International Journal of Engineering &Technology, 13 (2) (2024) 388-397

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Effects of process parameters variations and optimization of biodiesel production from waste cooking soya oil

Ugwu Hyginus Ubabuike [1] *, Ezere Yagazie Prosper [1], Igri O. Uket [1], Okon Jimmy Omini [2], Jacob Ukeme [3], Luke Uduak [3]

[1] *Department of Mechanical Engineering, Michael Okpara University of Agriculture, Umudike, Abia State, Nigeria*
[2] *Department of Mechanical Engineering, Faculty of Engineering, Cross River University, Cross River State, Nigeria*
[3] *Department of Mechanical Engineering, Faculty of Engineering, Akwa Ibom State University, Akwa Ibom State, Nigeria*
**Corresponding author E-mail: uket.igri@yahoo.com*

Abstract

Waste cooking soya oil (WCSO) in this study was transesterified with methanol in the presence of sodium hydroxide (NaOH) as catalyst. The effects of the process parameters (catalyst concentration, reaction time, reaction temperature, methanol/sample ratio and agitation speed) were studied individually and in matrix form to establish synergistic interactions. Process optimal conditions that gave the maximum bio-diesel yield of 94.70 % were: catalyst concentration (1 %), reaction time (60 minutes), reaction temperature (70 oC), methanol/sample ratio (6:1), and agitation speed (300 rpm), while those that caused the lowest yield of 66.20% were catalyst concentration of 0.25 % at reaction time of 30 minutes, under the reaction temperature of 50 oC with methanol to sample ratio of 2:1, and agitation speed of 150 rpm. The phys-iochemical properties of the yield investigated revealed that the developed biodiesel properties conformed within the American Society for Testing and Materials (ASTM) and European (EN) standard recommendations. From the analysis, Cetane index of 74.12, kinematic vis-cosity of 4.43 mm2/s, density of 876.6 kg/m3, flash point of 142 oC, fire point of 150 oC, cloud point of 8.5 oC and moistuure content of 0.04 % were obtained for the biodiesel. Overall, the findings demonstrated that the technique employed if harnessed and com-mercialized, is a safe clean energy technology which utilizes waste materials that would have been harmful to the environment for the enhancement of hu-man and environmental wellbeing.

Keywords: *Process Parameters; Optimization; Biodiesel Production; Waste Cooking Soya Oil; Transesterification; Safe Clean Energy Technology.*

1. Introduction

Environmental pollution and diminishing supply of fossil fuels according to [1] are the key factors leading to the search for alternative source of energy. This is because pollutants from fossil fuels are generated from non-renewable sources which are highly associated with climate change, global warming and wide spread of diseases through water and air contaminations. The effect of environmental pollution from fossil fuels action as the authors stated, was observed in Rivers State, Nigeria due to the industrial activities carried out by oil related companies such as gas flaring, crude oil exploration. Furthermore, environmental pollution from fossil fuels reduced drastically to about 9.6 % in 2021 during the COVID 19 pandemic, as observed globally. Because the transportation sector was not 100 % functional during the period, and the industries shut down, these resulted to a decline in the production of fossil fuel products and usage [2]. Today, based on this source, the world and the species living in it are considered endangered species because of fossil fuels activities carried out on a daily basis, which have raised concerns from researchers, world leaders, climate change enthusiast and common wealth organizations, etc. This has led to the search for an alternative fuel that can substitute fossil fuels, become environmental friendly, less expensive, and economical to the species living in the world [1]. Amongst other renewable products, biodiesel gotten from plants and agricultural wastes are also considered as substitutes to replace fossil fuels [2], [16]. Biodiesel as a fatty acid methyl ester (FAME) is a biomass derived renewable fuel which serves as an alternate to diesel fuel [3]. Derived from animal fats, and vegetable oils from non-edible seeds, because of its high viscosity and low volatility, biodiesels do not deplete the world food bank [2]. There are however, a lot of processes involved in biodiesel production but transesterification is seen as the most common process where fat or oil reacts with an alcohol to form esters or glycerol [4].

2. Materials and methods

2.1. Sample collection and preparation

Five (5) litres of pure soya oil were purchased with 5 kg of yam tubers procured from the local retailers at Aba main market, Abia State, Nigeria. The yam was washed, peeled and sliced. Each slice had a thickness of 20 mm (2 cm). The pure soya oil was poured into a 10 litres steel pot and heated using a gas cooker. The yam slices were divided into five parts, each having a weight of 1 kg. Each portion (1 kg) was fried for thirty minutes. After frying, the oil was allowed to cool, passed through 500 µm (0.5 mm) sieve to remove yam residues (impurities) and stored in transparent plastic containers. The oil was characterized and used for biodiesel production.

2.2. Soya oil characterization

The used fried soya oil was characterized to determine its density, refractive index, moisture content, saponification value, viscosity, acid value, peroxide value and iodine values as follows:

i) Density and Specific Gravity (SG) or Relative Density

The density and the specific gravity, otherwise, relative density of the bio-oil was determined using the method described in [5]. From the sample weight obtained, the density was determined by taking the ratio of the weight of the oil to the known volume (50ml) according to Eq. 1:

$$\text{Density}, \rho = \frac{\text{Sample weight}, W_S}{\text{Sample volume}, V_S} = \frac{(W_{Sgb} + W_S) - W_{Sgb}}{V_S} \quad (1)$$

Also, the specific gravity was determined using Eq. 2.

$$\text{Specific gravity}, S_g = \frac{\text{Weight of sample (50ml)}, W_S}{\text{Weight of water (50ml)}, W_W} = \frac{C - A}{B - A} \quad (2)$$

Where: Wsgb= weight of SG bottle, Ws = sample weight or weight of sample, Vs = sample volume, A = weight of empty SG bottle, B = weight of SG bottle + water, C = weight of SG bottle + sample, B - A = weight of water (Ww) and C - A = weight of sample (Ws) respectively.

