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Synthesis and characterization of Argania spinosa (Argan oil) biodiesel by sodium hydroxide catalyzed transesterification reaction as alternative for petro-diesel in direct injection, compression ignition engines

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ABSTRACT

In this research work, the optimization conditions for obtaining optimum biodiesel yield from argan oil as well as the quantification of degree of interactions between reactants and biodiesel yield were investigated by using a response optimization model and response surface methodology (RSM) respectively. Similarly, a regression polynomial model was used to develop a unified equation for predicting the expected yield of Argan biodiesel for different values of reactant variables and a regression coefficient of 92.56% was obtained.

The Argan oil was extracted from its kernel by using a soxhlet extractor with hexane as extraction solvent and 54.50% oil yield was obtained. The fatty acid compositional analysis was done by using a Shimadzu GCMS QP2010 SE Gas-chromatograph-mass spectrometer.

The spectrometer analysis shows that the oil has 80.90% of unsaturated fatty acid with oleic and linoleic acid constituting larger percentages respectively. A sodium hydroxide catalyzed transesterification reaction was used to convert the triglyceride in the oil to fatty acid methyl ester under standard conditions and the fuel properties of the oil and its ester were measured by using the American society for testing and materials (ASTM) procedures. A Fourier transform infrared spectroscopic (FTIR) technique was used for qualitative characterization of biodiesel functional groups in order to affirm the complete conversion of the oil into biodiesel.

Results showed that the cold flow behaviour in terms of cloud point, pour point, cold filter plugging point (CFPP) and Low temperature flow test (LTFT) and critical properties such as cetane number, calorific value, iodine value, density, flash point, ash percentage and carbon residue of the Argan biodiesel showed a good agreement with ASTM D6751-07b and European committee for standardization (EN 14214) standard requirements. Hence, its application in compression ignition engines will pose no threat as far as performance, combustion and emission qualities are concerned. Finally, the Argan biodiesel has a very high higher heating value (HHV) of 40,665 kJ/kg which is very uncommon of other vegetable oils methyl esters and thus facilitate better heat release during combustion and improves engine performance.

1. Introduction

The insatiable desire for a green environment devoid of various forms of environmental pollution coupled with the unsustainability and non-renewable nature of fossil fuels has always been the impetus for extensive search for a more environmentally benign and technically viable alternative fuel from biomass in compression ignition engines. The American society for testing and materials defines biodiesel as fatty acid methyl ester or mono alkyl esters of long chain fatty acids derived from vegetable oils (Plant Origin) or animal fats and other biomass derived oil for use in compression-ignition (diesel) engines.

The process of finding alternative to diesel in compression-ignition engines started with the direct use of plants oils either wholly or as blend with petroleum diesel without any major chemical and or physical modification [1, 2].

However, these plants oils were able to solve the environmental problems associated with the use of diesel in terms of its emission characteristics but posed a huge technical problem in its performance and combustion characteristics. Notable among those technical issues are abnormally high viscosity and density resulting in poor atomization and combustion in the combustion chamber, injector coking, engine deposits and lubricant thickening which consequently lead to poor performance,

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higher exhaust emissions and reduced engine life [3, 4, 5, 6].

In order to annul these ugly scenarios, an insight into various methods of chemically and or physically refining these plant oils prior to direct usage as fuels began to emerge. Various methods of processing the plant oils include thermal and catalytic cracking, electrolysis and the widely known transesterification reaction.

Transesterification involves the reaction of lower alcohols such as methanol and ethanol, with higher vegetable oil fatty acids in the presence of acidic or alkaline catalysts such as sodium hydroxide (NaOH) or potassium hydroxide (KOH). The reaction products are fatty acid alkyl ester and glycerol.

However, biodiesel yield and quality from transesterification reaction is dependent on a lot of factors. These are reaction time, type of alcohol and alcohol to oil molar ratio, reaction temperature and pressure, concentration and type of catalyst, water content and free fatty acid level in fats and oils.

The industries embraced methanol as primary alcohol for biodiesel synthesis regardless of its toxicity and chemical origin as a result of the following technical and economic advantages:

i. Very cheap
ii. Prevents soap formation
iii. High reactivity
iv. Easy method of recovery due to non-formation of azeotropes [7].

Various edible oils such as soybean oil, palm kernel oil and sunflower oil are being widely used in commercial quantities as biomass feed stocks in united states of America, Argentina and Europe respectively. However, in order to forestall the eventual depletion of edible-oil supply worldwide arising from competition by biofuel demands, various non-edible oil sources have been investigated by researchers. These include: Madhuca indica, bitter Almond oil, Jatropha curcas, Karanja oil and Pongamia pinnata [8].

Abdelrahman et al 2019 [9] evaluated the viability of non-edible Radish seed oil (**Raphanus sativus**) as possible feed stock for biodiesel production. An oil yield of 33.50 wt.% was obtained by solvent extraction of the radish seed and an optimized base catalyzed transesterification of the oil with methanol, ethanol and mixed methanol-ethanol yielded 95.55.wt.% of Fatty acid methyl esters (FAMEs), 90.66wt.% of Fatty acid ethyl esters (FAEEs) and 93.33.wt.% of Fatty acid methyl-ethyl esters (FAMEEs) respectively. The ultimate conclusion was that the synthesized biodiesel corresponds to standard limits requirement by ASTM D6751.

Similarly, the optimum conditions for transesterification of non-edible **Jatropha curcas** seed oil for biodiesel production has been investigated by **Dena et al 2018** [10]**.** Based on their findings, the optimum operating conditions for Jatropha oil transesterification process are methanol to oil molar ratio of 6:1, KOH catalyst concentration of 1% by weight, reaction temperature of 60°C and duration of 60 min. An ester yield of 94% was observed. **Gupta et al 2016** [11] conducted an investigation into the biodiesel fuel properties of a mixture of edible and non-edible vegetable oil (thumba oil, karanja oil, linseed oil and palm oil). A biodiesel yield of 97% that conforms with the stipulated biodiesel quality standards was obtained with methanol to oil molar ratio of 8.8:1, KOH catalyst concentration of 1.9g/100cc oil, temperature of 43.50°C and reaction time of 58.4 min.

Fadhil and Mohammed 2018 [12] examined the biodiesel potential characteristics of non-edible bitter almond oil by co-solvent transesterification with hexane as solvent and potassium hydroxide catalyst (KOH) as alternative fuel to diesel in compression engines. It was reported that the properties of the biodiesel and its blends complied with the limits prescribed by ASTM D7467-17.

However, biodiesel production from ethanol route provides us with a completely environmentally friendly fuel because of non-toxicity and renewable nature of ethanol.

