

## Evaluation of Properties and Optimization of Biodiesel from Used Soya Oil as an Alternative to Diesel Fuel

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**ABSTRACT:** Biodiesel is now acclaimed to be the foremost alternative to replace petro-diesel, but is beset with the problem of its feedstock being mainly edible oil. As this is envisaged to result in high cost of food and the biodiesel produced thereof, concerted research efforts are geared towards evaluating non-edible oil and waste cooking oil (WCO) or used cooking oil (UCO) as suitable feedstock. This research work focused on evaluation of properties and optimization of biodiesel from used soya oil as an alternative to diesel fuel. Solvent extraction was employed for extraction of oil from soya seed. Used soya oil was prepared by frying food (yam, potato plantain etc) with virgin soya oil for a total of 72 hours (Issaryakul 2008). The oil was characterized based on American Society for Testing and Materials (ASTM) method. The fatty acid profile of used soya oil (USO) was analyzed using gas chromatography mass spectroscopy (GC MS) while the functional groups of the triglyceride were determined using Fourier transform infrared spectroscopy. The effects of process parameters on the yield of used soya oil fatty acid methyl ester (USOFAME) was investigated using one factor at a time method. The oil was pretreated to reduce the free fatty acid level below 1% and then was transesterified using methanol in the presence of sodium hydroxide catalyst. The fuel properties of the USOFAME produced were determined based on ASTM standards. Optimization of USO biodiesel was carried out using response surface methodology. The physicochemical properties of USO, density, acid value, free fatty acid, saponification value, iodine value, flash point, pour point, moisture content, kinematic viscosity, cloud point, calorific value gave the values of, 962kg/m<sup>3</sup>, 4.20%, 2.10 %, 187mgKOH/g, 75.4gI<sub>2</sub>/100g,

180°C, -5°C, 0.2%, 47.78mm<sup>2</sup>s<sup>-1</sup> @ 40°C, 5°C, 34.20MJ/Kg respectively. The fatty acid profile of USO consist of saturated fatty acids; myristic acid, palmitic acid, stearic acid and arachidic acid;

unsaturated fatty acids, oleic acid, linoleic acid, linolenic acid and lignoceric acid. The fuel properties of the USOFAME which is within the ASTM standards were determined as acid value 0.4mgKOH/g, density 863mm<sup>2</sup>/s, kinematic viscosity 4.60mm<sup>2</sup>s<sup>-1</sup>, flash point 162°C, cetane number 61.0, calorific value 40.06MJ/Kg, pour point 4°C, cloud point 7°C, iodine value 30.60gI<sub>2</sub>/100g. The use of quadratic regression model from design expert version 12.0 for response surface methodology (RSM) showed optimal biodiesel yield of 91% at the optimum reaction conditions of methanol to oil molar ratio 7:1, catalyst concentration 1%wt. reaction temperature 65°C, and reaction time 60 minutes and agitation speed 300rpm

**Key words:** biodiesel, characterization, optimization, transesterification, Used soya oil.

### I. INTRODUCTION

The growing concern due to environmental pollution caused by the conventional fossil fuels and the fact that they are non-renewable has led to research for environmentally friendly and renewable fuels. Among various options investigated for diesel fuel, biodiesel obtained from vegetable oil and other sources has been universally recognized as one of the contenders for reduction of exhaust gas emission [1]. Presently, the bulk of biodiesel produced all over the world has edible oil as its feedstock. This has therefore raised the fear of many researchers that the continuous use of edible oil for biodiesel production might stress the food uses, prize,

production and availability of these oils. Consequently this has ignited research into the use of non-edible oil for biodiesel synthesis

A mono-alkyl ester of long chain fatty acid, biodiesel is known to have characteristics similar to diesel with additional advantages of high lubricity, high cetane number, being biodegradable and environmentally friendly [2]. Burning of fossil fuel results in environmental pollution such as emission of green house gasses, including sulphur oxides (SO<sub>x</sub>), nitrogen oxides (NO<sub>x</sub>) and methane [3]. Biodiesel is produced by the reaction of oil or fat with an alcohol usually in the presence of catalyst which could be a base, acid or an enzyme. If an alcohol typically monohydric alcohol like methanol contacts a fatty acid, it will bond to form biodiesel [4]. Various processes have been adduced for production of biodiesel, including, micro-emulsion with alcohol, catalytic cracking, pyrolysis and transesterification [5, 6, 7, 8]. Among these processes, transesterification has proved to be the most useful means of converting oil or fat into environmentally safe biodiesel [9, 10,].

Although, biodiesel is gaining popularity, more than 95% of the renewable resources used for its production is edible oil [11], which will in a long term have serious implications on food availability and the cost of biodiesel as it may be more expensive than petro-diesel. Worldwide, biodiesel production is mainly from edible oils such as soybean, sunflower and canola oils etc. Utilization of edible oils as feedstock for biodiesel production poses a lot of concerns as this practice competes with food supply leading to high cost of edible vegetable oil, and consequently results in relative increase in biodiesel production cost. Therefore, concerted research efforts are geared towards evaluating non-edible oils and waste cooking oil (WCO) or used cooking oil (UCO) as suitable feedstock. Used cooking oil or used oil for short refers to used vegetable oil obtained from cooking or frying of food. Repeated frying for preparation of food make such an oil unsuitable for consumption due to high free fatty acid content [12]. In order to minimize the market prize of edible oil and stem the contentious debate on the ill-effects of use of edible oil for biodiesel production, research is now geared towards the use of UCO feedstock [13, 14, 15]. The resulting USO from various sources all over the world now stands at 15million tons yearly. The very high rate of generation of UCO has considerable environmental impact as 1 liter of UCO can foul 1000liters of water. The main drawback of used cooking oil is that its previous exposure to high temperature with

food contact, increases the moisture, free fatty acid and particulate material contents in the oil. The high free fatty acid leads to soap formation with alkali catalyst and thus retard the dispersion and mixing efficiency of the reaction mixture and thus reduce the formation of biodiesel. The particulate matter in the oil persist in the formed biodiesel and may result in carbon deposit, plugging of fuel lines, fouling piston heads and sticking of the rings. The moisture contained in the oil can react with base catalyst to give emulsion [16]. thus favoring the reverse reaction. Used cooking oil polymerizes on heating and storage and thus exhibit increase in molecular weight and viscosity [16, 18]. This research work is focused on evaluation of properties and optimization of biodiesel from use soya oil. In order to carry out the research on a particular used oil (soya oil), used soya oil was prepared by frying foods (yam, potato plantain etc) in a virgin soya oil for a total of 72 hours [19]. The resulting used soya oil was synthesized to biodiesel, characterized and optimized.

Optimization of used soya oil was carried out using response surface methodology of central composite design (CCD) in order to determine the optimum reaction conditions for biodiesel production. The five processing factors, methanol to oil molar ratio, catalyst concentration reaction temperature, reaction time, and agitation speed are the independent variables while percentage biodiesel yield is the dependent variable or response. Design expert software version 12.0 was used for the design of experiment and optimization of the reaction conditions.

## II. MATERIALS AND METHODS

### A Materials

Used soya oil, reagents, glass wares, equipments including gas chromatography mass spectrometer (GC-MS), Fourier transform infrared spectroscopy (FTIR), viscometer, magnetic hot plate, waterbath, soxhlet extractor, design expert software version 12.0 etc.

### B Preparation of used soya oil

20 liter of pure soy oil was purchased from Ogboete main market Enugu. 10 liters of the oil was introduced into a 20 liter steel pot. Heating was done using gas cooker. The oil was used for frying food for duration of 72 hours (8 hours a day for 9 days) to make waste cooking oil [19]. A test of the acid value of the used soy oil showed much increase compared to the unused one, from 0.22mg/g oil to 4.20mg/g oil.

### C Characterization of used soya oil

The physiochemical properties of the used soya oil was characterized based on American Society for Testing Materials, ASTM 6751 (1973) method. Analytical equipments, GC- MS (QP2010 plus Shimadzu, Japan) and FTIR (M530 Bulk scientific FTIR ) were used to determine the fatty acid profile and the functional groups of the oil respectively.

