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Compression Ignition Engine Fuel Property Evaluation and Optimization of Biodiesel from Avocado Pear Oil

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ABSTRACT: The world energy demand is increasing by day as a result of increase in population and high spate of industrialization. This has therefore resulted in the search of alternative energy sources to replace the fast depleting fossil fuels. This research work is therefore focused on compression ignition engine fuel property evaluation and optimization of biodiesel from avocado pear oil.. The avocado pear oil (APO) was extracted using solvent extraction method. Avocado pear oil was characterized based on American Society for Testing and Materials (ASTM) method. The fatty acid profile was determined using gas chromatography mass spectrometry while the functional group of the oil was analyzed using Fourier transform infrared spectroscopy. The effect of process parameter on the yield of avocado pear oil fatty acid methyl ester (APOFAME) was investigated using one factor at a time method. The APO was pretreated to reduce the free fatty acid below 1% and then traesterified using ethanol in the presence of potassium hydroxide (KOH) catalyst. The fuel properties of the APOFAME produced was determined based on ASTM standards. The physiochemical properties of APO , free fatty acid, saponification value, iodine value , kinematic viscosity, fire point, flash point, cloud point, pour point, density , moisture content, gave the values 7.15%, 201.4mgKOH/g, 74.8gI_2/100g, 38.5mm^2s^{-1} @ 40^0C, 169^0C, 120^0C, 13^0C, 3^0C 919Kg/m^3, 6% respectively. The fatty acid profile of APO shows the constituents to be lauric acid 12.30%, palmitic acid 24.20%, stearic acid 18.20%, myristic acid 14.54%, while the unsaturated fatty acid constituents are linolenic acd 10.61%,, sapentaenoic acid 12.57%, and linoleic acid 7.55%. The experimentally determined properties of the APOFAME; acid value, density, kinematic viscosity, fire point, flash point, cetane number, refractive index, calorific value, iodine value, cloud point and pour point gave the values, 0.45, 873Kg/m^3, 4.95mm2s-1, 160^0C, 154^0C, 62.69, 1.5464, 34.683MJ/Kg, 43.2gI_2/100g, 7^0C, 4^0C respectively. The optimum conditions suggested by the result analysis for maximum APOFAME yield of 87.57% within the ranges studied were: methanol to oil molar ratio 6:1, catalyst concentration 1.0%wt, reaction temperature of 50^0C, reaction time of 65 minutes .Actual experiment based on the optimum conditions produced 90% yield of GSOFAME.

Key words: Avocado pear oil, optimization, synthesis, transesterification

I. INTRODUCTION

The main sources of world energy needs are petroleum, coal and natural gas. Global energy demand is sky-rocketing due to increasing world population and high spate of industrialization. The world has been heavily dependent on coal, petroleum and natural gas for energy and feedstock for industrial production. These energy sources are commonly termed as fossil or nonrenewable resources [1]. These resources are extracted from the earth's crust, processed and burnt as fuel or used as feedstock in the chemical industries. The burning of fossil fuels result in environmental concerns such as greenhouse gas emission, which is the major substance responsible for climate change. Other harmful substances released during fossil fuel production and utilization includes sulphur oxides (SO_X), nitrogen oxides (NO_X) and methane [2]. These shortfalls of fossil fuels have prompted researchers to look for other sources of energy that are sustainable, renewable, with less negative effect on the environment. 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 [3]. Biodiesel is a promising choice for compression ignition engine due to its renewable nature and superior emission characteristics [2]. However the bulk of biodiesel produced all over the world now has edible oil as its feedstock. This has therefore raised the fear of many researchers that the

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continuous use of edible oil for biodiesel production might stress the food uses, prize, production and availability of these oils. However the edible oils are known to produce higher oil yield per acre and contain less fatty acid than the none-edible oils which are conditions necessary for high yield of biodiesel.