ii) Refractive Index

Refractive index was determined using a digital tabletop refractometer (H196800) manufactured by Hanna Instruments, Romania adopting the AOAC (2000) method described in [5].

iii) Moisture content

Moisture content of the sample was determined by dry oven method described in [3]. Five (5) g synthesized sample (a) was weighed into an already weighed Petri dish (b). The sample in the Petri dish was transferred into the oven and left for an hour at 105 ^{o}C and thereafter allowed to cool in desiccators. The second weight of the sample was taken after oven heating (c), and the percentage moisture calculated using Eq. 3.

$$\%\text{moisture} = \frac{(a+b)-c}{a} \times 100\% \quad (3)$$

iv) Saponification value

Saponification value (SV) was determined according to the method of [6] reported in [5]. This is the milligram of KOH required to neutralize the fatty acids resulting from the complete hydrolysis of 1g of the sample. Half (0.5) gram of the sample was weighed (ws) into a conical flask and 50 ml of 0.5N ethanolic KOH added to the sample. The mixture was refluxed to saponify the sample. The unreacted KOH was titrated back with 0.5N hydrochloric acid (HCl) using three drops of phenolphthalein as indicator. The saponification value of the sample thus was calculated as:

$$\text{Saponification value}, SV = \frac{T_V \times N_{HCl} \times 56.1}{W_S} \quad (4)$$

where: N_{HCl}= normality of HCl acid = 0.5N; 56.1 g/mol = molecular weight (molar mass) of KOH (MwKOH) and titre value,T_V = titre value of the sample, V_1- titre value of the blank, V_2.

v) Viscosity

The U-tube viscometer manufactured by Poulten Selfe and Lee Ltd (PSL ASTM- IP 350) was used to determine the kinematic viscosity. Micro pipette was used to introduce the sample into the viscometer. Sample flow time was determined in seconds at 40 ^{o}C.

Hence:

$$\text{Kinematic vicosity}, \nu = \frac{\text{Dynamic vicosity}, \mu}{\text{Density}, \rho} \text{ cSt or mm}^2\text{S}^{-1} \quad (5)$$

$$\text{Where; dynamic viscosity is given as:} \mu = \frac{\text{measured viscosity value of sample from viscometer reading (Pa.S)}}{10^{-3}} \text{ (cP)} \quad (6)$$

vi) Acid value or free fatty acid value

The acid value, also known as the free fatty acid (FFA) value of the samples was performed according to the method of [7]. Half (0.5) g of the sample was weighed into a conical flask, and 20 ml of ethanol and three drops of phenolphthalein indicator thereafter introduced. The solution was titrated with 0.5N KOH with constant agitation until a faint, pink end point appeared and persisted for thirty seconds. The volume of the titrant at end point was recorded. From the readings obtained, the acid value was evaluated using the Eq. 7.

$$\text{Acid value}, AV = \frac{T_V \times N_{KOH} \times 5.61}{W_S} \text{ (mgKOH/g)} \quad (7)$$

Where: N_{KOH}= normality of KOH = 0.5N and 5.61 = M_{WKOH} divided by 10

vii) Peroxide Value

Peroxide value (PV) was determined according to the method of [6] reported in [7], where 0.5 g of the sample weighed into a conical flask with 25 ml glacial acetic acid and chloroform mixed together was added in the ratio of 2:1. Afterwards, 1ml of 10% potassium iodide (KI) was added and shaken vigorously, covered and kept in the dark for one minute, and 35 ml of starch indicator thereafter added. The whole solution was titrated with 0.02N sodium thiosulphate solution as solutions turns from pale black to white. Titration was also made for blank. PV thus was calculated by Eq. 8.

$$\text{Peroxide value, PV} = \frac{(100)\times(V_1-V_2)\times(N)}{W_S} \quad (8)$$

Where: 100 = milliequivalent conversion factor, N = normality of titrant = 0.02N of sodium thiosulphate ($Na_2S_20_3$)

viii) Iodine Value

Iodine value (IV) was determined according to the method of [6] reported in [7]. Half (0.5) g of the sample was weighed and 15ml of chloroform added to the weighed sample. Thereafter, 25 ml of Wiji's solution was added and mixed vigorously. It was covered tightly and placed in the dark for 30 minutes. Afterwards, 20 ml of 10% KI and 150 ml of distilled water were added. The solution was observed as it turned red, and 5 ml of 5% starch solution indicator added to the solution and further observed as the solution turned blue-black. The solution afterwards was titrated with 0.1N Na2S2O3 solution until the black precipitates appeared colourless. Titration was also made for blank, and the iodine value then calculated using Eq. 9.

$$\text{Iodine value, IV} = \frac{(12.69)\times(V_2-V_1)\times(N)}{W_S} \quad (9)$$

Where: 12.69 = molecular weight of iodine and N = normality of titrant = 0.1N of ($Na_2S_20_3$) solution

ix) Ester Percentage

The percentage of the ester formed was calculated using the Eq. 10 according to [8]

$$\text{Ester percent, IV} = \frac{100\times(IS-IA)}{IS} \quad (10)$$

Where: IS represents index of saponification, and IA is the index of FFA

2.3. Biodiesel production

2.3.1. Transesterification

The transesterification reactions were carried out in a 250 ml, three neck, glass spherical reactor, provided with a thermometer, sampling outlet, and condensation system. The heating system was an electromagnetic hot plate which heated the reactor and rotated the metal knob in the reactor through an electromagnetic field. The reactor was preheated to 75 ^oC to eliminate moisture and then 50 ml of the used soya vegetable oil added for each of the experiment. When the reactor reached the temperature established for the reaction, the methanol and the catalyst were added in the amount required for the experiment. The stirring system afterwards was switched on at the desired speed, taking this moment as time zero of the reaction. Each mixture was vigorously stirred and refluxed for the required reaction time. After methanolysis reaction had finished, the transesterification product was allowed to stand for twelve hours in a separating funnel (Fig. 1) for glycerol separation. The crude glycerol thus was removed through the funnel tap leaving the methyl ester (biodiesel) behind.

