out where a lower value of CV% indicates a better precision and reliability of the experiments carried out. The predicted R^2 of 0.8090 is in reasonable agreement with the adjusted R^2 of 0.9217 with a difference less than 0.2. Adeq precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 17.888 indicates an adequate signal. This model can be used to navigate the design space.

The coefficient estimate represents the expected change in response

per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings. When the factors are orthogonal the VIFs are 1; VIFs greater than 1 indicate multi-collinearity, the higher the VIF the more severe the correlation of factors. As a rough rule, VIFs less than 10 are tolerable. The regression analysis produced the following coded equation:

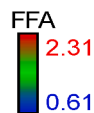
$$\text{Biodiesel Yield} = 61.17 + 5.92A - 1.17B + 10.33C + 1.33D + 2.50AB - 5.12AC + 0.88AD - 0.25BC - 1.00BD - 0.87CD - 1.31A^2 + 0.19B^2 - 1.69C^2 - 1.69D^2.$$

The linear effect of A and C, the interaction effect of AB and AC and the quadratic effect of C^2 and D^2 are the general determining factors of transesterification of beef tallow as they have the larger coefficients.

In this statistical analysis the reaction temperature (factor C) has the highest coefficient among the four independent variables. This implies that the transesterification of beef tallow relies greatly on this factor.

Fig. 17 shows the graph of the predicted value vs the actual values obtained in the transesterification of beef tallow. It was observed that the actual data was in agreement with the predicted data by the model.

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X1 = A: Acid Catalyst Amount
X2 = B: Methanol:Oil ratio

Actual Factors
C: Temperature = 52.50
D: Time = 85.00

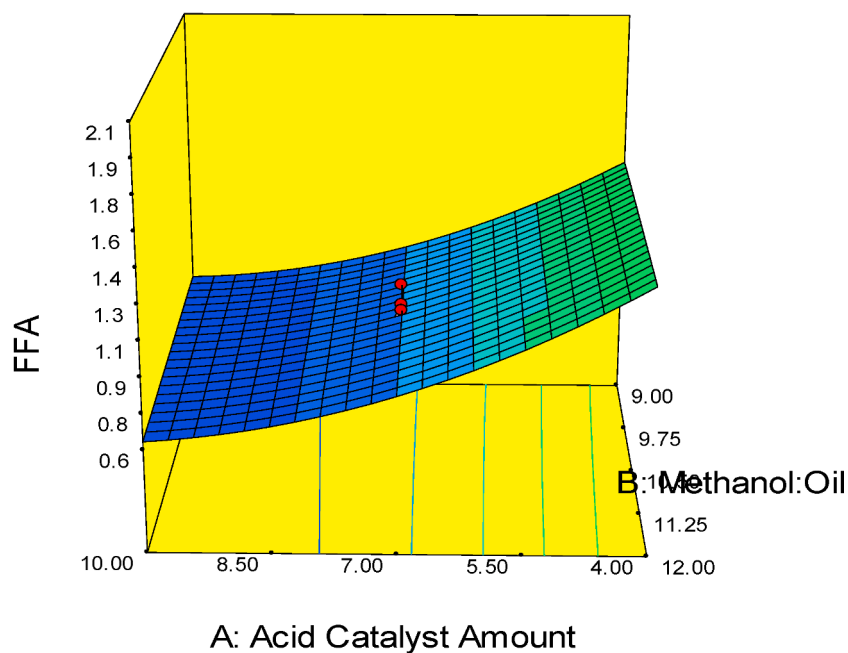
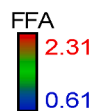


Fig. 11. Response surface plot of the interaction effect of methanol. oil ratio and acid catalyst amount on FFA.

Design-Expert® Softw are



X1 = B: Methanol:Oil ratio
X2 = C: Temperature

Actual Factors
A: Acid Catalyst Amount = 7.00
D: Time = 85.00

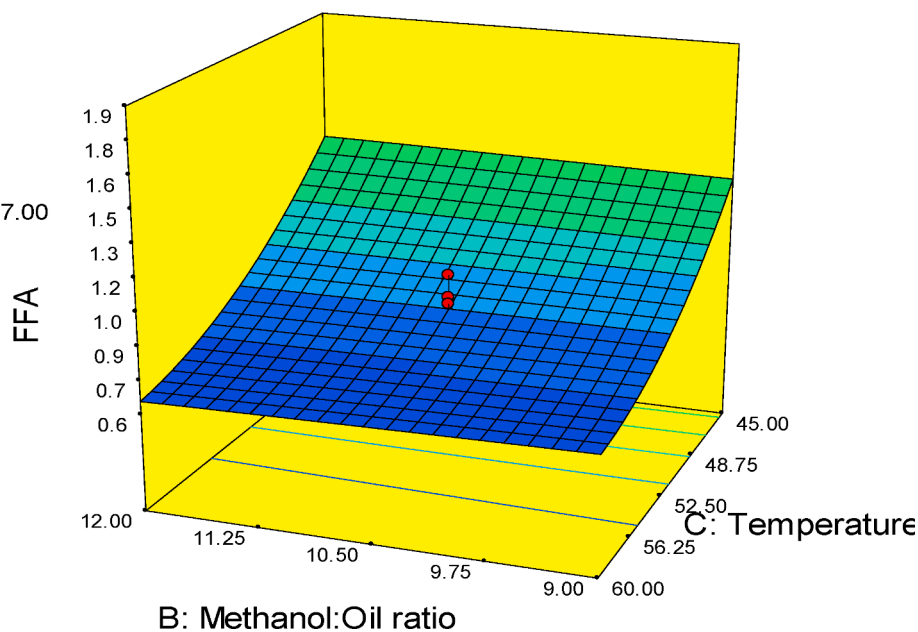
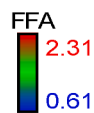


Fig. 12. Response surface plot of the interaction effect of methanol: oil ratio and reaction temperature on FFA.

Design-Expert® Software



X1 = B: Methanol:Oil ratio
X2 = D: Time

Actual Factors
A: Acid Catalyst Amount = 7.00
C: Temperature = 52.50

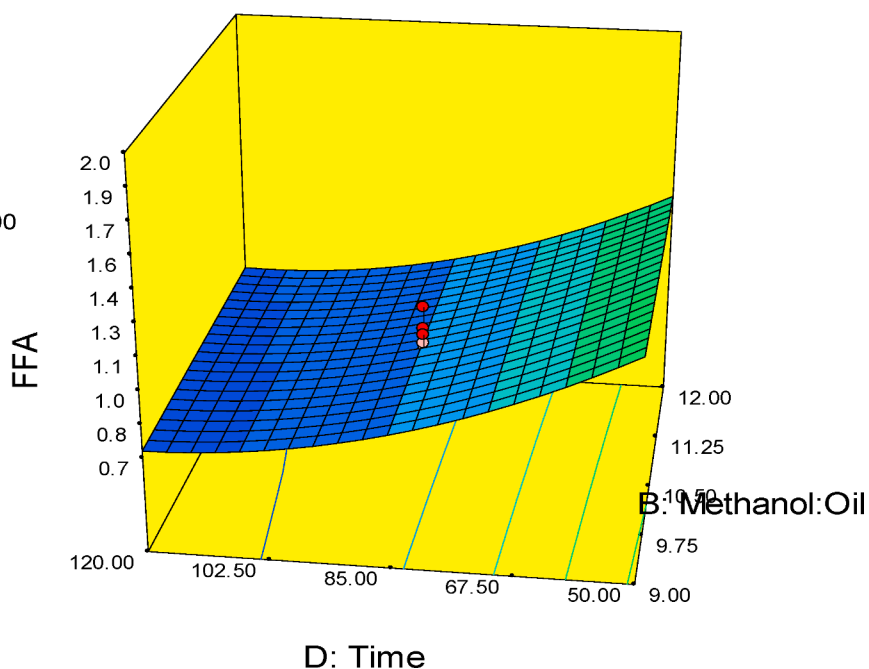
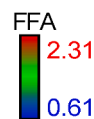


Fig. 13. Response surface plot of the interaction effect of methanol: oil ratio and reaction time on FFA.

