



Parametric optimization by Taguchi L9 approach towards biodiesel production from restaurant waste oil using Fe-supported anthill catalyst

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ABSTRACT

Restaurant waste oil is easily obtainable from local restaurants, while anthills grow widely in Oro, Nigeria. The anthills were first carbonized, then steam activated to prepare an inert, porous support capable of functional group adsorption. The support was then doped with Fe (II) using FeSO_4 and the Fe/A catalyst was used in biodiesel synthesis from the RWO. L9 Taguchi OA was chosen to optimize the transesterification process parameters comprising of catalyst concentration, methanol to oil ratio, reaction temperature and reaction time. The optimization revealed that methanol concentration does not affect the biodiesel yield significantly, while reaction time has the highest contribution. A biodiesel yield of 99.73 % was attained at 60 °C for 1.5 h with 1.2 % catalyst and 6:1 methanol:oil ratio. GC analysis showed the product to be rich in methyl esters. Fuel characterization tests show that the product has properties exceeding the standards set by ASTM. Kinetic studies show the process adheres to pseudo 1st order kinetics and has high reaction rate and frequency factor (A) with low E_A , while the catalyst shows very efficient retention of functional groups, as evident from its reusability up to 7 times. Thus the process is energy and cost efficient, with a potential for commercialization.

1. Introduction

In recent times, biodiesel has gained more attention for research as an energy rich alternative fuel due to diminishing reserves and concurrent price hike of petro-fuels. The significant advancements in global industrialization and motorization has resulted in rising pollutant levels, impacting human health [2]. This is coupled with the increase in energy demands considering limited resources [3]. Thus, alternate fuels are needed that will come from renewable sources, meet energy and environmental crisis and have cleaner burning properties compared to petro-fuels. Also, biodiesel possesses properties such as being non-toxic, biodegradable, eco-friendly and high combustion efficiency due to low GHG emissions [7]. Biodiesel is prepared from renewable sources such as oil crops and micro algae, and an appropriate feedstock can potentially reduce one third of the total cost for biodiesel production [21].

Oil crops are grouped into edible and non-edible oils. The edible oils used are soybean oil, peanut oil, coconut oil, corn oil, palm oil, sunflower oil while non-edible oils are *Jatropha curcas*, neem oil, Jojoba, apricot seed, cotton seed oil, and tobacco seed. Also, animal

fats, waste vegetable oil (WVO), lard are used for making biodiesel [5]. For reducing production cost of biodiesel, WVO can be employed, since procurement of this oil does not involve additional costs. The non-edible oil is also used to avoid competition with food [19]. Furthermore, biodiesel can be produced by various techniques such as pyrolysis, micro – emulsification, dilution and transesterification [4]. The most widely used method is transesterification (even in commercial production), which is a reversible reaction amid vegetable oils and alcohol when the reaction is facilitated by a catalyst. The process is also accompanied by esterification, which progresses rapidly when an acid catalyst is used, and FFAs present in the oil can be converted into esters through this process. These processes involve catalysts which can either be homogenous or heterogeneous [7]. Since homogeneous catalysts have a lot of limitations which hinder their use in biodiesel production such as problem of separation and purification of product and increased wastewater generation due to excessive washing of biodiesel [18]. Hence, heterogeneous catalysts are better since they can overcome the drawbacks of homogenous catalysis [8], being easily separable, reusable with minimum leaching of catalytic groups, therefore requiring far less complicated purifications resulting in drastically reduced

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wastewater generation, and improved glycerol quality. Since resistances during mass transfer diffusion lower the reaction rate, hence a catalyst support is necessary for increasing surface area that increases the reaction rate in addition to improved catalyst stability [11,13,15]. The diffusional resistances in heterogeneous catalysis again affect the final yield by decreasing the reaction rate. Still, this process can be practiced effectively by using catalyst supports or structure promoters which will provide large number of reactive sites and surface area for conversion of triglycerides into fatty acid methyl esters (FAME) [15]. Various catalyst supports in heterogeneous transesterification like zinc oxide and aluminum oxide were commonly used due to their porous characteristics. Many heterogeneous catalysts such as mixed oxides, Amberlyst – 15, Zirconia, alkali and alkaline earth oxide have been studied but none of the catalysts were efficient enough for biodiesel production [6,14,16]. Moreover, there is a need for development of cheap heterogeneous catalyst in a commercially feasible way for biodiesel production that incurs low costs. Biomass waste or clay can be used in preparing an inert support for catalytic group doping since they have a microporous structure that offers a large number of reaction sites [9,19]. Making an inert support from clay minimizes resistances in diffusion because of increased surface area that facilitates the conversion (esterification of FFAs and transesterification of glycerides) that result in a high biodiesel yield [1,4]. Anthill is a clay deposited by termites which serve as a waste and are found everywhere in almost all states in Nigeria. Thus this waste can be appropriately utilized as a support to develop activated clay (silica) catalyst with high surface area [10,17]. In our previous works, the use of anthills as a catalyst was done by calcination of the anthills to develop an activated anthill catalyst without doping of any functional groups or transition metals [29]. As such, the biodiesel yield noted was less than 95 % w/w with high methanol concentration (9:1 molar ratio of methanol to oil) and reaction temperature (65 °C). In another of our works, activated anthill clay was mixed with calcined eggshells, and the resulting catalyst was inefficient in transesterification, resulting in only 70.7 % w/w biodiesel yield with high methanol concentration (12:1 methanol to oil molar ratio), 3 h reaction duration, 3% w/w catalyst load when the anthill and calcined eggshells were mixed in a 80–20 ratio. It was seen that catalysts prepared using lower amounts of anthills with a corresponding higher amount of eggshell resulted in lower biodiesel yield, and therefore anthills were noted to be a far more efficient catalyst of the transesterification process [27]. Also, Dhawane *et al.* had reported the successful catalytic transesterification of low-FFA rubber seed oil using a Fe(II) doped *Delonix regia* catalyst, with 96.31 % biodiesel yield [30]. Hence, it was reasoned that transition metal doped on to activated anthill doped with Fe(II) can be a very effective catalyst in the transesterification of waste oils for high biodiesel production. Also, since the presence of zirconia makes the anthill support hard and resistant to mechanical damage from high agitation, reusability of the catalyst was also tested.

For optimization of the heterogeneous catalyzed transesterification process, manual optimization techniques can be used, but the process is unnecessarily repetitive, requiring very high amounts of time and resources. Therefore, software guided approaches can be effectively used that use a limited number of experimental runs and analyze the obtained results for their accuracy through statistical ANOVA (analysis of variance). Among these, RSM (response surface methodology) based approaches such as CCD (central composite design) and BBD (Box-Behnken design) still use repetitive runs around the central points for optimizing the conversion process. An alternative and better approach are factorial approaches such as Taguchi OA (orthogonal array) and PBD (Plackett Burmann design) which use a drastically reduced number of runs with no repetitions and present the results as effects of individual parameters on the process response, as opposed to RSM approaches which show interactive effects on the process response.

To produce biodiesel, the discussed study uses an inert support of activated silica based catalyst made from anthill clay that was

impregnated with iron (II) (using FeSO_4 solution) to synthesize an aboriginal Fe/Silica heterogeneous catalyst (called Fe/A). The study is optimized by means of an L9 Taguchi matrix, which denotes the combination of parametric factors required for process optimization with the least number of experiments. Estimation of influential parameters for the studied process and their discrete impacts on the process was done through analysis of variance (ANOVA), which also aptly compares the obtained data with mathematically predicted values and shows experimental accuracy through statistically relevant factors [8,20]. The process kinetics were also examined and reported through tests conducted under optimum conditions at different temperatures. Fuel properties were also tested for quality assurance. The catalyst was also tested under optimal conditions for its reusability which is directly proportional to functional group retention within the catalyst support. So far, no reports exist on optimized biodiesel production using restaurant waste oil (RWO) through silicified anthill catalyst.