2.3.2. Biodiesel production by wet production method

One mil (1m) of sulphuric acid was prepared and added drop-wise to the biodiesel in a separating funnel. Hot distilled water was added as well, and shaken vigorously. The mixture afterwards was allowed to settle and separate (water and water soluble impurities at the lower end and biodiesel layer at the top) into 2 phases and separated using the funnel tap. The washed water lower layer was decanted into a beaker and removed, while the upper washed biodiesel layer was further washed to ensure complete separation. The biodiesel produced was characterized to ascertain its cloud and pour points, flash and fire points, anisidine point, fuel gravity, Cetane index or cetane number respectively.

2.5. Effects of process parameters on the produced biodiesel yield

These process parameters were studied to determine their respective effects on the biodiesel yield produced.

2.5.1. Effect of catalyst concentration

The effect of catalyst concentration was studied by applying NaOH as catalyst at varied concentrations ranges of 0.25 to 1.5 % (0.25, 0.50, 0.75, 1.00, 1.25 and 1.50).

2.5.2. Effect of time

The effect of time on the yield of methyl ester (biodiesel) was studied applying different time intervals, ranging from 15 to 90 minutes (15, 30, 45, 60, 75, and 90).

2.5.3. Effect of temperature

The temperature effect was ascertained by production at varied temperatures (30, 40, 50, 60, 70, 80 ^oC).

2.5.4. Effect of methanol/sample molar ratio

The methanol/sample ratio was varied at 2:1, 4:1, 6:1, 8:1, and 12:1.

2.5.5. Effect of agitation speed

The rotation (stirling or agitation) speed for the test was varied from 150 to 350 rpm (150, 200, 250, 300 and 350 rpm) respectively.

3. Results and discussion

3.1. Characterization of the waste soya oil

The characterization of some essential physicochemical aspects of the waste soya oil before application to biodiesel production was helpful to evaluate the quality of the raw material, as regards deterioration. The results in Table 1 obtained from the characterization helped in determining the best handling method relating to biodiesel production process to generate greater yield

Table 1: Characterization Test Results of Waste Soya Oil for Biodiesel Production

Acid value (mgKOH/kg)	Saponification (mgKOH/kg)	Peroxide value (PV) (meq/kg)	Iodine value (IV) (mg/100g)	Refractive index @29ºC	Moisture (%)	Density (g/ml)	Viscosity @ 40ºC (mm^2s^{-1})
0.22	193.71	1.56	48.33	1.4622	0.07	0.921	63.163

The peroxides in oils help in assessing the degradation level, which can occur mainly due to exposure to high temperatures. The iodometric titration method used for peroxide index (IP) determination supported the assertion by [8] which suggested that the method was fast, inexpensive and reasonably precise when PVs are higher than 1 meqO2kg^{-1}. The oxidation level of refined soya bean oil as they stated was considered low when the IP is between 1.0 and 5.0 meqO2kg^{-1} of oil; moderate when IP is between

5.0 and 10.0 meqO2kg^{-1}of oil, and high if the IP is greater than 10 meqO2kg^{-1} of oil. Considering the above criteria, the 1.56 meqO2kg^{-1} PV for the experimental sample obtained was considered low, suggesting very good stable oil against deterioration or congealing when kept or stored for a longer period.

Free fatty acid (FFA) and PVs are qualitative properties and reflect the amount of FFAs present in the samples. FFAs have different origins, such as high temperatures, when residual frying oil is used, or oxidation that can occur in the presence of peroxides or light [9]. The initial FFA of the waste soya oil was at 4.07 mgKOH/kg, and the sample after being neutralized came down to 0.22 mgKOH/kg. FFA values greater than 3.5 mgKOH/kg impair the transesterification reactions when base catalysts are used, causing the formation of saponified product [8]. Saponification according to them, leads to the formation of salts of fatty acids, and can be used for a quick assessment of the potential formation of esters whose percentage was determined using the Eq.

10. Consequently, the ester percentage of the oil was calculated as 99.89%. The ester percentage (99.89%) obtained based on [8] minimum recommended value of 96.5% at that level, was considered highly sufficient as an excellent yield for biodiesel production

3.2. Characterization of the biodiesel produced from waste soya oil

Optimal conditions obtained during the study of the effects of the process parameters were applied to produce an enhanced product (biodiesel). The characterization test results as obtained are presented in Table 2.

Table 2: Physicochemical Properties of the Synthesized Biodiesel

Properties	ASTM D6751 range	EN 14214 range	Synthesized biodiesel
Kinematic viscosity at 40ºC (mm^2/s)	1.9-6.0	3.50-5.00	4.43
Density (kg/m^3)	860-894	860-900	876.6
Flash point (ºC)	>120	>120	142.00
Fire point (ºC)	-	-	150.00
Moisture content (%)	<0.05	<0.05	0.04
Acid value (mgKOH/g)	< or = 0.5	<0.5	0.13
Cloud point (ºC)	-	-	8.50
Pour point (ºC)	-	-	3.00
Anisidine point (ºC)	-	-	22.00
API gravity	-	-	33.69
Cetane index	-	-	74.12
Iodine number (gI2/100g)	<120	<120	28.85
Calorific value (J/g)	-	-	41286
Methyl ester content (%)	>96.5	>96.5	97.84
Monoglyceride (% mass)	-	<0.8	0.52
Diglyceride (% mass)	-	<0.2	0.14
Triglyceride (% mass)	-	<0.2	0.09
Glycerol (% mass)	0.02	0.02	0.01

Kinematic viscosity of the produced biodiesel from the result was 4,43 mm^{2}s^{-1} which was thin the recommended standard ranges prescribed by ASTM D6751 and EN 14214. This also conformed within the standard recommendation limit of 6.0mm^{2}s^{-1} for biofuel viscosity advocated in [8].