Biodiesel is a mono-alkyl ester of long chain fatty acid that is produced by the reaction of fat or oil with monohydric alcohol. It has properties that approximate that of diesel with added advantages of high lubricity, high cetane number and being highly biodegradable. It is a promising nontoxic alternative fuel used in the transport sector. Compression ignition engine or diesel engine is adapted for heavy duty applications and therefore are the preferred engine of choice for agricultural and earth moving construction equipment, marine and rail transportation devices and electricity generation. In order to minimize the environmental impact and yet maintain high thermal efficiency of the engine, biodiesel is used as fuel for diesel engine because it efficiently powers the existing engines without the need for

In the course of this research, the use of avocado pear oil as a possible feedstock for production of biodiesel of comparable quality as diesel will be considered. Avocado (Persea americana Mill.) of the plant family Lauraceae produce fruit with high oil content (Mooz et al [12]. The pulp or mesocarp (fleshy part of the fruit) make up 60 to 75% of the total weight of avocado fruit [13]. Mesocarp is composed of parenchyma cells that surround uniformly distributed specialized oil containing idioblast cells [14]. The endocarp (stony part of the fruit) makes up 13% of the total weight of the fruit. Avocado is a tropical fruit that stands out for its high nutritional value [12]. The oil contains mainly of saturated fatty acid and low amount of polyunsaturated fatty acid [15]. Avocado oil has been used for cooking, cosmetics, and treating diseases, but has not been widely studied as a good source of oil for renewable energy [16]. Optimization of APOFAME 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.

modification [4]. Various processes have been adopted for biodiesel production from vegetable oil and animal fat, namely; micro-emulsion with alcohol, catalytic cracking, pyrolysis and transesterification [5],[6],[7],[]8]. Among these methods, transesterification is the key and the most important process for production of a cleaner and environmentally safe biodiesel [9],

[10].Transesterification means conversion of one type of ester to another. During transesterification a basic catalyst breaks the fatty acid from the glycerine one by one. If an alcohol typically methanol contacts a fatty acid, it will bond and form biodiesel [11].

The global trend towards increased use of renewable energies has led to investigation of non-traditional oil producing crops. Some crops have been discovered in the tropical Sub-Saharan regions of Africa that have potential for use as bio-fuel feed stocks. Oil seeds and feedstock such as Jatropha, cotton, palm kernel, soy beans and rice bran has been proposed as potential sources of oil for biodiesel production.

II. MATERIALS AND METHODS

2.1 Materials

Avocado pear, 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.

2.2 Experimental Methods

2.2.1 Sample preparation

The avocado pear fruits used were bought from Ogboete market Enugu in Enugu state, Nigeria. The seed, seed coat and skin were removed and the pulp was sundried for 7 days followed by oven drying till it was sufficiently dry for application of solvent extraction..

2.2.2 Extraction of oil from avocado pulp

Solvent extraction was used for extraction of oil from the dried avocado pulp. Ethanol was employed in the extraction of oil from the dried avocado pulp. The solvent choice of ethanol for extraction of oil from avocado pulp was based on the study by[17],[18], Both researchers reported higher yield of oil from ethanol extraction when compared to extraction with n-hexane.

Soxhlet extractor was used for extraction and determination of the oil content of the seed while the bulk of oil used in experimentation was extracted thus; 3 kg of the dried, ground pulp was

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introduced into a plastic container containing 3 liters of ethanol.

The mixed content of the container were vigorously shaken after covering the container. The container was made air tight to prevent evaporation of the ethanol and then kept to macerate for a day. Then the dissolved oil in ethanol was decanted and the slurry filtered. The filtrate was then distilled to recover the ethanol at 65^0C [19]. The percentage oil yield was calculated as:

$$\% \text{ oil yield} = \text{weight of oil obtaind} \div \text{weight of seed sample x } 100 \quad (1)$$

2.2.3 Characterization of avocado pear oil

The physiochemical properties of the oil extracted from avocado pear 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.

2.2.5 Pretreatment of the oil extracted.

The avocado pear oil 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 60^0C for 120 minutes at an agitation speed of 450rpm. The mixture was then transferred into a 250 ml separating funnels where it later separated into three layers comprising of water at the bottom, pre-treated oil in the middle and methanol at the upper layer. The mixture of components were carefully separated by removal 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 105^0C until the residual water evaporated completely. After this process, the pre-treated oil was ready for transesterification [20].

2.2.6 Production of Biodiesel

2.2.6.1Transesterification reaction

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 transesterfied 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.

2.2.6.2 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 the 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 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 after testing for its neutrality 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 105^0C on a laboratory hot plate until all residual water molecules is evaporated. The percentage biodiesel yield is given by the expression

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

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2.2.7 Determination of the fuel properties of the avocado pear oil biodiesel

The properties of the avocado pear oil biodiesel were characterized based on ASTM D6751 biodiesel fuel standards. The properties characterized for include density, viscosity, cetane number, flash point, cloud point, water and sediment, acid value, iodine value, saponification value etc

2.2.8 Design of Experiment for Transesterification of APO

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 percentage biodiesel yield obtained by transesterification of the avocado pear oil. The level of factors of the independent variables are given in table1.The choice of level of factors were based on the earlier experiments performed on the effects of process veriables on APO biodiesel yield by [22]. The experimental design matrix for transesterification of avocado pear oil is 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 value of $2^{n/4}$, where n is the number of factors [23]. 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 3.