Design-Expert® Software



X1 = A: Acid Catalyst Amount
X2 = C: Temperature

Actual Factors
B: Methanol:Oil ratio = 10.50
D: Time = 85.00

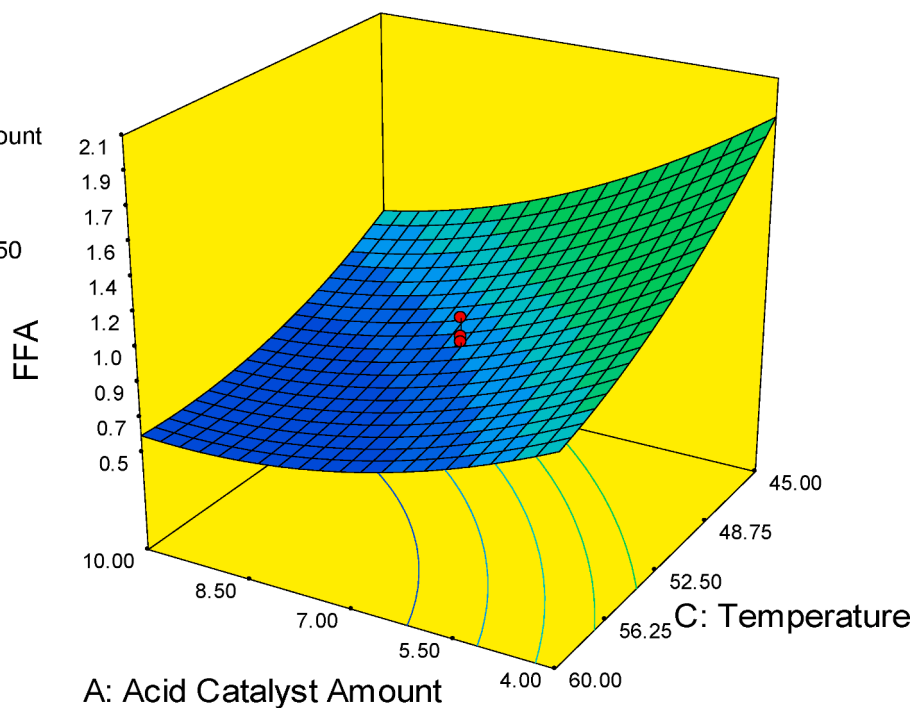
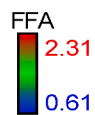


Fig. 14. Response surface plot of the interaction effect of acid catalyst amount and reaction temperature on FFA.

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X1 = A: Acid Catalyst Amount
X2 = D: Time

Actual Factors
B: Methanol:Oil ratio = 10.50
C: Temperature = 52.50

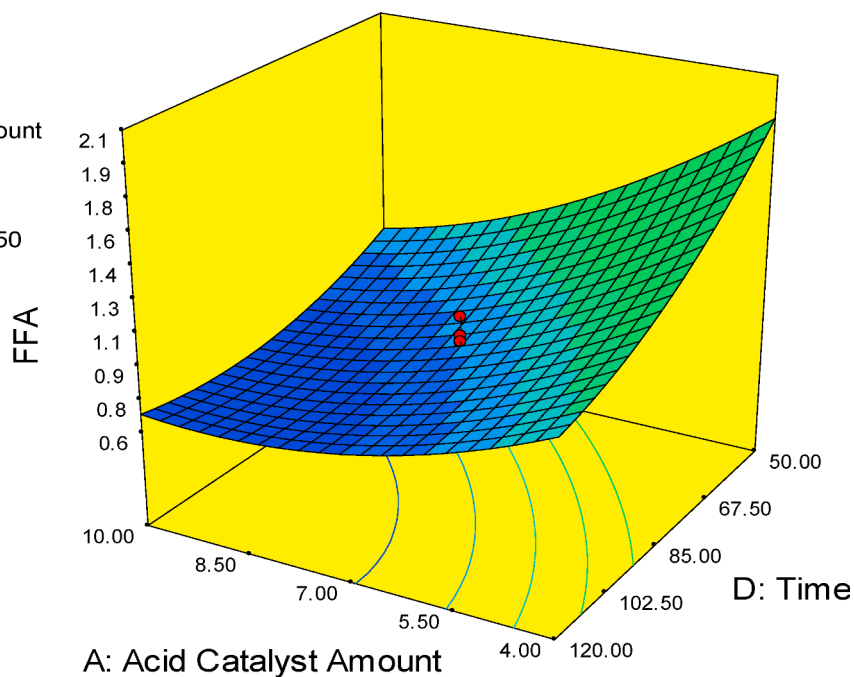
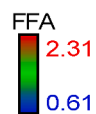


Fig. 15. Response surface plot of the interaction effect of acid catalyst amount and reaction time on FFA.

Design-Expert® Softw are



X1 = C: Temperature
X2 = D: Time

Actual Factors
A: Acid Catalyst Amount = 7.00
B: Methanol:Oil ratio = 10.50

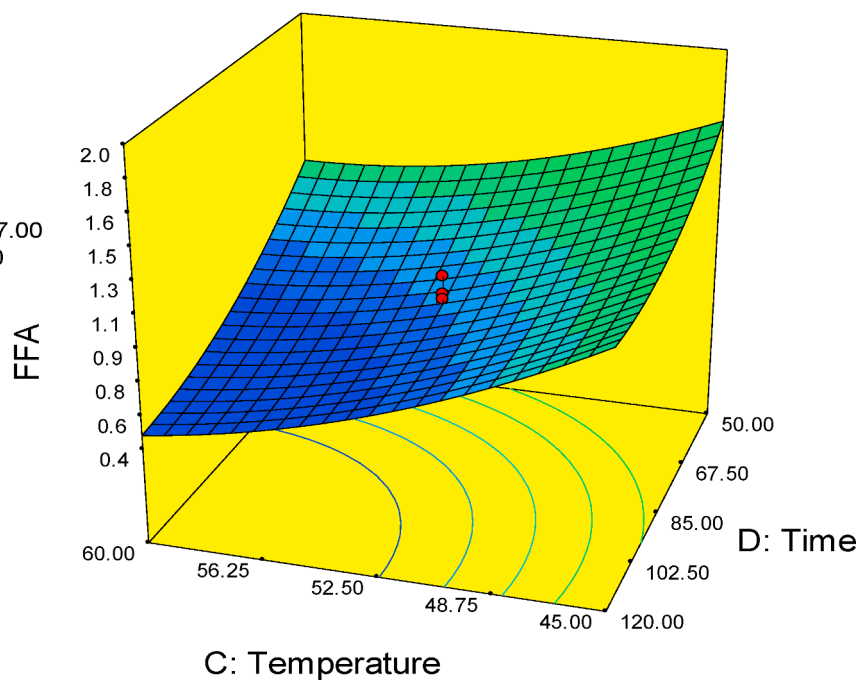


Fig. 16. Response surface plot of the interaction effect of reaction temperature and reaction time on FFA.

Table 11
Analysis of Variance of the transesterification of Beef Tallow.

Source	Sum of Square	Degree of Freedom	Mean Square	F Value	p-value Prob > F
Model	4213.62	14	300.97	25.40	0.0001
A- Methanol to Oil ratio	840.17	1	840.17	70.90	0.0001
B- Catalyst Loading	32.67	1	32.67	2.76	0.1176
C- Reaction Temperature	2562.67	1	2562.67	216.26	0.0001
D- Reaction Time	42.67	1	42.67	3.60	0.0772
AB	100.00	1	100.00	8.44	0.0109
AC	420.15	1	420.15	35.46	0.0001
AD	12.25	1	12.25	1.03	0.3254
BC	1.00	1	1.00	0.084	0.7754
BD	16.00	1	16.00	1.35	0.2634
CD	12.25	1	12.25	1.03	0.3254
A ²	47.25	1	47.25	3.99	0.0643
B ²	0.96	1	0.96	0.081	0.7793
C ²	78.11	1	78.11	6.59	0.0214
D ²	78.11	1	78.11	6.59	0.0214
Residual	117.75	15	11.85		
Lack of Fit	134.92	10	13.49	1.57	0.3216
Pure Error	42.83	5	8.57		
Cor Total	4391.37	29			

Table 12
Fit Statistics.

