

Production, Characterization and Optimization of Biodiesel from Gmelina Seed Oil

Umezuegbu J. C., Ezennajiego E.E., Onukwuli O. D.

Abstract— Among the various alternatives for fossil fuel, biodiesel is emerging as a promising choice for compression ignition engine due to its renewable nature and superior emission characteristics. This research work focused on the production, characterization and optimization of gmelina seed oil fatty acid methyl ester (GSOFAME). Solvent extraction was employed for extraction of oil from gmelina seed. The oil was characterized based on American Society for Testing and Materials (ASTM) method. The fatty acid profile of gmelina seed oil (GSO) 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 GSOFAME was investigated using one factor at a time method. The oil was pretreated to reduce the free fatty acid below 1% and then transesterified using methanol in the presence of potassium hydroxide catalyst. The fuel properties of the GSOFAME produced were determined based on ASTM standards. Optimization of gmelina seed oil biodiesel was carried out using response surface methodology. The physicochemical properties of the oil for density, free fatty acid, saponification value, iodine value, flash point, pour point, moisture content gave the values of, 896kg/m³, 2.04%, 181.31mgKOH/g, 64.12gI₂/100g, 2400C, 20C, 4%, respectively. The fatty acid profile of GSO consist of saturated fatty acids; lauric acid 15.05%, myristic acid 5.85%, palmitic acid 54.94% and stearic acid 4.57% and unsaturated fatty acids; oleic acid 8.4%, linoleic acid 1.98%, and linolenic acid 8.9%. The main constituent functional groups of GSO are alkene group, hydroxyl group, carboxylic group, alkyne group, amine group etc. The process parameters of methanol to oil molar ratio, catalyst concentration, reaction temperature and reaction time immensely affected the biodiesel yield as their increase resulted in the increase of biodiesel yield until an optimum value was attained when the yield started decreasing. The fuel properties of the GSOFAME which is within the ASTM standards were determined as acid value 0.5mgKOH/g, density 874.1mm²/s, flash point 5%, cetane number 64.2, calorific value 38.33MJ/Kg, pour point 30C, iodine value 34.2gI₂/100g. The use of quadratic regression model from design expert version 12.0 for response surface methodology (RSM) showed optimal biodiesel yield of 91.5% at the optimum reaction conditions of methanol to oil molar ratio 9:1, catalyst concentration 1%wt, reaction temperature 500C, and reaction time 65 minutes.

Index Terms— characterization, gmelina seed oil, optimization, transesterification.

I. INTRODUCTION

The world energy demand is soaring by day as a result of rapid population increase and high spate of industrialization. The sources of world energy needs are petroleum, coal and natural gas, all of which are fossil-derived and non-renewable. Burning of the fossil fuels causes environmental concerns such as emission of green house gases (GNG) which is the major substance responsible for climate change. Other hazardous substances released by burning of fossil fuels include sulphur oxides(SO_x), nitrogen oxides(NO_x) and methane [1]. 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 emission [2]. 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, price, production and availability of these oils. Consequently this has ignited research into the use of non-edible oil for biodiesel synthesis

Biodiesel, a mono-alkyl ester of long chain fatty acid has properties that approximate that of diesel with added advantages of high lubricity, high cetane number and been highly biodegradable. It is a promising nontoxic alternative fuel used in the transport sector. Biodiesel is produced by the reaction of fat with monohydric alcohol. Various processes have been adopted for biodiesel production from vegetable oil and animal fat, namely; micro-emulsion with alcohol, catalytic cracking, pyrolysis and transesterification [3, 4, 5, 6]. Among these methods, transesterification is the key and the most important process for production of a cleaner and environmentally safe biodiesel [7, 8]. Transesterification means conversion of one type of ester to another. During transesterification a basic catalyst breaks the fatty acids from the glycerine one by one. If an alcohol typically methanol contacts a fatty acid, it will bond and form biodiesel [9].

The source of oil feedstock gmelina arborea is a big forest tree popular for its wood used for making furniture and as building materials. It is a fast growing tree which grows to about 40m in height. The tree is commonly planted as a garden and an avenue tree. The fruit contains very little kernel that is rich in oil, containing 53% by weight of oil [10]. This seeds are usually neglected and underutilized thereby serving no commercial purpose. The research work deals with the

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synthesis of gmelina seed oil fatty acid methyl ester (GSOFAME) by transesterification with methanol in the presence of potassium hydroxide catalyst. Optimization of GSOFAME was also carried out using response surface methodology of central composite design (CCD), in order to determine the optimum reaction conditions for biodiesel production. The four processing factors, reaction temperature, reaction time, catalyst concentration and methanol to oil molar ratio 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

Gmelina seeds as picked from the plantation (plate 2.1), reagents, glass wares, equipments including gas chromatography mass spectrometer (GC-MS), Fourier transform infrared spectroscopy (FTIR), viscometer, magnetic hot plate, soxhlet extractor. design expert software version 12.0 etc.

B. Sample preparation

The collected gmelina seeds were left for the pulp to start rotting when the seeds were de-pulped. The depulped seeds were then air dried for 7 days, and this was followed by oven drying at 40°C for 6 hours for 5 consecutive days, so as to obtain moisture free seed samples. After oven drying, the seeds were ground with a mechanical grinder.



Plate 2.1: Gmelina seeds

C. Extraction of oil from gmelina seed

Solvent extraction was used to extract the oil from the seeds. 5kg of the dried, ground seed was measured into a plastic container containing 3 liters of n-hexane. The mixed content of the container were vigorously shaken after covering the container. The container was made air tight to prevent evaporation of the hexane and then kept to macerate for a day. Then the dissolved oil in hexane was decanted and the slurry filtered. The filtrate was then distilled to recover the n-hexane at 65°C [11]. The percentage oil yield was calculated thus,

$$\% \text{ oil yield} = \text{wt of oil extracted} + \text{wt of seed sample} \times 100 \quad (1)$$

D. Characterization of gmelina seed oil

The physiochemical properties of the oil extracted from gmelina seed was characterized based on American Society for Testing and 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.

E. Effect of process parameters on biodiesel yield

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

F. Pretreatment of the Oil Extracted.

A pre-treatment procedure was performed on the extracted gmelina oils as its free fatty acid (FFA) is in excess of 1%. The FFA was reduced below 1.% using methanol and concentrated sulphuric acid as catalyst prior to transesterification reaction.