2. Materials and procedure

2.1. Materials required

Anthill clay was selected as the antecedent material because of it being abundantly available in Irepodun LGA of Oro, Kwara state, Nigeria for making the inert support that can be impregnated with desired functional group(s). The feedstock chosen was restaurant waste oil (RWO) from Chicken Republic Tanke, Ilorin, Nigeria in order to produce biodiesel. For transesterification, the reactant selected was methanol (purchased from Central Research Lab, Nigeria). Iron (II) sulphate was used for impregnation of iron (II) as catalytic group on activated anthill-clay surface acquired from Central Research Lab, Nigeria. Deionized water was used in the study to prevent ion contamination after collection from Central Research Lab, University of Ilorin, Nigeria. KOH, 2-propanol and phenolphthalein (Merck, India) was used to estimate FFA conversion, through titration of a fixed amount of sample dissolved in 2-propanol against KOH with phenolphthalein as end point indicator.

2.2. Synthesis of catalyst

The anthill harvested from Oro in Nigeria was cleaned to get rid of impurities and dirt. The clay was oven dried at 110 °C for 12 h for moisture removal. Grinding increases the surface area within 100–200 μm . Calcination in a muffle furnace under 900 °C for 4 h with subsequent optimized superheated steam activation under a temperature of 350 °C and duration of 1.5 h gives the necessary inert support [9]. The activated siliceous clay of termite acquired was used for preparing an inert support for doping iron (II) in making Fe/A catalyst [7]. Various amounts of iron (II) sulphate were liquefied in 150 mL deionized water. The support was doped with load amounts = 3.5, 4, 4.5 wt %. For 2 g of activated clay, solution of iron (II) sulphate was made accordingly with varying concentrations. The set quantity of activated clay can be mixed with every solution of iron (II) sulphate at 500 rpm agitation under 40 °C temperature for a time period of 15 h [27]. The process, (called a 'wet impregnation approach') can be performed under optimal conditions reported by Dhawane *et al.* [9] that maximizes biodiesel yield [8]. After impregnation, 0.5 M NaOH solution in the required quantity was added to the slurry (acidic in nature) till final pH was 12. After that, the mixture was poured onto filter paper for separation after stirring for 40 min, and aged for a day after separation. The Fe/A cake thus acquired was ground and placed at 600 °C for 1 h in a muffle furnace for use as a catalyst in the transesterification of the RWO [26].

2.3. Characterization of silica based catalyst

X-ray fluorescence (XRF) characterization was conducted using a

Varian 102WXRf analyzer to determine the chemical composition of the minerals that are present in the anthill clay sample. The termite clay (called catalyst support) and synthesized catalyst (Fe/A) were characterized using energy dispersive analysis by X-ray (EDAX) and scanning electron microscopy (SEM). SEM was obtained by means of Quanta FEG 450 Model Scanning Electron Microscope to obtain information about the sample surface morphology while EDAX allowed calculation of the elemental conformation of the sample [23]. A surface area analyzer using Bruanner Emmett Teller (BET) approach was used to gain insight into the sample's pore volume and surface area [24]. The X-ray diffraction (XRD) analysis is useful in determining the crystalline structure of a compound, and was performed on using a diffractometer (Philips PW1710) with parallel beam Cu K α radiation; the patterns for the synthesized catalyst observed were recorded. Detection of the various functional groups that have been adsorbed onto the surface of the inert support is possible by a thermo scientific Nicolet IS 10 Fourier Transform Infrared (FTIR) Spectrometer in the spectral range 500–4500 cm⁻¹, which uses a KBr pellet blank and pellet of sample mixed with KBr for analysis [25]. The biodiesel produced was analyzed for ester composition using gas chromatography (GC).

2.4. Design of experiments by Taguchi method

The one factor approach (OVAT) is not useful for efficient optimization of a process, since many overlapping experiments need to be run for the process to be thorough and the cost of optimization as well as the time required in greatly increased [23]. Hence, software guided approaches are preferable which include response surface methodology (RSM) consisting of Box Behnken Design (BBD) and Central Composite Design (CCD), or one factor approaches consisting of Taguchi OA and Plackett Burman Design (PBD). Among these, Taguchi OA uses orthogonal arrays to determine the minimum of significant runs within interactive variables at different levels of each variable that are sufficient in predicting the optimum response within a drastically reduced number of experimental runs. This results in a very few number of absolute runs which are needed for an accurate prediction of the response. The runs were systematically randomized to reduce analytical errors [24]. Methanol was varied at 6:1, 9:1 and 12:1. Reaction time was varied at 1, 1.5 and 2 h. Reaction temperature was varied at 50, 60, 70 °C; catalyst concentration was varied at 0.7, 1.2 and 1.7 % w/w of the oil. These levels were chosen based on literature and preliminary experiments [8,22]. Table 1 summarizes the parameters chosen for optimization and the levels taken for each parameter during the study.

2.5. Experimental procedure

The reaction between restaurant waste oil (RWO) and methanol was done under varying conditions. The temperature used in the reaction was kept at different temperatures (50, 60 and 70 °C), mostly around the boiling temperature of methanol (64.7 °C), to minimize evaporation losses aided by a reflux condenser that circulated the methanol vapor back into the reaction vessel [23]. A primary study was also performed for determining whether biodiesel would be formed at the minimum values of the varied conditions. The experiment run sheet containing parametric variations for each run along with the obtained response (in

Table 1
Parameters chosen at three levels for L9 design.

Parameters	Variables	Levels		
		1	2	3
Reaction Temperature (°C)	A	50	60	70
Reaction time (h)	B	1	1.5	2
Catalyst Loading (w/w%)	C	0.7	1.2	1.7
Methanol to Oil ratio	D	6:1	9:1	12:1

Table 2

Experimental design matrix by Taguchi method.

Run No.	Reaction Temperature (°C)	Reaction Time (h)	Catalyst Load (w/w%)	Methanol : oil ratio	Biodiesel yield (%)
1	70	1.5	0.7	12:1	71.13
2	60	1	1.2	12:1	87.19
3	50	1.5	1.2	9:1	69.86
4	60	1.5	1.7	6:1	81.8
5	70	2	1.2	6:1	82.77
6	60	2	0.7	9:1	93.72
7	70	1	1.7	9:1	90.7
8	50	1	0.7	6:1	84.03
9	50	2	1.7	12:1	77.74

terms of biodiesel yield%) has been reported in Table 2. All experimental runs were repeated in triplicates for elimination of errors and only consistent values were considered.

A fixed amount of RWO was used in the transesterification reaction. The value of methanol, catalyst concentration, reaction time and temperature depend on the run being carried out. At the end of each run, 5 mL of n-hexane and 5 mL of distilled water was added. Water and n-hexane are two immiscible liquids which would form two distinct layers. The glycerol formed from the reaction dissolves in the water phase while the biodiesel dissolves in the n-hexane phase. A separating funnel is used to separate the layers. The hexane layer is then filtered to remove all trace of catalyst in the solvent. n-hexane boils off at 68 °C; the mixture is then heated to around 75 °C to get rid of the n-hexane, to leave only the biodiesel. The biodiesel obtained was weighed and then used to calculate the yield using Eq. 1, where Y denotes the biodiesel yield.

$$Y(\%) = \frac{\text{weight of biodiesel}}{\text{weight of oil}} * 100 \quad (1)$$

2.6. Physico-chemical properties of raw oil and biodiesel

ASTM (American Society for Testing and Materials) standard methods were used to get the physicochemical properties of the raw oil before the biodiesel production process was performed and to characterize the biodiesel produced. Free fatty acid (FFA) denotes the residual acid content of the sample, while acid value denotes the corrosiveness of the fuel produced. Both can be assayed through a titrimetric assay using KOH of known normality and phenolphthalein as the end point indicator. A known quantity of sample is dissolved into a fixed amount of 2-propanol and 2 drops of phenolphthalein are added, to which KOH is added drop wise till a stable faint pink color is observed. The FFA and AV of the feedstock and the product are estimated using Eq. 3 and 4. The formation of esters was confirmed using gas chromatography (GC), carried out by Agilent Technologies GC system 7820A using a DB-23 wax column with N₂ as a carrier gas, while the reference material for confirming ester components was Supelco 37 FAME mix (Sigma-Aldrich). Both the sample fuel and the standard had been diluted in dichloromethane (CH₂Cl₂) for ease in peak identification.