### D Effect of process parameters on biodiesel yield

The effects of process parameter on biodiesel yield from USO were investigated based on one factor at a time method involving keeping a factor constant at a time and varying the others in turn. The five factors investigate are, molar ratio of methanol to oil, catalyst concentration, reaction time, reaction temperature and agitation speed.

### E Pretreatment of the used soya oil

A pre-treatment procedure was followed to reduce the excess free fatty acid of the used soya oil below 1%. The oil sample was first heated on a heating mantle at 110°C for 10 minutes for any available moisture to be driven off. The sample was cooled to 60°C in a water bath, and then weighed into 500ml three necked round bottomed flask. Then methanol of 60%w/w of oil mixed with concentrated sulphuric acid of 7% w/w of oil was added. A reflux condenser was fitted into the middle arm of the flask and water circulated at the outer jacket of the condenser. A thermometer was inserted into the sample in the flask from one of the side arms. The whole setup was placed on a magnetic heating mantle and heated at 60°C for 120 minutes at an agitation speed of 450rpm. The mixture was then transferred into 500ml separating funnel where it later separated into three layers comprising water at the bottom, pre-treated oil in the middle and methanol at the upper layer. The various components were carefully tapped off, water first, followed by the oil and finally methanol. Hot distilled water was poured into the oil in a separating funnel, shaken and allowed to stand when it separated into water and oil layers below and above the funnel respectively. The water layer was tapped off from the separating funnel and the pre-treated oil was poured into 250ml beakers and dried carefully in an oven regulated at a temperature of 105°C until the residual water evaporated completely. After this process, the pre-treated oil was made ready for transesterification [20].

### F Production of biodiesel by transesterification

The oil was transesterified using methanol and sodium hydroxide catalyst. A 500ml three-necked round bottomed flask fitted with a condenser on the middle arm, a thermometer and sample outlet on the side arms respectively served as the reactor. The heating system consists of an electromagnetic hot plate which heats the reactor and rotates the metal knob in the reactor through an electromagnetic field. Specified quantity of the oil sample was introduced into the flask and the flask content heated to the temperature established for the reaction. Then methanol and the catalyst (NaOH) mixture was added in the amount established for the reaction, and the stirrer switched on at a specified speed, taking this moment as zero time of the reaction. The reaction mixture was vigorously stirred and refluxed for the required reaction time. At the end of methanolysis, the transesterified product was made to stand for a day in a separating funnels where it separates into the upper biodiesel layer and the lower glycerol layer. The lower glycerol layer was tapped off first followed by the upper biodiesel layer.

### G Biodiesel purification by wet washing

After transesterification, the upper ester layer may contain traces of methanol and glycerol. The remaining un-reacted methanol has safety risk and might corrode engine components, and glycerin within the biodiesel will lessen the fuel lubricity and cause injector coking and other deposits [21]. Such trace of methanol is soluble in water and is therefore removed by wet washing. The methyl ester or biodiesel layer was gently washed with hot distilled water in the ratio of 3:1 water to methyl ester. The methyl ester was gently washed to prevent its loss due to formation of emulsion that results in complete phase separation [22]. The washed biodiesel was dried by heating at 105°C on a laboratory hot plate until all residual water molecules is evaporated. This conforms with the findings of [23]. The percentage biodiesel yield is given by the expression of equation (1)

$$\begin{aligned} \% \text{ biodiesel yield} &= \text{Volume of biodiesel produced} \\ &\div \text{volume of oil used} \times 100 \quad (1) \end{aligned}$$

### H Determination of the fuel properties of used soya oil biodiesel produced

The properties of the biodiesel fuel were characterized based on ASTM standards. The properties characterized for include density, viscosity, iodine value, saponification value, cetane number, acid value, free fatty acid, calorific value, flash point etc.

**I Design of experiment for transesterification of used soya oil catalyzed by NaOH**

Design Expert software (version 12) was used in this study to design the experiment and to optimize the reaction conditions. The experimental design employed in this work was a two-level-five factor fractional factorial design, including 32 experiments. Reaction temperature, catalyst concentration, methanol to oil molar ratio, reaction time and agitation speed were selected as independent factors for the optimization study. The response chosen was the methyl ester yields obtained from transesterification of used soya oil. 2<sup>5</sup> (2<sup>n</sup>) factor fractional factorial experiments, 10(2n) star points and 6 center points were carried

out in order to predict a good estimation of errors and experiments were performed in a randomized order. The actual and coded levels of each factor are shown in Table 1. Alpha is defined as a distance from the center point which can be either inside or outside the range, with the maximum value of 2<sup>n/4</sup>, where n is the number of factors [24]. It is noteworthy to point out that the software uses the concept of the coded values for the investigation of the significant terms, thus equation in coded values is used to study the effect of the variables on the response. The empirical equation is represented as shown in equation (2) below:

**Table 1:** Experimental range and levels of independent process variables for biodiesel production.

Independent Variables	Units	Range and Level				
		-α	-1	0	1	+α
Molar Ratio( X <sub>1</sub> )	Mol/mol	2:1	4:1	6:1	8:1	10:1
Catalyst Concentration (X <sub>2</sub> )	Wt %	0.25	0.50	0.75	1.00	1.25
Temperature (X <sub>3</sub> )	°C	50	55	60	65	70
Reaction time (X <sub>4</sub> )	Min.	30	45	60	75	90
Agitation speed (X <sub>5</sub> )	Rpm	150	200	250	300	350

**Table 2** Experimental design Matrix for transesterification studies of neem oil FAME

Run order	Methanol/Oil molar ratio X <sub>1</sub>		Catalyst conc. (wt %) X <sub>2</sub>		Temperature (°C) X <sub>3</sub>		Time (Mints) X <sub>4</sub>		Agitation Speed (Rpm) X <sub>5</sub>		Biodiesel Yield (%)
	Code d	Real	Code d	Real	Coded	Real	Coded	Real	Code d	Real	
1	-1	4	-1	0.5	-1	55	-1	45	+1	300	
2	+1	8	-1	0.5	-1	55	-1	45	-1	200	
3	-1	4	+1	1	-1	55	-1	45	-1	200	
4	+1	8	+1	1	-1	55	-1	45	+1	300	
5	-1	4	-1	0.5	+1	65	-1	45	-1	200	
6	+1	8	-1	0.5	+1	65	-1	45	+1	300	
7	-1	4	+1	1	+1	65	-1	45	+1	300	
8	+1	8	+1	1	+1	65	-1	45	-1	200	
9	-1	4	-1	0.5	-1	55	+1	75	-1	200	
10	+1	8	-1	0.5	-1	55	+1	75	+1	300	
11	-1	4	+1	1	-1	55	+1	75	+1	300	
12	+1	8	+1	1	-1	55	+1	75	-1	200	
13	-1	4	-1	0.5	+1	65	+1	75	+1	300	
14	+1	8	-1	0.5	+1	65	+1	75	-1	200	
15	-1	4	+1	1	+1	65	+1	75	-1	200	
16	+1	8	+1	1	+1	65	+1	75	+1	300	

17	-2	2	0	0.75	0	60	0	60	0	250
18	+2m	10	0	0.75	0	60	0	60	0	250
19	0	6	-2	0.25	0	60	0	60	0	250
20	0	6	+2	1.25	0	60	0	60	0	250
21	0	6	0	0.75	-2	50	0	60	0	250
22	0	6	0	0.75	+2	70	0	60	0	250
23	0	6	0	0.75	0	60	-2	30	0	250
24	0	6	0	0.75	0	60	+2	90	0	250
25	0	6	0	0.75	0	60	0	60	-2	150
26	0	6	0	0.75	0	60	0	60	+2	350
27	0	6	0	0.75	0	60	0	60	0	250
29	0	6	0	0.75	0	60	0	60	0	250
30	0	6	0	0.75	0	60	0	60	0	250
31	0	6	0	0.75	0	60	0	60	0	250
32	0	6	0	0.75	0	60	0	60	0	250

$$Y = \beta_0 + \sum_{i=1}^5 \beta_i X_i + \sum_{i=1}^5 \sum_{j=i+1}^5 \beta_{ij} X_i X_j + \sum_{i=1}^5 \beta_{ii} X_i^2 \quad (2)$$