The oil samples 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 a 150 ml 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 mixture components were carefully separated by removing the water first, followed by the oil and finally the methanol. Hot distilled water was poured into the oil, shaken and allowed to stand. This was done to wash the esterified oils. After a while, 2 layers were observed; water (below) and oil (above). The water was tapped off from the separating funnel .The pre-treated oil was poured into 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 the transesterification process [12].

G. Transesterification reaction

The oil will react with methanol in the presence of potassium hydroxide (KOH) to produce methyl esters of fatty acids (biodiesel) and glycerol.

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 mixture (KOH) 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 funnel 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.

H. Biodiesel purification

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 [13]. Such traces of methanol is soluble in water and therefore is removed by wet washing. A drop of 1M sulphuric acid was added to the biodiesel in a separating funnel. Hot distilled water was as well added and the mixture vigorously shaken. The mixture was allowed to settle when it separates into two, the upper layer consisting of the biodiesel and the lower layer consisting of water and water soluble impurities.

The water was discarded and tested with three drops of phenolphthalein indicator. Washing was continued until the waste water was bright and does not turn pink when tested with phenolphthalein. The washed sample was dried by heating at 105⁰C on a laboratory hot plate until all residual water molecules is evaporated. The percentage biodiesel yield is given by the expression,

$$\% \text{ biodiesel yield} = \text{Volume of biodiesel produced} \div \text{volume of oil used} \times 100 \quad (2)$$

I. Determination of the fuel properties of the Gmelina seed oil biodiesel

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 and flash point.

J. Optimization of the biodiesel produced

Design of experiment and optimization of the reaction conditions were carried out using design expert software version 12.0. The experimental design employed is two-level four factor fractional factorial design including 30 experiments. The independent factors involved are methanol to oil molar ratio, catalyst concentration, reaction temperature and reaction time, while the dependent factor or response was

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

Independent variable	Units	+α	High level	Mid-range	Low level	- α
Reaction time	Min	102.5	90	65	40	27.5
Temperature	⁰ C	65	60	50	40	35
Catalyst conc.	Wt%	1.75	1.5	1	0.5	0.25
Methanol/Oil ratio	mol/mol	10.5	9	6	3	1.5

Table 2: Experimental design matrix for transesterification of GSO (coded values)

Std	Reaction time	Temperature	Catalyst Concentration	Methanol ratio
1	-1	-1	-1	-1
2	1	-1	-1	-1
3	-1	1	-1	-1
4	1	1	-1	-1
5	-1	-1	1	-1
6	1	-1	1	-1
7	-1	1	1	-1
8	1	1	1	-1
9	-1	-1	-1	1
10	1	-1	-1	1
11	-1	1	-1	1
12	1	1	-1	1
13	-1	-1	1	1
14	1	-1	1	1
15	-1	1	1	1
16	1	1	1	1
17	-α	0	0	0
18	+α	0	0	0
19	0	- α	0	0
20	0	+α	0	0
21	0	0	- α	0
22	0	0	+α	0
23	0	0	0	- α
24	0	0	0	+α
25	0	0	0	0
26	0	0	0	0
27	0	0	0	0

28	0	0	0	0
29	0	0	0	0
30	0	0	0	0

Table 3: Experimental design matrix for transesterification of GSO(uncoded values)

Std	Run	Reaction time	Temperature	Catalyst conc.	Methanol ratio	Yield
1	18	40.00	40.00	0.50	3.00	
2	13	90.00	40.00	0.50	3.00	
3	30	40.00	60.00	0.50	3.00	
4	25	90.00	60.00	0.50	3.00	
5	8	40.00	40.00	1.50	3.00	
6	10	90.00	40.00	1.50	3.00	
7	1	40.00	60.00	1.50	3.00	
8	22	90.00	60.00	1.50	3.00	
9	14	40.00	40.00	0.50	9.00	
10	2	90.00	40.00	0.50	9.00	
11	23	40.00	60.00	0.50	9.00	
12	21	90.00	60.00	0.50	9.00	
13	20	40.00	40.00	1.50	9.00	
14	12	90.00	40.00	1.50	9.00	
15	16	40.00	60.00	1.50	9.00	
16	3	90.00	60.00	1.50	9.00	
17	26	27.50	50.00	1.00	6.00	
18	9	102.50	50.00	1.00	6.00	
19	28	65.00	35.00	1.00	6.00	
20	19	65.00	65.00	1.00	6.00	
21	4	65.00	50.00	0.25	6.00	
22	15	65.00	50.00	1.75	6.00	
23	6	65.00	50.00	1.00	1.50	
24	11	65.00	50.00	1.00	10.50	
25	7	65.00	50.00	1.00	6.00	
26	27	65.00	50.00	1.00	6.00	
27	17	65.00	50.00	1.00	6.00	
28	5	65.00	50.00	1.00	6.00	
29	29	65.00	50.00	1.00	6.00	
30	24	65.00	50.00	1.00	6.00	

percentage biodiesel yield obtained by transesterification of the gmelina oil. The level of factors of the independent variables are given in table 1. The experimental design matrix for transesterification of gmelina seed oil are in coded and un-coded forms as shown in tables 2 and 3 respectively. Alpha (α) is defined as a distance from the center point which can be either inside or outside the range, with the maximum

$$Y = \beta_0 + \sum_{i=1}^4 \beta_i X_i + \sum_{i=1}^4 \sum_{j=i+1}^4 \beta_{ij} X_i X_j + \sum_{i=1}^4 \beta_{ii} X_i^2 \quad (3)$$

Where Y is the predicted yield of biodiesel (%), X_i and X_j represent the transesterification process variables, β_0 is the offset term, β_i is the coefficient of linear (single) effect, β_{ij} is the coefficient of interaction effect and β_{ii} is the coefficient of quadratic effect.

III. RESULTS AND DISCUSSION

A. Physiochemical properties of GSO

value of $2^{n/4}$, where n is the number of factors [14]. It is noteworthy to point out that the software uses the concept of the coded values for 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 2.3

The summary of the characteristics of GSO are as shown in table 4. From the table, it could be seen that the fatty acid and therefore free fatty acid of gmelina seed oil are relatively low. However the free fatty acid and the moisture content of the oil are in excess of 1%, a condition required for high yield of biodiesel by alkali catalyzed transesterification.