Fire point denotes the temperature at which the fuel gives off sufficient quantity of vapor to maintain a flame, while at flash point the fuel's vapors are just sufficient to give a brief flash. Both properties denote the thermal stability of the fuel. The fire and flash points of the fuel can be tested using a closed cup Pensky Martens apparatus. Kinematic viscosity (KV) of a fuel represents the fluidity of the fuel and its ease in atomization during spray. This can be measured using a Redwood viscometer at a certain temperature, with variations in temperature resulting in different KV values. The energy content of the fuel is also an important quality parameter that determines how energy efficient the fuel is, and this can be measured using a bomb calorimeter

which is used in determining the calorific value of the fuel. The presence of paraffins are highly recommended in a fuel due to their clean burning characteristics, and this can be measured using aniline point, which is the temperature at which equal volumes of aniline and an oil sample become miscible in an aniline point measurement apparatus. The cetane number (CN) of a fuel denotes its quality and is indicative of ignition delay. Cetane number can also be used to calculate diesel index (DI) using Eq. 2:

$$CN = (0.72 * DI) + 10 \quad (2)$$

$$FFA = \frac{28.2 * N * t}{m} \quad (3)$$

$$AV = \frac{56.1 * N * t}{m} \quad (4)$$

Here, 28.2 denotes the weight of 0.1 M of oleic acid (weight of 282 g/mol), 56.1 is the molar weight of KOH, N is the normality of the KOH solution used for titrimetric analysis of FFA and AV, t is the titre value in mL and m is the mass of oil or fuel taken for titration.

3. Results and discussion

3.1. Proximate analysis of restaurant waste oil

The RWO used was analyzed to gain insight into its properties to determine if a direct transesterification using methanol was feasible without any acid pretreatment. The result was stated in Table 3 below. The percentage of free fatty acid observed is lower than 2% implying that the feedstock can be directly transesterified without an acid esterification step. Kinematic viscosity noted was high enough for the oil to be incompatible for direct use in blending with petro-diesel. The calorific value of the oil is high enough, implying that the product obtained may be rich in energy content. The relatively high moisture content in the oil meant that drying was necessary to avoid hydrolysis during transesterification.

3.2. Catalyst characterization

The chemical composition of anthill clay is summarized in Table 4 as had been determined by XRF. The result obtained revealed that the anthill contains mainly silica (SiO_2), alumina (Al_2O_3), zirconia (ZrO_2), and titania (TiO_2). From the result obtained, the anthill could be classified as siliceous fire clay [28]. However, the presence of ZrO_2 in the anthill sample is a unique find since it is absent in natural clay [26]. The presence of zirconia also explains the high thermal resistance and increased resistance to wear (zirconia confers increased hardness in the microscopic structure of the siliceous clay) after transition metal doping, since the clay was seen to be able to withstand high agitation speeds with little loss in catalytic activity even after the 7th reuse. It was observed from the Table 5 and Fig. 1 that the elemental composition of the catalyst could be attributed majorly to the siliceous clay and the principal catalyst contained a considerable amount of iron and silica. Also absence of nitrate compound in the elemental composition indicates proper calcination of the catalyst. The XRD pattern of silica based catalyst is shown in Fig. 2. The existence of numerous chemical

Table 4

Chemical composition analysis of Anthill by XRF.

Constituent	Chemical composition (% w/w)
Silicon oxide (SiO_2)	60.56
Aluminum oxide (Al_2O_3)	21.12
Zirconium Oxide (ZrO_2)	1.51
Calcium oxide (CaO)	1.85
Titanium oxide (TiO_2)	4.72
Magnesium oxide (MgO)	0.84
Sodium oxide (Na_2O)	0.06
Potassium oxide (K_2O)	2.10
Manganese oxide (MnO_2)	7.188
Zinc oxide (ZnO)	0.05
Iron(II) Oxide (FeO)	0.002
Total	100

Table 5

The elemental composition of the Fe/A catalyst by atomic weight.

Element	C	Si	Al	O	K	Ti	Mn	Fe	Total
Wt%	7.56	43.32	15.87	21.95	0.64	1.1	2.56	7.01	100

compounds and the crystallinity is observed at the peaks at various 2 θ values. The sharp peaks at 20.2°, 28.7°, 38.0° and 51.2° indicate that the synthesized catalyst is crystalline. The highest peak represents quartz (SiO_2) present in the clay which is a highly crystalline substance. The remaining points on the graph represent the presence of montmorillonite ($\text{Na}_x(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$) in the catalyst composition which is the component of the siliceous clay used. Hence, XRD analysis reveals that the catalyst produced can be efficient and easily separated.

BET was used to determine the pore volume and surface area of the catalyst support. The numerical values of the pore volume and surface area were 0.4510 cm^3/g and 762.5 m^2/g respectively. This property means that the support can provide high number of active catalytic sites for the transesterification reaction to proceed which will result into high yield of biodiesel produced. Thus, the activated clay is efficiently utilized as an inert support. Additionally, pore volume and surface area of synthesized catalyst were also determined to confirm the adsorption of iron (II) onto the inert support. It was observed that pore volume and surface area were 0.0525 cm^3/g and 120 m^2/g respectively. From the BET analysis it is clear that after the doping of Fe(II) on to the siliceous anthill support, the available surface area is drastically reduced, which indicates that large quantities of the functional group had been doped, and as was further noted from the biodiesel yield, the doping of large quantities of Fe(II) result in the development of a catalyst with high capacity for facilitating transesterification between the oil and methanol. Surface morphologies of the catalyst support and synthesized catalyst were examined by SEM as represented in Fig. 3a and b respectively. The figures illustrate dissimilar crystal patterns and crystal structures for every sample. The catalyst support (Fig. 3a) is observed to be an agglomerate of big particles. The cubic crystals with large pores account for increase in the activated clay surface's surface area. The SEM image in Fig. 3b shows a particle's asymmetrical shape with varying sizes; there exist a few surface micropores due to blockage accompanied by a decrease in measured surface area, this characteristic is preferable for a good catalyst. Hence the adsorption of iron (II) can be considered as successful [9]. The successful adsorption and impregnation on the catalyst support can also be confirmed by an EDAX quantitative analysis of elements (Fig. 1). The elemental composition of the Fe/A catalyst by atomic weight was observed: carbon 7.56 %, oxygen 21.95 %, aluminium 15.87 %, silicon 43.32 %, potassium 0.64 %, titanium 1.1 %, manganese 2.56 % and iron 7.01 %. This elemental composition of the Fe/A catalyst shows successful impregnation of the iron (II) on the activated clay surface. Thus, it could be used as a heterogeneous catalyst in the transesterification process.

Table 3

Proximate Analysis of Waste Restaurant Oil.

Property (unit)	Values
Acid value (mg KOH/g)	3.945 $\pm$ 0.02
Free fatty acid content (%)	1.973 $\pm$ 0.01
Kinematic viscosity (mm^2/s) at 40 °C	10.34 $\pm$ 0.2
Specific gravity	0.91 $\pm$ 0.04
Calorific value (MJ/kg)	39 $\pm$ 0.5
Moisture content (%)	2.1 $\pm$ 0.05

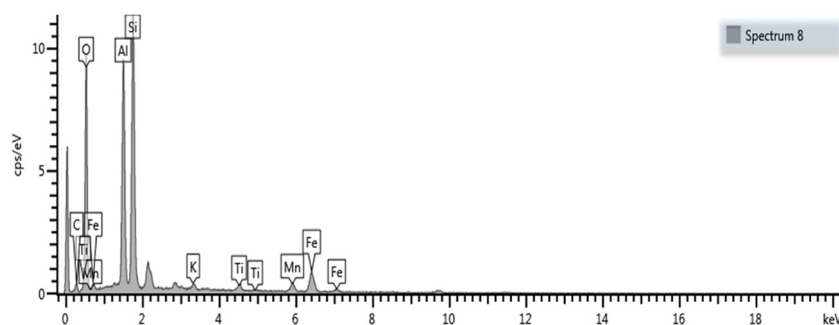


Fig. 1. EDAX structure of the synthesized catalyst.