Where Y is the predicted yield of FAME (%),  $X_i$  and  $X_j$  represent the transesterification process variables,  $\beta_0$  is the offset term,  $\beta_i$  is the coefficient of linear (single) effect,  $\beta_{ij}$  is the coefficient of interaction effect and  $\beta_{ii}$  is the coefficient of quadratic effect. Selection of levels for each factor was based on the experiments performed to study the effects of process variables on the yield of biodiesel by alkali catalyzed transesterification of used soy oil. The lower level of temperature was 50°C since below that the reaction rate is relatively slow and the upper level of temperature was 70°C. The levels of methanol to oil molar ratio were selected between 2:1 and 10:1 and the catalyst concentration was limited between 0.25 wt% and 1.25wt%(based on the initial weight of the oil) with agitation speed range of 150 rpm to 350 rpm. The range and levels of the independent variables and the experimental design matrix for the transesterification are presented in Figure 1 and 2 respectively

### III. RESULTS AND DISCUSSION

#### A Characteristics of Used Soya Oil

The summary of the characteristics of used soya oil are presented in the Table3, From the table, it is seen that the free fatty of the used soya oil (2.10%) is greater than 1%, a condition inimical to high yield of biodiesel by alkali transesterification. This is an unacceptable levels of free fatty acid for alkali transesterification reaction because of high tendency for soap formation, reduction in biodiesel formation as a result of inhibition of the separation of esters from glycerol [25]. After the pre-treatment, the free fatty acid

values were reduced to less than 1% which is within the acceptable level for alkali transesterification reaction. The kinematic viscosity measures the flow resistance of the fuel while the density of the oil determines the quantity measured since this is volumetrically made.

The kinematic viscosity and the density of the oil (47.78mm<sup>2</sup>s<sup>-1</sup> and 962kg/m<sup>3</sup>) are higher than that of the biodiesel produced from it (4.60mm<sup>2</sup>s<sup>-1</sup> and 880kg/m<sup>3</sup>) and even much higher than that of diesel (4.2mm<sup>2</sup>s<sup>-1</sup> and 835kg/m<sup>3</sup>). High density and viscosity makes atomization of the oil in internal combustion engine difficult and has

been associated with increase in engine deposits, hence they cannot be used directly as bio-fuel [26]. The determined density of the oil 966kg/m<sup>3</sup> is in agreement with the literature findings of [23, 27], but at variance with [28, 29].

Iodine value, a measure of degree of un-saturation of the oil was obtained as 75.4gI<sub>2</sub>/g.oil which is below 100gI<sub>2</sub>/100g oil, indicative of the oil being nondrying and therefore suitable for biodiesel production. High iodine value of oil corresponds to high degree of un-saturation of the fatty acid in the triglyceride. If heated, such an oil is prone to thermal oxidation and polymerization of the triglyceride causing formation of deposits. The calorific value of used soya oil like that of any oil is relatively lower than that of diesel. The determined calorific value of the oil 34.20MJ/kg is in conformity with literature values for used cooking oils [27, 29]. The cloud and pour point of 5°C and -0.5°C respectively determined for the used soya oil are relatively low but not to the extent of being suitable for operation and handling during cold weather especially in cold climates. Peroxide value, an index of rancidity obtained as 9.5meq/kg was high and indicative of poor resistance of the oil to per-oxidation during heating, storage and

handling. The saponification value determined as 187.5 is in agreement with literature findings of [30, 31]. The flash point of 220°C is in agreement with literature values [30]. The high flash point of 180°C shows that the oil is not prone to fire hazard as the ignition temperature is high.

**Table 3 Physiochemical properties of USO oil**

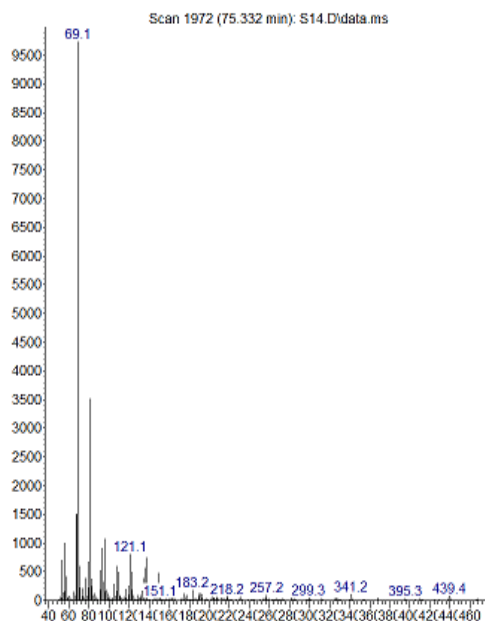
Properties	Unit	USO
Acid value	mgKOH/g	4.20
Free fatty acid	%	2.10
Saponification value	mgKOH/g	187.5
Iodine value	(gI <sub>2</sub> /100g oil)	75.4
Peroxide value	meq/kg	9.5
Kinematic viscosity	mm <sup>2</sup> s <sup>-1</sup> @ 40°C	47.78
Fire point	°C	280
Flash point	°C	180
Cloud point	°C	5
Pour point	°C	-5
Refractive index		0.4112
Specific gravity		0.962
Moisture content	%	0.2
Density	Kg/m <sup>3</sup>	962
Calorific value	MJ/kg	34.20

**B The Fatty Acid Profile of Used Soya Oil (GC-MS)**

The fatty acid profile of used soya oil was carried out with the aid of gas chromatography mass spectrometry (GC-MS). Figure1 shows the GC-MS spectra of used soya oil. The summary of fatty acid composition of used soya oil is shown below in Table 4. Used soya oil consist of 32.64% of saturated acids (myristic acid, stearic acid, palmitic acid and arachidic acid ) and 53.67% unsaturated acids (oleic acid, linoleic acid , linolenic acid and lignoceric acid ). The dominant monounsaturated fatty acid of the oil is oleic, which accounted for 50.5% of the total fatty acid content, hence, the oil belongs to oleic acid category [32]. The oleic acid content of used soya oil is comparatively higher than 7-40% reported for coconut oil, palm oil and cottonseed oil [33, 34]. This shows that used soya oil is highly unsaturated triglycerides. Nevertheless, the fatty acid components of the used soya oil were found to be consistent with the fatty acids present in typical oils used for producing biodiesel.

**C Fourier Transform Infrared (FT-IR) Spectra Analysis of Used Soya Oil**

The FTIR spectral analysis of used soya oil was carried out and shown in Figure2. From the result, obvious peaks of note were recorded .The region 723.8 cm<sup>-1</sup> ( 679.61 cm<sup>-1</sup> – 886.65 cm<sup>-1</sup>) indicate the presence of =C-H(alkenes) functional groups. They possess bending type of vibrations appearing at low energy and frequency region in the spectrum and they are all double bounded. They are attributed to olefin (alkenes) functional groups and are unsaturated. The characteristics peak found in the region 1114.5 cm<sup>-1</sup> (1050.15 – 1297.23 cm<sup>-1</sup>) indicate stretching vibrations of C-O and C-O-C.

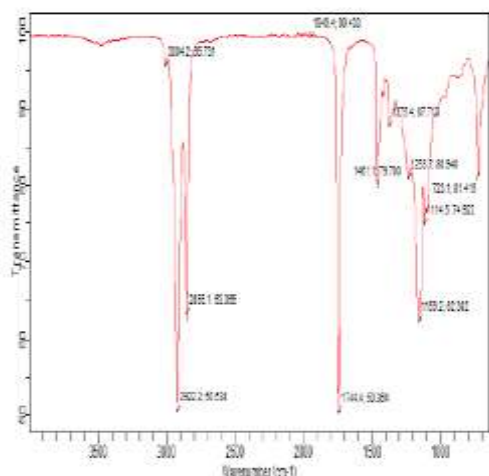


**Figure1: GC-MS Spectra of used soya oil**

**Table 4: Summary of fatty acid composition of used soya oil.**

Fatty Acid	Structure	Compos ition (%)	Molecular weight (g/mol)
Myristic acid	C14:0	0.85	228.30
Oleic acid	C18:1	50.5	282.465
Stearic acid	C18:0	10.56	284.48
Palmitic acid	C16:0	20.56	256.4
Arachidic acid	C20:0	0.67	304.470
linoleic acid	C18:2	1.80	294.48
linolenic acid	C18:3	1.05	278.43

Lignoceric acid	C24:1	0.22	368.63
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**Figure 2:** FT-IR spectra of used soya oil.