1.1. Historical background of Argan oil

Argan oil is a plant oil that is extracted from the kernels of argan tree fruit (Argania spinosa, family Sapotaceae) which is cultivated on a large scale in Southwestern Morocco and covering areas such as Essaouira, Agadir, Chtouka Ait Baha, Tiznit and Taroudant [13]. The Argan tree is a slow growing spiny tree with robust adaptation mechanisms for drought and other harsh environmental conditions that are characteristic of South Western Morocco [14]. In Morocco, the Argan forests cover about 8, 280km^2 and they are tagged as UNESCO biosphere reserves.

Edible Argan oil is not refined and it is obtained from slightly roasted kernels whereas the non-edible (cosmetic grade oil) oil comes from non-roasted kernel [15]. Although Argan tree grows naturally exclusively in South Western Morocco, the kernels can also be exported to other countries for oil extraction and processing. The oil serves as source of essential fatty acids and Vitamin E with extensive medicinal applications.

Argan oil share some similarities with olive oil and almond in the following regards. They are cold-press oils, they are produced from a tree fruit, they contain about 80% unsaturated fatty acid with oleic and linoleic acid being the two major unsaturated fatty acid while palmitic and stearic acids form the two main saturated fatty acids in all the three oil samples [16, 17].

1.2. Seed processing and exraction of Argan oil

The quality and properties of argan oil obtained from the argan nut is dependent on two major factors, namely: extraction method and secondly, processing and storage methodologies and conditions. There are two methods of removing the argan kernels from the ripe fruits. Mechanically cracked nuts provide us with an argan kernel of high quality oil in terms of composition, taste and shelf, whereas the traditional method of goat-digested fruit yield kernels whose extracted oil has an unacceptable chemical composition that is different from those of peeled fruit derived oil [18].

For this research work, two (2) sacks, each of 50kg of argan kernels were mechanically pressed by a grinding machine to obtain pressed cakes. The cakes were then taken into a soxhlet apparatus with hexane as solvent in order to extract the oil. The process was repeated in a number of times in order to obtain the required quantity of oil for the transesterification process.

1.3. Oil yield

The percentage (%) of oil yield was calculated by using Eq. (1)

$$\text{Percentage Yield} = \frac{\textit{weight of oil obtained}}{\textit{Weight of samples (argan kernels)}} \times 100 = 54.5\% \quad (1)$$

2. Materials and methods

2.1. Fatty acid compositional analysis of Argania spinosa (Argan oil)

After the extraction of the argan oil from the kernel, the composition of the fatty acids in the oil was determined by using Schimadzu Gas-Chromatograph with mass spectrometer detector and the absolute values are presented in Table 1. We couldn't rely on the compositional information that exist in the literature because of increasing degree of reported cases of argan oil adulteration with olive oil [19, 20]. There are five (5) essential components of the gas chromatography system. These are: the column with the stationary phase, the carrier gas system, the split or splitless sample introduction system, GC detectors or the detection system and the computer station or integrator. The GC has a capillary column with an internal diameter (I.D) of 0.25mm. This diameter was selected because it provides adequate plates per meter, allows acceptable sample capacity

Table 1
Fatty acids composition of Argania spinosa oil (Argan Oil) as determined from GC-MS analysis.

Fatty acid	Molecular formular	Molecular structure	Structural formular	% composition
Myristic	$C_{14}H_{28}O_2$	14:0	$CH_3(CH_2)_{12}COOH$	0.08
Palmitic	$C_{16}H_{32}O_2$	16:0	$CH_3(CH_2)_{14}COOH$	12.50
Palmitoleic	$C_{16}H_{30}O_2$	16:1	$CH_3(CH_2)_5CH = CH(CH_2)_7$ COOH	1.20
Stearic	$C_{18}H_{36}O_2$	18:0	$CH_3(CH_2)_{16}COOH$	5.90
Oleic	$C_{18}H_{34}O_2$	18:1	$CH_3(CH_2)_7CH = CH(CH_2)_7$ COOH	43.60
Linoleic	$C_{18}H_{32}O_2$	18:2	$CH_3(CH_2)_4CH = CHCH_2$ CH = $CH(CH_2)_7$ COOH	35.80
Linolenic	$C_{18}H_{30}O_2$	18:3	$CH_3CH_2CH = CHCH_2$ CH = $CHCH_2CH = CH(CH_2)_7$ COOH	0.30
Arachidic	$C_{20}H_{40}O_2$	20:0	$CH_3(CH_2)_{18}COOH$	0.40
Behenic	$C_{22}H_{44}O_2$	22:0	$CH_3(CH_2)_{20}COOH$	0.15

and lower ID gives higher capillary column efficiency. A film thickness of 0.25μm was selected for sharper peaks, increase resolution and reduced column bleed. While a column length of 30metres was chosen for better resolution balance, analysis time and required column head pressure. Hence the column dimension was [30 m × 0.25 mm x 0.25μm]. The stationary phase consists of chemically bonded, DB5-5% phenyl methyl silicone. This was selected based on the polarity of Fatty acid and its methyl ester. The stationary phase is the most essential aspect of the capillary column because it determines selectivity and the column's ability to separate sample components. The Schimadzu, GC-2010 SE has oven temperature and injector port temperature of up to 450°C with AFC pressure range of zero to 970kpa. The mass spectrometer has a direct connection with capillary column and with temperature range of 50 to 350°C. The detector was a secondary electron multiplier with the patented overdrive lens and conversion dynode. The injector temperature was set at 230°C while the oven temperature of the column was initially set at 100°C and held constant for 30s before it was increased to 150°C at the rate of 10°C/min and held for 5min. The column oven temperature was finally increased to 220°C at the rate of 5°C/min and held for 5.50 min. About 5μL of heptane derivatized sample were injected into the GC-MS for separation and analysis. The mobile phase (carrier gas) was helium and was pumped at a flow rate of 0.5 μL/min for 30 min (30). The difference between chemical and physical properties of the injected sample and their interactions with the stationary phase are the basis of the separation process. As the sample travels through the length of the column, separation of the molecules occur as a result of different chemical properties of the molecules in the mixture and their affinity for the stationary phase. The molecules were retained in the column and eluted from the column at different times called the retention time and this allows the mass spectrometer to capture, ionize, accelerate, deflect and detect the ionized molecules separately. This was done by breaking each molecule into ionized fragments and detecting these fragments using their mass to charge ratio. The retention times identified by the gas chromatograph were then correlated by the computer to a spectrum library to see if its characteristics were present for some samples in the library. Also, the compound can be analyzed by measuring the peaks in relation to one another and the total mass of the unknown compound is normally indicated by the parent peak. This value of the parent peak can be used to fit with a chemical formula containing the various elements which are in the compound.

