(RESEARCH ARTICLE)

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Effect of process parameters on biodiesel yield produced from palm kernel shell oil (PKSO) using eggshell as catalyst

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Abstract

Effect of process parameters on biodiesel produced from PKSO and eggshell catalyst is investigated. The study showed the significant effect of the process parameters and properties on biodiesel yield. The appropriate reaction parameters that had the maximum biodiesel yield of 79.53% were 3% catalyst concentration, 150 minutes reaction time, 65°C reaction temperature, 12:1 methanol/oil molar ratio, and agitation speed of 300 rpm. Critical fuel properties such as; density, kinematic viscosity, flash point, fire point, cloud point, pour point, free fatty acid, aniline point, diesel index, API gravity, cetane, and fuel calorific values of the biodiesel obtained from all operating parameters were found to be between 0.8461 – 0.8831kg m^{-3}, 5.31 – 7.84 mm^{2}s^{-1}, 97 – 141 °C, 107 – 150 °C, 4.14 – 6.5 °C, 1.5 – 4.5 °C, 0.318 – 0.931mgKOH/kg, 45 – 52 °C, 31.83 – 41.17, 28.165 – 33.258, 28.8313 – 41.1519, and 16 – 18% respectively. These values are within the accepted standard limits for diesel fuels.

Keywords: Process parameters; Biodiesel yield; Egg shell catalyst; Palm kernel shell oil; Characterization

1. Introduction

Currently, the world is facing environmental challenges due to the release of toxic and harmful substances into the environment from fossil fuels as a result of internal combustion engines, and the burning of waste aided by fossil fuels [1, 2]. This has increased the emission of CO_2, SO_2, and NOx globally [3]. Due to the usage of this fossil fuels, the world is challenged with climatic issues, global warming, disease (related to breathing), and has also caused a decrease of fossil fuels from the world's oil reservoirs [4,5]. For instance, some industrial cities are environmentally polluted with 'black soot' which is caused by an incomplete combustion of these fossil fuels [6,7,8]. Since these fossils are not properly burnt, they react with air and water molecules [9]. [10], also observed that globally, the transportation sector has made so much use of these fossil fuels, and affected nations are still besieged with a swift in energy mix or transition to alternative fuels. Today, the rate of fossil consumption in the world energy is about 84% [11,12]. According to NASA and BP Statistical Review of World Energy, the several lockdowns during the COVID 19 pandemic reduced the emission rate of CO_2 in the world due to the fact that industries were not working as much as they did in previous years. Thus, reduced the emission rate to about 9.6% of CO_2 compared to 60-77% of CO_2 released duration. Research and development of substitute fuels to fossil has become a very vital problem. Therefore, it has become essential that substituted fuel to fossils be renewable, eco-friendly, locally available, efficient, and viable, for environmental sustainability and economic growth. Biodiesel is one of the alternative fuels that can substitute fossil fuels [13,14]. Biodiesel is a fatty acid methyl ester (FAME), a biomass derived renewable fuel which can serve as an alternate to diesel fuel [15,16]. Biodiesel fuel is mostly gotten from vegetable oils because of its high viscosity and low volatility and trans-esterification which can be used in the production process to help reduce the high viscosity of the bio-oil [17,18,19]. Trans-esterification has been viewed as an excellent process for biodiesel production, because it helps in removing the glycerides present in the bio-oil, thereby allowing the oil esters of the vegetable oil to mix with alcohol [20,21]. In the trans-esterification process,

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either homogenous or heterogeneous catalyst can be utilized to enhance the rate of reaction. According to [22], catalysts that are homogenous are less efficient because during the production process, it can be used once. Therefore, as a circumvent, catalysts that are heterogenous for transesterification (such as: biochar and solid-acid based catalysts) has evolved, and offers better advantages due to its eco-friendliness, synthesis, easy separation, high efficiency and reusability, less corrosive nature, dual production process, cost effectiveness, functional surface, etc. [23]. Today, efforts in terms of research and development of heterogeneous catalysts are rapidly gaining relevance. Recent studies on the use of a homogenous (palm kernel shell biochar) catalyst has been carried out by [24], to produce biodiesel from waste cooking oil. Conversely, based on reviewed literature studies of [25], and [26], egg shell catalyst has been identified to have a great potential when utilized as a biodiesel synthesizer or carbon catalyzer, and has been used by other researchers to produce biodiesel from different biooils and it blends. However, studies on the use of PKSO to produce biodiesel with egg shell as catalyst has not yet been considered. This study focuses on producing biodiesel from PKSO with an egg shell-based catalyst through a transesterification process, characterization of the catalyst and oil to determine production yield, and examining the effect of process parameters on biodiesel yield.