Oil of free fatty acid and moisture content in excess of 1% has the tendency for soap formation, inhibition of glycerol separation from biodiesel and therefore retardation of biodiesel production. The oil is rather pretreated or esterified before being transesterified. Again oil of high moisture content is prone to oxidation. The kinematic viscosity and the density of the oil are higher than that of the biodiesel

produced from it and much higher than that of diesel. 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 [15]. Iodine value, a measure of degree of un-saturation of the oil obtained is below 100gI₂/100g oil, indicative of the oil being nondrying and therefore suitable for biodiesel production. High iodine value of the oil corresponds to high degree of unsaturation of the fatty acid in

the triglyceride, and if heated, such an oil is prone to thermal oxidation and polymerization of the triglyceride causing formation of deposits. The cloud and pour point of 9^oC and 2^oC respectively determined for the seed oil are relatively high and unsuitable for operation and handling during cold weather. Peroxide value, an index of rancidity obtained as 9meq/kg was high and indicative of poor resistance of the oil to peroxidation during storage and handling.

Table 4: Physiochemical properties of gmelina seed oil

Properties	Unit	GSO
Acid value	mgKOH/g	3.08
Free fatty acid	%	1.54
Saponification value	mgKOH/g	181.31
Iodine value	(gI ₂ /100g oil)	64.12
Peroxide value	meq/kg	9
Kinematic viscosity	mm ² /s	36.4
Fire point	^o C	292
Flash point	^o C	240
Cloud point	^o C	9
Pour point	^o C	2
Refractive index		1.441
Specific gravity		0.896
Moisture content	%	4
Density	Kg/m ³	896

B. Fatty acid profile of gmelina seed oil

The Fatty acid profile of gmelina seed oil was determined using GC-MS analysis. The individual peaks of the gas chromatogram were identified as shown in figure 1. The relative percentage of fatty acids were calculated from total ion chromatography by computerized integrator and results are presented in the table 5. The saturated fatty acid constituents of the oil were identified as palmitic acid (C16:0) 54.94%, lauric acid (C12:0). 15.05%, myristic acid (C14:0) 5.85% and stearic acid (C18:0) 4.57%.. The mono-, di-, and tri-unsaturated fatty acid constituents of the oil are oleic acid (C18:1) 8.4%, linoleic acid (C18:2) 1.98%, and linolenic acid (C18:3) 8.9% respectively.

C. Fourier transform infrared (FTIR) spectra analysis of gmelina seed oil

The fourier transform infrared spectra of gmelina seed oil

was analysed using fourier transform infrared spectroscopy (M530 Buck scientific FTIR). This analysis was carried out in order to detect the various functional groups contained in the oil.. Figure 2 Shows the FTIR spectrum of gmelina seed oil. Table 6. represent the functional group and its compositional analysis. The strong absorbance peaks at 3033cm⁻¹ and 3293 cm⁻¹ both represent OH stretch showing the presence of carboxylic and hydroxyl group respectively. The OH stretching at 3464 and 3598 cm⁻¹ depicts the presence of alcohol. The C≡N stretch at 2239 cm⁻¹ showed the presence of Alkyne. The bending vibration of OH (alcohols) were evident at 1314 and 1354 cm⁻¹.The presence of alkenes and conjugated alkenes with bending and stretch vibrations were determined by vibrations and peak values at 838 and 1612 cm⁻¹

Table 5: Summary of Fatty Acid Profile of GSO

Components Common Name	Systematic Name	Structural Formulas	Concentration (%)
Lauric Acid C12	Dodecanoic	CH ₃ (CH ₂) ₁₀ cooh	15.05
Myristic Acid C14	tetradecanoic	CH ₃ (CH ₂) ₁₂ COOH	5.85
Palmitic acid C16	Hexadecanoic acid	CH ₃ (CH ₂) ₁₄ COOH	54.94
Stearic acid C18	Octadecanoic	CH ₃ (CH ₂) ₁₆ COOH	4.57
Oleic Acid C18:1	Cis-9- Octadecenoic acid	C ₉ H ₁₈ =C ₈ H ₁₅ COOH	8.4
Linoleic Acid C18:2	Octadeca-9, 12-Dienoic Acid	C ₆ H ₁₂ =C ₃ H ₄ =C ₇ H ₁₄ COOH	1.98

α Linolenic acid C18:3
 Octadeca-9, 12,15
 Trienoic Acid $C_3H_6=C_3H_4=C_3H_4=C_8H_{15}COOH$ 8.9