2.2. Determination of the percentage of free fatty acid of the Argan oil

The free fatty acid in the argan oil was determined by chemical titration method [21].

Fifty-six grams of well-mixed sample of each refined vegetable oil was accurately measured into a 300ML Erlenmeyer flask. Also, 50ML of ethyl alcohol (95% ethanol) containing 2ML of phenolphthalein indicator was heated to a temperature of 60°C by using water bath to prevent evaporation because ethanol boils at 78°C. The mixture of hot, neutralized ethanol was then added to the vegetable oil in the flask and titrated with 0.1N sodium hydroxide solution (NaOH). The mixture was shaken constantly until a pink colour which persisted for thirty seconds (30s) was observed in the alcohol layer above the sample.

2.3. Calculations

Argan oil free fatty acids (%) were calculated in terms of % oleic by using Eq. (2).

$$\textit{Free fatty acid}\ (\%) = \frac{V \times N \times 28.2}{W} \tag{2}$$

where V = volume in ml of standard sodium hydroxide solution used.
N = normality of standard sodium hydroxide solution used.
W = mass(g) of oil sample used.

2.4. Estimation of degree of unsaturation and long chain saturation factor for Argania spinosa (Argan oil)

Total saturated fatty acid = 19.03%

Total monounsaturated fatty acid (MUFA) = 44.80%

Total polyunsaturated = 36.10%

The total unsaturated Fatty Acid = 80 90%

Hence the degree of unsaturation = $MUFA + 2PUFA$ =117

The long chain saturation factor LCSF = $(0.1 * wt\%\ \ of\ C16 : 0) + (0.5 * wt\%\ \ of\ C18 : 0) + (1 * wt\ \%\ of\ C20 : 0) + (1.5 * wt\ \%\ \ of\ C22 : 0) + (2.0 * wt\%\ \ of\ C24 : 0)$ = 4.825

2.5. Transesterification reaction

Transesterification process was used to convert the triglyceride or triacylglycerol (TAG) present in Argan oil to methyl esters and glycerol (propane 1,2,3 triol) using methanol in the presence of sodium hydroxide catalyst (NaOH) which helped to chemically breakdown the triglyceride molecules in the vegetable oils, remove the glycerol chains from the triglycerides and replace them with alkyl radicals from the methanol used. Various researchers [22, 23, 24] have opined that one of the best conditions for the conversion of Fatty Acids to biodiesel are:

1 Catalyst total content of 1.5% for potassium hydroxide catalyst and 1.0% for sodium hydroxide catalyst.
2 Methanol to Oil molar ratio of 6:1
3 Reaction time of 2–3 h
4 Temperature range of 60°C-65°C

The schematic representation of the chemical reaction is shown in Fig. 1.

2.5.1. Selection of suitable alcohol for the formation of alkoxide

The two major alcohols that are widely used in transesterification reaction are methanol and ethanol. However, methanol was used in this experiment because of its technical and economic advantages over ethanol which includes less cost, prevention of soap formation, high

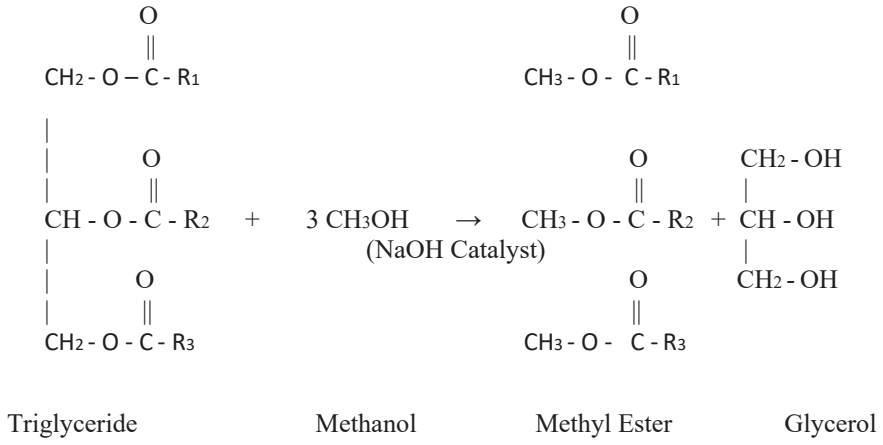

Fig. 1. Schematic representation of transesterification reaction.

reactivity, its recovery is easier because it does not form azeotropes and its short chain molecular size helps in the avoidance of steric hindrance effect.

2.6. *Argania spinosa (Argan oil) biodiesel production process*

The various stages of producing Argania spinosa Biodiesel (ASB) via alkali–catalyzed transesterification reaction can be summarized into a Four-Stage production process under the following sub headings.

2.6.1. *Preparation of sodium methoxide solution*

250 ml of methanol (analytical grade) was measured by using a measuring cylinder and poured inside a 1000ml Erlenmeyer flask. The glass was capped with glass lid to prevent evaporation and 28.50gram of Sodium Hydroxide (NaOH) pellets was measured by using a digital weighing balance and was quickly added to the methanol thereby minimizing its exposure to air. The alcohol-sodium hydroxide mixture was stirred continuously with the aid of a magnetic stirrer until the catalyst was completely dissolved in the alcohol to form sodium methoxide solution. The solution was heated to a temperature of 50°C and maintained at this temperature which is below the boiling temperature of methanol (65°C).

2.6.2. *Main transesterification reaction*

Because the free fatty acid content (FFA) of argan oil is 1.50 %, hence there was no need for acid esterification prior to the main transesterification. For other vegetable oils such as coconut oil, with free fatty acid content above 2.0–2.5%, an acid transesterification is necessary as a preliminary stage to reduce the level of Free Fatty Acid content (FFA) before the main transesterification reaction [25].

Hence, 1500ml of Argan oil was measured and placed in 5000ml Erlenmeyer flask and was heated to 65°C by using electric oven. While stirring the warmed oil, the sodium methoxide solution that was already prepared and maintained at 50°C was slowly added to avoid any possible drop in the temperature of the reaction mixture. The solution became cloudy. The reaction mixture was then heated to a temperature of 65°C and continuously stirred with the aid of a magnetic stirrer which was maintained at 500 revolutions per minute in order to increase mass transfer between the immiscible phases because alcohols and oils do not mix at room temperature. The reaction was left for 2 h to reach completion.

The reaction mechanism has three main steps as shown in Eqs. (3), (4), and (5). The first step involves an attack by the alkoxyde ion, to form a tetrahedrical intermediate. The second step involves the generation of alkoxyde by the reaction between the intermediate produced in the first step with an alcohol molecule. While in the last step, ester and diglycerides are produced with the liberation of three ester molecules and glycerol (propane 1,2,3 triol).