They can also indicate the bending vibration of O-CH<sub>3</sub> in the spectrum 35, 36].

The band region of 1375 cm<sup>-1</sup> can be ascribed to the bending vibration of C-H methyl groups, while the band at 1401cm<sup>-1</sup> (1400-1800 cm<sup>-1</sup>) is ascribed to C=C bending vibrations [37]. The peaks at 2855.75 cm<sup>-1</sup> and 2922cm<sup>-1</sup> indicate symmetric and asymmetric stretching vibrations of C-H alkane groups respectively. They could be methyl (CH<sub>3</sub>) or methylene groups and they require high energy to cause stretching vibrations within their bond when compared to the ordinary C-H bending vibrations of alkene groups detected at low energy and frequency region [38, 39]. The peak at 3004cm<sup>-1</sup> is attributed to the stretching vibration of =C-H alkene groups. They are detected above wave number 3000 cm<sup>-1</sup> in the spectrum compared to corresponding alkane C-H stretching groups detected below 3000 cm<sup>-1</sup>

### C Effects of Process Parameter on used soya oil biodiesel yield

#### Effect of methanol to oil molar ratio on USOFAME yield

The effect of methanol to oil molar ratio on used soya oil biodiesel yield is shown in figure 3 which reveals that USOFAME yield increased with increase of methanol to oil molar ratio until a maximum yield was attained at 6:1 methanol to oil molar ratio when the yield started decreasing. The decrease in yield beyond the optimal methanol to oil molar ratio of 6:1 is attributed to the fact that while the increase in methanol to oil molar ratio

favors transesterification reaction, very high ratio of methanol to oil decreases the catalytic activity of the catalyst, resulting in the reduction of biodiesel produced. This is in agreement with the findings of [40, 41]. Again Rashid and Anwar (2008) reported that when too much alcohol is used in transesterification reaction, the polarity of the reaction mixture is increased, thus increasing the solubility of glycerol which promote the reverse reaction between glycerol and biodiesel, thereby decreasing the biodiesel yield.

#### Effect of catalyst concentration on USOFAME yield

Catalysts provide alternative reaction pathways for breaking of bonds in chemical reaction. The activation energy for this new pathway is often less than the activation energy of the normal pathway. Sodium hydroxide was used as a base catalyst for the transesterification reaction in this work. The effect of sodium hydroxide concentration expressed as weight percentage of the oil on the USOFAME yield is presented in Figure 4. The yield of methyl ester increased with increase in catalyst weight up to 0.75%wt for used soya oil, and then began to decrease. Initially the amount of catalyst helped to accelerate the reaction by increasing the reaction rate. The higher yield of ester with increase in catalyst weight is due to the higher reaction rate due to high catalyst concentration. Increasing the catalyst weight beyond 1.0%wt for used soya oil led to the decrease in ester yield. This observation could be explained by the fact that initially increase in catalyst concentration helped to accelerate the rate of reaction. However, on exceeding the optimal catalyst concentration of 1wt%, the excess catalyst react with the triglyceride to form soap which increases the viscosity of the reaction mixture, hinders effective dispersion and mixing of the reactants and also separation of glycerol from biodiesel which gives rise to reduction of biodiesel production. This is in agreement with the findings of [17, 42].

#### Effect of temperature on biodiesel yield.

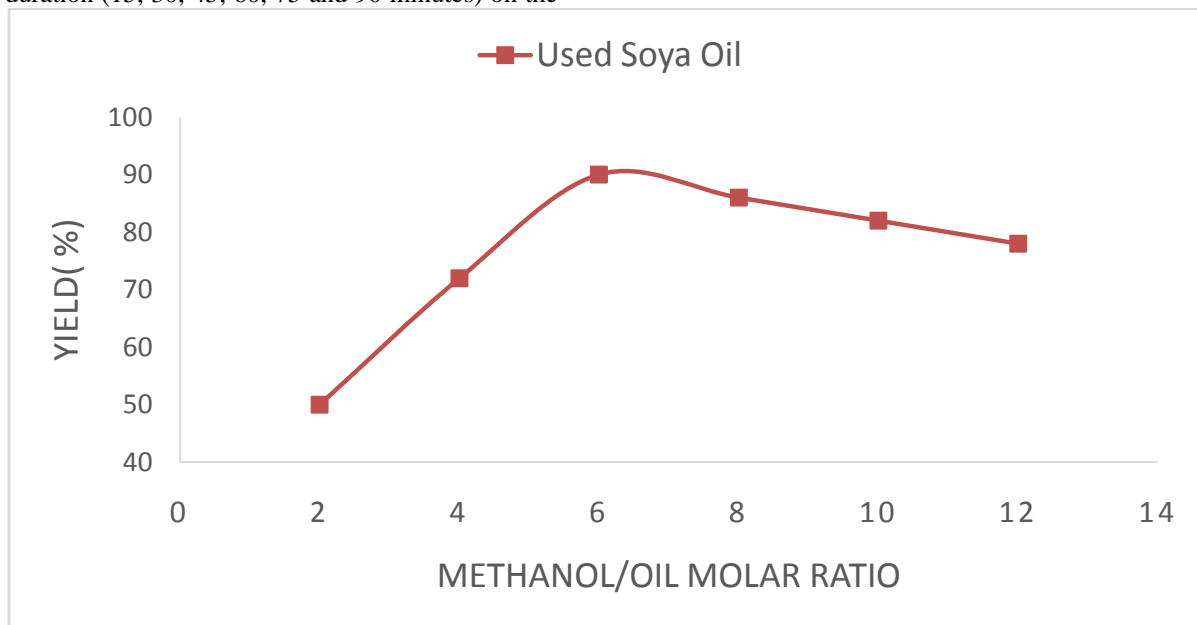
The rate of chemical reaction is accelerated at higher reaction temperature. For the study of the effect of temperature on the yield of the transesterification reaction, the reaction temperature was varied thus; 50°C, 55 °C, 60°C, 65°C, 70°C and 75°C while the other parameters (catalyst concentration, methanol to oil molar ratio, reaction time and agitation speed) were kept constant. As shown in Figure 5, USOFAME yield first increased and then decreased with increased in

reaction temperature beyond 65°C for used soya oil. This may be explained thus. At a temperature below the boiling point of methanol ester formation was favored, but about the boiling point of methanol, the backward reaction is favoured coupled with much amount of methanol lost by evaporation thus reducing the biodiesel yield. This trend conforms with the findings of [7].

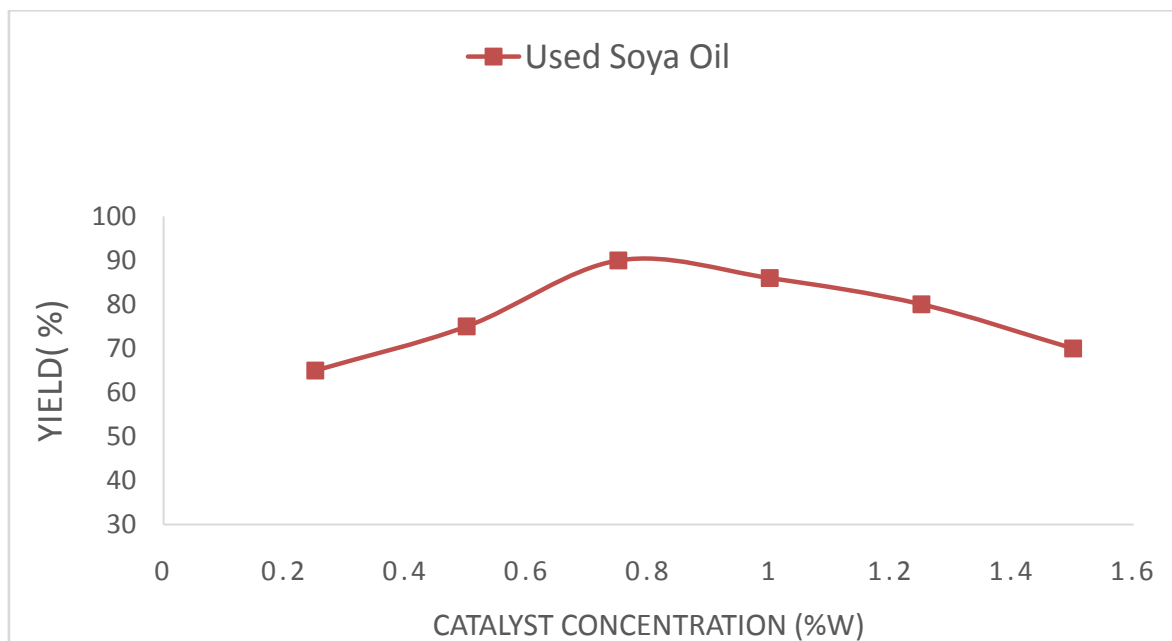
**Effect of reaction time on biodiesel yield.**