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

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.

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 APO (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

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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 APO (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	

III. RESULTS AND DISCUSSION

3.1 Charateristics of avocado pear oil

3.2.1 Physiochemical properties of APO

The summary of characteristics of avocado pear oil are as shown in table 3.1. From the table, it could be seen that the acid value and the free fatty acid of APO, 14.30mg and 7.15% respectively are high.

The free fatty acid and the moisture content of the oil are each greater than 1% which is the maximum required of the oil for high yield of biodiesel from alkali transesterification. Oil of high moisture content like APO is prone to hydrolytic oxidation. Again oils of high free fatty acid and moisture content has the tendency for soap formation which inhibits glycerol separation from

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biodiesel and therefore retards biodiesel production. The oil is therefore pretreated or esterified before being transesterified. 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 biodiesel [24].

Iodine value, a measure of degree of un-saturation of the oil obtained is below 100gI_2/100g 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, and if oil of high iodine value is heated, it undergoes thermal oxidation and polymerization of the triglyceride, causing formation of deposits. The cloud and pour point of 13^0C and 3^0C respectively determined for the oil are high and therefore unsuitable for cold weather. Peroxide value, an index of rancidity obtained as 16meq/Kg was high and indicative of poor resistance of the oil to per-oxidation during storage and handling.

Table 4: Physiochemical properties of APO

Properties	Unit	APO
Acid value	mgKOH/g	14.30
Free fatty acid	%	7.15
Saponification value	mgKOH/g	201.4
Iodine value	(gI_2/100g oil)	74.8
Peroxide value	meq/kg	16
Kinematic viscosity	mm^2s^{-1} @ 40^0C	38.5
Fire point	^{0}C	169
Flash point	^{0}C	120
Cloud point	^{0}C	13
Pour point	0C	3
Refractive index		1.4614
Specific gravity		0.919
Moisture	%	6
content		
Density	Kg/m^3	919

3.2.2 Fatty acid profile of avocado pear oil

The Fatty acid profile of APO was determined using GC-MS analysis. The individual peaks of the gas chromatogram were identified as shown in figure 1. The percentage fatty acids were calculated from total ion chromatography by computerized integrator and results are presented in table 5. As shown in the table the saturated fatty acid constituents of the oil were identified as palmitic acid (C16:0) 24.20%, lauric acid (C12:0). 12.30%, myristic acid (C14:0) 14.54% and stearic acid (C18:0) 12.57%.. The di-, tri-, and polyunsaturated fatty acid constituents of the oil are linoleic acid (C18:2) 7.55%, linolenic acid (C18:3) 10.61% and sapentaenoic acid 12.57% respectively.

3.2.3 Fourier transform infrared spectra analysis (FTIR) of avocado pear oil

The Fourier transform infrared spectra of APO was analyzed using Fourier transform infrared spectroscopy (M530 Buck scientific FTIR). This analysis was carried out in order to detect the various functional groups contained by the oil. The FTIR spectrum of APO oil is shown in figure 2. The different group assignments of the FTIR spectra of APO are summarized in table 6, showing the presence mostly of alkane, alkynes and hydroxyl groups. The presence of hydroxyl groups are detected at 3853.171, 3539.869, 3149.224, 1390.83 cm^{-1} with O-H stretching. The C-H bending vibration of alkanes were evident at 775.3272 and 878.8254 cm^{-1}. The C≡C stretching at 2042.03 and 2201.238 cm^{-1} shows the presence of alkynes. While the C-H stretch at 2805.394 and1 852.449cm^{-1} depicts the presence of aldehydes and aromatic compounds respectively. The presence of conjugated alkane was also detected by the C=C stretch at 1622$cm^{-1.}$

Tetradecanoic Acid $CH_3(CH_2)_{12}COOH$ 4

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Table 5: Summary of fatty Acid Profile of APO