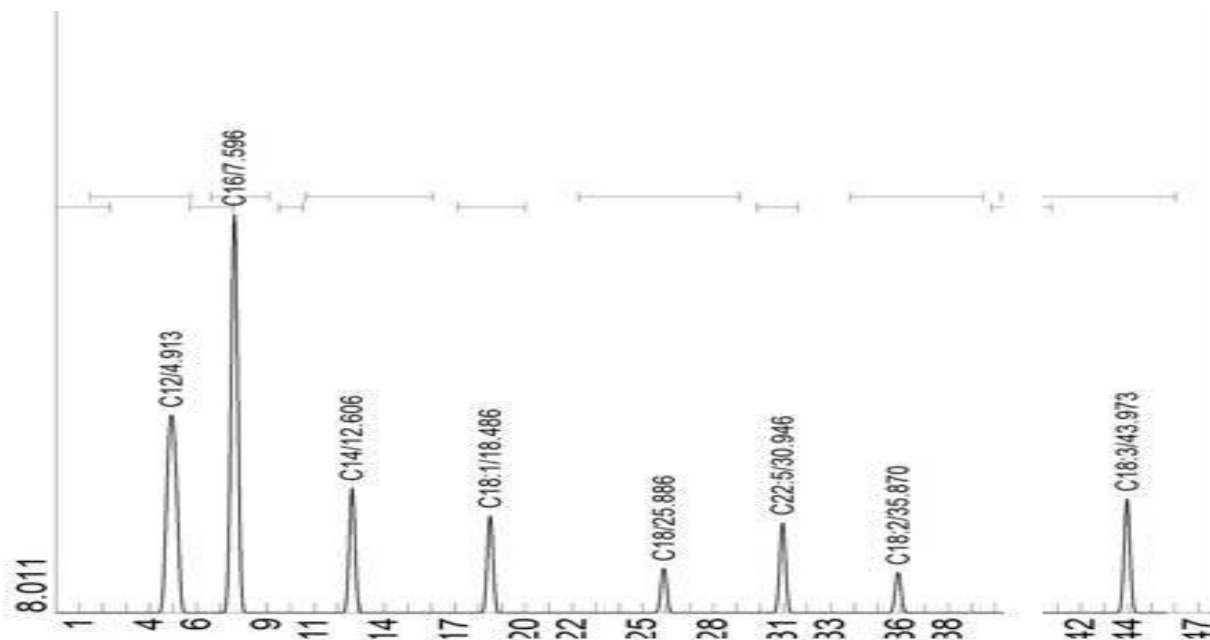


Fig1: GC-MS plot of Gmelina Seed Oil

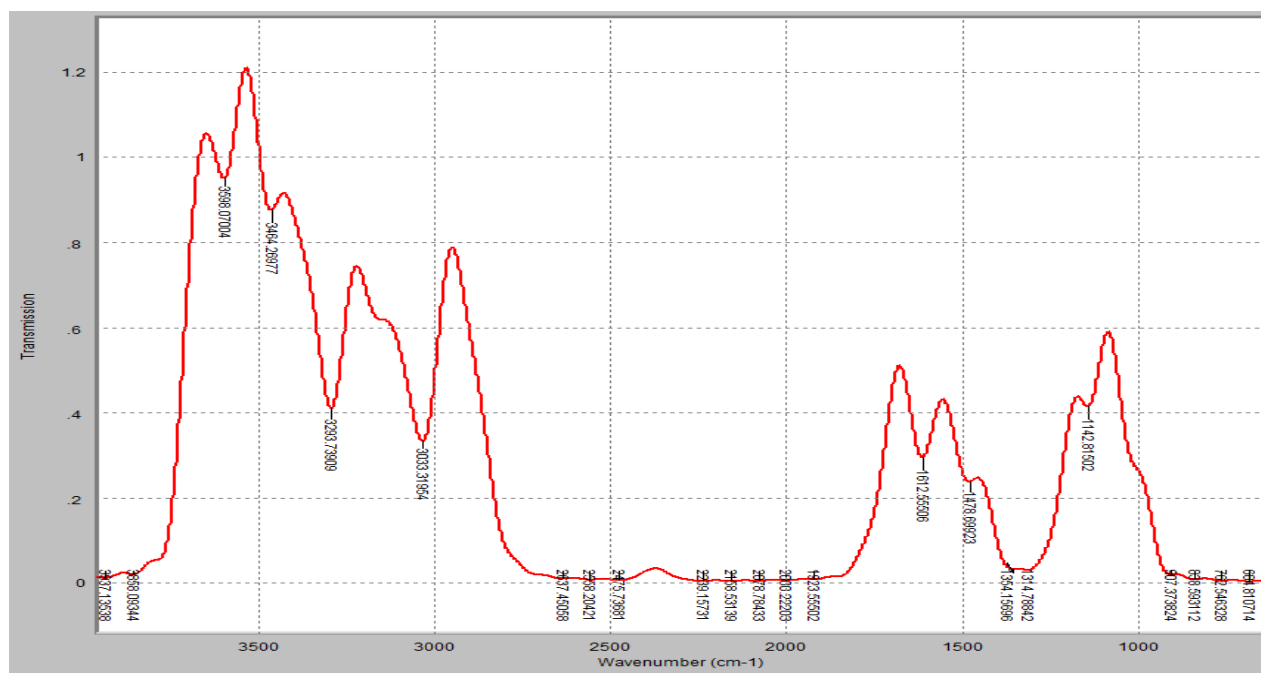


Fig 2 FTIR Spectra of gmelina seed oil

Table 6: FTIR functional group frequencies of GSO

Frequency wave number (cm ⁻¹)	Types of Vibration	Functional Group
838.5931	Bending	C=C (Alkene)
1142.815	Stretch	C-N (Amine)
1314.788	Bending	O-H Alcohol
1354.157	Bending	O-H (Alcohol)
1612.555	Stretch	C=C (conjugated alkene)
2000.222	Bending	c-H (Aromatic compounds)
2239.157	Stretch	C≡N (Alkyne)
2558.204	Stretch	O-H (Thiol)
3033.32	Stretch	O-H (Carboxylic group)

3293.739
 3464.27
 3598.093

Stretch
 Stretch
 Stretch

0-H (Hydroxyl group)
 0-H (alcohol)
 0-H (alcohol)

Effect of Process Parameters on gmlina seed oil biodiesel yield

Effect of methanol to oil molar ratio on GSOFAME yield

The effect of methanol to oil molar ratio is shown in figure 3 which reveals that GSOFAME yield increased with increase of methanol to oil molar ratio until a maximum yield was attained at 9:1 ratio when the yield started decreasing. The decrease in yield beyond the optimal methanol to oil molar ratio of 9:1 is attributed to the fact that while the increase in methanol to oil molar ratio favours 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 [16,17]. Again it has been 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 [18].

Effect of catalyst Concentration on GSOFAME yield

The effect of catalyst concentration on the biodiesel yield is depicted in figure 4. The biodiesel yield increased with increase in catalyst concentration and reached a maximum value at catalyst concentration of 1% when the yield started to decrease. The decrease in yield beyond the optimal catalyst concentration results as the excess catalyst react with the triglyceride to form soap which hinders effective dispersion and mixing of the reaction mixture and retards the separation of glycerol from biodiesel and thus giving rise to reduction of

biodiesel production. This is in conformity with the findings of [19].

Effect of reaction temperature on GSOFAME yield

Gmlina seed oil biodiesel yield increased with increase in temperature until the maximum value was attained at 65°C when the yield starts to decrease. This is shown in figure 5. The decrease in biodiesel yield beyond the optimum temperature of 65°C results because below the boiling point of methanol (65°C) production of biodiesel is favoured but beyond the optimum temperature of 65°C most of the methanol is lost by evaporation, leaving a reaction mixture with higher concentration of catalyst that favour soap formation. The formation of soap retards proper dispersion and mixing of the reaction mixture and hinders separation of glycerol from biodiesel and thus reduced the ester yield. This trend conforms with the findings of [5].

Effect of reaction time on GSOFAME yield

The effect of reaction time on the yield of gmlina seed oil biodiesel is shown on figure 6. The yield of the biodiesel increased with increase in reaction time and attained a maximum value at the reaction time of 60 minutes when it started decreasing. The decrease of biodiesel yield beyond the optimum reaction time of 60 minutes may be attributed to the reversal nature of transesterification reaction. For the process conditions used, the forward reaction leading to ester formation is favored below 60 minutes while the reverse condition leading to ester depletion is favoured at reaction time beyond 60 minutes.