The flash point as a very significant property in engine performance represents the temperature at which the fuel becomes a potentially flammable mixture when exposed to a spark or flame [8]. Both the ASTM and EN guidelines stipulated that biodiesel must have a value >120 °C for this property. Consequently, the synthesized optimal biodiesel value of 142 ºC obtained fitted into this description.

Water content is another important factor in quality control of the biodiesel as its presence can promote not only microbial growth, but leads to the corrosion of tanks, participates in emulsion formation and stimulates mainly the hydrolysis of esters [8]. For these reasons, the minimum limit of moisture or water content established by both the ASTM and EN recommended standards at 0.05 % validated the 0.04 % result obtained in this study.

The iodine (I2) number based on the ASTM D6751 and EN 14214 recommendations should ideally stay below 120 g of I2 to 100 g of sample (<120 g I2/100 g) as under this value, fuels are less susceptible to oxidation and polymerization processes, thus allowing storage with fewer issues in terms of conservation [9]. This suggests that the 28.85gI2/100g value obtained for the synthesized biodiesel presents the fuel as a good candidate. Also, the density of the optimal biodiesel yield of 876.6 kg/m^3 was below the density of the starting feed stock (921 kg/m^3) but however, was within the recommended ASTM D6751 and EN 14214 ranges. Fuel densities beyond the recommended ranges will cause depositions on the combustion engine.

Methyl ester conversion was at 97.84%. This fits within the acceptable minimum value of >96.5 % prescribed by both the ASTM and the EN standards. This is an indication of high conversion efficiency. Monoglyceride, diglyceride and triglyceride are components of vegetable oil. They were well converted (0.52, 0.14 and 0.09%) to methyl ester in the final product (biodiesel) within the acceptable EN 14214 ranges (<0.8, <0.2 and <0.2%) respectively. As noted, higher content of glycerides in the ester, especially triglycerides, may cause formation of deposits at both the injection nozzles and the valves [10]. In general, the product conversions evidently from the study were satisfactory.

3.3. Effects of process parameters on the biodiesel yield

3.3.1. Effect of catalyst concentration on biodiesel yield

Catalyst concentration is a major factor that directly affects the yield of biodiesel during the transesterification reaction. It was hence essential to obtain the optimal catalyst concentration for the process. Fig. 2 presents the trend of biodiesel yield at varied catalyst concentrations, while other parameters were kept constant.

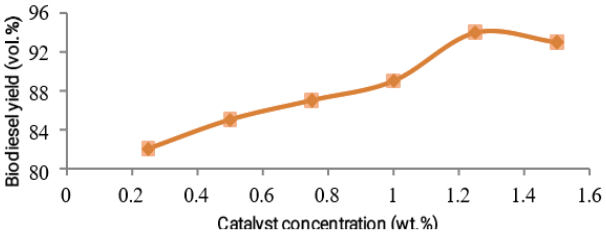


Fig. 1: Biodiesel Yield Against Catalyst Concentration for Biodiesel Produced Using Waste Soya Oil.

Biodiesel yield from the figure was directly proportional to catalyst concentration up till the 1.25% weight of the sample with a maximum yield of 94%. As catalyst concentration increased beyond 1.25 to 1.50 %, the biodiesel yield decreased to 93% volume. This is as a result of the difficulty in triglyceride conversion to biodiesel higher concentration, resulting in the production of lesser biodiesel.

3.3.2. Effect of reaction time on biodiesel yield

Time is one of the major factors that considerably affect the conversion of triglycerides to methyl esters. In the study, reaction time was varied at six points, ranging from 15 to 90 minutes. The variation of the biodiesel yield with the reaction time is presented in Fig.2.

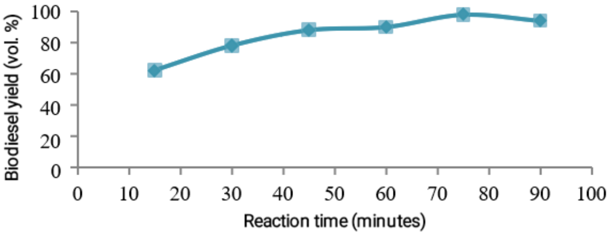


Fig. 2: Biodiesel Yield Against Reaction Time for Biodiesel Produced Using Waste Soya Oil.

Biodiesel yield increased progressively from 15 minutes (62 %) to the maximum yield at 75 minutes (98 %). Increase in time permits greater contact among active sites of the reacting molecules (methanol and oil). Beyond 75 minutes, at 90 minutes, there was reduction (94 %) in the biodiesel yield. This can be attributed to the reduction of methoxy species at the active sites.

3.3.3. Effect of reaction temperature on biodiesel yield

One of the essential factors that affect the rate of transesterification reaction is the reaction temperature following its endothermic nature [11]. Increase in the reaction temperature increases the frequency of collisions among the reacting molecules which causes gain in kinetic energy, hence permitting the miscibility and mass transfer between the phases [12]. The plot of biodiesel yield as reaction temperature varies is shown in Fig. 3.

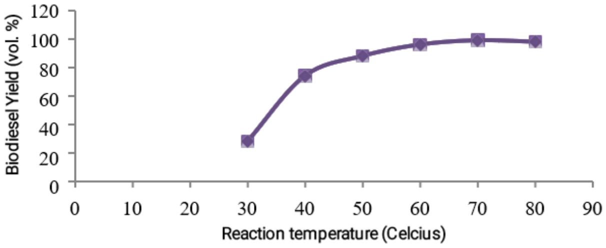


Fig. 3: Biodiesel Yield Against Reaction Temperature for Biodiesel Produced Using Waste Soya Oil.