Components Common Name	Systematic Name	Structural Formula	Concentration (%)
Lauric C12	Dodecanoic Acid	$CH_3(CH_2)_{10}COOH$	12.30
Palmitic Acid C16	Hexadecanoic Acid	$CH_3(CH2)_{14}COOH$	24.20
∝ Linolenic Acid C18:3	Octadeca-9, 12,15 Trienoic Acid	$C_{17}H_{29}C0_2H$	10.61
Sapentaenoic Acid C20:5	Icosa-5,8,11,14,17-Pentaenoic Acid	$C_{19}H_{29}C0_2H$	12.57
Stearic Acid C18	Octadecanoic	$CH_3(CH_2)_{16}COOH$	18.20
Linoleic Acid C18:2	Octadeca-9, 12-Dienoic Acid	$C_{17}H_{31}C0_2H$	7.55
Myristic Acid C14	Tetradecanoic Acid	$CH_3(CH_2)_{12}COOH$	14.54

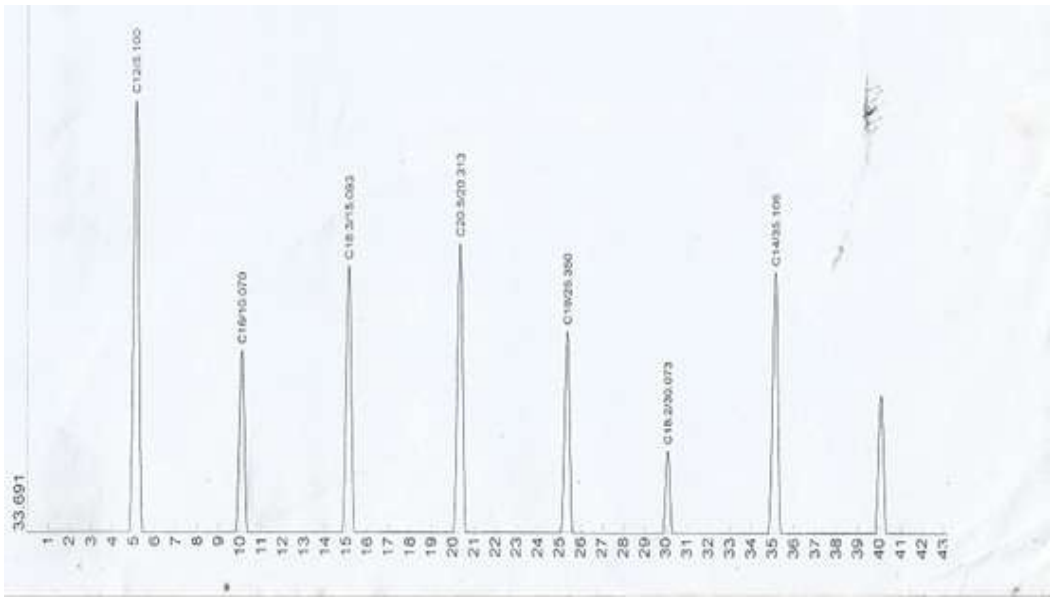

Figure 3.1 GC-MS plot of avocado pear oil

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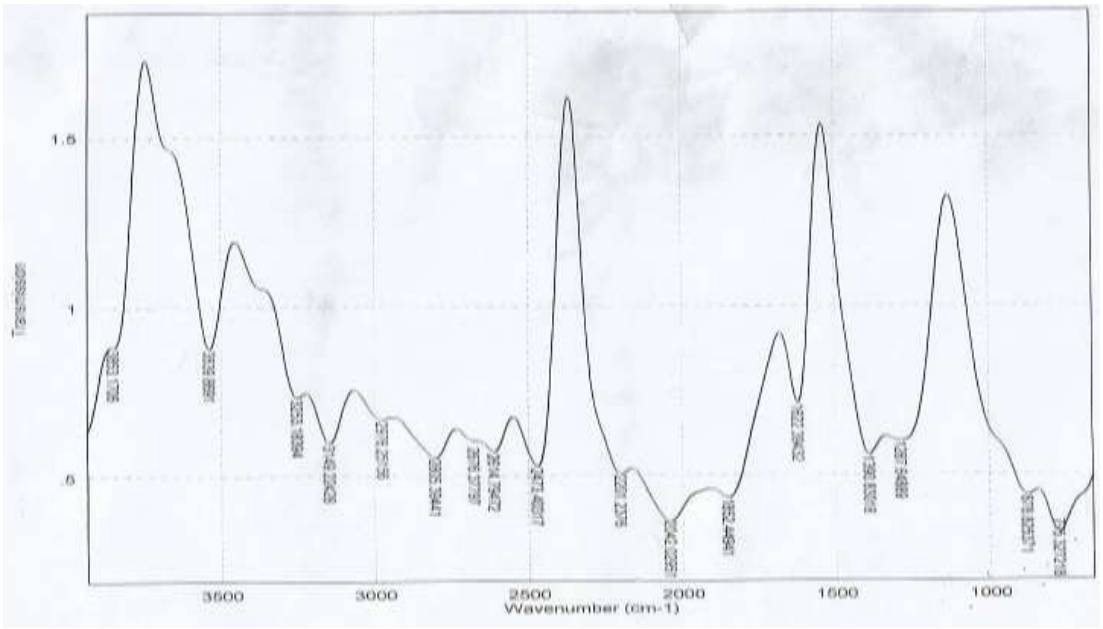