In this work, the effect of reaction duration (15, 30, 45, 60, 75 and 90 minutes) on the

yield of biodiesel from used soya oil was investigated. It was found that reaction time of 60 minutes was needed for a maximum yield of USOFAME for oil investigated and beyond this the yield decreased as shown in Figure 6. The decrease in the yield after 60 minutes may be due to reversible reaction of transesterification resulting in loss of esters [40]. Also longer reaction time most times allow the fatty acid present to react with alkali resulting in soap formation. The presence of soap retards the formation of ester [7, 20].

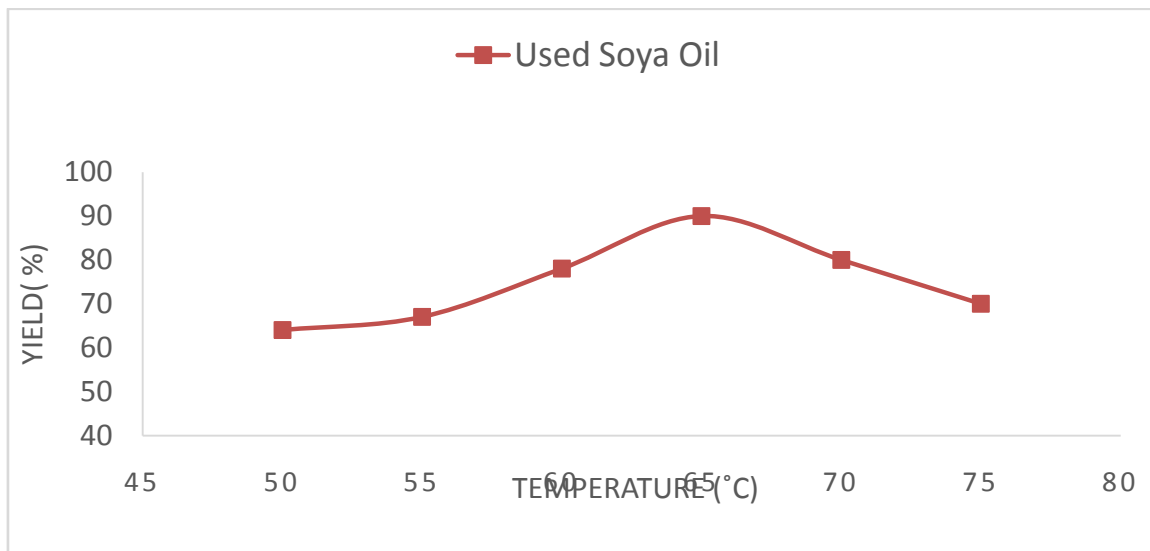


**Figure 3:** Effect of methanol to oil molar ratio on biodiesel Yield.

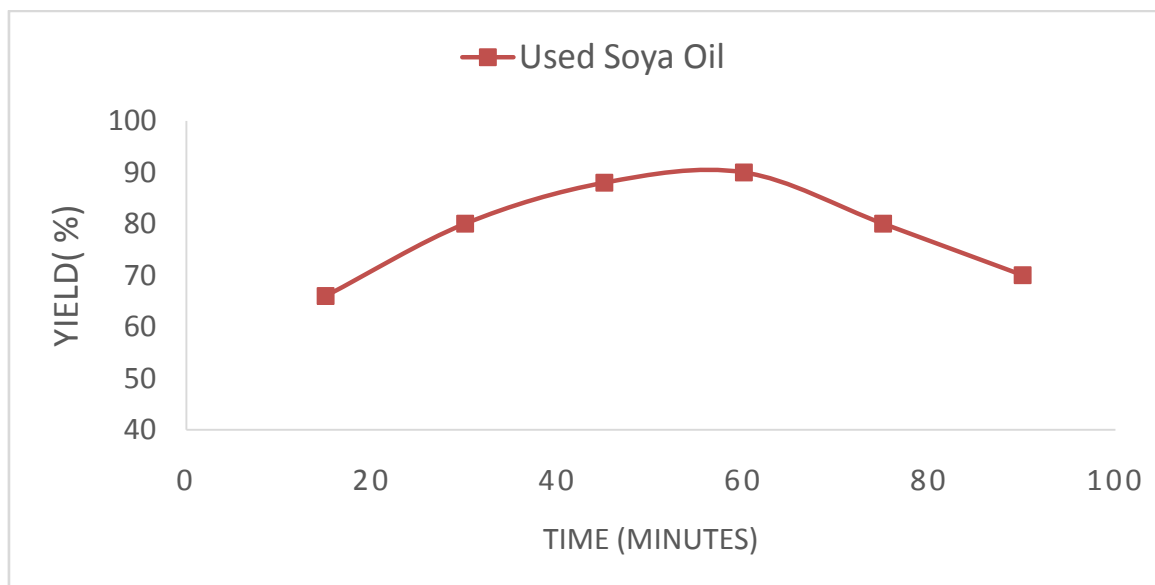


**Figure 4:** Effect of catalyst concentration on biodiesel yield





**Figure 5:** Effect of temperature on biodiesel yield.

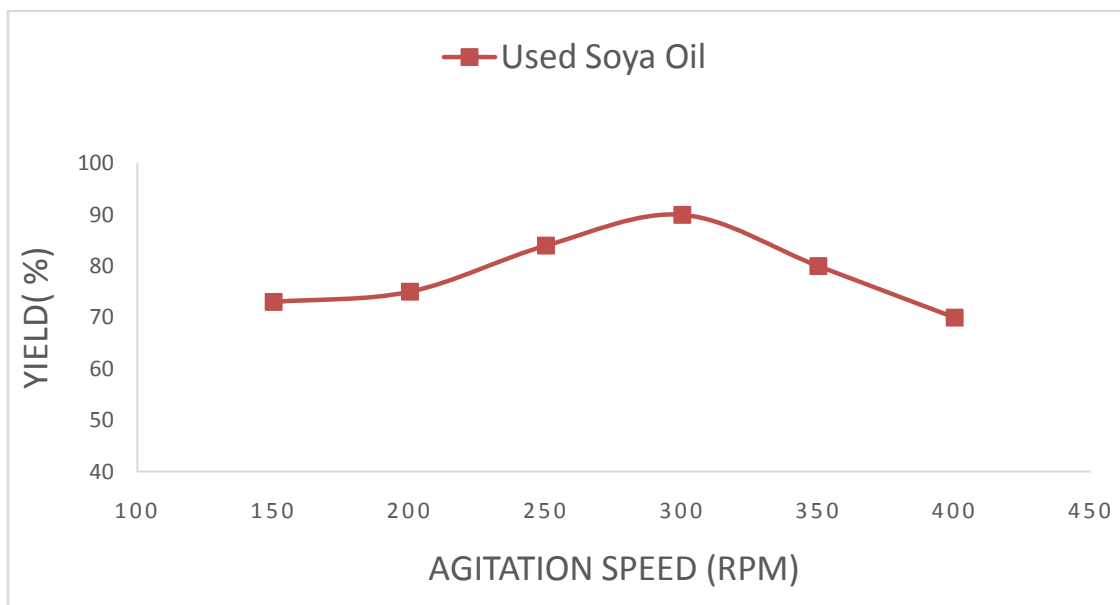


**Figure 6:** Effect of reaction time on biodiesel yield

**Effect of agitation speed on biodiesel yield.**

Transesterification was conducted in this study at different agitation rate of 150, 200, 250, 300, 350 and 400 revolutions per minutes (rpm). Mixing is particularly very important for transesterification process as it ensures homogeneity within the reaction mixture. The biodiesel yield at different rate of mixing is shown in Figure 7. At the lowest stirring speed of 150rpm it was observed that the reaction of methanolysis was practically incomplete as it only exhibited a yield which was difficult to separate. The yield was

observed to decrease as the stirring rate went above 300 rpm for used soya oil. The backward reaction may have been favored when mixing intensity was accelerated beyond the above condition, thereby retarding the formation of biodiesel. These results are in conformity with observations made by Ogunsuyi (2015), who studied the effect of agitation speed on the transesterification of non-edible oils and concluded that higher agitation promoted the homogenization of the reactants and thus led to higher yields.