From reaction temperature of 30 ^{o}C with biodiesel yield of 28 %, the yield increased consistently to 99 % at 70 ^{o}C. Biodiesel yield was enhanced at higher temperatures which enabled the carbonyl group of triglyceride molecules became more activated. This favoured the methanol nucleophillic attack on the triglyceride and enabled the transesterification reaction in the forward direction to produce higher biodiesel yield [13]. Also, beyond 70^{o}C (at 80 ^{o}C), biodiesel yield decreased slightly to 98 %. This reduction in yield was as a result of increased volatilization of methanol in the reaction medium, hence, reducing the amount of methanol available for reaction with the triglyceride. Moreover, as the transesterification reaction was reversible, following this effect of reduced product at higher temperature (optimum), it was evident that high temperature favoured the backward reaction between glycerol and methyl esters on the surface of the catalyst. It is therefore glaring that the optimum reaction temperature for production of biodiesel from the waste soya oil, using sodium hydroxide as catalyst was 70 °C which produced a yield of 98 %.

3.3.4. Effect of methanol/sample molar ratio on biodiesel yield

Methanol to oil molal ratio as another factor considered during biodiesel production from the waste soya oil was varied at 2:1, 4:1, 6:1, 8:1, 10:1 and 12:1. The variation is shown in Fig. 4.

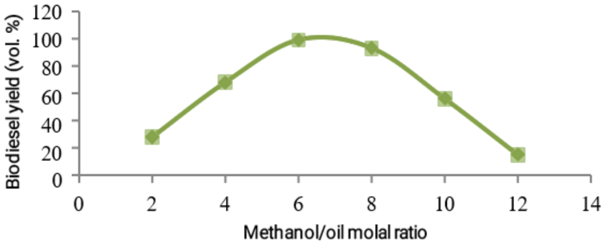


Fig. 4: Biodiesel Yield Against Methanol/Oil Molal Ratio for Biodiesel Produced Using Waste Soya Oil.

The yield of biodiesel as seen in Fig. 5, increased from the initial ratio to the highest value of 99% at molal ratio of 6:1. However, beyond the optimum molal ratio (6:1), there was noticeable decrease in the biodiesel yield of 93, 56 and 15 % for molal ratios of 8:1, 10:1 and 12:1 respectively. The maximum biodiesel yield at this optimum methanol to oil molal ratio of 6:1 was due to the formation of methoxy species on the active sites present on the surface of solid heterogeneous catalyst. This pushed the transesterification reaction in the forward direction to produce maximum biodiesel [14]. From the yield obtained, it was therefore evident that the molal ratio, 6:1 provided the most effective contact point for biodiesel production from the waste soya oil using NaOH as catalyst. When NaOH was used to catalyze biodiesel production, two distinct phases existed in the reaction mixture. These were the oil and the sodium methoxide phases. These two phases were not mixable, hence, the need to agitate or stir the mixture during the synthesis of the biodiesel.

3.3.5. Effect of agitation speed on biodiesel yield

For the agitation speed, the biodiesel production was varied at 150, 200, 250, 300 and 350 rpm respectively. This variation with the biodiesel yield is presented in Fig. 5.

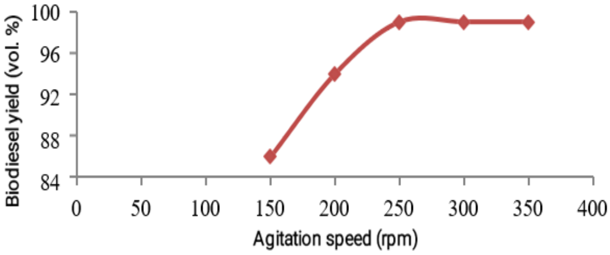


Fig. 5: Biodiesel yield against agitation speed for biodiesel produced using waste soya oil

From the figure, the biodiesel yield increased as agitation speed increased, until at the agitation speed of 250 rpm when the optimum product yield of 99% was obtained. Beyond this speed, there was no noticeable increase in the product yield, as the yield remained unchanged at 300 and 350 rpm. This was an indication that among all the agitation speed varied, 250 rpm was the most suitable speed to minimize the mass transfer limitations of the reaction.

3.4. Experimental matrix using the fractional factorial design

3.4.1. Analysis of variance (ANOVA) for quadratic model

Presented in Table 3 is the analysis of variance (ANOVA) result obtained using the quadratic model where the factors were coded. The ANOVA was applied to estimate the significance of the model at 5% significant level. A model is considered statistically significant if the p-value (significance probability value) is less than 0.05 (typically
≤0.05).

From the table, the model F-value of 2668.55 implied that the model was significant. There was only a 0.01% chance that an F-value as large of that could occur due to noise. The P-value less than 0.0500 indicated that the model terms were significant. In this case, the linear terms: A, B, C, D and E, the interaction terms: AB, AC, AD, AE, BC, BD, BE, CD, CE, DE and the quadratic terms: A^2, B^2, C^2, D^2 and E^2 were statistically significant models, while the values greater than 0.1000 indicated that the model terms were not significant.