2. Material and methods

2.1. Egg shell sample collection, preparation and modification

Egg shell was locally sourced in selected areas in Cross River State, Nigeria. The sample was allowed to dry in hot air oven for 24 hours at 60^oC. After drying, it was milled to powdery form using an industrial ball mill. The milled sample was sieved. The sieved sample was submerged in distilled water and allowed to stand for an hour. This is to separate the egg shell (lower portion) from impurities (upper portion) which floats on water. The overlaying water portion was decanted to remove all impurities in the sample. The sample afterwards was placed in hot air oven at 60^0C to dry. For thermal modification of the dried sample, the egg shell sample was weighed into a flat bottom, round flask. Phosphoric acid (100ml of concentrated phosphoric acid made up to 1L using distilled water) was added to the egg shell in the flask. Reflux condenser with water circulation tubes was fitted to the flask. The whole set up was placed on a heating mantle to reflux for 2 hours. While refluxing, water was allowed to circulate at the outer jacket of the reflux condenser. This was done to prevent the loss of steam from the flask. The mixture was allowed to cool and filtered using qualitative filter paper (240 mm). The residue which is the egg shell was dried in hot air oven at 60^0C, and the sample thereafter was transferred into ceramic crucibles and carbonized in a muffle furnace for 4 hours at 600^0C.

2.2. Palm kernel shell oil extraction

Palm kernel shell, being a waste product gotten after processing of palm kernel, was obtained from the local mills' residue dump sites in the study region. It was air-dried and sorted to remove impurities. It was further grounded using industrial blender. The sample was weighed into a semi-permeable cotton material and placed into the thimble of a 500ml Soxhlet extractor. N-hexane was measured afterwards into a 500ml flat bottom round flask. The Soxhlet with the extraction thimble containing the sample in a semi-permeable membrane was connected with the condenser which was fitted to the flat bottom round flask containing n-hexane. The Soxhlet extraction system was then heated on a hot plate while water was allowed to circulate at the outer jacket of the condenser. The extraction was discontinued when the oil was completely extracted from the sample. The de-fatted sample in the semi permeable membrane was discarded, while the oil and n-hexane mixture in the flat bottom flask were separated by distillation. During distillation, the n-hexane was distilled over while the extracted oil remained in the flask.

2.3. Oil characterization

The extracted oil from the palm kernel shell was characterized to determine their density, refractive index, moisture content, saponification value, viscosity, acid value, peroxide value and iodine value following these procedures

2.3.1. Density

An empty beaker was weighed and the weight recorded. 50ml of the oil sample was introduced into a 50ml density bottle. The weight of the density bottle and the sample was taken. Sample weight was obtained by subtracting the weight of the empty density bottle from the weight of the sample and the density bottle. From the sample weight obtained, the density was determined by taking the ratio of the weight of the oil to the known volume (50ml) in SI unit as presented in Eq. 1.

$$h = \frac{wt}{v} \quad \text{.......................} \quad (1)$$

2.3.2. Refractive Index

The refractive index was determined using a digital table-top refractometer. The device was initially calibrated to zero using distilled water, and the sample placed at the glass prism and read off using the refractive index key.