Reaction Mechanism

$$\text{Step 1 Triglycerides} + CH_3OH \xrightarrow[\text{Temperature } (65^{o}\boldsymbol{C})]{\text{NaOH catalyst}} Di-glycerides + \text{Methyl ester} \quad (3)$$

$$\text{Step 2 Di}-\text{glycerides} + CH_3OH \xrightarrow[\text{Temperature } (65^{o}\boldsymbol{C})]{\text{NaOH catalyst}} Monoglycerides + \text{Methyl ester} \quad (4)$$

$$\text{Step 3 Monoglycerides} + CH_3OH \xrightarrow[\text{Temperature } (65^{o}\boldsymbol{C})]{\text{NaOH catalyst}} \text{Methyl ester} + \text{Glycerol} \quad (5)$$

2.6.3. *Fatty acid methyl Ester(FAME) and glycerol phase separation*

After the completion of the transesterification reaction, the reaction mixture was immersed in a cold water bath and distilled water of about 15% of the initial volume of oil used (225ml) was added to the system and the entire reaction mixture was re-stirred for thirty (30) minutes in order to prevent further reaction occurring as a result of unreacted catalyst and alcohol. At the end of 30 min, the reaction mixture was transferred to a separating funnel and was allowed to settle for twelve hours (12hrs) for the separation of the fatty acid methyl esters (FAME) and the glycerol layer under gravity. The mixture of the fatty acid methyl ester was decanted into another beaker by opening the separating funnel tap leaving behind the glycerol. As a result of different chemical affinities, most of the catalyst and excess alcohol were concentrated in the lower phase (glycerol) while most of the mono-, di- and tri-glycerides were concentrated in the upper phase (Methyl esters).

2.6.4. *Purification of biodiesel*

After the separation of glycerol, the Fatty acid methyl ester (FAME) mixture contains impurities such as unreacted alcohol and catalyst, mono-, di- and tri-glycerides. These impurities usually bring about undesirable characteristics to the biodiesel produced. For instance, increased cloud point and pour point and lower flash point. Hence the mixture of FAME obtained from the alkali-catalyzed transesterification reaction must be purified in order to comply with established quality standards for biodiesel (ASTM and EN Standards) and for the following reasons.

1 Unreacted methanol must be removed because it degrades some plastics and elastomers, very corrosive and can lower flash point to unsafe levels (fire safety).
2 Unconverted or partly converted oils (bound glycerin) can result in very poor cold flow properties (Pour point, cloud point and Kinematic Viscosity, injector and in-cylinder deposits and thus results in potential engine failure.
3 Free glycerin results in injector deposit, clogged fuel filters and undesirable deposits at the bottom of the fuel storage thank
4 Unreacted catalyst (Caustic- NaOH) causes excessive injector, fuel pump wear, piston and ring wear, filter plugging and lubricant issues [26].

The volume of the biodiesel produced was measured after separation from the glycerol layer to know the quantity of acidified and warm water required. The methyl ester was washed with acidified water of about 20% of the produced ester volume in order to neutralize the mixture of the esters. The acid-free ester was then washed with ordinary water and dried to produce a pure biodiesel.

2.7. Conversion efficiency of the transesterification process

The conversion efficiency of the biodiesel transesterification process was deduced by using Eqs. (6) and (7) below.

$$\%\ \text{yield of Fatty Acid Methyl Este} = \left[\frac{\textit{Volume of FAME produced}}{\textit{Volume of Argan Oil used}}\right] \times 100 \quad (6)$$

$$\%\ \text{yield of Biodiesel} = \left[\frac{1240}{1500}\right] \times 100 \quad (7)$$

$$\%\ \text{yield of Biodiesel} = 82.67\%$$

2.8. Optimization of Argan oil biodiesel production parameters

A response optimization model (Fig. 2) was used to predict the optimization conditions for obtaining an optimum yield of 88.85%. Based on this model, the optimum conditions are sodium hydroxide (NaOH) catalyst concentration of 1.08%, methanol to oil molar ratio of 6:4, reaction time of 1.57hours and reaction temperature of 59 °C with a response desirability of 0.9239. Similarly, a Response surface methodology (RSM) was used to quantify the degree of interactions between the response or output variable (Biodiesel yield) and the input variables (catalyst concentration, methanol to oil molar ratio, temperature and time) and the surface response plots of these interactions are presented in Figure 3a, b and c. A regression polynomial model was used to develop a unified equation (eq. 8) for predicting the expected yield of Argan biodiesel for different values of reactant variables and a regression coefficient of 92.56% was obtained by plotting the experimental values against the predicted yield (Fig. 4).

$$\text{Regression (polynomial) Model} = Y\ (\text{yield}) = -414.644 + 214.036X_1 + 26.755X_2 + 116.627X_3 + 7.115X_4 - 98.765X_1^2 - 2.086X_2^2 - 37.044X_3^2 - 0.060\ X_4^2 \quad (8)$$

$$R^2 = 92.56\%,\ R^2(\text{Adj}) = 84.06\%$$

where:
X_1 = catalyst concentration (wt.%).
X_2 = alcohol to oil molar ratio.
X_3 = time (hour).
X_4 = temperature (°C).

2.9. FTIR Analyses

The presence of one or more aromatic rings in a structure is indicated by C–H and C=C–C ring related vibrations. The C–H stretching group occurs above 3000cm^{-1} and it occurs as a multiplicity of weak to moderate bands compared with the aliphatic C–H stretch. In FTIR spectra, a well-defined absorption of one but typically two sets of bands with wave number in the region of 1615cm^{-1}-1495cm^{-1} for aromatic ring stretch is representative of aromatic compounds [27]. This is conspicuously present in diesel FTIR spectrum (Fig. 5c) but absent in the parent argan oil and its produced biodiesel spectra (Fig.5a&b). This indicates the non-toxicity of methyl esters (biodiesel). The diesel FTIR spectrum has an aromatic ring stretch in the region of 1604.84cm^{-1}-1460.73cm^{-1} and an aromatic C–H stretch of wave number 2954.09cm^{-1} -2923.16 cm^{-1} (Fig. 5c). From Fig. 5b, the biodiesel has a methyl C–H asymmetrical stretch in the region with group frequency of 2970cm^{-1}-2950cm^{-1} while symmetrical stretch