Table 3: ANOVA for Quadratic Model (Response 1: Biodiesel Yield)

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	2190.64	20	109.53	2668.55	<0.0001	significant
A-Molal ratio	51.63	1	51.63	1257.83	<0.0001	
B-Catalyst concentration	76.62	1	76.62	1866.78	<0.0001	
C-Reaction temperature	16.73	1	16.73	407.67	<0.0001	
D-Reaction time	207.82	1	207.82	5063.24	<0.0001	
E-Agitation speed	64.82	1	64.82	1579.24	<0.0001	
AB	5.71	1	5.71	139.23	<0.0001	
AC	8.10	1	8.10	197.31	<0.0001	
AD	19.33	1	19.33	470.85	<0.0001	
AE	35.53	1	35.53	865.52	<0.0001	

BC	1.33	1	1.33	32.42	0.0002	
BD	73.92	1	73.92	1800.94	<0.0001	
BE	0.3362	1	0.3362	8.19	0.0169	
CD	21.05	1	21.05	512.75	<0.0001	
CE	1.08	1	1.08	26.30	0.0004	
DE	10.70	1	10.70	260.60	<0.0001	
A^2	705.02	1	705.02	17176.45	<0.0001	
B^2	51.02	1	51.02	1243.06	<0.0001	
C^2	5.94	1	5.94	144.79	<0.0001	
D^2	1.09	1	1.09	26.59	0.0004	
E^2	15.08	1	15.08	367.35	<0.0001	
Residual	0.4105	10	0.0410			
Lack of fit	0.0755	5	0.0151	0.2252	0.9362	Not significant
Pure error	0.3350	5	0.0670			
Cor total	2191.05	30				

Moreso, the lack of fit (F-value) of 0.23 implied that it was not significant relative to the pure error. Hence, there was a 93.62% chance that a Lack of Fit F-value of this dimension could occur due to noise. Thus, a non-significant Lack of Fit is good as the expectation of the result is for the model to fit. Generally, from the Table 3, it was evident that among the five variables (parameters) studied, exposure time (D) had the largest effect on biodiesel yield as it has the highest F-test value of 5063.24 for the single effect, which the least was the reaction temperature (C) that showed the lowest F-test value of 407.67.

3.4.2. Fit statistics

From the statistical analysis, the regression coefficient ($R^2 = 0.9998$), the predicted R^2 of 0.9985 presented in Table 4 are in reasonable agreement with the adjusted R^2 value of 0.9994, which implied a difference of less than 0.2. The coded equations as presented were useful for identifying the relative impact of the factors by comparing the factor coefficients. Also, since the Adequate precision measures the signal to noise ratio, the value of 170.225 obtained for this study indicated an adequate signal where model could be used to navigate the design space, as a ratio greater than 4 is desirable. Overall, other test results from the statistical analysis perspective are as presented in the Table 5.

Table 4: Fit Statistics

Parameter	Value	Parameter	Value
Std. Dev.	0.2026	R^2	0.9998
Mean	81.38	Adjusted R^2	0.9994
C.V. %	0.2490	Predicted R^2	0.9985
Glycerol (% mass)	0.02	Adeq Precision	170.2248

3.4.3. Coefficient estimate

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 from the Table 5 were adjustments around the average based on the factor settings. When the factors are orthogonal, the VIFs are 1 while the VIFs greater than 1 indicate multi- colinearity [15]. But since variance inflation factor (VIF) based on the authors, provides a measure of multi-colinearity among the independent variables in a multiple regression model, then, the higher the VIF, the more severe the correlation of factors would be. Hence, as a rough rule as they stated, VIFs less than 10 are tolerable. Consequently, the VIFs for all the factors studied were tolerable and thus accepted for the analysis.

Table 5: Coefficients in Terms of Coded Factors

Factor	Coefficient estimate	df	Standard error	95% CI low	95% CI high	VIF
Intercept	94.12	1	0.1106	93.87	94.36	
A-Molal ratio	1.89	1	0.0532	1.77	2.00	1.27
B-Catalyst concentration	2.08	1	0.0481	1.97	2.19	1.16
C-Reaction temperature	1.02	1	0.0504	0.9044	1.13	1.31
D-Reaction time	3.58	1	0.0503	3.47	3.69	1.16
E-Agitation speed	1.90	1	0.0479	1.80	2.01	1.15
AB	-0.6885	1	0.0583	-0.8185	-0.5585	1.21
AC	0.8645	1	0.0615	0.7273	1	1.27
AD	1.36	1	0.0626	1.22	1.50	1.24
AE	-1.86	1	0.0632	-2.00	-1.72	1.17
BC	-0.3357	1	0.0590	-0.4670	-02043	1.23
BD	2.47	1	0.0583	2.34	2.60	1.16
BE	0.1678	1	0.0586	0.0372	0.2985	1.24
CD	-1.45	1	0.0641	-1.60	-1.31	1.36
CE	0.3074	1	0.0599	0.1738	0.4410	1.28
DE	0.9834	1	0.0609	0.8477	1.12	1.17
A^2	-12.11	1	0.0924	-12.32	-11.91	1.43
B^2	-3.62	1	0.1027	-3.85	-3.39	1.43
C^2	-1.20	1	0.0997	-1.42	-0.9780	1.21
D^2	-0.4762	1	0.0924	-0.6820	-0.2704	1.22
E^2	-1.86	1	0.0970	-2.08	-1.64	1.27

3.4.4. Predicted and experimental or actual values

Presented in Fig.6 is the plot of the correlation between the experimental and the predicted biodiesel yield. After the actual or experimental values were fed into the analytical software, the values were found to be same with the predicted value which are 66.2 and 94.7 respectively, thus statistically acceptable. Data points on the plot were linearly distributed, indicating a good relationship between the experimental and the predicted values of the response. It also suggested that the quadratic model was proper and adequate in predicting the response variables for the experimental data.

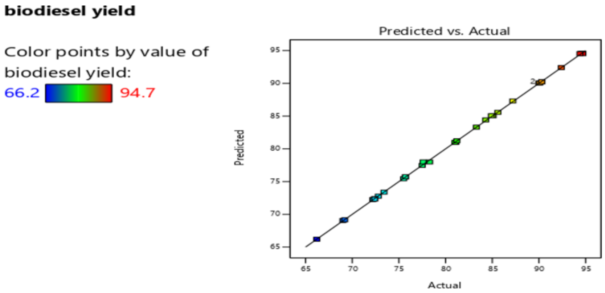


Fig. 6: Predicted Versus Actual Plot.