Std. Dev.	Mean	C.V. %	R ²	Adjusted R ²	Predicted R ²	Adeq Precision
3.44	57.57	5.98	0.9595	0.9217	0.8090	17.8880

From Fig. 26 the minimum predicted value of the biodiesel obtained from the transesterification of beef tallow was 72%, while the actual experimental value is 74%. The optimization solution obtained shows that a biodiesel yield of 72.0% was obtained at a methanol to oil ratio of 7:1, a catalyst loading of 4%, a reaction temperature and time of 60 °C and 106 min respectively.

Fig. 17 the actual values obtained from the study lie close to the regression line as such they correlated with the predicted values generated by design expert. This shows that there is no much disparity between the actual and predicted results and this quadratic model is suitable model for this study.

Regression analysis for transesterification

The effects of each of the parameters and how they affect the acid catalyzed esterification of beef tallow are studied. These parameters

which include the methanol: oil ratio, the catalyst concentration, the reaction time and the reaction temperature.

From the plot of Fig. 18 it was observed that an increase in methanol to oil ratio led to increment in the biodiesel yield. This trend panned out at a methanol oil ratio of 8:1 where further increment in the methanol to oil ratio resulted in a drop in the biodiesel yield as was observed at a methanol to oil ratio of 12:1 with a biodiesel yield of 68%. Similar findings were reported by Xinyu *et al.* (2013).

From the plot of Fig. 19 it was observed that an increase in the catalyst loading resulted in a increase in the biodiesel yield. This trend panned out at a biodiesel yield of 75 % at a catalyst loading of 7 %. Further increment in the catalyst loading resulted in a decrement in the biodiesel yield as was observed at catalyst loading of 10 % and 13 % with biodiesel yields of 71 % and 62 % respectively with similar findings reported by Widayat *et al.* (2016).

From the plot of Fig. 20, it was observed that an increase in the reaction temperature resulted in an increase in the Biodiesel yield with higher temperatures resulting in higher biodiesel yield. Reaction temperatures of 51, 60 and 69 °C gave biodiesel yields of 68, 74 and 75%. Similar findings were reported by Sanjel *et al.* (2014).

From the plot of Fig. 21, it was observed that an increase in the reaction time resulted in an increase in the biodiesel yield. This trend panned out at a reaction time of 90 min with biodiesel yield of 75%. Further increment in the reaction time brought about a decline in the

Table 13
Coefficients in Terms of Coded Factors.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	61.17	1	1.41	58.17	64.16	
A-Methanol:Oil ratio	5.92	1	0.7027	4.42	7.41	1.0000
B-Catalyst Loading	-1.17	1	0.7027	-2.66	0.3310	1.0000
C-Reaction Temperature	10.33	1	0.7027	8.84	11.83	1.0000
D-Reaction Time	1.33	1	0.7027	-0.1644	2.83	1.0000
AB	2.50	1	0.8606	0.6657	4.33	1.0000
AC	-5.13	1	0.8606	-6.96	-3.29	1.0000
AD	0.8750	1	0.8606	-0.9593	2.71	1.0000
BC	-0.2500	1	0.8606	-2.08	1.58	1.0000
BD	-1.0000	1	0.8606	-2.83	0.8343	1.0000
CD	-0.8750	1	0.8606	-2.71	0.9593	1.0000
A ²	-1.31	1	0.6573	-2.71	0.0885	1.05
B ²	0.1875	1	0.6573	-1.21	1.59	1.05
C ²	-1.69	1	0.6573	-3.09	-0.2865	1.05
D ²	-1.69	1	0.6573	-3.09	-0.2865	1.05

Table 14

Effect of Repeated Use of Catalyst on Biodiesel Yield.

Times of repeated run	1	2	3	4	5	6	7
Biodiesel yield (%)	72	64	61	53	44	41	34

Table 15

Independent Factors used for kinetics study.

Time (minutes)	Yield		
	55 °C	60 °C	65 °C
30	10	28	52
40	17	33	55
50	52	56	58
60	66	71	72

biodiesel yield as was observed at reaction times of 120 and 150 min with biodiesel yields of 74 and 61% respectively. Similar findings was reported by Sanjel *et al.* (2014).

The effect of interaction between process parameters for transesterification

The Three-dimensional response surfaces are plotted on the basis of the generated model equation to investigate the interaction among variables and to determine the optimum condition of each factor for maximum biodiesel yield.

Fig. 22 represents the 3D plot of the interaction effect of methanol: oil ratio and catalyst loading on the biodiesel yield at reaction time of 90 min and reaction temperature of 51 °C. From the plot it was observed that the plane was inclined towards both x and z axes indicating a decline in the catalyst loading resulted in an increase in the biodiesel yield similarly as the methanol to oil ratio increased from 6:1 to 10:1 so did the biodiesel yield increase progressively. In terms of the interaction of the methanol to oil ratio and the catalyst loading on the biodiesel yield, it was observed that an optimum biodiesel yield of 67.19% was obtained at a methanol to oil ratio of 10:1 and catalyst loading of 10% at a constant reaction temperature and time of 51 °C and 90 min respectively.

Fig. 23 represents the 3D plot of the interaction effect of methanol: oil ratio and reaction temperature on the biodiesel yield at reaction time of 90 min and catalyst loading of 7%. From the plot, the plane was inclined towards the z-axis (reaction temperature). It was observed that an increase in the methanol to oil ratio resulted in an increase in biodiesel yield. A similar trend was observed in the case of reaction time because as it increased from 42 to 60 °C so did biodiesel yield increase. In terms of interaction effect of the methanol to oil ratio and the reaction temperature on the biodiesel yield. An optimum biodiesel yield of 69.85% was obtained at a methanol to oil ratio of 9:1 and a reaction temperature of 60 °C at a constant catalyst loading and reaction time of 7% and

Table 16

Characteristics of Produced Biodiesel from Beef Tallow.

S/N	Property	Unit	Result Obtained	ASTM D6751
1.	Density 40 °C	g/cm ³	0.928	–
2.	Flash Point	°C	154	130
3.	Kinematic Viscosity at 40 °C	mm ² /s	5.4	1.9 – 6.0
4.	Cetane Index		56	47
5.	pH Value		7.2	–
6.	Color		Amber Yellow	–
7.	Pour Point	°C	5	18 max
8.	Cloud point	°C	11	–
9.	Iodine Value	mgI/100 g	54.4	120 max
10.	Ester Value	wt. %	141.3	96.5
11.	Acid value	mgKOH/g	0.836	0.8 max
12.	FFA	wt %	0.418	–

90 min.

Fig. 24 represents the 3D plot of the interaction effect of methanol: oil ratio and reaction time on the biodiesel yield at a reaction temperature of 51 °C and a catalyst loading 7%. From the plot it was observed that as the methanol to oil ratio increased from 6:1 to 10:1 so did the biodiesel yield increase progressively. Similarly, an increase in the reaction time resulted in an increase in biodiesel yield although this trend panned out at a reaction time of 100 min with further increment in the reaction time resulting in a dip in the biodiesel yield. In terms of interaction effect of the methanol: oil ratio and reaction time on the biodiesel yield at a reaction temperature of 51 °C and a catalyst loading 7% an optimum biodiesel yield of 66.35% at a methanol to oil ratio and reaction time of 10:1 and 115 min.

From Fig. 25, the 3D plot was inclined along both x and z axes. This shows that increase in both parameters led to increase in biodiesel yield. Catalyst loading and reaction temperature played significant role in transesterification. Optimum biodiesel yield of 71.31% at reaction time of 90 min, methanol to oil ratio of 8:1, catalyst concentration of 4% and reaction temperature of 60 °C.

From Fig. 26, the 3D plot is slightly inclined on both x-axis and z-axis. This shows interaction between biodiesel yield and reaction time and catalyst loading. Optimum biodiesel yield of 63.31% was observed at reaction temperature of 51 °C, methanol to oil ratio of 8:1, catalyst concentration of 4% and a reaction time of 108 min.