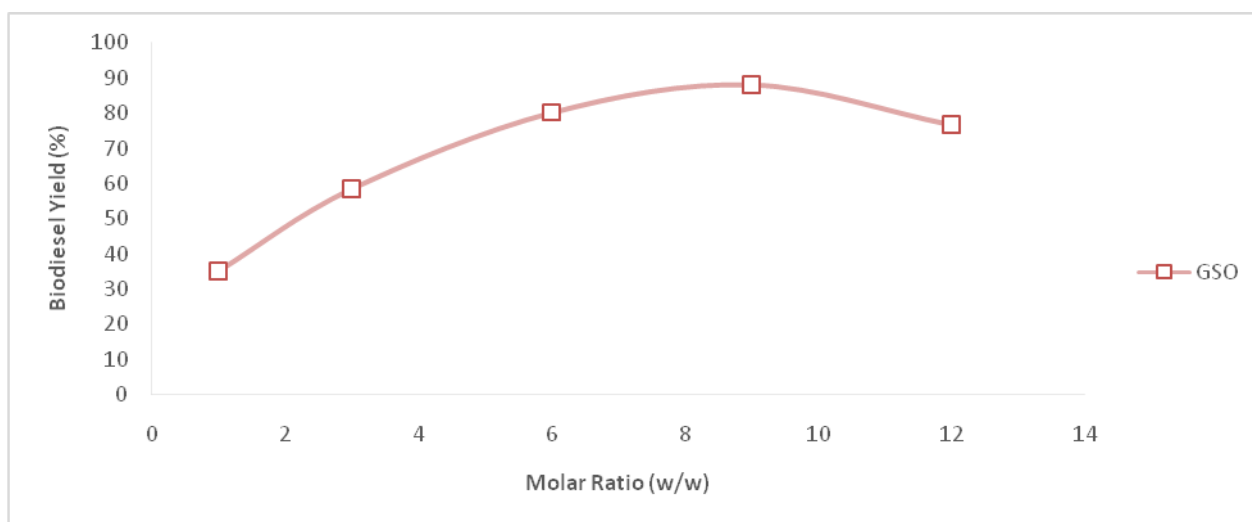


Fig 3: Effect of methanol to oil molar ratio on GSOFAME

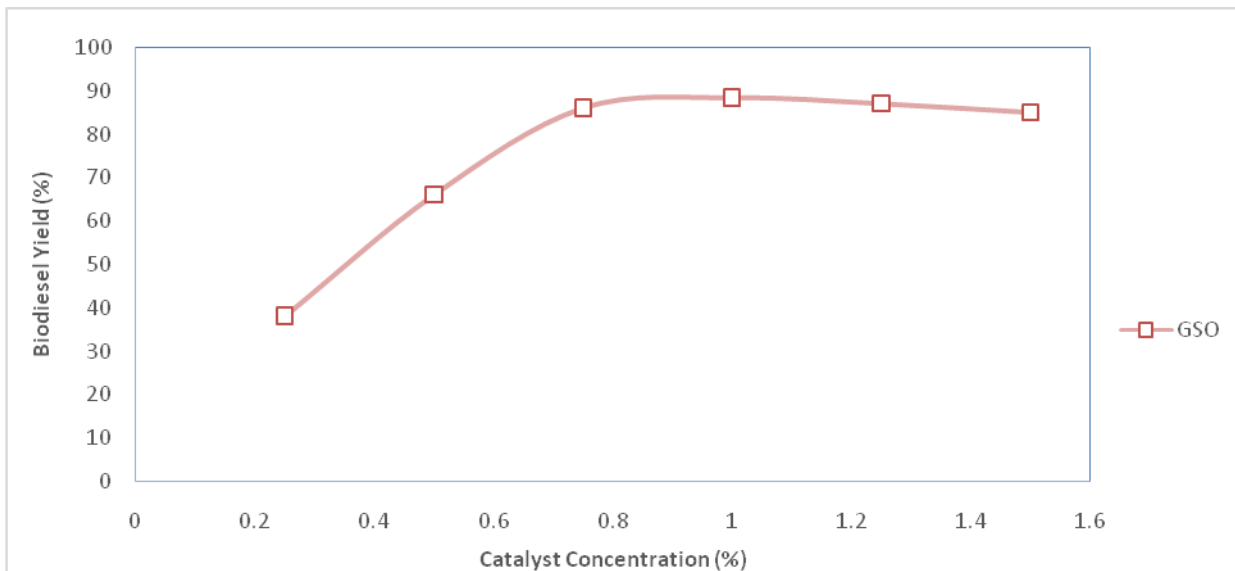


Fig 4: Effect of Catalyst Concentration on GSO FAME Yield

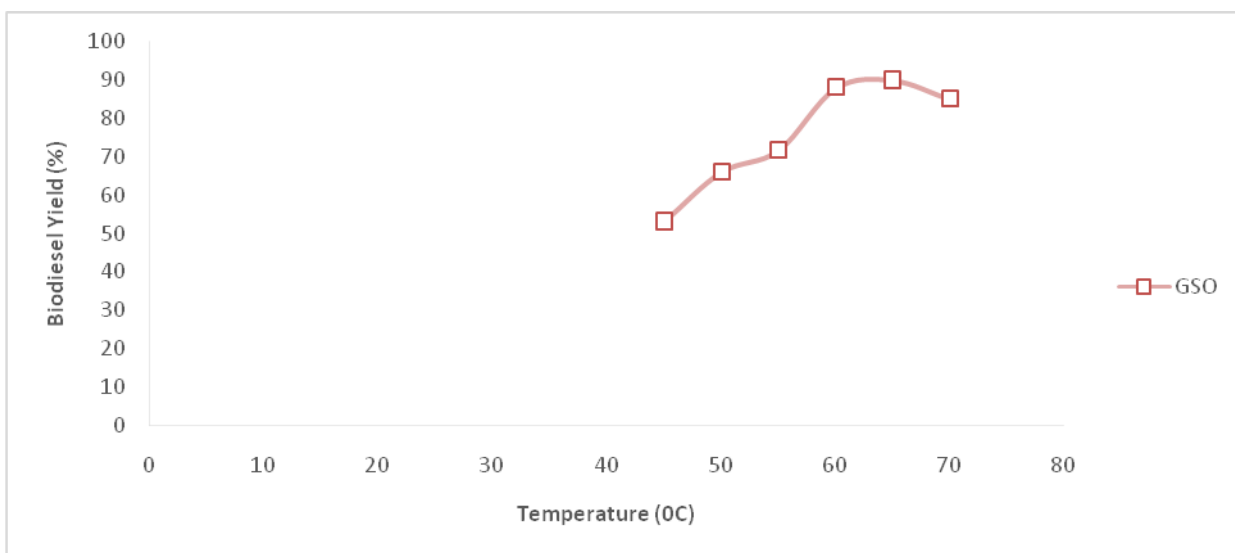


Fig 5: Effect of reaction temperature on GSO FAME yield

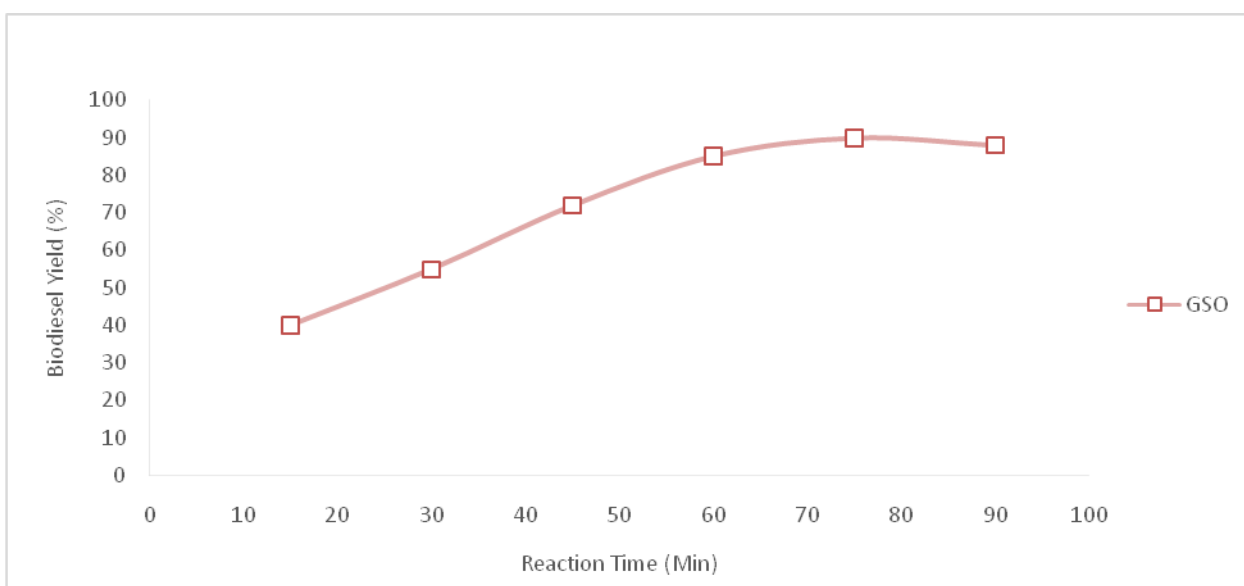


Fig 6: Effect of reaction time on GSO FAME yield

E. Fuel properties of gmelina seed oil biodiesel

The fuel properties of GSO FAME produced are given in table 7. Biodiesel generally has a higher density than

petro-diesel. This has a significant impact on fuel consumption as the fuel introduced into the combustion chamber is determined on volume basis. The density of the

biodiesel was evaluated to be 874kg/m³ which is within the ASTM limit for biodiesel. The biodiesel density is however lower than that of the oil from which it was derived. This underscores the essence of transesterification in reducing the density of oil to a level where it could be properly atomized in the engine in order to exhibit good combustion characteristics.

The kinematic viscosity of the biodiesel produced was evaluated as 4.794mm²/s and is therefore within the ASTM limit. High kinematic viscosity of biodiesel result in poor atomization and incomplete combustion which give rise to cocking of injector tips and hence engine power loss. This conforms with the findings of [20]. The viscosity of biodiesel is typically higher than that of diesel [21]. On the other hand very low viscosity fuel produces very subtle spray which cannot properly get into the combustion cylinder, thus forming a fuel rich zone that give rise to soot formation [22,23].

Flash point measures the degree of flammability of the fuel. The ASTM standard for flash point is $\geq 1300^{\circ}\text{C}$. However during biodiesel production and purification, some traces of methanol may remain in the fuel making the flash point to be less than 1300°C and thus making it flammable and dangerous to handle or store. The flash point of the GSOFAME is 1540°C and thus is within the ASTM standards which make it safe for handling and storage. Cetane number