3.4.5. Contour and 3-dimensional (3D) plots interactions of the process parameters

i) Interactions between methanol/sample molal ratio and catalyst concentration

Fig. 7 shows the contour and three (3) dimensional (3D) plots for the interactions between methanol/sample molal ratio and catalyst concentration. Consistent red concentric lines around the region indicate an almost consistent optimal yield region with a yield of 94.7 %. Other side curvatures indicate increase in yield as molal ratio and other individual parameters increase, up to the point of six and their gradual decrease beyond six.

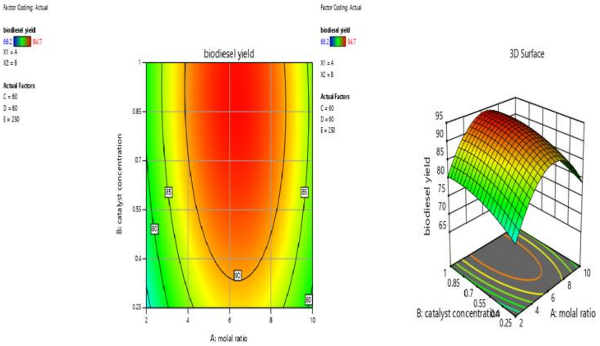


Fig. 7: Contour and 3D Plots Interaction for Methanol/Sample Molal Ratio and Catalyst Concentration.

ii) Interactions between reaction time and temperature on biodiesel yield

Fig. 8 shows the contour and 3D plots for the interaction between the exposure (reaction) time and temperature. The figures indicate that biodiesel yield increased with increase in time and temperature. This increase was attributed to the positive quadratic effect of the reaction temperature.

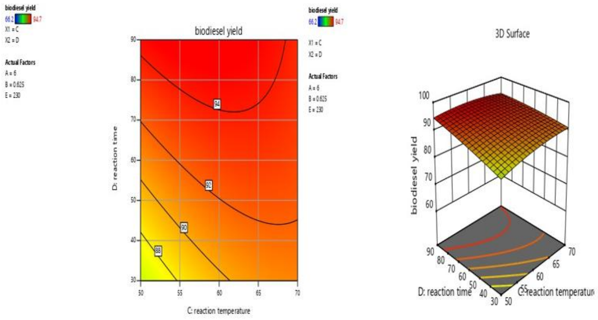


Fig. 8: Contour and 3D Plots Interaction for Reaction Time and Reaction Temperature.

iii) Interactions between agitation speed and reaction time

Fig. 9 shows the contour and 3D plots for the interaction between the exposure (reaction) time and the agitation speed. No static or concentric region from the figures was noticed. As reaction time and agitation speed increased, the biodiesel yield all increased likewise. This increase was attributed to the positive quadratic effect of the reaction (exposed) temperature.

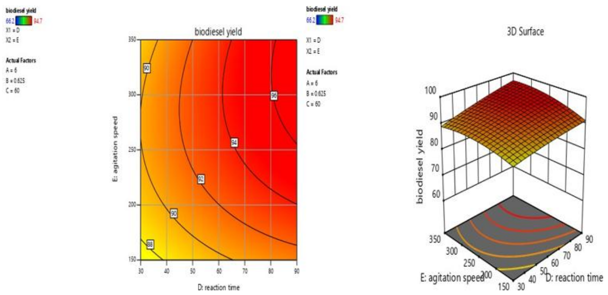
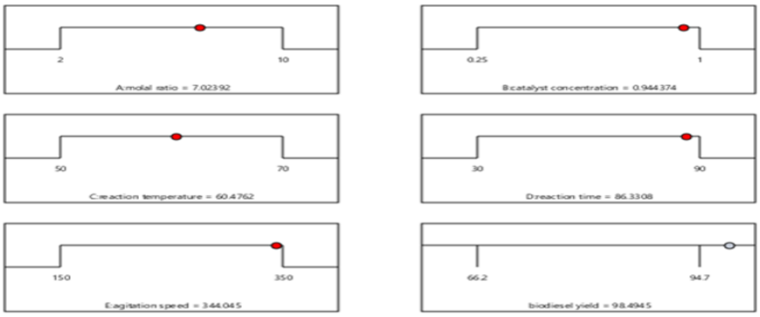


Fig. 9: Contour and 3D Plots Interaction for Reaction Time and Agitation Speed.

3.4.6. Biodiesel optimization

Presented in Fig. 10 are the optimized results showing the optimum, desirability, standard error and the optimized biodiesel yield values from the input parameters (temperature, catalyst concentration, methanol/oil molal ratio, reaction time and agitation speed). The optimized biodiesel yield and the optimum values were obtained through iterations of one hundred (100) solutions and the best yield established at F.



Desirability = 1.000
Solution 75 out of 100

Fig. 10: Ramp Showing the Optimum Values, Standard Error, Desirability and Biodiesel Yield.