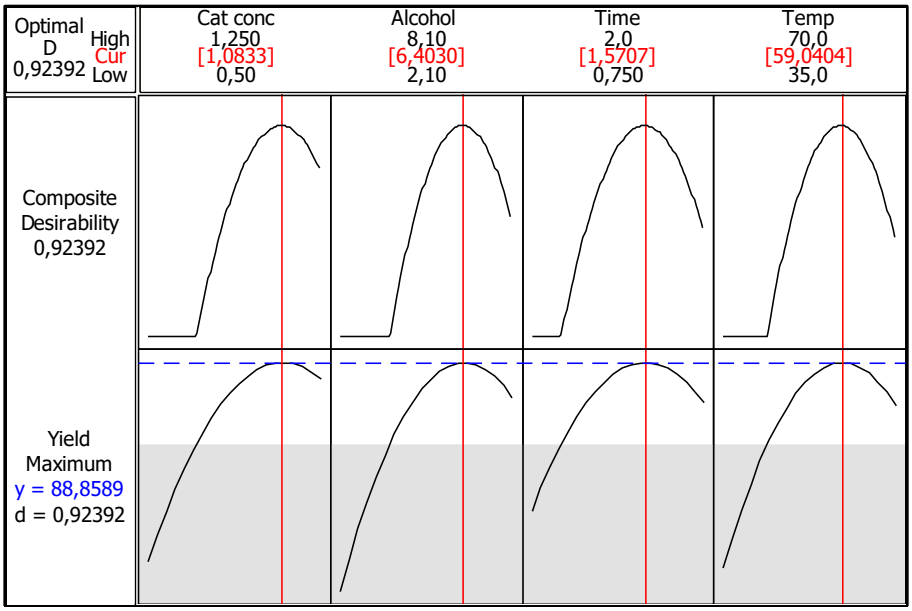

Fig. 2. Response optimization Model.

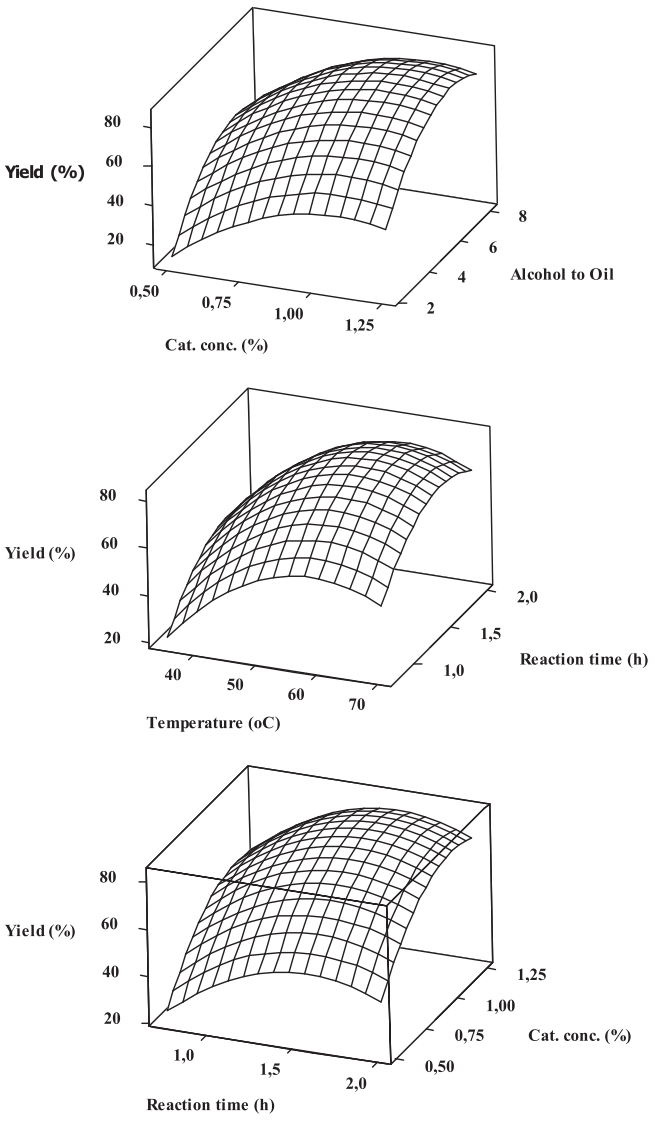

Fig. 3. a: Surface response plot for Yield (%) with catalyst concentration and alcohol to oil molar ratio interactions. b: Surface response plot for Yield (%) with reaction Temperature and Time interactions. c: Surface response plot for Yield (%) with reaction Time and Catalyst concentration interactions.

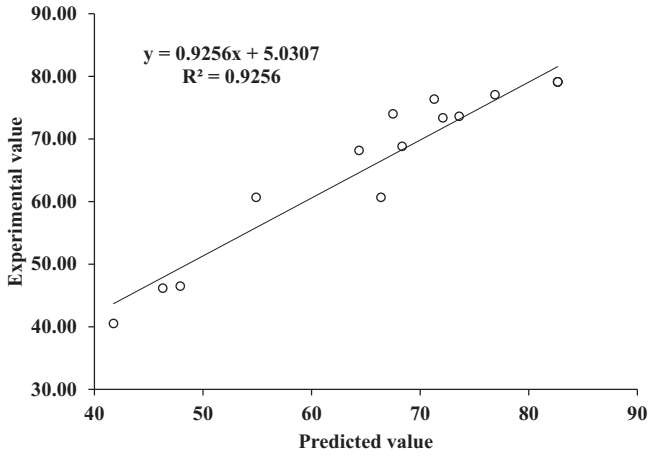

Fig. 4. Experimental versus predicted values from polynomial model.

occurs between 1470cm^{-1} and 1430cm^{-1} with a symmetrical bend in the region of 1380–1370cm^{-1}. Also, the Argan oil fatty acid methyl ester has a characteristics vibration group frequency in the region between 1750cm^{-1} and 1725cm^{-1}. This shows a qualitative conversion of the triglycerides in the vegetable oil to fatty acid methyl ester.

3. Results and discussion

(1) Cold flow properties: The cold flow properties of vegetable oil and its alkyl ester (biodiesel) is an intrinsic characteristics of the degree of saturation and branching of its fatty acid.

(a) Cloud Point:

The cloud point is the temperature at which wax crystals begin to form in a liquid as it is cooled. It can also be seen as the temperature at which an oil starts to solidify. Knowing the cloud point is very essential in determining storage ability of the fuel because storing formulations at temperature significantly higher than the cloud point may result in phase separation and instability [28]. The argan oil has a cloud point of 8°C (Table 2), this makes the argan oil to be susceptible to start up and performance problems when the compression engine and the fuel system are subjected to cold temperatures because at temperatures below the cloud point, larger crystals fuse together and form large globules that can restrict or cut off flow through fuel lines and filters [29, 30, 31]. Upon transesterification, the cloud point decreased to -3°C (Table 4) which makes its application in cold climate less problematic. However, when the biodiesel was blended with cold flow improver at ratios B_{30}, B_{50} *and* B_{80} , there was a significant improvement in the cloud point as seen in Table (8). It must be noted that when operating an engine at temperatures below its cloud point, heating will be necessary in order to avoid waxing of the fuel.