serves as a measure of ignition quality of the fuel. Fuels with low cetane number shows an increase in emission due to incomplete combustion. The higher the cetane number the better the fuel burns in the combustion chamber of the engine. Since biodiesel is composed of long chain hydrocarbon groups with virtually no branching or aromatic structure, it typically has higher cetane number than petro-diesel [21]. The ASTM lower limit for cetane number is 47. The cetane number of the GSOFAME is 62.69. Thus it is within the ASTM standards and therefore of good ignition quality. Calorific value which is an important property for measuring the energy content of the fuel suggest the suitability of GSOFAME as an alternative to petro-diesel as its determined calorific value of 38.2MJ/Kg approximate that of diesel of 44.34MJ/Kg. The lower calorific value of a methyl ester is usually attributed to the presence of oxygen in the ester.

Cloud point and pour point are cold flow properties which indicate the ease of handling and storage during cold weather. Cloud point which is the temperature of first appearance of waxlike material on cooling the biodiesel was determined as 50°C . Pour point which is the lowest temperature at which the fuel will still pour was obtained as 30°C . The cloud point and the pour point of the biodiesel are not sufficiently low and therefore might give rise to handling and storage problems during cold weather especially in the temperate and cold regions. However this problem could be overcome by the use of cloud point and pour point depressants or by blending with diesel [24].

Table 7: Fuel properties of GSOFAME

Properties	Unit	GSOFAME	ASTM Standards
Acid value	mgKOH/g	0.23	0.50
Density	Kg/m ³	874	860-900
Kinematic viscosity at 40 ^o C	mm ² s ⁻¹	4.794	1.9-6
Fire point	^o C	195	197
Flash point	^o C	178	100-170
Cloud point	^o C	5	-3-15
Cetane number		64.2	48-65
Refractive index		1.4500	1.38
Specific gravity	Kgm ⁻³	0.874	0.860-0.900
Calorific value	MJ/Kg	38.33	42.06
Pour point	^o C	3	0.5
Iodine value	gI ₂ /100g oil	34.2	42-46

Statistical analysis of transesterification using central composite design (CCD)