Fig. 4 showed the FT-IR spectra of iron (II) impregnated on anthill clay (Fe/A), and the numerous existing functional groups are in the range $500 - 4000 \text{ cm}^{-1}$. The broad band located in 3626.39 cm^{-1} showed the presence of $-\text{OH}$ stretches. The peak between 2500 and 2000 cm^{-1} showed that triple bonds are present ($\text{C}\equiv\text{C}$). The peak 1634.83 cm^{-1} is due to $\text{C}=\text{C}$ stretching vibration, $\text{C}-\text{SO}_4$ stretching vibrations. SO_4 and $\text{C}=\text{O}$ functional groups (sulphate and carboxylic acid salt). The peak at 1479.68 cm^{-1} , 1425.86 cm^{-1} and 1378.36 cm^{-1} showed the presence of $\text{C}-\text{H}$ deforming vibration. The peak at 1036.41 cm^{-1} specifies the existence of a $\text{C}-\text{O}$ stretching vibration. 916.09 cm^{-1} , 871.77 cm^{-1} and 792.61 cm^{-1} peaks are due to the presence of a $\text{C}-\text{H}$ deforming vibration. The peak 665.95 cm^{-1} shows $\text{C}-\text{I}$ stretching vibration. Peaks at 523.48 cm^{-1} and 472.82 cm^{-1} are due to the presence $\text{S}-\text{S}$ stretching vibration. The FT-IR result shows that there are traces of silicon compounds, alkynes, alkenes, sulphate compounds, carboxylic acids and sulphur compounds.

3.3. Regression model equation and statistical analysis

Signal to noise ratio (SNR) or adequate precision (AP) value is calculated as a measure of standard deviation (SD) of every response from the mean of the responses obtained for every combination of the matrix experimentally tested. The data is then fed into a regression model developed [32]. The ANOVA also provides statistical parameters that show the significance of every reaction parameter and their impact on the response, as well as other relevant statistical parameters that are useful in understanding the fit (or lack thereof) of the experimentally obtained data with the mathematically predicted values. This can be obtained as a regression model equation as in Eq. 5, and the experimentally obtained vs. mathematically predicted data can be seen in

Fig. 5. Other relevant values such as sum of squares (SS) values for the model in overall as well as the individual parametric SS values, F-value and p-value of the model are obtained through ANOVA study as shown in Table 6, where it is evident that catalyst concentration is not mathematically significant for the process, and therefore its lowest value can be considered as optimal. Each of the values for every reaction parameter come assured with a high Fischer's test value (F-value), which denoted the significance of a particular parameter. A high F-value can be obtained when the model chosen fits well with the data obtained, or due to high noise. This is verified by the probability value (p-value); values within 0.05 indicate that the F-value is not due to noise. The present model has a F-value of 1388.29, with a p-value of only 0.0007, thereby indicating a 0.07 % chance of error. Also, as seen from Table 7, precision value of the fit characteristics for the model chosen should be at least 4, and other statistically relevant parameters such as R^2 values are also deemed important.

$$\text{Biodiesel yield (\%)} = 82.10 - 2.67 * A[1] + 6.21 * A[2] - 6.04 * B[1] + 6.64 * B[2] - 3.54 * C[1] + 4.78 * C[2] \quad (5)$$

Eq. 6 treating all optimized factors as numerical (instead of categorical as in Eq. 5) has been also depicted here, and here it can also be seen that methanol:oil ratio has the lowest impact on the biodiesel yield [30,31].

$$\text{Biodiesel yield (\%)} = 7.36 - 0.043 \times A + 5.45 \times B + 2.30 \times C + 0.02 \times D \quad (6)$$

In these equations, A = reaction temperature, B = reaction time and C = catalyst concentration and D = methanol:oil ratio, a '+' sign indicating a positive effect while a '-' sign indicates a negative effect on

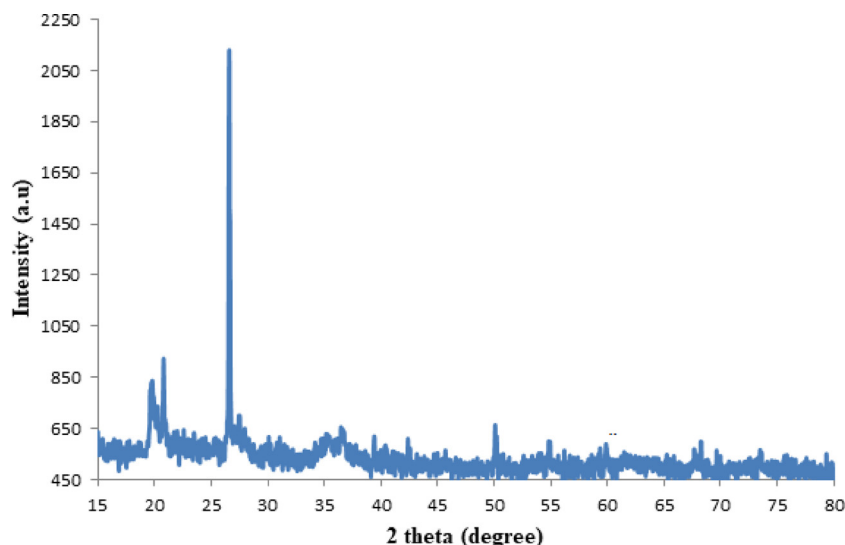


Fig. 2. XRD pattern of synthesized Fe/A catalyst.

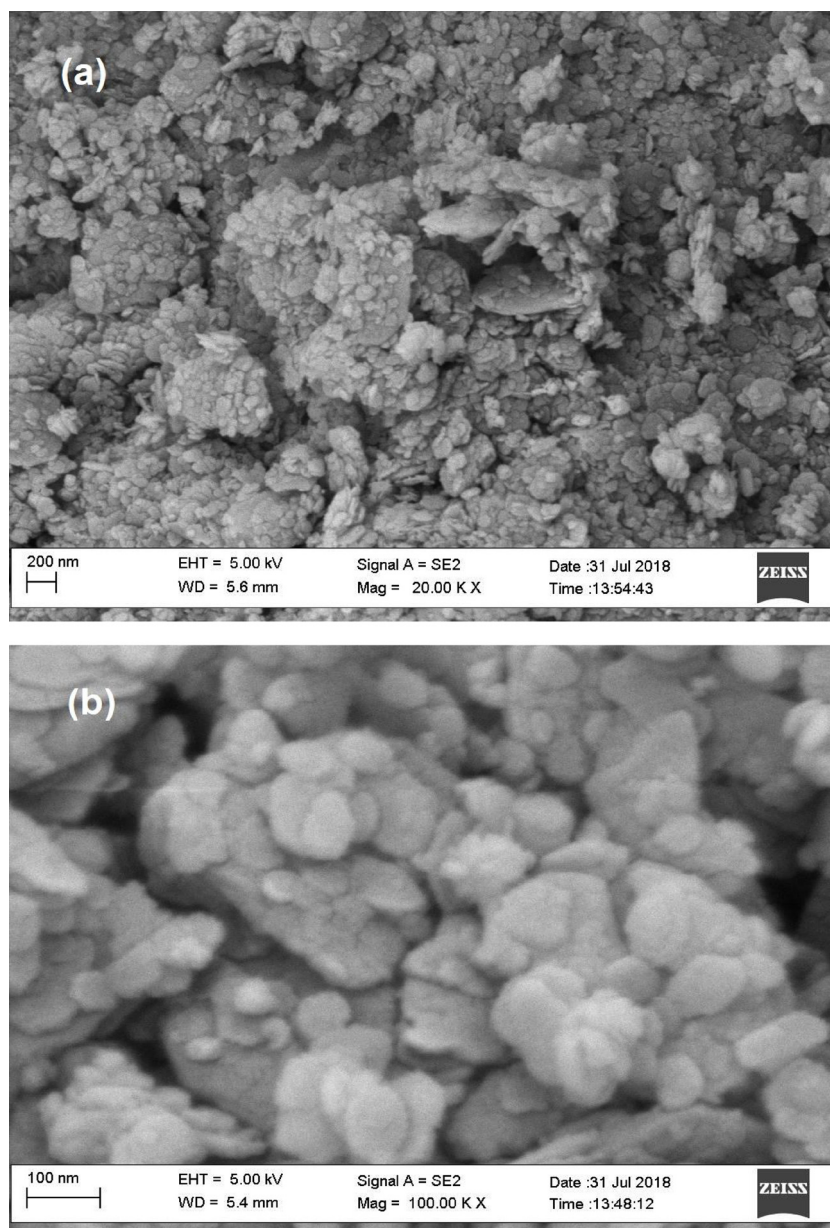


Fig. 3. SEM image of (a) catalyst support (b) Fe/A catalyst.