4. Conclusion

In this study, the use of alkaline based catalyst (NaOH) has proven to be efficient in converting waste used soya oil to more useful bioenergy resource. Though soya oils can be used to operate diesel engines, they cannot be applied for a very long time, which necessitated the transesterification of the used soya oils to obtain the lighter derivative (biodiesel), which is more combustible. The results obtained indicated that all the process parameters studied had significant effects on the biodiesel yield. The combined interactions of these process conditions had various effects on the quantitative yield of the biodiesel developed, which necessitated the satisfactory conversion of the oil triglycerides to methyl ester. Also, the ANOVA from the experimental matrix design indicated that the process parameters analysed gave satisfactory results. Moreso, an increase in reaction temperature and time affected the biodiesel yield positively which had a value of 94.70 % initially, but presented an optimized result of 98.48 % afterwards. The statistical models developed for predicting the yield showed good agreement with other literatures. Overall, from the experimental analysis, catalyst concentration of 1 %, reaction time of 60 minutes, reaction temperature at 70 ^{o}C, methanol/sample molal ratio of 6:1, and agitation speed of 300 rpm were obtained at the optimal conditions, which were validated with the actual biodiesel yield of 94.70 %. In view of the findings, other waste vegetable oils were suggested to be exploited using same achieved optimal process conditions established in this study. In the alternative, other feasible methods to convert waste vegetable oils to biodiesel, which is conveniently combustible in present day diesel engines without modification could also be exploited.

References

[1] Igri Omini Uket and Hyginus Ubabuike Ugwu (2023). Effects of Process Parameters Variations and Optimization of Biodiesel Production from Orange Seed Oil Using Raw and Thermal Clay as Catalyst. International Journal of Frontiers in Engineering and Technology Research, 05(01) – 001-0. https://doi.org/10.53294/ijfetr.2023.5.1.0018.

[2] Samuel Oliver Effiom (2023). Effect of Process Parameters on Biodiesel Yield Produced from Palm Kernel Shell Oil (PKSO) Using Egg Shell as Catalyst. International Journal of Frontiers in Engineering and Technology Research, 04(01) – 001-0.017 https://doi.org/10.53294/ijfetr.2023.4.1.0012.

[3] Carneiro, J.D.S; Nogueira, R.M; Martins, M.A; Valladão, D.M.D.S. and Pires, E.M. (2018). The oven-drying method for determination of water content in Brazil nut. Bioscience Journal, 34(3): 595-602. https://doi.org/10.14393/BJ-v34n3a2018-37726.

[4] Demirbaş, A. (2005). Biodiesel production from vegetable oils via catalytic and non- catalytic supercritical methanol transesterification methods. Progress in Energy Combustion Science, 31: 466-487. https://doi.org/10.1016/j.pecs.2005.09.001.

[5] Yau, D; Ibrahim, M; Salihu, I; Abdulhadi, M; Sani, M.M; Sulaiman, A.A. and Umar, A.U. (2020). Extraction, production and characterization of biodiesel from shea butter (Vitellaria paradoxa C.F. Gaertn)obtained from Hadejia, Jigawa State, Nigeria. GSC Biological and Pharmaceutical Sciences, 11(03): 208-215. https://doi.org/10.30574/gscbps.2020.11.3.0168.

[6] Boerlage, G. D. and Broeze, J.J. (1990). Determination of saponification, iodine and peroxide values. Progress Report of Volunteer Group for Fuel Research Society of Automotive Engineers, 21:289-305.

[7] Food Safety and Standards Authority of India: FSSAI. (2015). Manual of methods of analysis of foods (oils and fats). https://www.google.com/url?Sa=t&rct=j&q=&esrc=S&source=web&Cd=&ved=2ahUKEw illp40Rwq3xAhUKDMA-KHbZAwOQFjABegQIBhAD&url=https%3A%2F%2Fold.fssai.gov.i n%2FPortals%2FO%2FPdf%2FManual_Oil_Fat_25_05_2016.pdf&usg=AovVawOoWNoF C9Ld-cjtEFVn9VA5. Retrieved: 23-06-2020.

[8] Canesin, E.A; deOliveir, C.C; Matsushita, M; Dias, L.F; Pedro, M.R. and de Souza, N.E. (2014). Characterization of residual oils for biodiesel production. Electronic Journal of Biotechnology, 17:39–45; https://doi.org/10.1016/j.ejbt.2013.12.007.

[9] Akoh, C.C. (2017). Food Lipids: Chemistry, Nutrition and Biotechnology, 4 th ed. CRC Press, Boca Raton, FL, 1047; https://doi.org/10.1201/9781315151854.

[10] Vicente, G; Martinez, M. And Aracil, J. A. (2006). Comparative study of vegetable oils for biodiesel production in Spain. Energy Fuels, 20:394-398. https://doi.org/10.1021/ef0502148.

[11] Jain, S., Sharma, M.P. and Rajvanshi, S. (2011). Acid base catalyzed transesterification kinetics of waste cooking oil. Fuel Process Technology, 92: 32-38. https://doi.org/10.1016/j.fuproc.2010.08.017.

[12] Noureddini, H. and Zhu, D. (1997). Kinetics of transesterification of soybean oil. Journal of American Oil Chemist Society, 74: 1457-1463. https://doi.org/10.1007/s11746-997-0254-2.

[13] Ngamcharussrivichai, C., Totarat, P. and Bunyakiat, K. (2008). Ca and Zn mixed oxide as a heterogeneous base catalysts for transesterification of palm kernel oil. Applied Catalysis A: General, 341: 77-85. https://doi.org/10.1016/j.apcata.2008.02.020.

[14] Ramachandran, K., Sivakumar, P., Suganya, T. and Renganathan, S. (2011). Production of biodiesel from mixed waste vegetable oil using an aluminium hydrogen sulphate as a heterogeneous acid catalyst. Bioresource Technology, 102: 7289-7293. https://doi.org/10.1016/j.biortech.2011.04.100.

[15] Sivakumar, P; Prabhakaran, D. and Thirumarimurugan, M. (2018). Optimization studies on recovery of metals from printed circuit board waste. Bioinorganic Chemistry and Applications, 2-8. https://doi.org/10.1155/2018/1067512.

[16] Smith, J., & Johnson, M. (2023). "Improving Biodiesel Production Efficiency through Catalyst Optimization." Journal of Renewable Energy, 45(2):123-136.