Figure 1: FTIR spectra of avocado pear oil

Table 6: FTIR functional group frequencies of APO

Frequency wave number (cm^{-1})	Types of Vibration	Functional Group
775.3272	Bending	C-H (Alkane)
878.8254	Bending	C-H (Alkane)
1287.649	Stretch	C-O (Aromatic)
1390.83	Bending	0-H (Phenol)
1622.394	Stretch	C=C (conjugated alkene)
1852.449	Stretch	C-H (Aromatic Compound)
2042.03	Stretch	C≡C (Alkyne)
2201.238	Stretch	C≡C (Alkyne)
2805.394	Stretch	C-H (aldehyde)
2976.252	Stretch	C-H (alkane)
3149.224	Stretch	0-H (alcohol)
3253.184	Stretch	Normal polymeric O-H
3539.869	Stretch	O-H
3853.171	Stretch	O-H

3.3 Fuel properties of avocado pear oil biodiesel

The fuel properties of APOFAME 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 volumetrically.The density of the APO biodiesel was evaluated to be 873kg/m^3 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 4.95mm^2/s and is therefore within the ASTM limit. High kinematic viscosity result in poor atomization and incomplete combustion of biodiesel, giving rise to cocking of injector tips and hence engine power loss. This conforms to the findings of [6]. The viscosity of biodiesel is typically higher than that of diesel [25]. 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 sooth formation [26],[27].

Flash point measures the degree of flammability of the fuel. The ASTM standard for flash point is ≥ 130^{0}C. However during biodiesel

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production and purification, some traces of methanol may remain in the fuel making the flash point to be less than 130^0C and thus making it flammable and dangerous to handle or store. The flash point of the APOFAME is 160^0C and thus is within the ASTM limit, 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 show 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 biodieel is composed of long chain hydrocarbon

Table 7: Fuel properties of APOFAME

Properties	Unit	APOFAME	ASTM Standards	Test method
Density	Kgm^{-3}	873	860-900	D93
Kinematic viscosity	mm^2s^{-1}	4.95	1.9-6.0	D445
Cetane number		62.69	47min.	D613
Flash point	^{0}C	160	100-170	D93
Cloud point	^{0}C	7	-3-15	
Water &sediment	%	0.7	0.5	D2209
Acid value	$mgKOHg^{-1}$	0.45		D664
Calorific value	$MJKg^{-1}$	38.2	42.06	D35
Iodine value	gI_2100g^{-1}oil	43.2	42-46	D4067
Fire point	^{0}C	180	197	

groups with virtually no branching or aromatic structure, it typically has higher cetane number than petro-diesel [25]. The ASTM lower limit for cetane number is 47. The cetane number of the APOFAME 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 APOFAME as an alternative to petro-diesel as its determined calorific value of 38.2MJ/Kg approximate that of diesel of 44.34MJ/Kg The low calorific value of 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 wax like material on cooling the biodiesel was determined as 7^0C. Pour point which is the lowest temperature at which the fuel will still pour was obtained as 4^0C. 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 [28].