From Fig. 27, the plot was inclined on both x and z axes. This shows that reaction time and temperature were significant factors in transesterification reaction. At reaction time of 99 min and reaction temperature of 60 °C optimum biodiesel yield of 69% was observed at constant values of 7% catalyst loading and methanol to oil ratio of 8:1.

Overall, the process parameters affect biodiesel yield as the combination of any of the process parameters results in a minimum biodiesel yield of 63.31% while a maximum biodiesel yield of 71.31% was obtained at a catalyst concentration of 4% and a reaction temperature of 60 °C when the methanol to oil ratio and the reaction time parameters were kept constant at 90 min and 8:1 respectively.

Catalyst reusability test

The result of reusability test shows how many times the same catalyst can be used to produce biodiesel. It was observed that at repeated 4th run, biodiesel yield using the same calcium oxide catalyst dropped below 50 %.

Kinetics data for biodiesel production

The kinetics of the reaction was determined by measuring the effect of the reaction time and temperature. Several assumptions were made,

Table 17

Chemical Composition of Synthesized Biodiesel.

Peak No.	Retention time (min)	Compound Name	Molecular Formula	Area (%)	Height (%)
1	4.661	Methyl butanoate	C ₅ H ₁₀ O ₂	17.66	1.79
2	5.277	Tetracosanoic acid methyl ester	C ₂₅ H ₅₀ O ₂	0.53	17.48
3	5.468	Docosanoic acid Methyl ester	C ₂₃ H ₄₆ O ₂	5.20	2.09
4	13.629	Hexadecanoic acid methyl ester (Methyl Hexadecanoate).	C ₁₇ H ₃₄ O ₂	18.66	15.51
5	18.997	Methyl 15-methylhexadecanoate (Methyl Hexadecanoate)	C ₁₇ H ₃₄ O ₂	10.34	4.62
6	21.083	11,14-Eicosadienoic acid methyl ester (Methyl Eicosanoate)	C ₂₁ H ₃₈ O ₂	0.99	13.52
7	21.132	Methyl 11-octadecenoate (Methyl Octadecanoate)	C ₁₉ H ₃₆ O ₂	27.60	17.86
8	21.472	Eicosanoic acid methyl ester (Methyl Eicosanoate)	C ₂₁ H ₄₂ O ₂	18.71	25.86
9	26.159	2H-1-Benzopyran-6-ol	C ₃₁ H ₅₂ O ₃	0.31	1.28

one of which was that the catalyst used was of sufficient amount with respect to the oil in other to cause a change in the reaction equilibrium bringing about the formation of FAME [36].

According to Permsuwan *et al.* [37] the mechanism governing the conversion of triglycerides to methyl esters are in three steps;



TG = Triglycerides, DG = Diglycerides, MG = Monoglycerides, MeOH = Methanol, ME = Methyl esters.

According to Permsuwan *et al.* [37] and Alam *et al.* [38] the reaction

can be assumed to be a single one step esterification reaction.



The overall reaction rate is given as.

$$-r_A = -\frac{d[\text{TG}]}{dt} = k[\text{TG}][\text{MeOH}]^3 \quad (4.3)$$

The overall reaction follows a second order reaction rate law. But due to the high molar ratio of methanol to oil ratio the change in the methanol concentration can be assumed to be constant during the reaction as such the reaction behaves as a first order chemical reaction [36].

The overall rate of reaction reduces to.

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Biodiesel Yield

Color points by value of
Biodiesel Yield:

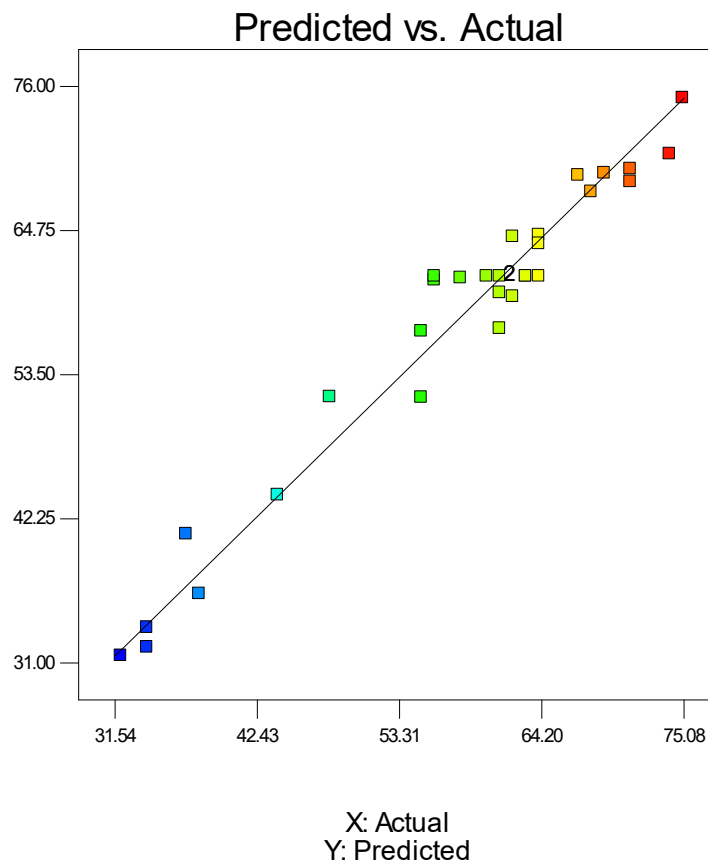
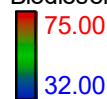


Fig. 17. Graph of predicted values vs. actual values obtained from the transesterification of beef tallow.

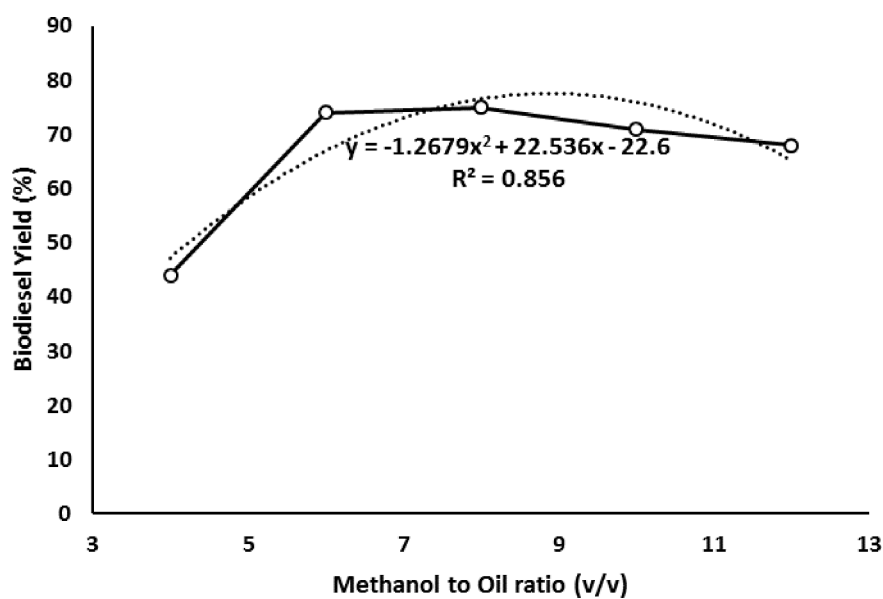


Fig. 18. Regression graph of the effect of methanol to oil ratio on biodiesel yield.

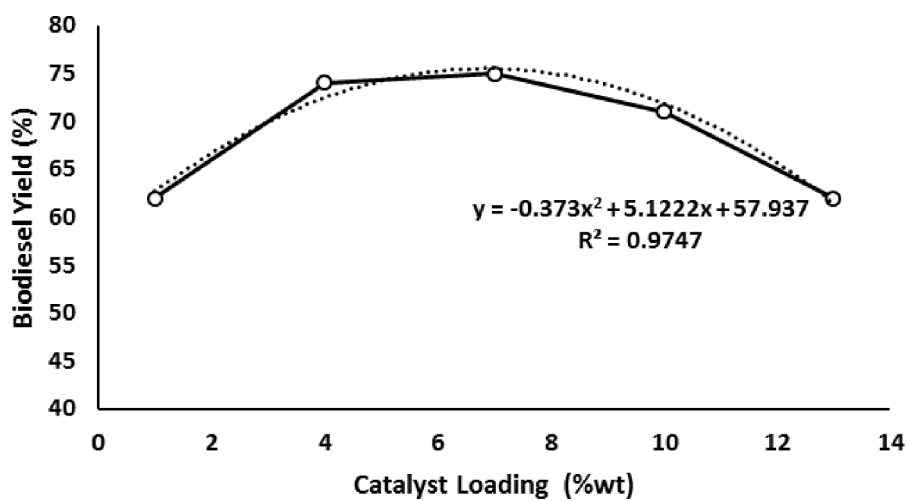


Fig. 19. Regression graph of the effect of catalyst loading on biodiesel yield.