**Figure 7:** Effect of agitation speed on biodiesel yield.

#### D Fuel Properties of the FAME Produced.

Table 5 gives the summary of the fuel properties studied in the course of this research work.

Biodiesel generally has a higher density than petro-diesel. This has a significant impact on fuel consumption as fuel introduced into the combustion chamber is determined volumetrically. The density was evaluated as  $863 \text{ kg/m}^3$  for used soya oil biodiesel and this is within the ASTM limits for biodiesel. The biodiesel has lower density compared to the density of used soya oil ( $962 \text{ kg/m}^3$ ).

The value of kinematic viscosity obtained for the biodiesel produced from used soya oil is  $4.6 \text{ mm}^2/\text{s}$  as shown in Table 5, and it could be observed that it is within the standard range of ASTM limit. The increase in viscosity results in poor atomization, incomplete combustion which leads to coking of injector tips and engine power loss. Low-viscosity fuel produces a very subtle spray which cannot get into the combustion cylinder, thus forming the fuel rich zone which lead to the formation of soot [43, 44]. From the result it could be inferred that FAME from used soya oil has a good injection and atomization performance. Furthermore it will offer superior lubrication and protection for the moving parts of engine than the diesel.

The flash point is a determinant for flammability classification of materials. The typical flash point of pure methyl ester is  $\geq 130^\circ\text{C}$ , classifying them as “non-flammable”. However,

during production and purification of biodiesel, not all the methanol may be removed, making the fuel flammable and dangerous to handle and store if the flash point falls below  $130^\circ\text{C}$ . The flash point of USOFAME is  $156^\circ\text{C}$ . This is within the ASTM standard as shown in Table 5, indicative of the safety of USOFAME in handling and storage.

Cetane number serves as a measure of ignition quality of the fuel. This is the most pronounced change from vegetable oil to the transesterified product. Fuels with low cetane number show an increase in emission due to incomplete combustion. The lower limit for cetane number by ASTM and EN standards are 47 and 51 respectively. The values obtained for used soya oil biodiesel is 61.00. Thus the obtained result which are within the acceptable ASTM limits indicates that the produced biodiesel possess good ignition response.

The cloud point which is the lowest temperature of first appearance of wax-like material on cooling the biodiesel was determined as  $7^\circ\text{C}$  for used soya oil biodiesel. The pour point which is the lowest temperature at which the fuel will still pour was determined as  $4^\circ\text{C}$  for used soya oil biodiesel. The characteristics of the biodiesel produced is within the ASTM standards for biodiesel, as shown in Table 5. However the cloud and pour points might give rise to cold flow problems in cold season. This problem however could be overcome by addition of suitable cloud and pour point depressants or by blending with diesel oil [45, 46].

**Table 5:** Fuel properties of USOFAME

Properties	Unit	USOFAME	ASTM Standards
Acid vlue	mgKOH/g	0.400	o.50
Density	Kg/m <sup>3</sup>	863	860-900
Kinematic viscosity@ 40 <sup>o</sup> C	mm <sup>2</sup> /s	4.60	1.9-6.0
Fire point	<sup>o</sup> C	171	197
Flash point	<sup>o</sup> C	162	100-170
Cloud point	<sup>o</sup> C	7	-3-15
Cetane number		61.00	48-65
Refractive index		1.4710	1.38
Specific gravity	Kg/m <sup>3</sup>	0.873	0.860-0.900
Calorific value	MJ/Kg	40.28	42.06
Pour point	<sup>o</sup> C	4	0.5
Iodine vlue	gI <sub>2</sub> /100g	30.60	42.46

### E Statistical Analysis of Transesterification Using Central Composite Design (CCD)

To optimize transesterification of used soya oil, central composite design (CCD), a response surface methodology (RSM) was used to determine the optimum values of the process variables. Fractional factorial design was used to obtain a quadratic model, consisting of factorial trials to estimate quadratic effects. To examine the combined effect of the five different factors; catalyst concentration, methanol to oil molar ratio, reaction temperature, reaction time and agitation speed, on biodiesel yield and derive the model, a two-level- five –factor (2<sup>5-1</sup> + 2\*5 + 6) central composite response design = 32 experiments were performed. The factors levels are shown in Table 1. The matrix for the five variables was varied at two levels (-1 and +1). The lower level of variable was designated as “-1” and higher level as “+1”. The experiments were performed in random order to avoid systematic error. Equations 3 and 4 represent the mathematical model relating the transesterification reaction of used soya oil with the independent process variables obtained with the

Design Expert 12. The design of the experimental matrix of transesterification of used soya oil with the experimental values of the biodiesel yield are presented in Tables 6. The response was expressed as % yield, calculated as  $\{(V_b)/V_o\} \times 100$  where V<sub>o</sub> is the initial volume of oil and V<sub>b</sub> is the volume of biodiesel produced.

### F Transesterification of Used Soya Oil.

The design plan as shown in Table 1 was used to optimize the yield of FAME production from used soya oil. The coded and un-coded values of the test variables were used to optimize the variables .The experimental values of percentage yield were presented in table 6. The percentage yield of FAME produced depends on the results, if there is significant variation for combination of process parameters. The empirical relationship between yield (Y) and the five variables in coded values obtained by using the statistical package Design-Expert 12 for determining the levels of factors which gives optimum percentage yield is given by equation 3 which is a quadratic regression equation that fitted the data is:

$$Y_{FAME (Used Soya Oil)} = 91.73 + 4.08A + 3.42B + 2.08C + 3. D + 1.58E + 2AB - 0.875AC - 0.75AD + 1.75AE + BC - 0.375BD + 0.875BE - 1.25CD + 2.25CE + 1.38DE - 13.85A^2 - 2.23B^2 - 1.6C^2 - 1.850D^2 - 1.98E^2 \quad (3)$$

Where Y<sub>FAME (Used Soya Oil)</sub> is the response of the variables (percentage yield of FAME) and A-E are the coded values of the independent variables. The above equation represents the quantitative effect of the factors (A, B, C, D, and E) upon the response (Y). Equation 3 suggested that the yield of FAME has linear and quadratic effects on the five variables studied. Coefficients with one factor represent the single effect of that particular factor while the coefficients with more than one factor represent the interaction between

those factors. Positive sign in front of the terms indicates synergistic effect while negative sign indicates antagonistic effect of the factors. The adequacy of the above proposed model was tested using the Design Expert sequential model sum of squares and the model test statistics. From the statistical analysis, the regression coefficient (R<sup>2</sup> = 0.9964) is reasonable , and the predicted R<sup>2</sup> of 0.980 is in a reasonable agreement with the adjusted R<sup>2</sup> of 0.909. This test result is shown in Table 7.