3.4 Comparison of APOFAME with diesel (CI engine) Fuel

Table 8 gave a comparison between the properties of the avocado pear oil biodiesel produced and compression ignition (diesel) fuel. From the obtained property values in the table, it could be seen that the APO biodiesel properties approximate that of diesel or compression ignition engine fuel. A major difference lies with the cloud point and pour point of which the value for APO biodiesel is higher and therefore unsuitable for use in cold weather. However these property values could be improved by the use of cloud point and pour point depressants

Table 8: Comparison between APOFAME and CI engine (Diesel) Fuel

Property	Unit	NSOFAME	Diesel	Test Method
Density	Kgm^{-3}	873	850	D93
Kinematic Viscosity	mm^2s^{-1} at 40^0C	4.95	1.9-4.1	D445
Cetane number	^{0}C	62.69	40	D613
Flash point	^{0}C	160	100	D93
Cloud point	^{0}C	5	Varies	D2500
Water & sediments	%	0.60	0.5	D2209
Acid value	mgKOH/g	0.420		D664

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3.5: Statistical Analysis of Transesterification Using Central Composite Design (CCD)

To optimize transesterification of avocado pear 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 to 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 factor levels are shown in Table 1. 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 avocado pear oil with the independent process variables obtained with the design Expert version12.0. The design of the experimental matrix of transesterification of avocado seed oil with the experimental values of the biodiesel yield are presented in Tables 9.The design plan as shown in table 9 was used to predict the optimum biodiesel yield and the values of optimum variables as presented in table10.The coded and un-coded values of the test variables were used to optimize the variables namely catalyst concentration, methanol to oil molar ratio, reaction temperature and reaction time. The experimental values of percentage yield were presented in Table 10. 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:

Biodieselyield (APO)=+87.57+3.71A+4.63B+3.27C+7.15D-1.69AB-0.4375AC-1.06AD-0.8125BC+0.3125BD-3.44CD\-1.39A²-4.50B²-0.4972C²-2.94D² (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 model was tested using 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 11.

$\mathbf{Y_{APO}}$=+87.57+3.71A+4.63B+3.27C+7.15D-1.69AB-3.44CD-0.4972C²-2.94D² (5)

Table 9: Optimization results for biodiesel yield of APO

Std	A:Time Min	B:Temperature °C	C:Catalyst conc Wt%	D:Methanol Mol/Mol	Biodiesel yield %
1	40	40	0.5	3	54
2	90	40	0.5	3	69
3	40	60	0.5	3	68
4	90	60	0.5	3	70
5	40	40	1.5	3	69
6	90	40	1.5	3	80
7	40	60	1.5	3	78
8	90	60	1.5	3	86
9	40	40	0.5	9	75
10	90	40	0.5	9	86
11	40	60	0.5	9	91
12	90	60	0.5	9	94
13	40	40	1.5	9	81
14	90	40	1.5	9	85
15	40	60	1.5	9	88
16	90	60	1.5	9	89

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17	27.5	50	1	6	75
18	102.5	50	1	6	89
19	65	35	1	6	65
20	65	65	1	6	85
21	65	50	0.25	6	78
22	65	50	1.75	6	90
23	65	50	1	1.5	68
24	65	50	1	10.5	89
25	65	50	1	6	89
26	65	50	1	6	89
27	65	50	1	6	89
28	65	50	1	6	89
29	65	50	1	6	89
30	65	50	1	6	89

Table 10: Actual and predicted values of the yield of biodiesel from APO

Std	Time (Min)	Temperature (°C)	Catalyst concentration (Wt. %)	Methanol (mol/mol)	Actual Yield (%)	Predicted yield (%)
1	40	40	0.5	3	54	52.37
2	90	40	0.5	3	69	66.16
3	40	60	0.5	3	68	66.01
4	90	60	0.5	3	70	73.05
5	40	40	1.5	3	69	68.28
6	90	40	1.5	3	80	80.32
7	40	60	1.5	3	78	78.67
8	90	60	1.5	3	86	83.96
9	40	40	0.5	9	75	75.03
10	90	40	0.5	9	86	84.57
11	40	60	0.5	9	91	89.93
12	90	60	0.5	9	94	92.72
13	40	40	1.5	9	81	77.20
14	90	40	1.5	9	85	84.99
15	40	60	1.5	9	88	88.84
16	90	60	1.5	9	89	89.88
17	27.5	50	1	6	75	78.89
18	102.5	50	1	6	89	90.01
19	65	35	1	6	65	70.50
20	65	65	1	6	85	84.40
21	65	50	0.25	6	78	81.55
22	65	50	1.75	6	90	91.35
23	65	50	1	1.5	68	70.23
24	65	50	1	10.5	89	91.67
25	65	50	1	6	89	87.57
26	65	50	1	6	89	87.57
27	65	50	1	6	89	87.57
28	65	50	1	6	89	87.57
29	65	50	1	6	89	87.57
30	65	50	1	6	89	87.57