To optimize transesterification of melina seed 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 four different factors; catalyst concentration, methanol/oil molar ratio, reaction temperature, and reaction time on biodiesel yield and derive a model, a two-level- four-factor (2^{4-1} + 2*4 + 6) central composite response design = 30 experiments were performed. The factors levels are shown in Table 2. The matrix for the four 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 4 and 5 represent the mathematical model relating the transesterification reaction of melina seed oil with the independent process variables obtained with the design expert version 12.0. The design of the experimental matrix of transesterification of melina seed oil with the experimental values of the biodiesel yield are presented in Tables 8. The design plan as shown in Table 8 was used to predict the optimum biodiesel yield and the values of optimum variables as presented in table 9. The coded and un-coded values of the test variables were used to optimize the variables namely catalyst concentration, methanol/oil molar ratio, reaction temperature and reaction time. The experimental values of percentage yield were presented in Table 9. The empirical relationship between yield (Y) and the four variables in coded values obtained by using the statistical package design-expert version 12.0 for determining the levels of factors which gives optimum percentage yield is given by equation 4, a quadratic regression equation that fitted the data:

$$\text{Biodiesel yield (GSO)} = +84.85+4.63A+4.68B+4.00C+7.39D-2.00AB-1.87AC-0.8750AD-1.37BC-0.3750BD-3.50CD-1.72A^2-4.83B^2-0.8297C^2-3.27D^2 \quad (4)$$

Equation 4 suggested that the yield of FAME has linear and quadratic effects on the four variables studied. Coefficients with one factor represent the single effect of that particular factor while 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 coefficient of determination, $R^2 = 0.9541$ is reasonable, and the predicted R^2 of 0.8260 is in a reasonable agreement with the adjusted R^2 of 0.9111. This test result is shown in Table 10.

$$Y_{GSO} = +84.85+4.63A+4.68B+4.00C+7.39D-2.00AB-1.87AC-3.50CD-1.72A^2-4.83B^2-3.27D^2 \quad (5)$$

H. Predicted versus actual yield of GSO FAME

The plots of predicted versus actual yield of GSO FAME is given in figure 7. The plot is used to check whether the points will follow a straight line in which case we conclude that the residuals follow a normal distribution. From figure 7, it could be seen that the points were closely distributed to the straight line of the plot, it confirms the good relationship between the experimental values and the predicted values of the response. This plots equally confirm that the selected model was adequate in predicting the response variables in the experimental values.

I. Optimization of process parameters of GSO FAME

The optimization of process variables in this study was

G. Analysis of variance (ANOVA) for optimization of GSO FAME

The ANOVA results for the model terms are given in Table 10. ANOVA was applied to estimate the significance of the model at 5% significance level as shown in the Table. A model is considered significant if the p-value (significance probability value) is less than 0.05. From the ANOVA table 3.5 it can be stated that the linear, interactive and quadratic terms A, B, C, D, AB, AC, CD, A^2 , B^2 , D^2 are the significant terms for GSO transesterification. Therefore, eliminating the insignificant terms the final model equation becomes as expressed in equation 5 below

carried out using design expert version 12.0. The optimum conditions suggested by the result analysis for maximum GSO FAME yield of 90.23% within the ranges studied were: methanol/oil molar ratio 6:1, catalyst concentration 1.0%wt, reaction temperature of 500C, reaction time of 65 minutes. Actual experiment based on the optimum conditions produced 91.5% yield of GSO FAME. The small percent error difference between the predicted and actual yield of 1.41% indicates 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 gmelina seed oil.

Table 8: Optimization results for biodiesel yield of GSO

Std	A:Time Min	B:Temperature °C	C:Catalyst conc Wt%	D:Methanol Mol/Mol	Biodiesel yield %
1	40	40	0.5	3	41
2	90	40	0.5	3	66
3	40	60	0.5	3	65
4	90	60	0.5	3	67
5	40	40	1.5	3	66
6	90	40	1.5	3	78
7	40	60	1.5	3	75
8	90	60	1.5	3	80
9	40	40	0.5	9	71
10	90	40	0.5	9	83
11	40	60	0.5	9	80
12	90	60	0.5	9	86
13	40	40	1.5	9	78
14	90	40	1.5	9	82
15	40	60	1.5	9	85
16	90	60	1.5	9	86
17	27.5	50	1	6	72
18	102.5	50	1	6	86
19	65	35	1	6	62
20	65	65	1	6	82
21	65	50	0.25	6	75
22	65	50	1.75	6	87
23	65	50	1	1.5	65
24	65	50	1	10.5	86
25	65	50	1	6	91
26	65	50	1	6	91
27	65	50	1	6	91

28	65	50	1	6	91
29	65	50	1	6	91
30	65	50	1	6	91

Table 9: Actual and Predicted values of the yield of biodiesel from GSO

Std	Time (Min)	Temperature (°C)	Catalyst concentration (Wt. %)	Methanol (mol/mol)	Actual Yield (%)	Predicted Yield
1	40	40	0.5	3	41	40.22
2	90	40	0.5	3	66	66.88
3	40	60	0.5	3	65	62.14
4	90	60	0.5	3	67	68.65
5	40	40	1.5	3	66	64.27
6	90	40	1.5	3	78	79.67
7	40	60	1.5	3	75	74.56
8	90	60	1.5	3	80	80.02
9	40	40	0.5	9	71	70.43
10	90	40	0.5	9	83	82.11
11	40	60	0.5	9	80	80.89
12	90	60	0.5	9	86	88.24
13	40	40	1.5	9	78	76.13
14	90	40	1.5	9	82	81.02
15	40	60	1.5	9	85	83.77
16	90	60	1.5	9	86	86.80
17	27.5	50	1	6	72	70.56
18	102.5	50	1	6	86	86.88
19	65	35	1	6	62	64.22
20	65	65	1	6	82	80.77
21	65	50	0.25	6	75	76.35
22	65	50	1.75	6	87	85.67
23	65	50	1	1.5	65	65.12
24	65	50	1	10.5	86	84.56
25	65	50	1	6	91	90.23
26	65	50	1	6	91	90.23
27	65	50	1	6	91	90.23
28	65	50	1	6	91	90.23
29	65	50	1	6	91	90.23
30	65	50	1	6	91	90.23

Table 10: Analysis of variance (NOVA) for optimization of GSOFAME

Source	Sum of Squares	Df	Mean Square	F-value	p-value	Significant
Model	3306.02	14	236.14	22.23	< 0.0001	Significant
A-Time	440.24	1	440.24	41.44	< 0.0001	
B-Temperature	449.56	1	449.56	42.32	< 0.0001	
C-Catalyst conc	328.00	1	328.00	30.88	< 0.0001	
D-Methanol	1119.62	1	1119.62	105.39	< 0.0001	
AB	64.00	1	64.00	6.02	0.0268	
AC	56.25	1	56.25	5.29	0.0361	
AD	12.25	1	12.25	1.15	0.2999	
BC	30.25	1	30.25	2.85	0.1122	
BD	2.25	1	2.25	0.2118	0.6520	
CD	196.00	1	196.00	18.45	0.0006	
A ²	33.61	1	33.61	3.16	0.0956	