(b) Pour Point:

Pour point represents the lowest temperature at which a liquid will began to flow. The argan oil has a pour point of 5°C. Hence, the high pour point results in extensive crystal agglomeration which prevents free pouring of fluid under cold temperature conditions. Whereas, the synthesized biodiesel has a pour point of -7°C (Table 4) which invariably means that little stresses are needed to be overcome before the fuel begins to flow. Meanwhile, blending with petro diesel cold flow improver, tremendously reduced the pour point to -14, -19 and -31 for the three blends of B_{30}, B_{50} *and* B_{80} respectively (Table 8).

(c) Cold Filter Plugging Point (CFPP) and Low Temperature Flow Test (LTFT)

The cloud point and pour point are relatively easy to measure, but the CP over-estimate the cold temperature limit at which start up or performance issues begin to occur in a fuel system whereas the pour point tends to be optimistic [32, 33].

The CFPP describes the lowest temperature at which a 20-ML sample of a liquid passes through a 45-μm wire mesh under 0.0194 atm vacuum within 60s. While the low temperature flow test (LTFT) is the lowest temperature at which 180-ML sample of Argania spinosa (Argan oil) or its methyl ester passes through a 17-μm wire mesh filter under 0.197atm vacuum within 60s.The Argan oil has a relatively high CFPP and LTFT (Table 2), hence, higher susceptibility to filter plugging and flow operational problems are inevitable in cold temperature climates. This is because when wax molecules in the oil tends to crystallize at low temperatures, crystals agglomerate to form large masses which invariably causes filter plugging and eventually solidify the oil. However, a remarkable improvement in these properties was seen in the Argania spinosa biodiesel and upon blending with petrodiesel.

Summarily, the synthesized Argan biodiesel has better cold flow

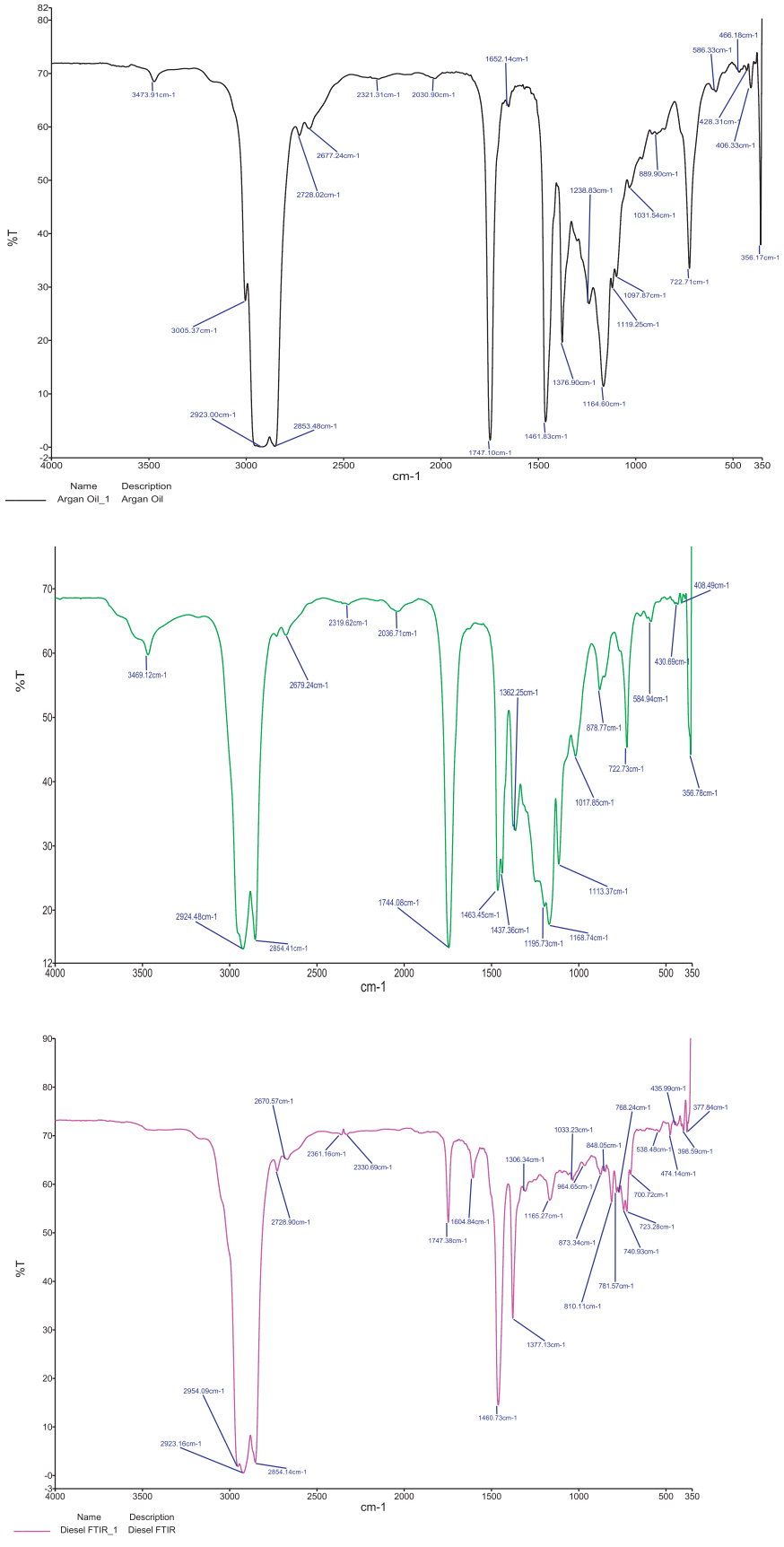

Fig. 5. a: Argan oil FTIR spectrum. b: Argan oil Methyl ester FTIR spectrum. c: Diesel FTIR spectrum.

Table 2
Cold flow properties of Argania spinosa Oil.

Fuel property	Method of estimation	Result
Cloud Point (°C)	ASTM D2500	8
Pour Point (°C)	ASTM D97	5
CFPP (°C)	ASTM D6371	4.5
LTFT (°C)	ASTM D4539	10

Table 4
Cold flow properties of Argania spinosa biodiesel.

Fuel property	Method of estimation	Result
Cloud Point (°C)	ASTM D2500	-3
Pour Point (°C)	ASTM D97	-7
CFPP (°C)	ASTM D6371	-6
LTFT (°C)	ASTM D4539	-2.5

properties than the Jatropha and Olive oil biofuels because of its higher degree of unsaturation. According to **Eboibi et al 2018** [34], Jatropha curcas methyl ester (biodiesel) has a cloud point of 8°C and pour point of 2°C (Table 6). While methanol trans-esterified olive oil under optimum conditions has a cloud point of -2°C and pour point of -3°C [35].