the biodiesel yield.. For Eq. 5 [1], and [2] represent the levels of the reaction parameters. The SS values can be also converted into a percentage of contribution for the process product, according to Eq. 7, where SS_f = SS value for individual parameter, SS_T = SS value for the model. The contribution factors for every reaction variable are summarized in Table 8 along with their optimal values.

$$\text{Contribution factor (\%)} = \frac{SS_f}{SS_T} * 100 \quad (7)$$

As can be seen from Table 7 and Fig. 5, the predicted and actual data are well in agreement with the difference between adjusted R^2 (= 0.999) and predicted R^2 (= 0.9951) values being only 0.0039, which is much less than the acceptable margin of 0.2, thereby indicating further that no block effect is present in the chosen model and the experimental data are accurate. AP value of a model should be greater than 4, and for the current study it is 107.4385, indicative of a strong signal.

3.4. Parametric effects on biodiesel yield

Biodiesel production from the RWO depends on the influence of every reaction parameter chosen for optimization. The study reported was aimed at optimizing catalyst concentration, methanol : oil ratio, reaction temperature and reaction time for the production of fuel grade esters. Optimal conditions have been summarily reported in Table 8.

3.4.1. Impact of reaction temperature

As seen in Fig. 6a, the reaction temperature affects the reaction rate as well as the yield of product. Under a range of 50 °C–70 °C at 3 distinct levels, 60 °C is seen to be the optimal temperature for the reaction to proceed at the highest rate. This is due to the methanol being used as the reactant. Since methanol has a boiling point of 64.7 °C, the reflux of methanol beyond 60 °C is not sufficient enough to maintain the molar ratio of oil to methanol. However, as seen from Table 8, this parameter has a contribution factor of 33.06 %, therefore, even at the lowest level of optimization, the reaction temperature plays a pivotal role in product formation. It can also be seen from Fig. 7a–c that the interactive effect

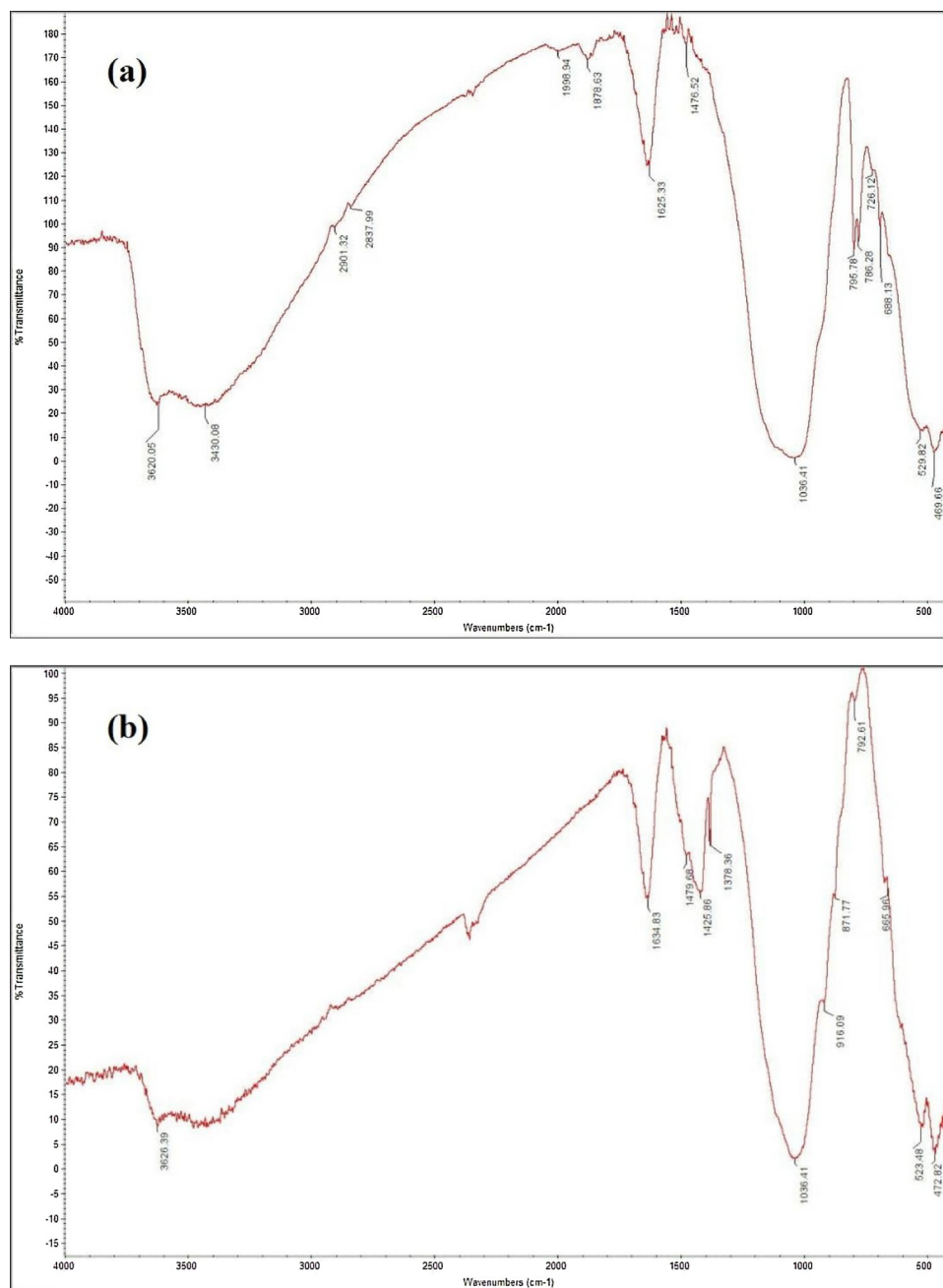


Fig. 4. FT-IR spectra of (a) catalyst support (b) synthesized Fe/A catalyst.

of temperature with other factors on the biodiesel yield is also significant. Reports from Karmakar *et al.* [12] and Dhawane *et al.* [7,8,10] were observed to be similar.

3.4.2. Impact of reaction time

For proper conversion of oil into its esters, sufficient time should be provided for the reactants to undergo sufficient molecular interactions. Therefore, reaction time was also considered for optimization in the reported work. The reaction time was optimized at 3 levels between 1 h–2 h. As seen in Fig. 6b, a reaction time of 1.5 h is optimal, with higher reaction durations resulting in backward reaction and loss of product. With a SS value of 242.75 and highest contribution factor of 45.96 %, the reaction duration is seen to be the most influential parameter in the biodiesel production process. It can also be seen from Fig. 7a, d and e that the interactive impacts of reaction duration with other parameters on the biodiesel yield is significant. The importance of

reaction time is also seen in reported works by Dhawane *et al.* [7,8,10] and Karmakar *et al.* [12].