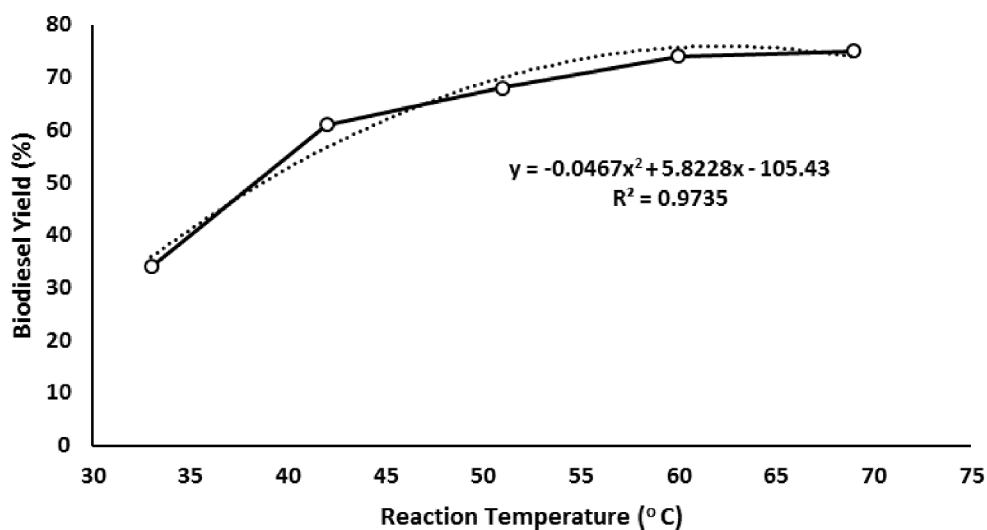


Fig. 20. Regression graph of the effect of reaction temperature on biodiesel yield.

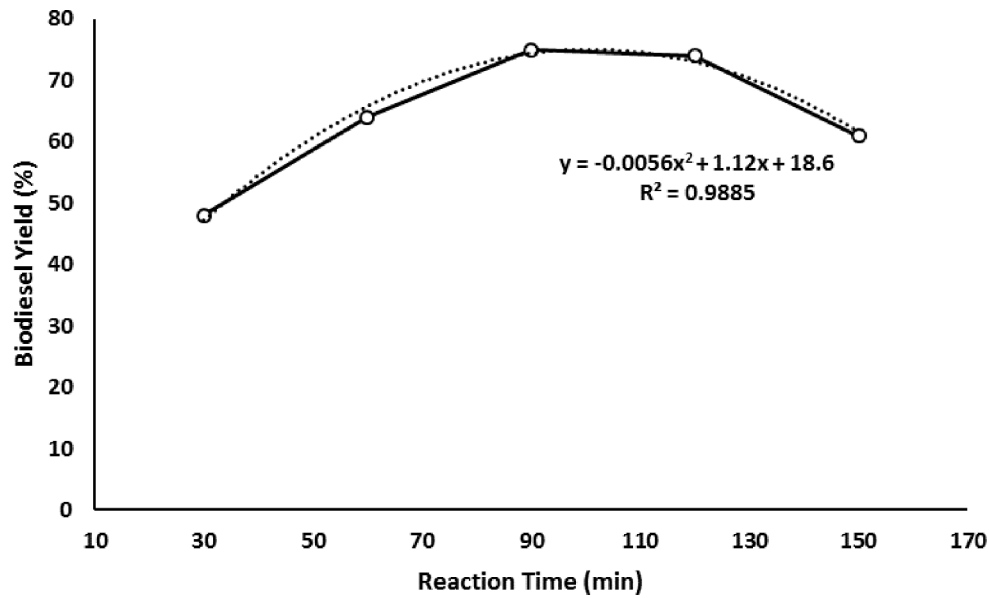


Fig. 21. Regression graph of the effect of reaction time on biodiesel yield.

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Biodiesel Yield



X1 = A: Methanol:Oil ratio

X2 = B: Catalyst Loading

Actual Factors

C: Reaction Temperature = 57.00

D: Reaction Time = 90.00

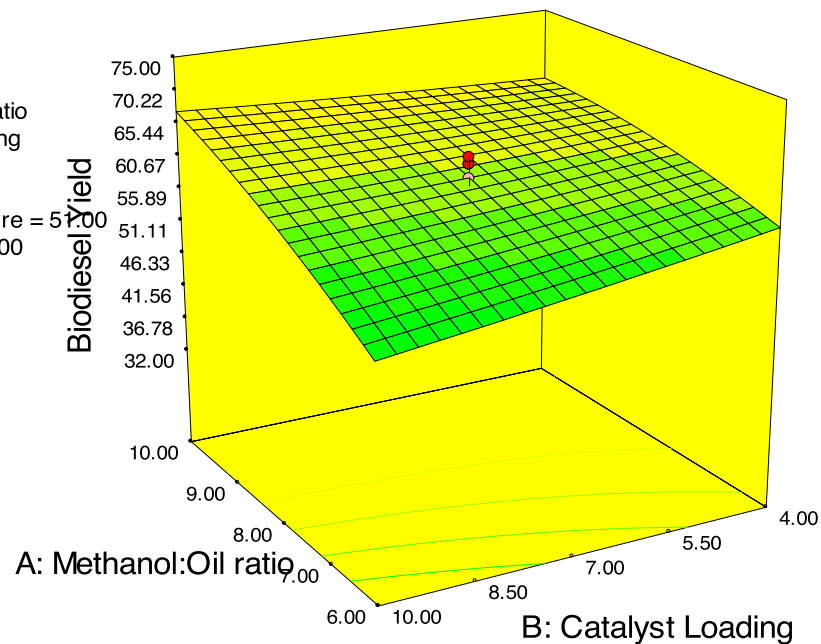


Fig. 22. Response surface plot of the interaction effect of methanol: oil ratio and catalyst loading on the biodiesel yield.

$$-r_A = -\frac{d[TG]}{dt} = k[TG]$$

Hence the overall reaction rate obeys a pseudo first order kinetic.

$$-\frac{d[TG]}{dt} = k[TG]$$

Rearranging Equation 4.5 and integrating gives.

$$-\int_{TG_0}^{TG_t} \frac{1}{[TG]} d[TG] = k \int_{t=0}^{t=t} dt$$

Equation 4.6 becomes.

$$-\ln \frac{[TG_t]}{[TG_0]} = kt$$

Where $[TG_t]$ = triglyceride concentration at time t $[TG_0]$ = initial triglyceride concentration.

But from mass balance.

$$X_{fame} = 1 - \frac{[TG_t]}{[TG_0]} \quad (4.8)$$

Rearranging equation (4.8).