(2) Critical properties: These are properties that directly affect the performance, combustion and emission characteristic of the compression ignition engines upon the application of a designated fuel.

(a) Specific Gravity:

The argan oil biodiesel has a specific gravity of 0.865 at 15°C which is in good agreement with standard requirements. This density is high enough to increase energy concentration of fuel and thus minimize fuel leakage and enhance fuel atomization efficiency [36, 37]. Whereas the un-trans-esterified argan oil has an ignominious density of 910 kg/m^3 at the same temperature which corresponds to higher viscosity that results in poor combustion, performance and emission characteristics. In comparison of the Argan oil biodiesel to those of commercially available biodiesel fuels, **Pradeep and Sharma 2007** [38] evaluated the fuel characteristics of Jatropha oil biodiesel and a density of 878 kg/m^3 was obtained. These lower densities will ultimately give room for better air-fuel ratio and improvement of fuel atomization efficiency.

(b) Kinematic Viscosity.:

Kinematic viscosity is both cold flow and critical property of oil to be used in compression engines and it represents the degree of resistance to flow offer by the fluid. The argan oil has an extremely high viscosity of 33.15mm^2/s at 40°C (Table 3) which violates the ASTM and EN standard requirement for oil to serve as replacement for diesel in CI engines. This makes the oil to be susceptible to poor combustion, increased exhaust smoke and emissions when used directly as fuel in direct injection, CI engines. Upon transesterification, the Argania spinosa biodiesel yielded a kinematic viscosity value of 3.68 mm^2/s at 40°C(Table 3) which invariably conforms with the standard requirement of 1.9–6.0 and 3.5–5.0 for ASTM D6751 and EN14214 respectively. This sufficiently lower viscosity would help to prevent problems such as injector coking, poor fuel atomization, carbon deposits on piston and engine head, excessive engine wear and increased exhaust smoke and emission [39]. Whereas corn oil biodiesel has a higher kinematic viscosity value of 5.9 mm^2/s at 40°C [40] than Argan methyl ester of 3.68 mm^2/sat 40°C. **Avella et al 1992** [41] also recorded a value of 4.76mm^2/s at 40°C for canola oil methyl ester. Lower kinematic viscosity was experienced with Argan oil biodiesel because viscosity increases with chain length and degree of unsaturation of the fatty acid [42, 43].

(c) Flash Point:

The flash point is the lowest temperature at which a liquid can form an ignitable mixture in air near the surface of the liquid. Both the argan oil and its methyl ester (biodiesel) have a relatively high flash point that is comparable with that of Jatropha oil biodiesel of 162°C [44] and within the lower limit requirements by ASTM and EN standards (Table 3). Low flash point has its detriment in cold weather starting. However, minimum flash point temperatures are required for proper safety and handling of the fuel.

(d) Iodine Value:

The iodine value is a scale to numerically quantify the degree of unsaturation of fats and oil. From Table 1, the Argan oil has a high degree of unsaturation of 117 and hence, a higher iodine value of 105gI_2/100g of oil. Whereas, the Argan oil biodiesel has an iodine value of 101 gI_2/100g of biodiesel. All these values fall within the acceptable standard limits and thus make the biodiesel an efficient fuel due to high combustion rate and reduced oxidation and polymerization.

For methanol transesterification of Jatropha oil using NaOH catalyst, **Raja et al 2011** [45] obtained an iodine value of 101.7 gI_2/100g of biodiesel because of similar fatty acid profile. Also, **Abdur Rahman et al 2010** [46] recorded iodine values of 101.67 gI_2/100g of biodiesel for KOH catalyzed methanol trans-esterified sunflower oil. Iodine value significantly influences fuel oxidation and the type of aging products and deposits formed in diesel engine injectors. It has a relation with oxidative stability and reflects the tendencies of a fuel to oxidize and polymerize to form engine deposits.

(e) Cetane number:

The cetane number is a dimensionless descriptor of the ignition quality of a fuel and it a measure of the interval between the beginning of injection and auto-ignition of the fuel. Improper injection timing and consequent engine locking is the common catastrophe associated with fuels that have low cetane number [47]. The Argania spinosa oil has a cetane number of 52.50 which is in agreement with ASTM D6751 minimum value of 47 but violates the EN14214 minimum requirement of 51. Conversely, the Argan biodiesel has a cetane number of 54.20 which is good enough to forestall operational problems associated with poor ignition quality. Interestingly, the Argan biodiesel has a higher cetane number than the soybean and sunflower biodiesel (Tables 5 and

Table 3
Critical properties of Argania spinosa (argan oil).

Test property	Test method	Test result	ASTM D6751 standard	EN 14214 standard
Kinematic viscosity @ 40°C(mm^2/s)	ASTM D445	33.15	1.9–6.0	3.5–5.0
Specific Gravity @ 15°C	ASTM D1298	0.910	0.88	0.86–0.90
Flash Point (°C)	ASTM D93	164	93 min.	120 min
Cetane Number	ASTM D613	52.50	47 min.	51 min
Calorific Value kj/kg	ASTM D240	39,310	Sufficiently close to diesel	35 mj/kg
Iodine Value $\frac{gI_2}{100g\ of\ oil}$	ASTM D445	105	Report	130 max

Table 5
Critical properties of Argania spinosa (argan oil) biodiesel.

Test property	Test method	Test result	ASTM D6751 standard	EN 14214 standard
Kinematic viscosity @ 40°C(mm^2/s)	ASTM D445	3.68	1.9–6.0	3.5–5.0
Specific Gravity @ 15°C	ASTM D1298	0.865	0.88	0.86–0.90
Flash Point (°C)	ASTM D93	148	93 min.	120 min
Cetane Number	ASTM D613	54.20	47 min.	51 min
Calorific Value kj/kg	ASTM D240	40,665	Sufficiently close to diesel	35 MJ/kg
Iodine Value $\frac{gI_2}{100g\ of\ biodiesel}$	ASTM D445	101	Report	130 max

Table 6
Comparison of physico-chemical properties of plant oil methyl esters.

Plant oil	Property					
	K.V@40°C (mm^2/s)	Cetane number	H.V (Mj/kg)	Flash point (°C)	Cloud point (°C)	Pour point (°C)
Coconut[56a, 56b]	2.83	70	36.1	110	0	-3
Palmkernel[57a, 57b]	4.839	54.57	38.6	167	6	2
Soyabean [48]	4.18	49.6	39.823	190.6	-1.1	-3.9
Corn [40]	5.9	49	35.4	212	-2	-16
Olive [35]	4.7	61	37.29	≥110	-2	-3
Canola [41]	4.76	47.9	39.87	166	-3	-9
Jatropha [34, 44]	4.84	51.6	37.2	162	8	2
Sunflower oil [49, 62]	4.2	50	38.2	177	5	-2

Table 7
Less critical properties of Argania spinosa (argan oil) Biodiesel.