3.4.3. Impact of catalyst concentration

For conversions that do not involve the use of superheated and supercritical reactants, the reaction must always be facilitated by a catalyst that can enhance the reaction rate. For the present study, the developed siliceous anthill supported Fe/A catalyst prepared by doping of Fe(II) is seen to be very efficient in the conversion of the oil into esters since in the optimization, within a range of 0.7 % w/w to 1.7 % w/w set at 3 levels, 1.2 % w/w is sufficient for optimal conversion. Such high conversions of the oil at such low catalyst loads indicate a very effective doping of the functional group onto the inert support, as well as the catalytic efficiency of the doped functional group. Catalyst load also has a significant impact on the reaction, since it contributes 20.97 % of the variation in biodiesel yield. Dhawane *et al.* obtained similar

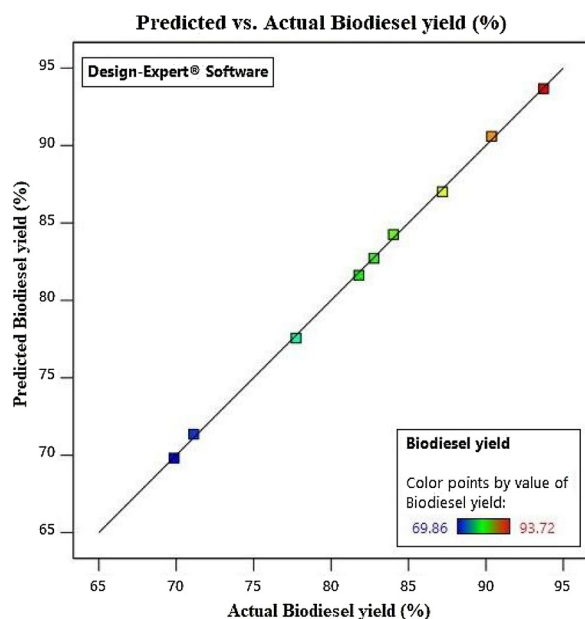


Fig. 5. Predicted vs. Actual Biodiesel yield from ANOVA study.

Table 6

ANOVA for the selected factorial model.

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	528.20	6	88.03	1388.29	0.0007	significant
A-Temperature	174.60	2	87.30	1376.75	0.0007	
B-Time	242.75	2	121.37	1914.06	0.0005	
C-Catalyst	110.85	2	55.42	874.05	0.0011	
Residual	0.1268	2	0.0634			
Cor Total	528.32	8				

Table 7

Fit and model comparison statistics for the model.

Std. Dev.	0.2518	R ²	0.9998	PRESS	2.57
Mean	82.10	Adjusted R ²	0.9990	-2 Log Likelihood	-12.82
C.V. %	0.3067	Predicted R ²	0.9951	BIC	2.56
		Adeq Precision	107.4385	AICc	113.18

Table 8

Parametric contribution factor (%) and optimum values.

Parameter	Contribution Factor (%)	Optimum value
Reaction temperature (°C)	33.06	60
Reaction time (h)	45.96	1.5
Catalyst load (% w/w)	20.97	1.2
Methanol:oil molar ratio	Insignificant (< 0.1)	6:1

results on Fe doped inert carbonaceous catalyst prepared from waste flamboyant pods for the conversion of rubber seed oil [7] as well as KOH doped waste flamboyant pods for the conversion of rubber seed oil into biodiesel [9,10]. From Fig. 7b, d and f it can be seen that the interactive effect of catalyst concentration with other reaction parameters on the biodiesel yield is also very noticeable.

3.4.4. Impact of methanol: oil molar ratio

For proper conversion of the feedstock used as reactant into its esters, the alcohol to oil ratio must be maintained at an optimal level, with higher and lower values mostly seen to have detrimental impacts on the yield. For the present study, the methanol to oil ratio was chosen

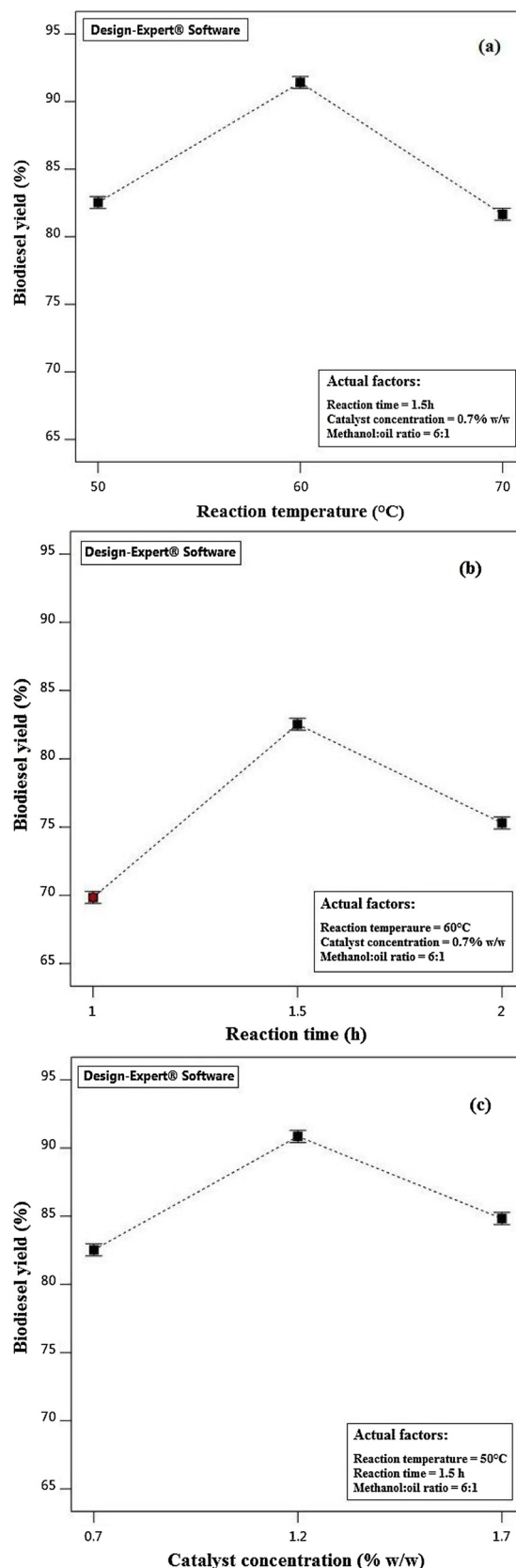


Fig. 6. Impact of individual parameters on biodiesel yield (a) Reaction temperature (b) Reaction time (c) Catalyst concentration.