2.3.3. Moisture

The moisture content of the sample was determined by the dry oven method. The sample was weighed into an already weighed petri-dish (a). The sample in the petri-dish was transferred into the oven and left for an hour at 105° C, and thereafter allowed to cool in a desiccator. The second weight of the sample thereafter, was taken after the oven-heating (b). Thus, the percentage moisture was obtained as given in Eq. 2.

$$\% \ a - \frac{b}{v} \times (100) \ \dots\dots\dots\dots\dots \ (2)$$

2.3.4. Saponification value

Saponification value was determined according to the method of [21]. This is the milligram of KOH required to neutralize the fatty acids resulting from the complete hydrolysis of 1g of the sample. Saponification value thus, is the measure of the molecular weight of the fatty acid in the sample. 0.5g of the sample was weighed into a conical flask and 50ml of 0.5N ethanolic KOH was added to the sample. The mixture was refluxed to saponify the sample. The unreacted KOH was titrated back with 0.5N hydrochloric acid (HCl) using three drops of phenolphthalein as indicator, and the saponification value of the sample calculated using Eq. 3.

$$Sv = \frac{(Tv) \ (HCl) \ (56.1)}{(wt)} \qquad \dots\dots\dots\dots\dots \ (3)$$

Where the normality of HCl acid is 0.5 and the molecular weight of KOH is 56.1g/mol

2.3.5. Viscosity

U-tube viscosity meter or viscometer manufactured by Poulten Selfe and Lee Ltd (PSL ASTM-IP 350) was used to determine the kinematic viscosity. Micropipette was used to introduce 5ml of the sample into the viscometer. The sample flow time from the upper meniscus to the lower meniscus was determined in seconds at 40° C. Hence, the oil viscosity was obtained using Eq. 4 as:

$$ct \ (mm^2 s^{-1}) \qquad \dots\dots\dots\dots\dots\dots \ (4)$$

Where c is the viscosity constant taken as 0.4891, and t is the time for the measurement.

2.3.6. Acid value

This is the number of milligrams of KOH required to neutralize the free fatty acid in 1g of the sample (ASTM, 2004). 0.5g of the sample was weighed into a conical flask. 20ml of ethanol and three drops of phenolphthalein indicator were introduced. The solution was titrated with 0.5N KOH with constant agitation until a faint, pink end point appeared and persisted for thirty seconds. The volume of the titrant at end point was recorded. From the readings obtained, the acid value was evaluated using Eq. 5.

$$Av \ = \frac{(Tv)(KOH)(5.61)}{(wt)} \quad \dots\dots\dots\dots\dots\dots \ (5)$$

2.3.7. Peroxide value

The peroxide value was determined according to the method of [21]. The peroxide value is the measure of the peroxides contained in the oil. It is used to determine the rancidity of a sample containing fat or oil subject to oxidation. Fresh oils according to the source, usually have peroxide values well below 10mEq/kg (milliequivalent/kg) of fat. A rancid taste often begins to be noticeable when the peroxide value is between 20 and 40mEq/kg. 0.5g of the oil sample was weighed into a conical flask and 25ml glacial acetic acid and chloroform mixed together added in the ratio of 2:1. 1ml of 10% potassium iodide (KI) thereafter was added and vigorously shaken, covered and kept in the dark for one minute, while a 35ml of starch indicator afterwards was added. The whole solution was then titrated with 0.02N sodium thiosulphate ($Na_2S_2O_3$) solution as the solution turned from pale black to white. Titration was also made for blank and the peroxide value calculated using Eq. 6.

$$Pv = \frac{(100)(V_1 - V_2)(\text{normality of titrant})}{\text{wt}} \quad \text{.....................} \quad (6)$$

Where: 100 = milliequivalent conversion factor; V_1 = titre value of the sample; V_2 = titre value of the blank; and the normality of the titrant = 0.02 of sodium thiosulphate solution.

2.3.8. Iodine value

The iodine value was determined according to the method of [21]. The iodine value of a sample as the source stated, is defined as the weight of iodine absorbed by 100 parts by weight of the sample. 0.5g of the sample will be weighed and 15ml of chloroform added. 25ml of Wiji's solution after that, was added and mixed vigorously. It was covered tightly and placed in the dark for thirty minutes. 20ml of 10% KI was added and also 150ml of distilled water. The solution was then observed as it turned red, and more so, 5ml of 5% starch solution indicator was added and observed as the solution turned blue-black. The solution was titrated with 0.1N sodium thiosulphate solution until black precipitates appeared in colorless solution. The titration was also made for blank and the iodine value calculated as in Eqn. 7.

$$IV = \frac{(12.69)(V_1 - V_2)(\text{normality of titrant})}{\text{wt}} \quad \text{.................} \quad (7)$$

Where; 126.9/10 = 12.69 = molecular weight of iodine in g/mol, V_1 = titre value of the sample, V_2 = titre value of the blank, and normality of titrant = 0.1N sodium thiosulphate solution respectively.