**TABLE 6:** Experimental Design Matrix for the Factorial Design of FAME Produced from Used Soya Oil

Run order	Methanol/Oil molar ratio X <sub>1</sub>		Catalyst conc. (wt %) X <sub>2</sub>		Temperature (°C) X <sub>3</sub>		Time (Mints) X <sub>4</sub>		Agitation Speed (Rpm) X <sub>5</sub>		FAME Yield (from used soya oil) (%)
	Coded	Real	Coded	Real	Coded	Real	Coded	Real	Coded	Real	
1	-1	4	-1	0.5	-1	55	-1	45	+1	300	54
2	+1	8	-1	0.5	-1	55	-1	45	-1	200	67
3	-1	4	+1	1	-1	55	-1	45	-1	200	62
4	+1	8	+1	1	-1	55	-1	45	+1	300	75
5	-1	4	-1	0.5	+1	65	-1	45	-1	200	65
6	+1	8	-1	0.5	+1	65	-1	45	+1	300	72
7	-1	4	+1	1	+1	65	-1	45	+1	300	71
8	+1	8	+1	1	+1	65	-1	45	-1	200	76
9	-1	4	-1	0.5	-1	55	+1	75	-1	200	71
10	+1	8	-1	0.5	-1	55	+1	75	+1	300	75
11	-1	4	+1	1	-1	55	+1	75	+1	300	68
12	+1	8	+1	1	-1	55	+1	75	-1	200	77
13	-1	4	-1	0.5	+1	65	+1	75	+1	300	73
14	+1	8	-1	0.5	+1	65	+1	75	-1	200	65
15	-1	4	+1	1	+1	65	+1	75	-1	200	69
16	+1	8	+1	1	+1	65	+1	75	+1	300	90
17	-2	2	0	0.75	0	60	0	60	0	250	27
18	+2m	10	0	0.75	0	60	0	60	0	250	44
19	0	6	-2	0.25	0	60	0	60	0	250	73
20	0	6	+2	1.25	0	60	0	60	0	250	91
21	0	6	0	0.75	-2	50	0	60	0	250	80
22	0	6	0	0.75	+2	70	0	60	0	250	89
23	0	6	0	0.75	0	60	-2	30	0	250	77
24	0	6	0	0.75	0	60	+2	90	0	250	90
25	0	6	0	0.75	0	60	0	60	-2	150	80
26	0	6	0	0.75	0	60	0	60	+2	350	86
27	0	6	0	0.75	0	60	0	60	0	250	92
28	0	6	0	0.75	0	60	0	60	0	250	92
29	0	6	0	0.75	0	60	0	60	0	250	92
30	0	6	0	0.75	0	60	0	60	0	250	92
31	0	6	0	0.75	0	60	0	60	0	250	92
32	0	6	0	0.75	0	60	0	60	0	250	92

**Table 7:** Significance of regression coefficients of the yield of FAME produced from used soya oil using design-expert version 12

Source	Mean Square	Degree of freedom	Sum of square	F-value	P-value (Prob>F)
Model	352.62	20	7052.32	152.70	< 0.0001
A	400.17	1	400.17	173.29	< 0.0001
B	280.17	1	280.17	121.32	< 0.0001
C	104.17	1	104.17	45.11	< 0.0001
D	216.00	1	216.00	93.54	< 0.0001
E	60.17	1	60.17	26.05	0.0003

AB	64.00	1	64.00	27.71	0.0003
AC	12.25	1	12.25	5.30	0.0418
AD	9.00	1	9.00	3.90	0.0740
AE	49.00	1	49.00	21.22	0.0008
BC	16.00	1	16.00	6.93	0.0233
BD	2.25	1	2.25	0.9744	0.3448
BE	12.25	1	12.25	5.30	0.0418
CD	25.00	1	25.00	10.83	0.0072
CE	81.00	1	81.00	35.08	< 0.0001
DE	30.25	1	30.25	13.10	0.0040
A <sup>2</sup>	5628.64	1	5628.64	2437.45	< 0.0001
B <sup>2</sup>	145.52	1	145.52	63.01	< 0.0001
C <sup>2</sup>	75.31	1	75.31	32.61	0.0001
D <sup>2</sup>	100.64	1	100.64	43.58	< 0.0001
E <sup>2</sup>	114.68	1	114.68	49.66	< 0.0001

R<sup>2</sup>=0.9964      Predicted R<sup>2</sup>=0.980      Adjusted R<sup>2</sup>=0.909

### G Analysis of variance (ANOVA) for the yield of FAME from used soya oil

The ANOVA results for the model terms are given in Table 7. ANOVA was applied to estimate the significance of the model at 5% significance level. From the p-values presented in the table, it can be stated that all the linear terms A, B, C, D and E, the interaction terms AB, AC, AE, BC, BE, CE, CD, DE and the quadratic terms A<sup>2</sup>, B<sup>2</sup>, C<sup>2</sup>, D<sup>2</sup> and E<sup>2</sup> are significant model terms. Based on this, the insignificant terms of the model AD and BD were removed and the adjusted model obtained for biodiesel produced from used soya oil as a function of the more significant variable is given in Equation 4.

$$Y_{\text{FAME (Used Soya Oil)}} = 91.73 + 4.08A + 3.42B + 2.08C + 3. D + 1.58E + 2AB - 0.875AC + 1.75AE + BC + 0.875BE - 1.25CD + 2.25CE + 1.38DE - 13.85A^2 - 2.23B^2 - 1.6C^2 - 1.850D^2 - 1.98E^2 \quad (4)$$

Also, the adjusted model obtained for FAME produced from used soya oil as a function of the more significant variables in real format, is given in Eq. 5.

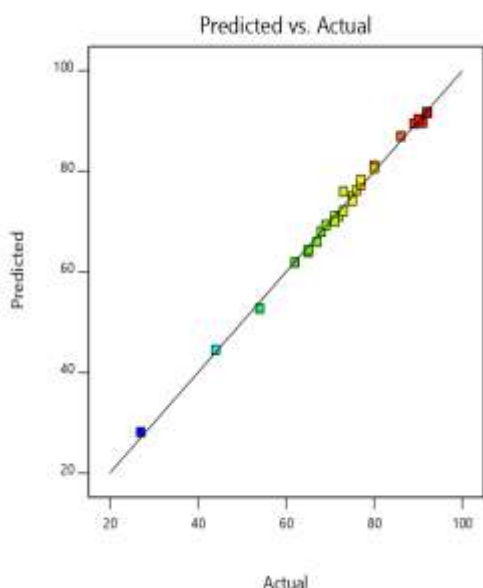
$$Y_{\text{FAME (Used Soya Oil)}} = 91.73 + 4.08\text{methanol oil ratio} + 3.42\text{catalyst conc} + 2.08\text{temperature} + 3\text{time} + 1.58\text{agitation speed} + 2\text{methanol oil ratio} \times \text{catalyst conc} - 0.875\text{methanol oil ratio} \times \text{temperature} + 1.75\text{methanol oil ratio} \times \text{agitation speed} + \text{catalyst conc} \times \text{temperature} + 0.875\text{catalyst conc} \times \text{agitation} - 1.25\text{temperature} \times \text{time} + 2.25\text{temperature} \times \text{agitation speed} + 1.38\text{time} \times \text{agitation speed} - 13.85\text{methanol oil ratio}^2 - 2.23\text{catalyst conc}^2$$

$$-1.6\text{temperature}^2 - 1.850\text{time}^2 - 1.98\text{agitation speed}^2 \quad (5)$$

From Table 7, it was clearly shown that among the five variables studied, methanol/oil molar ratio (A) has the highest effect on the yield of FAME from used soya oil as it has the largest F-test value (173) for single effect followed by the catalyst concentration (121). Agitation speed (E) showed the most insignificant single effect as it has the lowest F-test values.

### H Predicted and experimental or actual values for yield of FAME from used soya oil

Analysis was also carried out on the experimental data in Table 6 to check the correlation between the experimental and predicted FAME yield from used soya oil, the actual and predicted plot is shown in Figures 8. It could be seen that the data points on the plot were linearly distributed, indicating a good correlation between the experimental and predicted values of the response, and the underlying assumptions of the above analysis were appropriate. The result also suggests that the selected quadratic model was proper and adequate in predicting the response variables for the experimental data.



**Figure 8:** Plot of predicted value against the experimental values of FAME from used soya oil.

### I Optimization of Process Parameters of FAME from Used Soya Oil

The optimization of process variables in this study was carried out using design expert version 12. The optimum conditions suggested by the result analysis for maximum FAME yield of 91% within the ranges studied were: methanol to oil molar ratio 7:1, catalyst concentration 1.0%wt, reaction temperature of 65°C, reaction time of 60 minutes and agitation speed 300 rpm. Actual experiment based on the optimum conditions produced 93% yield of FAME with small percentage error of 2.2%. This percentage error of actual values compared to the predicted values indicate that the regression model developed in this study was accurate in representing the overall data and reliable in predicting the yield at any given conditions within the range studied for FAME produced from used soya oil. The validation of results for FAME yeild is as shown in table 8..