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Biodiesel Yield



X1 = A: Methanol:Oil ratio

X2 = C: Reaction Temperature

Actual Factors

B: Catalyst Loading = 7.00

D: Reaction Time = 90.00

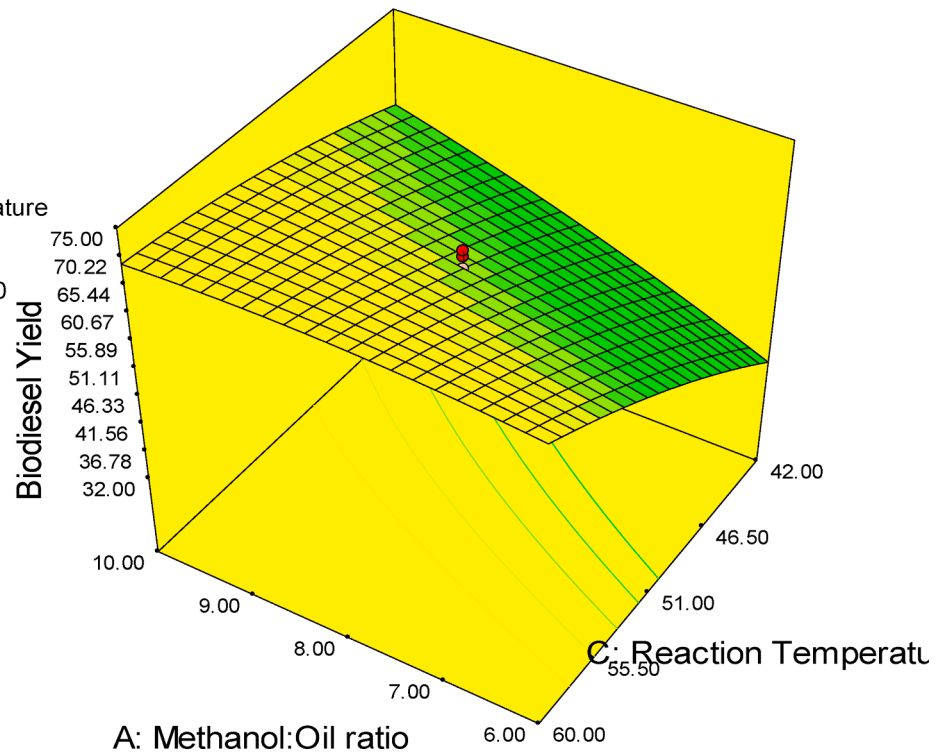
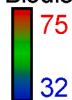


Fig. 23. Response surface plot of the interaction effect of methanol: oil ratio and reaction temperature on the biodiesel yield.

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Biodiesel Yield



X1 = A: Methanol:Oil ratio

X2 = D: Reaction Time

Actual Factors

B: Catalyst Loading = 7.00

C: Reaction Temperature = 55.50

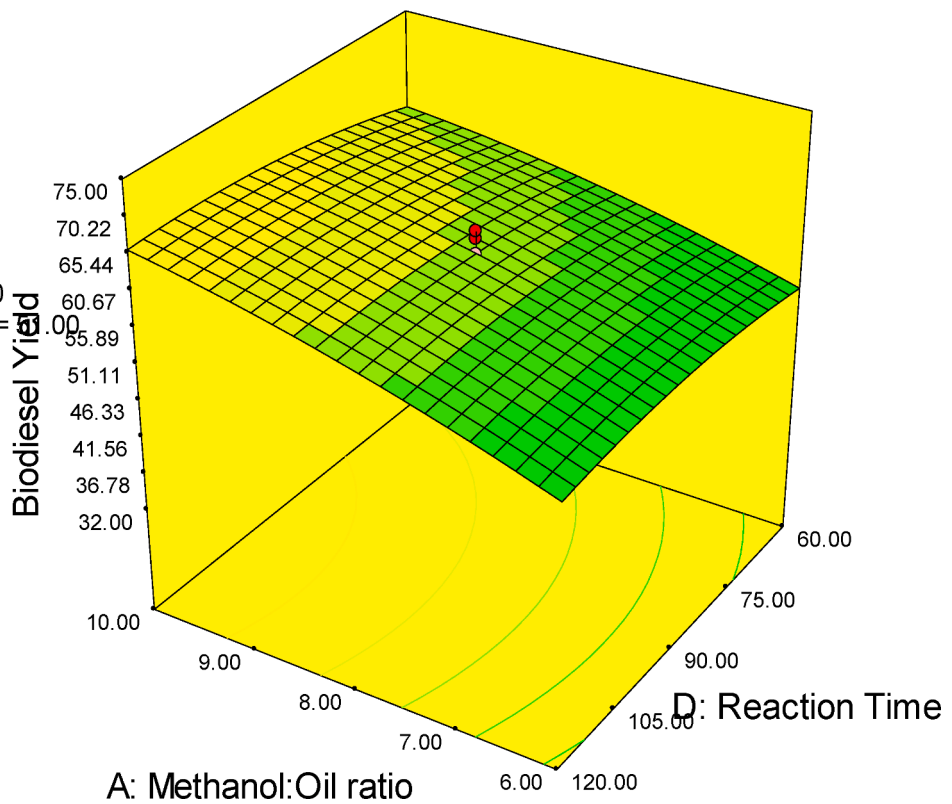


Fig. 24. Response surface plot of the interaction effect of methanol: oil ratio and reaction time on the biodiesel yield.

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Biodiesel Yield



X1 = B: Catalyst Loading

X2 = C: Reaction Temperature

Actual Factors

A: Methanol:Oil ratio = 8.00

D: Reaction Time = 90.00

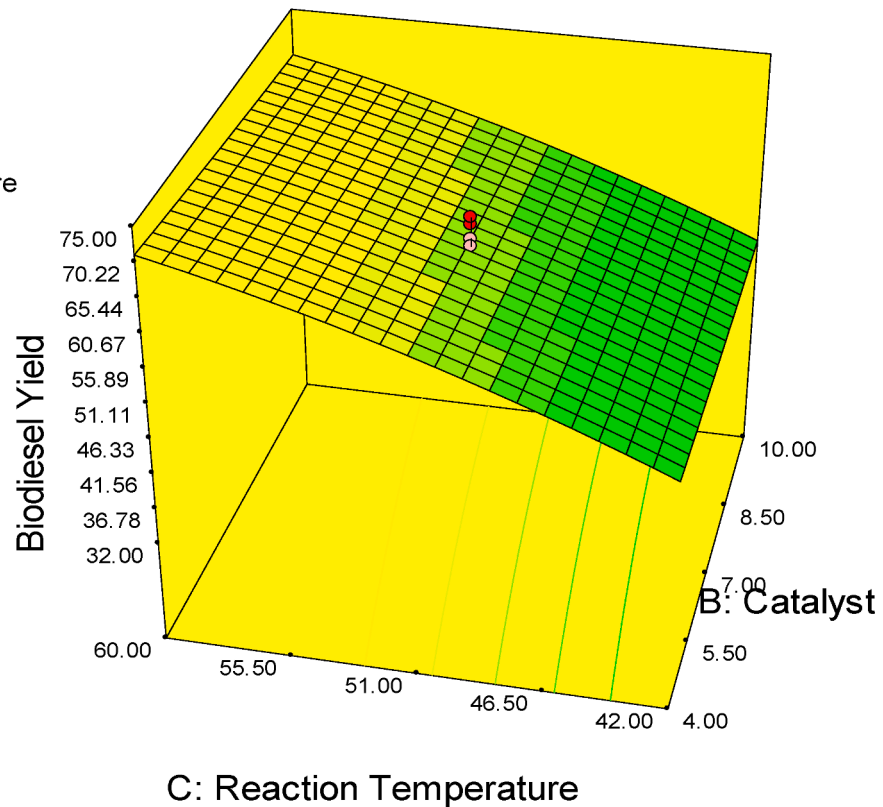


Fig. 25. Response surface plot of the interaction effect of catalyst loading and reaction temperature on biodiesel yield.

$$\frac{[TG_i]}{[TG_0]} = 1 - X_{fume}$$

Equation 4.9 becomes.

$$-\ln(1 - X_{fume}) = kt$$

From equation 4.10 $-\ln(1 - X_{fume})$ is plotted against t at selected temperatures of 55, 60 and 65 °C at a constant methanol to oil ratio of 8:1 and a catalyst loading of 7%.

Fig. 28 shows the plot of the $-\ln(1-X)$ versus reaction time at different temperatures with a constant methanol to oil ratio of 8:1 and a catalyst loading of 7 wt%. The k values obtained here (which is the slope of each plot at a particular temperature) is used to determine the activation energy and the pre exponential factor or frequency factor Figs. 29 and 30.

The Arrhenius equation.

$$k_A(T) = Ae^{-E/RT}$$

where k_A = Temperature dependent specific rate constant. A = pre exponential factor or frequency factor. E = Activation energy. R = gas constant (8.314 J/mol.K or 1.987 Kcal/mol.K).