2.4. Biodiesel production and characterization

2.4.1. Transesterification

The transesterification reactions to produce methyl ester was carried out in a 500 ml, round bottom, glass, spherical, three neck reactor. The glass reactor was set on a heating mantle equipped with electromagnetic field which actuates the agitation effect of the stirring nob when switched on. Initially, the reactor was preheated to eliminate residual moisture. A calculated amount of 'methanol' and modified 'catalyst' was added in the amounts established for each experiment and pre-stirred for 10 minutes for proper dissolution. After that, the palm kernel shell oil (bio-oil) was added. A reflux condenser with cold water circulating at the outer jacket was fitted to the mid neck of the reactor. Mercury in glass thermometer held in plastic bung was also fitted to the right neck of the reactor. The left neck of the reactor initially was left open for input of reactants (oil mixture, methanol and modified catalyst), and a capsular stirring nob place into the reactor through the left neck, after which it was closed using a plastic bung. The setup was placed on a magnetic heating mantle and switched on. The stirring system which was also maintained at an established speed and regulated at the required temperature, was switched on, taking this moment as the time zero of the reaction. Each reaction was allowed to last for the required 'time' at specific 'temperature'. When the methanolysis reaction had finished, the transesterification product was allowed to stand for twelve hours in a separating funnel for glycerol separation. The crude glycerol was removed through the funnel tap leaving the methyl ester (biodiesel) behind. The biodiesel was washed with hot water and dispensed into a 250 ml beaker, and thereafter heated at 105 $^{\circ}$C to remove any water molecules left from the biodiesel. The biodiesel was then allowed to cool and stored in calibrated (metric) specimen bottles.

2.4.2. Biodiesel characterization

The biodiesel produced was characterized by the cloud and pour point, flash and fire point, anisidine point, fuel gravity, cetane index and cetane number respectively.

Cloud point and pour point:

The bio-diesel sample was placed in a medium sized test tube and the test tube with its content was placed in a test tube rack, stored in a refrigerator and monitored. The temperature at which the heavier components form mass of colloids is the cloud point [27,28], while the temperature at which the sample solidify is the pour point [28,29]. The temperature was determined using mercury-in-glass thermometer.

Flash point and fire point:

The flash point and the fire point were determined by pouring the biodiesel sample in a glass petri-dish so that the surface of the dish was covered. A mercury-in-glass thermometer was immersed into the sample in the petri dish so that the tip of the thermometer came in contact with the biodiesel sample. The thermometer was held to position using a retort stand and clamp, while the sample was placed on a laboratory heating mantle. The sample was gradually heated

and a light source applied at intervals. The lowest temperature at which the sample just ignites and goes off is called the flash point [30], while the lowest temperature at which the sample ignites persistently is called the fire point [31].

Anisidine point

The anisidine point is the lowest temperature at which equal volume of anisidine and the biodiesel under test form a single phase. For the test, an anisidine oil was poured into a test tube, while the test biodiesel sample was also introduced into the test tube. Because both samples initially did not mix and so form double phase, the test tube in a test tube rack was placed in a refrigerator. The lowest temperature at which the anisidine oil and the biodiesel sample mixed together was the anisidine point [31,32].