B ²	265.39	1	265.39	24.98	0.0002
C ²	7.83	1	7.83	0.7373	0.4040
D ²	121.97	1	121.97	11.48	0.0041

Fit Statistics

R² = 0.9540 Adjusted R² = 0.9111 Predicted R² = 0.8250

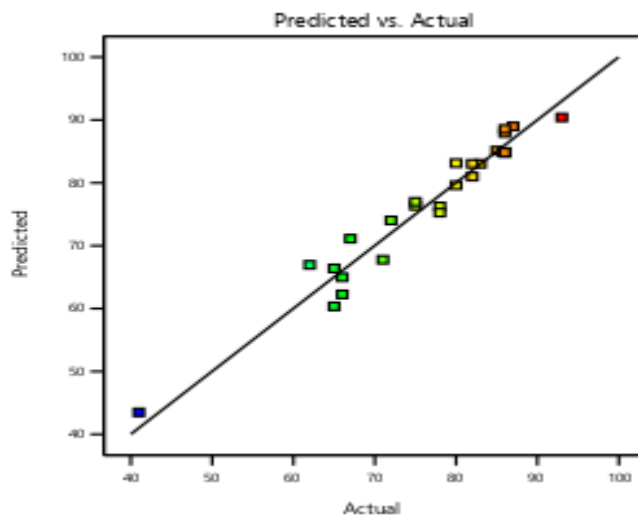


Fig 7: Plot of predicted versus actual yield of GSO FAME

J. Three dimensional (3D) response surface plots for FAME yield from gmelina seed oil

The 3D response surface plots of the different interaction effects were generated to estimate the effect the combinations of the independent variables on the FAME yield as typified by figures 8-10. Figures 8 depict the interaction effect between methanol to oil molar ratio and reaction temperature on FAME yield for gmelina seed oil. The figure indicated that the yield of FAME increases with increase in reaction temperature and methanol/oil molar ratio. This is as a result of a positive significant effect of methanol/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.

Figures 9 shows the interaction effect between reaction temperature and catalyst concentration on FAME yield for GSO. The figure indicated that the yield of FAME increased with increase in reaction temperature and catalyst concentration. This is as a result of the fact that more rapid reaction occur at high temperatures and high concentration of the catalyst which improved the yield. However, at higher catalyst concentration and reaction temperature above the optimal value, 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 GSO.

Figures 10 show that the amount of methyl ester yield increases with methanol/oil molar ratio and catalyst concentration. However, at higher catalyst concentrations a reduction in the yield was observed. This resulted because

very high concentration of catalyst and methanol to oil molar ratio has negative effect on the yield of FAME from GSO.

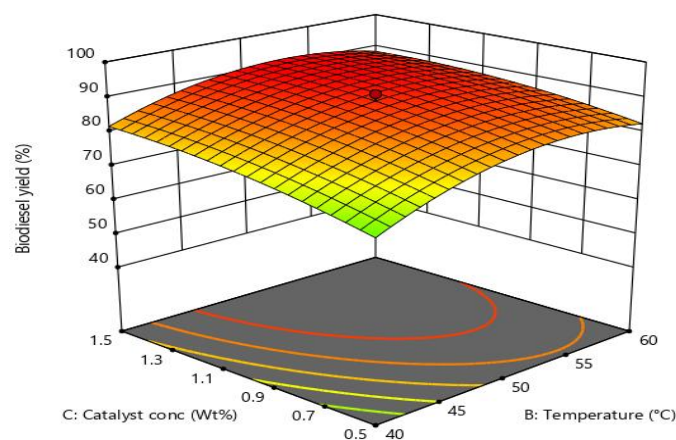


Fig 8: Response surface plot showing interaction between methanol to oil molar ratio and temperature on the yield of FAME from GSO

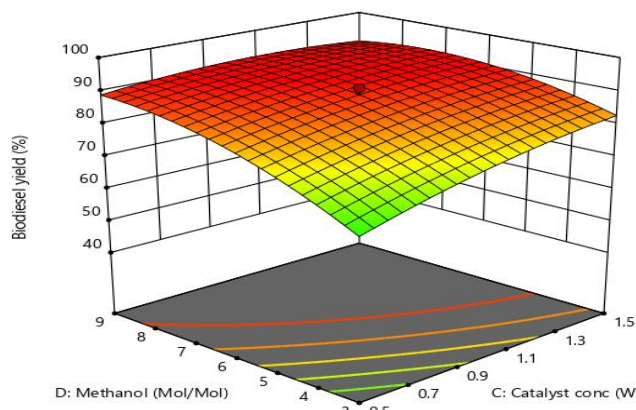


Fig 9: Response surface plot showing interaction effect between catalyst concentration and temperature on the yield of FAME from GSO

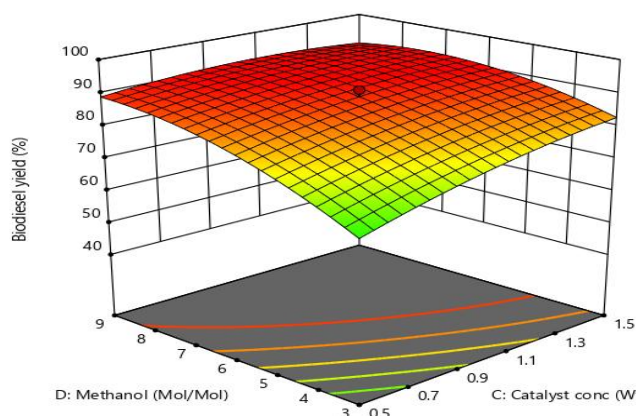


Fig10: Response surface plot showing interaction effect between methanol to oil molar ratio and catalyst concentration on FAME yield from GSO

IV. CONCLUSION

Gmelina seed oil biodiesel has properties that are within the ASTM standard limit and are therefore suitable for use as compression ignition engine fuel. The process parameters for transesterification of of gmelina seed oil significantly affected the biodiesel yield as their increase resulted in the increase of yield of biodiesel until the optimum parameter was reached when the yield started decreasing. The optimum GSO FAME obtained by the use of the optimum reaction parameter; methanol to oil molar ratio 6:1, catalyst concentration 1.0wt.%, reaction temperature 50°C and reaction time 65 minutes was 91.5%.

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