T = absolute temperature.

The Arrhenius equation is reduced to equation 4.12 after taking the natural logarithm of equation 4.11.

$$\ln k_A = \ln A - \frac{E}{R} \left(\frac{1}{T} \right)$$

The plot of $\ln k_A$ against $\left(\frac{1}{T} \right)$ is used to determine the activation energy E and the pre exponential factor A with the slope of the plot corresponding to $\frac{E}{R}$ and the intercept corresponding to $\ln A$.

From the plot the activation energy and the pre exponential factor

are calculated as 82.845 kJ/mol.K and $4.805 \times 10^{11} \text{ min}^{-1}$. The Arrhenius plot gives an R^2 value of 0.9109 which shows a correlation with the experimental data.

Biodiesel quality determination

The produced biodiesel is characterized and compared against established biodiesel standards such as the American Standards and Testing Materials. The ASTM D6751 serves as a guideline which provides information on the properties and quality of good Biodiesel.

GCMS analysis of synthesized biodiesel

One of the standards associated with biodiesel synthesis is the composition and structure of the fatty esters comprising the biodiesel. This analysis was carried out using the GC-MS where the relative peak areas in the GCMS analysis of the components are proportional to the weight proportion of the components (Sokoto et al., 2011). The components present in the biodiesel sample are presented in Table 17.

According to Hariram and Bharathwaaj, (2016) hydrocarbon grouping is differentiated as $< C_{15}$, $C_{15} - C_{20}$, $C_{20} - C_{30}$ and $> C_{30}$ with respect to the retention time of standard hydrocarbons like octadecane, heptadecane, eicosane, tricosane and molecular carbon chain length. From the GCMS analysis presented in Table 17 it revealed the presence of hexadecanoic acid methyl ester, methyl 11-octadecenoate, eicosanoic acid methyl ester, methyl butanoate, docosanoic acid methyl ester, 11,14-eicosadienoic acid methyl ester and tetracosanoic acid methyl ester as the methyl esters present in the biodiesel while 2H-1-benzopyran-6-ol is considered as an impurity. The major methyl ester is the hexadecanoic acid methyl ester. From the GCMS analysis the saturated fatty acids include methyl butanoate, tetracosanoic acid methyl ester, docosanoic acid methyl ester, hexadecanoic acid methyl ester and

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Biodiesel Yield



X1 = B: Catalyst Loading

X2 = D: Reaction Time

Actual Factors

A: Methanol:Oil ratio = 8.00

C: Reaction Temperature = 51.00

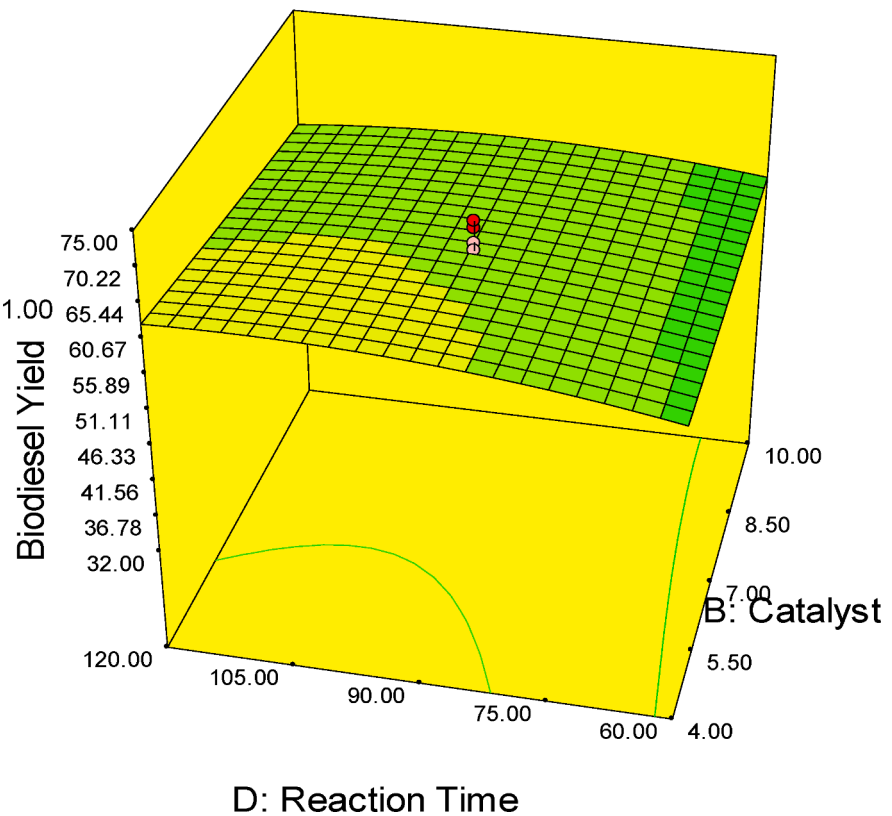


Fig. 26. Response surface plot of the interaction effect of catalyst loading and reaction time on the biodiesel yield.

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Biodiesel Yield



X1 = C: Reaction Temperature

X2 = D: Reaction Time

Actual Factors

A: Methanol:Oil ratio = 8.00

B: Catalyst Loading = 7.00

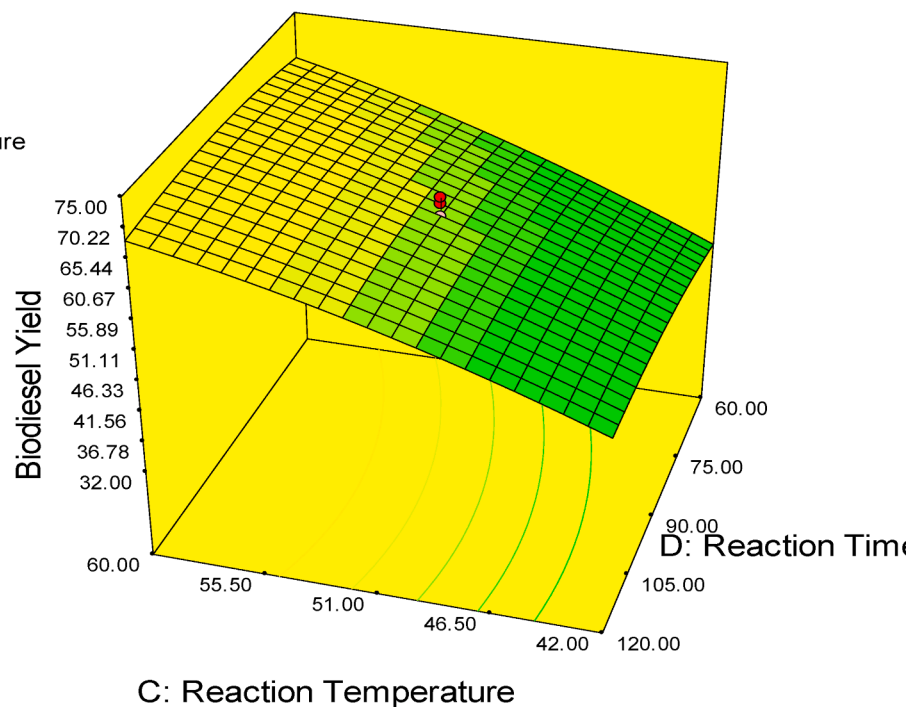


Fig. 27. Response surface plot of the interaction effect of reaction temperature and reaction time on the biodiesel yield.