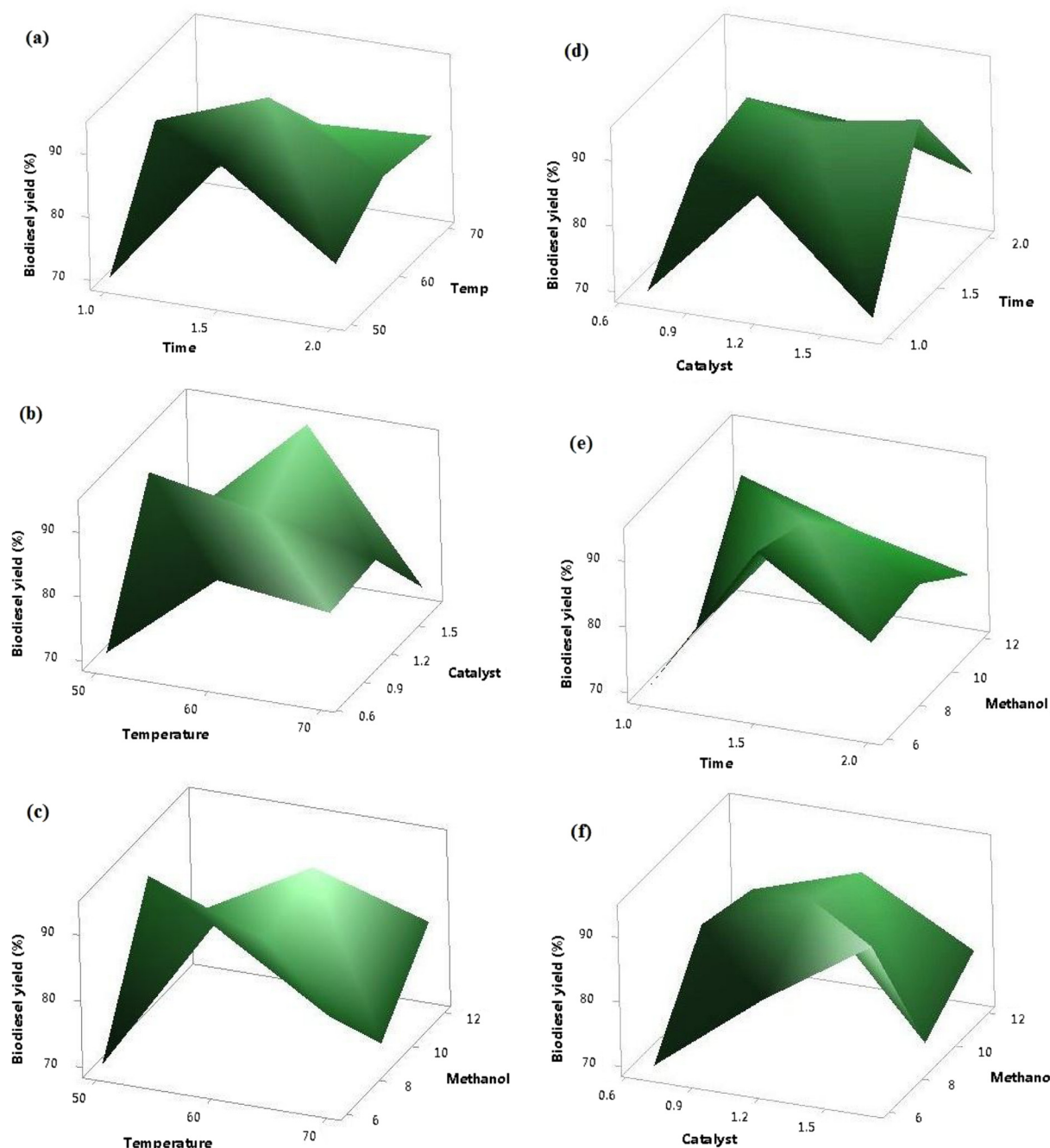


Fig. 7. 3D surface plots depicting combined effects of process parameters on biodiesel yield: (a) Temperature and time (b) Temperature and catalyst concentration (c) Temperature and methanol:oil ratio (d) Time and catalyst concentration (e) time and methanol:oil ratio (f) Catalyst concentration and methanol:oil ratio.

at 3 levels within a range of 6:1 to 12:1. It was seen that the lowest value, i.e. 6:1 is sufficient for the reaction to proceed at the maximum pace. This is due to the fact that stoichiometrically, a 3:1 molar ratio is required to be maintained during the entire course of the reaction, hence 6:1 is sufficient; on the other hand, higher alcohol amounts lead to dilution of the reaction system to the point that the reactant molecules and catalyst do not get interact enough for the reaction to process at a maximum pace. Thus, in this study, the variation of methanol concentration is not seen to have any significant impact on variation of biodiesel yield. From Fig. 7c, e and f it is clear that the interactive effect of methanol:oil ratio with other reaction parameters on the biodiesel yield is significant. Interestingly, many such observations have been made by other researchers, with Dhawane *et al.* [7] making a very similar observation about the dilution effect that higher methanol ratios

have on the reaction.

3.5. Characterization of biodiesel

The fuel produced under optimal conditions is subjected to physico-chemical characterization through various standardized ASTM test procedures. The product was tested for properties such as cetane number, fire point, viscosity, specific gravity, acid value, calorific value, aniline point, FFA content and flash point following ASTM standardized test procedures. Table 9 summarizes the various properties tested and their corresponding values obtained for the fuel produced. Low FFA content results in higher oxidative stability and longer shelf life, while low acid value corresponds to low corrosiveness of the fuel, resulting in no damage to the engine. High flash and fire point

Table 9
Properties of biodiesel produced from RWO.

Properties	ASTM Limit	Produced Biodiesel
Acid value (mg KOH/g)	~0.8	0.56
FFA (%)	~0.5	0.28
Flash point (°C)	> 93	130
Fire point (°C)	–	138
Aniline point	> 45	47
Cetane number	> 47	49
Diesel Index	–	54.2
Calorific value (MJ/kg)	35	37.9
Viscosity (mm ² /s) at 40 °C	5–6	2.94
Specific gravity at 30 °C	0.875–0.900	0.857
API gravity	–	33.61

Table 10
Ester composition of the produced biodiesel from RWO.

Retention time (min)	Component
3.300	Butyric acid methyl ester
3.750	Caproic acid methyl ester
3.882	Caprylic acid methyl ester
4.728	Capric acid methyl ester
5.405	Tridecanoic acid methyl ester
8.036	Pentadecanoic acid methyl ester
8.692	cis-10-Pentadecenoic acid methyl ester
8.818	Palmitoleic acid methyl ester
10.673	cis-10-Heptadecenoic acid methyl ester
11.695	Oleic acid methyl ester
12.038	Linoleic acid methyl ester
12.650	cis-8,11,14-Eicosatrienoic acid methyl ester
16.396	cis-5,8,11,14,17-Eicosapentaenoic acid methyl ester
23.558	cis-4,7,10,13,16,19-Deocosahexaenoic acid methyl ester

mean that the fuel has high thermal stability, proving to be safe for transportation. Aniline point is low, which indicates that the paraffin content of the fuel is high enough for clean burning. The fuel is also seen to be high in energy content as from high calorific value. Cetane number and diesel index are high, proving that the fuel is of good quality and combustion will be clean. A low viscosity of the fuel means good fuel flow, resulting in easy atomization of the fuel upon spray. Table 10 provides a comprehensive look at the various methyl esters that are obtained in the biodiesel produced through GC analysis which can be also seen in Fig. 8. It is clear that the values are well in

accordance with the set standards, hence the process shows prospect for production on a commercial level when scaled up accordingly.

4. Process kinetics

The heterogeneous catalyzed conversion process is able to convert both FFAs as well as glycerides to methyl esters with the progression of time. Therefore, for understanding the kinetics of the process, it is imperative to have a reference value that can be tallied against time. It was observed that as the reaction progresses, FFA concentration drops. It is well known that esterification and transesterification processes are reversible in nature, and therefore the methanol must be provided in an excess amount to shift the reaction equilibrium toward product formation. Since the amount of methanol thus remains constant, therefore the conversion is expected to be dependent only on the FFA concentration at any time [23].

The reaction rate (r) is the drop in the amount of FFA concentration, $d(C_{FFA0} - C_{FFAt})$ with change in time (dt). Since the FFA concentration decreases with time, the coefficient is negative as shown in Eq. 7:

$$r = - \frac{d(C_{FFA0} - C_{FFAt})}{dt} = (C_{FFA0} - C_{FFAt}) k(T) \quad (7)$$

k is the rate constant, dependent on temperature (T). From this, the Arrhenius equation can be written as in Eq. (8):

$$k(T) = Ae^{\frac{-E_A}{RT}} \quad (8)$$

Here, E_A is activation energy, A is the frequency factor while R is the gas constant. The derivative of C_{FFA} with respect to time t can be converted to logarithmic form by integration. Therefore, integrating Eq. 7 gives Eq. 9 which can be written as:

$$\ln(C_{FFA0} - C_{FFAt}) = kt \quad (9)$$

The slope of the plot of $\ln(C_{FFA(0)} - C_{FFA(t)})$ vs t is k . Eq. 8 can also be integrated to obtain Eq. 10, where the plot of $\ln k$ vs. $1/T$ gives $\ln A$ as the intercept and $-E_A/R$ as the slope. Knowing the value of R , the activation energy can thus be calculated, as can be the frequency factor A from antilog of the intercept.

$$\ln k = \ln A + \frac{-E_A}{RT} \quad (10)$$

The kinetics studies conducted at temperatures between 50–60 °C showed that within the optimal time, the conversion of FFAs progresses

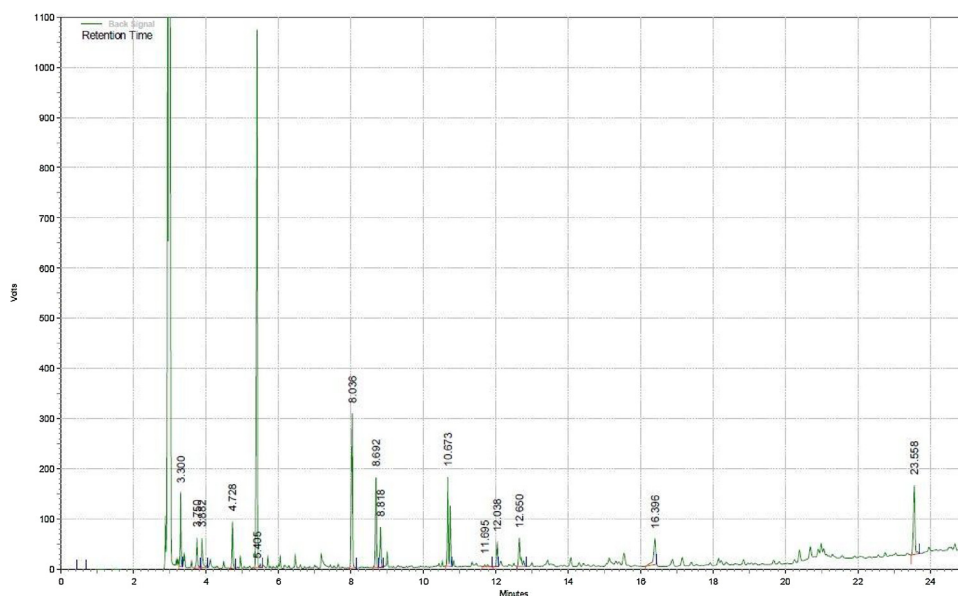


Fig. 8. GC chromatogram depicting ester composition of biodiesel from RWO.