**Table 8:** Validation of result for yield of FAME from used soya oil.

Methanol/Oil molar ratio	Catalyst concentration (wt %)	Temperature (°C)	Time (minutes)	Agitation speed (rpm)	Experimental FAME yield (%)	Predicted FAME yield (%)
7:1	1.0	65	60	300	93	91

### J Three dimensional response surface plots for FAME yield from used soya oil.

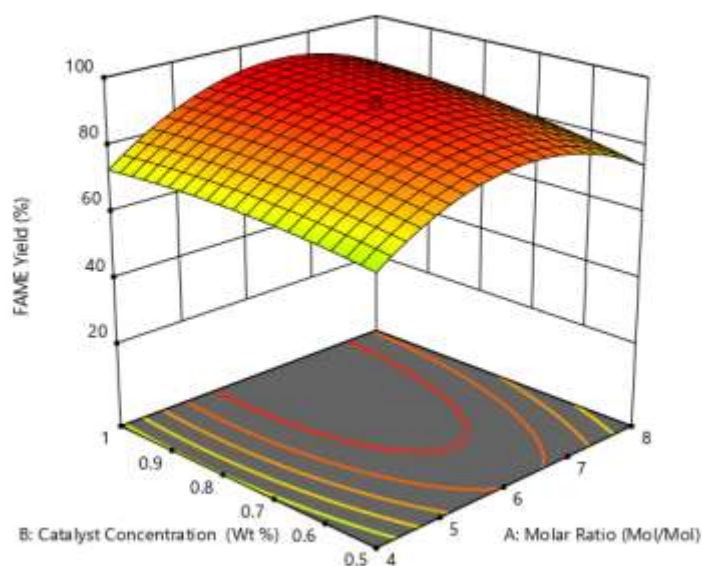
The 3D response surface plots of the different interaction effects were generated to estimate the effect of the combinations of the independent variables on the FAME yield. Figures 9 show that the amount of methyl ester yield increases with methanol to oil molar ratio and catalyst concentration. However, at higher catalyst concentration, a reduction in the yield was observed. This may be attributed to the fact that excess catalyst concentration has negative effect on the yield of FAME from used soya oil. High catalyst concentration encourage formation of soap which hinders and reduces ester formation.

Figures 10 depict the interaction effect between reaction temperature and methanol to oil molar ratio on FAME yield from used soya oil. The figure indicates that the yield of FAME increases with increase in reaction temperature and methanol to oil molar ratio. This is as a result of a positive significant effect of methanol to oil molar ratio and temperature interaction. However, at higher reaction temperature above boiling point of the alcohol used, a decrease in the yield was observed. This may be due to evaporation of methanol at higher temperature, and because the quadratic term of interaction between temperature and methanol to oil molar ratio is more significant with a negative effect.

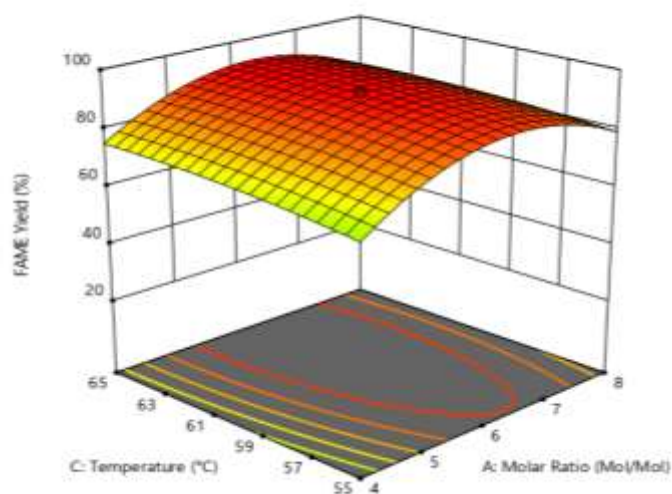
Figures 11 shows the interaction effect between methanol to oil molar ratio and agitation speed on yield of FAME from used soya oil. The figure shows that the FAME yield increases with methanol to oil molar ratio and agitation speed as a result of good homogeneity, good reaction rate and enough alcohol. However, at higher methanol to oil molar and agitation speed a reduction in the yield was observed. This may be due to poor contact between the reacting system, and the fact that the quadratic terms of the two factors are more significant with a negative effect on yield from used soya oil.

Figures 4.12 shows the interaction effect reaction temperature and catalyst concentration on FAME yield from used soya oil. The figure indicated that the yield of FAME increases with reaction temperature and catalyst concentration. This may be as a result of the fact that more rapid reaction rate could be obtained at high temperatures and high catalyst concentration which enhance yield. However, at higher catalyst concentration and reaction temperature above the optimum, a decrease in the yield was observed due to evaporation of

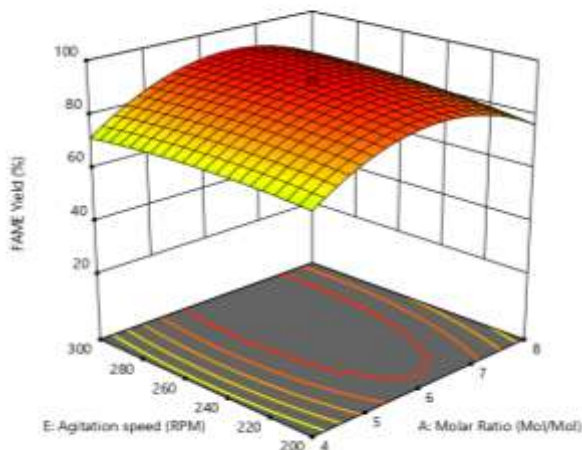
methanol at higher temperature and the fact that the quadratic terms of the two factors are more significant with a negative effect for yield of FAME from used soya oil.



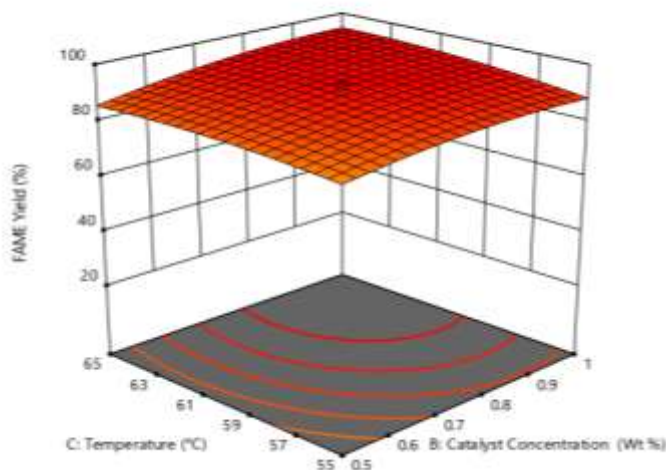
**Figure 9:** 3D response surface plot showing the effect of methanol/oil molar ratio and catalyst concentration on the yield of FAME from used soya oil.



**Figure 10:** 3D response surface plot showing the effect of methanol/oil molar ratio and temperature on the yield of FAME from used soya oil.



**Figure 4.11:** 3D response surface plot showing the effect of methanol to oil molar ratio and agitation speed on the yield of FAME from used soya oil.



**Figure 12:** 3D response surface plot showing the effect of temperature and catalyst concentration on the yield of FAME from used soya oil.

#### IV. CONCLUSION

Adequate pretreatment of used soya oil yielded biodiesel of standard. The properties of the used soya oil biodiesel produced are within the ASTM standards which closely approximate that of the diesel and even in some respects superior. The cetane number and the flash point for instance are

higher than that of diesel. By the use of optimal condition established in this work, that is methanol oil molar ratio 7:1, catalyst concentration 1% wt, reaction temperature 65°C, reaction time 60 minutes and agitation speed 300 rpm, an optimal used soya oil biodiesel yield of 91% was obtained.

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