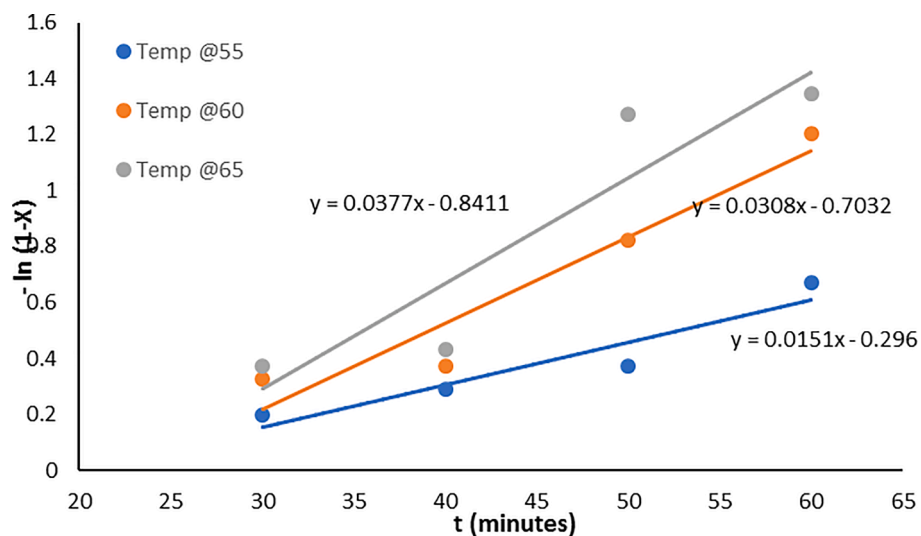


Fig. 28. $\ln(1-X)$ plot versus reaction time plot at different temperatures (methanol:Oil ratio of 8:1 and catalyst loading of 7 wt%).

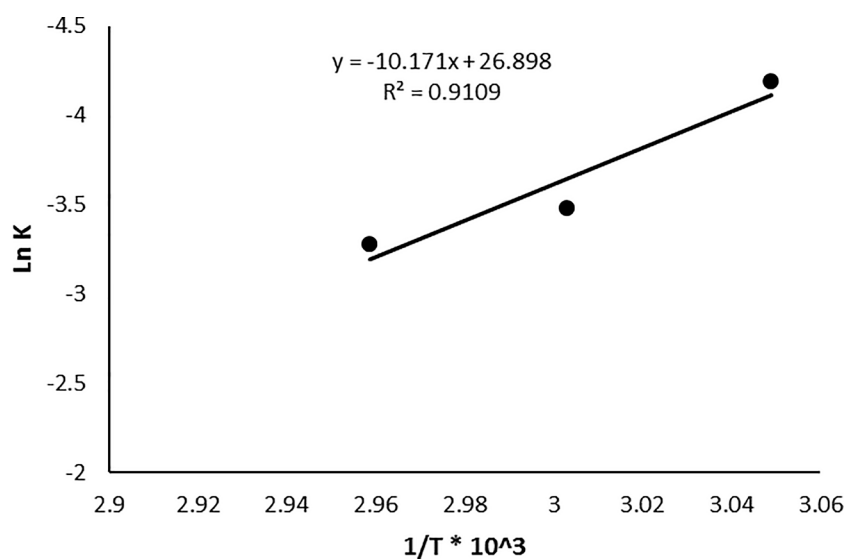


Fig. 29. Arrhenius plot of $\ln k$ versus $1/T \cdot 10^3$ for the transesterification of beef tallow by CaO derived from limestone.

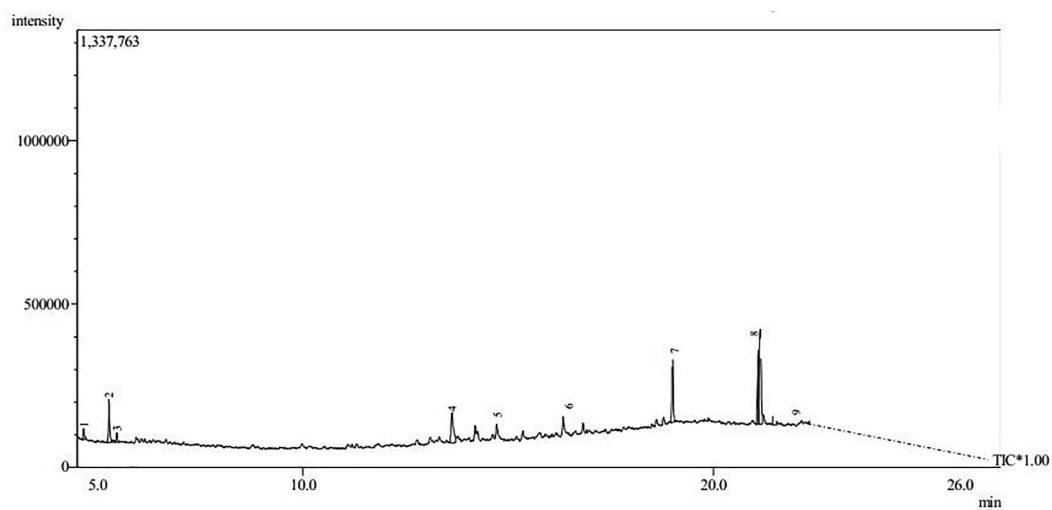


Fig. 30. GC-MS analysis of synthesized Biodiesel.

eicosanoic acid methyl ester which account for 71.1% of the biodiesel makeup. Similarly, 11,14-eicosadienoic acid methyl ester and methyl 11-octadecenoate (elaidic acid methyl ester) are unsaturated fatty acids and make up 28.59% of the biodiesel make up while 2H-1-benzopyran-6-ol accounts for 0.31% of the biodiesel makeup. According to Koria and Nithya, (2012) the presence of low level of unsaturated fatty acids is desirable as these unsaturated fatty acids results in poor oxidative stability of the fuel while a high presence of saturated fatty acids enhances the biodiesel fuel oxidative capacity. Similarly, Kaisan, [39] reported that higher degree of unsaturation in the fatty acid methyl esters limits its suitability for use as a fuel due to high polymerization tendency which is caused by peroxidation. Therefore, since the predominant methyl ester is methyl hexadecanoate which is a saturated fatty acid and as such has an affinity for oxygen therefore the tendency for peroxidation to occur in the car engine leading to engine failure would not occur.

Conclusion and future challenges

Optimization and kinetic study of biodiesel production from beef tallow using calcium oxide as a heterogeneous and recyclable catalyst, have been reported. From the findings, the quadratic model was selected as most suitable with a p value less than 0.0005. The significant factors from the ANOVA analysis are the methanol to oil ratio and the reaction temperature with p-values of 0.0001 respectively which is less than 0.05. The other significant factors are the interaction effect of the methanol to oil ratio and catalyst loading and the interaction effect of methanol to oil ratio and reaction temperature with p-values of 0.0109 and 0.0001. Similarly, the quadratic effects of the reaction temperature and the quadratic effect of reaction time are also significant factors with p-values of 0.0214 respectively. A value for the determination coefficient (R^2) of 0.9592 and 0.9595 and a value for the coefficient of variation (CV%) of 13.12 and 5.98 for both the esterification and transesterification stages were obtained from the study. The order of reaction for CaO catalyzed transesterification of biodiesel from beef tallow was pseudo first order reaction which resulted in activation energy and the pre-exponential factor of 82.845 kJ/mol.K and $4.805 \times 10^{11} \text{ min}^{-1}$ with the Arrhenius plot giving an R^2 value of 0.9109 which shows a correlation with the experimental data.

Finally, the four parameters studied in the acid catalyzed esterification of beef tallow resulted in an optimum FFA of 0.60 at operating conditions of acid catalyst amount of 7.1%, methanol to oil ratio of 9:1, reaction temperature of 60°C and a reaction time of 96 min. The obtained FFA from the actual experimental data showed a close correlation with the predicted FFA result where a predicted FFA of 0.61 was obtained. Thus, the experimental data and the predicted data showed a close fit. Secondly the produced biodiesel was characterized with its properties bearing a close correlation with ASTM and EN standards.

There is need to consider developments of novel catalysts possibly from wastes, with better catalytic performance than calcium oxide. These new types of catalysts should be useful for industrial application. This would become possible when catalysts preparation routes and treatment steps are modified to suit industrial application.

CRedit authorship contribution statement

Babatunde Esther Olubunmi: Conceptualization, Methodology, Investigation. **Aderibigbe Fatai Alade:** Investigation, Supervision. **Samuel Ogbeide Ebhodaghe:** Writing – original draft, Writing – review & editing. **Ogunjobi Tokunbo Oladapo:** Formal analysis, Validation, Data curation.

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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