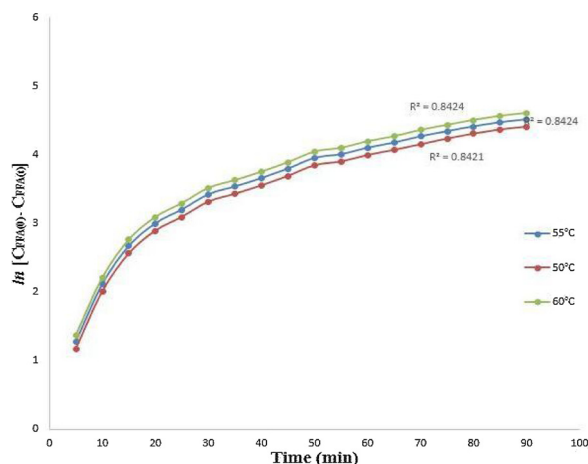


Fig. 9. Plot of $\ln C_{FFA(t)}$ versus time to determine rate constant k .

almost linearly with the logarithmic plot of FFA conversion vs time adhering to pseudo-first order kinetics, as reasoned before. This is also seen from Fig. 9, while the data for important kinetic parameters have been depicted in Table 11. It is seen that the reaction rate increases with rise in temperature, since the increased temperature results in a facilitated interaction between reactants. The R^2 values of the plots are high enough, confirming that the k values obtained adhere to Arrhenius' law. It is also seen from the plot of $-\ln k$ versus $1/T$ (multiplied by 100) in Fig. 10 and Table 12 that the energy of activation (E_A) is low enough (being only 2.219 kJ/mol) with a very high rate of molecular collision (frequency factor A) of 134.41 min^{-1} .

5. Catalyst reusability

The developed catalyst needs to be reusable in order for the process to be cost efficient since the catalyst support needs to be able to retain the functional groups even after the reaction and washing for subsequent uses. The reusability of the catalyst was tested by varying concentration of the catalyst while all other parameters were retained at their optimal levels. At each concentration, the fresh catalyst was tested for biodiesel yield, after which the catalyst was separated by filtration and washed with acetone to remove residual oil and impurities, followed by drying. The dry catalyst was then reused for production up to 7 times. After completion of the reaction, the oil and impurities that adhere to the catalyst block the active catalytic sites which can lead to inefficient conversion, therefore cleaning removes this possibility, however, during the cleaning process, the catalyst is susceptible to marginal inactivation due to functional group leaching. It was seen that the drop in biodiesel production varied anywhere between 6–8 % after the 7th reuse. The drop can be attested to the breaking of bonds between the inert support that compromises the structural integrity of the support as well as desorption of the functional groups from the matrix that is primarily responsible for the drop in catalytic activity. The leaching or desorption is caused by both mechanical forces caused by mixing provided to enhance reaction as well as the use of various reagents during washing of the catalyst. Table 11 comprehensively summarizes the various biodiesel yields that are obtained due to changing catalyst concentrations and reuse of the catalyst

Table 11
Kinetics study results for biodiesel production.

Temperature (°C)	Reaction rate constant (k) min^{-1}	R^2	Kinetic parameters	Values
50	0.0623	0.8421	Activation energy E_A (kJ/mol)	2.219
55	0.0656	0.8424	Frequency Factor A (min^{-1})	134.41
60	0.0682	0.8424		

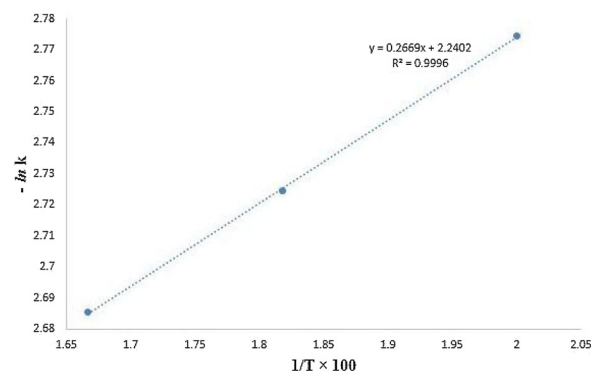


Fig. 10. Plot of $-\ln k$ versus $1/T$ ($\times 100$).

Table 12
Reusability of Fe(II) doped catalyst.

Catalyst	Level 1 (0.7 % w/w)	Level 2 (1.2 % w/w)	Level 3 (1.7 % w/w)
Fresh	95.32	99.73	96.91
1 st reuse	94.83	99.27	95.29
2 nd reuse	93.72	98.95	94.71
3 rd reuse	92.55	98.51	93.68
4 th reuse	91.99	96.72	93.26
5 th reuse	91.41	95.66	92.06
6 th reuse	90.41	93.01	91.65
7 th reuse	89.14	92.54	90.85

up to 7 times, after which the biodiesel yield drop can be considered significant enough for repeating the doping process on the activated inert support with fresh FeSO_4 . Tests to investigate the structural integrity of the catalyst support as evident from the catalytic activity of the recharged catalyst in terms of biodiesel production was also conducted, with results showing that the structural integrity of the activated inert support is not compromised and therefore it can be surmised that the prepared support can be used repeatedly, proving to be very cost-efficient.

6. Conclusions

For the present study, 2 types of waste material were chosen: the feedstock was restaurant waste oil which is easily obtainable from local restaurants and eateries, and the catalyst precursor chosen was anthill, harvested from Oro, Nigeria which was carbonized and steam activated to prepare inert support. The support was then doped with Fe(II) using FeSO_4 and the Fe/A obtained was used as a catalyst in the synthesis of biodiesel from the RWO. L9 Taguchi OA was chosen for optimization of the following process parameters: catalyst concentration, methanol : oil ratio, reaction temperature and reaction time. The optimization revealed that reaction duration had the highest impact on the biodiesel production, while methanol:oil ratio has an insignificant impact on variation of biodiesel yield. Fuel characterization shows that the product is comparable to commercially available biodiesel and is in accordance with the ASTM standards set for biodiesel, with high thermal stability, low acid value and residual FFA, high cetane number and diesel index as well as low kinematic viscosity. Also, GC analysis of the sample shows that the biodiesel produced is abundant in a variety of

methyl esters. Kinetic studies of the conversion against residual FFA showed that the conversion process adheres to pseudo first order kinetics with high reaction rate and frequency factor, while the activation is low enough for an economic process. Reusability studies of the developed Fe/A catalyst showed that the doping of Fe(II) is quite stable, and the adsorbent is able to retain the doped Fe(II) after repeated cycles of production and washing, with very low loss in catalytic activity. Thus the production process has potential for commercialization if scaled up accordingly, provided cost estimates are favorable.

CRedit authorship contribution statement

Babatunde E. Olubunmi: Conceptualization, Methodology, Investigation. **Bisheswar Karmakar:** Software, Writing - original draft. **Olutoye M. Aderemi:** Formal analysis, Data curation. **Akpan Uduak G.:** Investigation, Data curation. **Manase Auta:** Validation, Resources. **Gopinath Halder:** Supervision, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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