Test property	Test method	Test result	ASTM D6751 standard	EN 14214 standard
Sulphated Ash(%)	ASTM D 874	0.0095	0.020 max	0.020 max
Carbon residue (100% sample)	ASTM D 4530	0.038	0.050 max	0.30 for 10% dist res
Free Glycerin (%)	ASTM D6584	0.0085	0.020 max	0.020 max
Total glycerin (%)	ASTM D6584	0.115	0.240max	0.250 max
Water and sediment (%)	ASTM D2709	0.015	0.050 max	0.050 max

6). According to **Yahyah and Marley 2004** [48], the cetane number of soybean oil methyl ester was 49.6. While **Maria et al 2009** [49] obtained a value of 50 for sun flower oil biodiesel (Table 6).

Argan oil has a higher cetane value because of the presence of more saturated fatty acids in its profile (Table 1). Sunflower oil has about 59% polyunsaturated linoleic acid and 30% monounsaturated oleic with only 11% saturated fatty acids. Similarly, soybean oil has 61% poly unsaturated fatty acid and 23.4% monounsaturated fatty acid [50].

If cetane number is too high, combustion can occur before the fuel and air are properly mixed resulting in incomplete combustion and smoke. Whereas, low cetane number results in engine roughness, misfiring, higher air temperatures and slower engine warm up [51].

(f) Calorific Value:

The calorific value refers to the amount of heating energy released by the burning of a unit mass of fuel. Both the argan oil and its methyl ester (Biodiesel) have a very interesting heating value of 39,310 kJ/kg (Table 3) and 40,665 kJ/kg (Table 5) respectively. These values are sufficiently close to that of diesel of 45,310 kJ/kg [52]. Higher calorific value is desired for fuel because it facilitates the heat release during combustion and improves engine performance [53, 54, 55]. However, for methanol transesterification of coconut oil using potassium hydroxide (KOH) catalyst, **Bello et al 2015**[56a] obtained a lower calorific value of 36.1 MJ/kg (Table 6). Also, for palm kernel oil methyl ester, a calorific value of 38.6 MJ/kg was obtained by **Igbokwe and Obiukwu 2013**[57b] (Table 6). Biodiesel heating value increases with increase in carbon number in the ester molecule as well as with increasing ratio of carbon to hydrogen atoms [58].

(3) Less critical properties: The synthesized biodiesel has a low percentage of ash content of 0.0095 and carbon residue of 0.038% (Table 7). These values are very healthy as they help to prevent issues such as injector tip plugging, combustion deposits and injection system wears. A more than 0.02% sulphated ash indicates the presence of residual soap and catalyst. Sulphated ash in biodiesel can occur as a result of abrasive solids, unremoved catalysts and presence of soluble metallic soap [59]. High carbon deposits can invariably lead to fuel injector fouling and cylinder scoring within an engine. Free and total glycerine of the synthesized Argan biodiesel were evaluated by using ASTM D6584 procedures. The total glycerin quantifies the glycerol, mono, di and triglycerides present in the biodiesel and if it is too high, catastrophes such as fuel filter plugging and instability may arise. The free glycerin and total glycerin fall within the standard acceptable limit as seen in Table 7. For methanol trans-esterified Jatropha oil using NaOH catalyst, **Folaranmi 2013** [60] recorded a free glycerine value of 0.05% and a total glycerine value of 0.32%. Similarly, the free and total glycerine values obtained from the methanolysis of sunflower oil are 0.004 and 0.22% [61]. High total glycerine is an insignia of incomplete trans-esterification reaction and thus leads to production of crystals and deposits. Similarly, the water sediment was found to be 0.015% which is good for the synthesized biodiesel because excess free water in biodiesel can induce corrosion of fuel injection parts, appearance of free fatty acids and bacteria growths

Table 8
Cold flow properties of blends.

Fuel property	B_{30}	B_{50}	B_{80}
Cloud Point (°C)	-9	-15	-24
Pour Point (°C)	-14	-19	-31
CFPP (°C)	-12	-16	-27
LTFT (°C)	-8	-13	-21

that eventually clog filters.

4. Conclusion

The viability of Argania spinosa (Argan oil) biodiesel produced through alkali-catalyzed transesterification reaction as possible alternative to diesel fuel in compression ignition engines has been investigated via robust experimentation and analysis.

Alkali-catalyzed transesterification reaction is a reliable process which can help to bring about desirable properties on plant oils. For instance, the Argan oil specific gravity, kinematic viscosity, and iodine value were reduced by 4.95%, 88.90% and 3.81% respectively to conform to standard requirement. while an increase of 3.24% and 3.45% in cetane number and calorific value respectively was observed on transesterification. While the argan oil has an abysmal viscosity of $33.15 mm^2/s$ at 40°C that can make it to be susceptible to poor combustion, increased exhaust smoke and emissions when used directly as fuel in direct injection, CI engines. Whereas the its biodiesel has a low viscosity value of $3.68\ mm^2/s$at 40°C which gives room for reduced exhaust smoke emission, good fuel atomization and low engine wear. The biodiesel has a very good higher heating value of 40,665 kJ/kg which is very uncommon of other vegetable oils methyl esters and thus facilitate better heat release during combustion and improves engine performance. However, the Argan oil has abnormal cold flow properties that threatens its application in cold climates but the synthesized biodiesel has good cold flow properties which can be improved upon by addition of petro-diesel cold flow improver. Also, cetane number of 52.50 and 54.20 were obtained from the extracted oil and its biodiesel respectively. These values are sufficient enough for good ignition quality. Meanwhile, the amount of ash, carbon deposit, total glycerine and water sediment in the biodiesel showed that the fuel is free of any unreacted catalyst, soaps and glycerol and thus prevent issues such as injector plugging, injector fouling, filter plugging and corrosion of injector parts respectively.

Finally, from the results obtained, it can be concluded that the synthesized Argan biodiesel sufficiently fulfilled the upper and lower limits requirements of biodiesel by both the American society for testing and materials (ASTM) and the European union biodiesel standards.

Declarations

Author contribution statement

A. J. Folayan: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

P. A. L., Anawe: Concieved and designed the experiments; Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Data availability statement

The authors can boldly say that all the data used in this study were obtained from rigorous experimental research in the laboratory and not from any journal either in print or on line. We also declare that the data will be available for public use once the paper is published.

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