3.5.1Analysis of variance (ANOVA) for optimization of GSOFAME

The ANOVA results for the model terms are given in Table 11. ANOVA was applied to estimate the significance of the model at 5% significance level as shown in the table. A model is

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considered significant if the p-value (significance probability value) is less than 0.05

From the ANOVA table 11 it can be stated that the linear, interactive and quadratic terms A, B, C, D, AB, CD, B^2, D^2 are the significant terms for APO transesterification. Therefore, eliminating the insignificant terms the final model equation becomes as expressed in equation 6 below

Table10: ANOVA analysis for the optimization of biodiesel from APO

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	2743.20	14	195.94	21.68	< 0.0001	significant
A-Time	281.76	1	281.76	31.17	< 0.0001	
B-Temperature	440.24	1	440.24	48.70	< 0.0001	
C-Catalyst conc	218.98	1	218.98	24.22	0.0002	
D-Methanol	1046.94	1	1046.94	115.81	< 0.0001	
AB	45.56	1	45.56	5.04	0.0403	
AC	3.06	1	3.06	0.3388	0.5692	
AD	18.06	1	18.06	2.00	0.1779	
BC	10.56	1	10.56	1.17	0.2968	
BD	1.56	1	1.56	0.1728	0.6835	
CD	189.06	1	189.06	20.91	0.0004	
A^2	21.86	1	21.86	2.42	0.1408	
B^2	230.10	1	230.10	25.45	0.0001	
C^2	2.81	1	2.81	0.3111	0.5852	
D^2	98.45	1	98.45	10.89	0.0049	

R^2 =0.9529 Adjusted R^2 = 0.9089 Predicted R2 = 0.7592

$$Y_{APO}=+87.57+3.71A+4.63B+3.27C+7.15D-1.69AB-3.44CD-0.4972C^2-2.94D^2 \quad (6)$$

3.5.2 Prdicted versus actual yield of APOFAME

The plot of predicted versus actual yield of APOFAME is given in figure 7. The plot was employed, to check whether the points are linear, in which case we conclude that the residuals follow a normal distribution. From figure7 it could be seen that the points were closely distributed to the straight line of the plot, confirming the good relationship between the experimental values and the predicted values of the response. The values of the plot also confirm that the selected model was adequate in predicting the response variables in the experimental values.

3.5.3. Optimization of process parameters of GSOFAME

Optimization of process variables in this study was carried out using design expert version 12.0. The optimum conditions suggested by the result analysis for maximum APOFAME yield of 87.57% within the ranges studied were: methanol to oil molar ratio 6:1, catalyst concentration 1.0%wt, reaction temperature of 50^0C, reaction time of 65 minutes. Actual experiment based on the optimum conditions produced 90% yield of GSOFAME.

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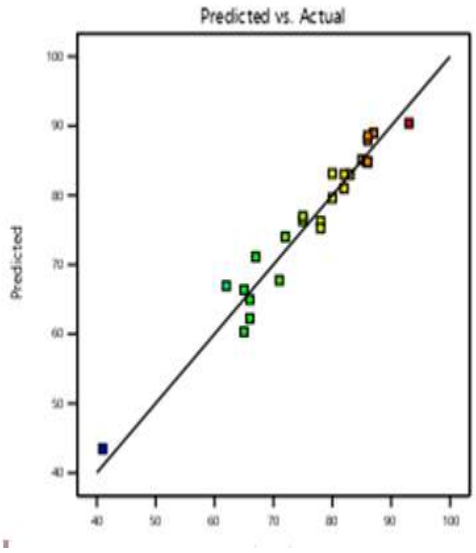

Fig 7: Plot of predicted versus actual yield of APOFAMEThe small percent error difference between the pedicted and actual yield of 2.6% indicates that the regression model developed in this study was accurate in representing the overall data and reliable in predicting the yield at any given conditions within the range studied for FAME produced from avacado pear oil.

IV. CONCLUSION

Avocado pear oil biodiesel has properties that are within the ASTM standards and compares favorably with the diesel. The additional advantages of the APOFAME over diesel are higher cetane number, higher lubricity, being biodegradable, renewable and environmentally friendly. However the cloud point and pour point values makes it unsuitable for use in cold climates especially during cold weather, but this could be surmounted by the use of pour point and cloud point depressants.

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