Gravity

The gravity is based on the American Petroleum Institute (API) gravity and was determined from the value of the specific gravity of the product and expressed in Eq. 8.

$$API = (141.5 / specific\ gravity\ at\ 60°F) - 131.5 \qquad .... (8)$$

Cetane index / cetane number:

The cetane index is a measure of the ignition quality of the biodiesel fuel [31,32]. The higher the cetane index, the easier it is to start a standard diesel engine. The cetane index was determined according to the method of [21], given in Eq. (9) as:

$$CI = \frac{Ap\ (°C) \times API\ Gravity}{10} \qquad .... (9)$$

2.5. Effects of process parameters on the produced biodiesel yield

To study the effects of process parameters (independent variables) which include catalyst concentration (wt. %), time (h), temperature (°C), methanol / oil molal ratio and agitation speed (rpm), the parameters were varied at points within the specified study range, while all the other parameters were kept constant. The optimal point for each level of parameter being studied was held constant for subsequent levels of study. The measurable outcome or response (dependent variable) was the volume of the biodiesel yield.

2.5.1. Effect of catalyst concentration

To study the effect of catalysts (thermal, acid and alkaline modifications) concentration on the biodiesel yield, the catalyst concentration in weight percent was varied at points; 1, 2, 3, 4 and 5 weight percent. At this study level, other parameters (temperature at 65° C, methanol / sample molal ratio of 10:1, reaction time of 120 minutes and agitation speed of 400 revolutions per minute, rpm) was held constant.

2.5.2. Effect of time

For the effect of time on the biodiesel yield, the time was varied as 30, 60, 90, 120 and 150 minutes, while the other conditions temperature at 65° C, methanol / sample molal ratio of 10:1 and agitation speed of 400 rpm and the value for the maximum catalyst concentration as obtained in sub-section 2.5.1 was held constant.

2.5.3. Effect of temperature

The temperature, being one of the process variables, was studied at different heating points at 35, 45, 55, 65 and 75° C, while other conditions for the studied parameters (methanol / sample molal ratio of 10:1 and agitation speed at 400 rpm) with the values for the maximum catalyst concentration and reaction time with the highest yield obtained in subsections 2.5.1 and 2.5.2 were held constant.

2.5.4. Effect of methanol / sample molal ratio

The effect of methanol/sample molar ratio was studied at the molal concentrations of 4:1, 6:1, 8:1, 10:1 and 12:1, while the other studied parameters (agitation speed of 400 revolutions per minute rpm) with the values for the maximum catalyst concentration, reaction time with the highest yield, and the heating temperature with the maximum yield as obtained in subsections 2.5.1, 2.5.2 and 2.5.3 were held constant.

2.5.5. Effect of speed

The rotational / agitation speed at which the sample is stirred in the reactor was varied at 100, 200, 300, 400 and 500 rpm, while the other variables studied (catalyst concentration with the maximum yield, reaction time with the highest yield in heating temperature with the maximum yield and the methanol/sample molal concentration with the maximum yield) as obtained in subsections 2.5.1, 2.5.2, 2.5.3, and 2.5.4 were held constant.

3. Results and discussion

3.1. Proximate and ultimate analysis of palm kernel shell oil

The proximate and ultimate analysis was carried out to characterize the feedstock to predict the actual condition of the oil. Table 1 presents the results obtained for the characterization of palm kernel shell oil.

Table 1 Biodiesel characterization

Parameters	Values
Refractive index @ 29oC	1.4664
Moisture (%)	4.23
Ash content	11.75
Density (g/ml)	0.927
Kinematic viscosity @ 40oC (mm2s-1)	32.994
Energy value (J/g)	29949
Flash point (oC)	247
Fire point (oC)	259
Cloud point (oC)	19.50
Pour point (oC)	15.00
Oil yield (%)	17.83
Acid value (mgKOH/kg)	0.5049
Saponification (mgKOH/kg	220.10
Peroxide value (meq/kg)	0.87
Iodine value (mg/100g)	18.30
Molecular weight (g/mol)	766.76

The palm kernel shell oil was extracted from palm kernel shell using Soxhlet extractor after it was grounded. Oil yield of 17.83 weight percent was obtained. Oil quality parameters evaluated include refractive index, moisture, density, kinematic viscosity, energy value, acid value, saponification, iodine value, molecular weight, flash and fire point, cloud and pour point.

Peroxide value is a test that provides information about the deteriorative state of the oil being studied [33,34]. It is a test for stability [34]. Oils exposed to increased temperatures have higher tendency to deterioration than oils preserved at room temperatures. This is because, oxidation is rapid at higher temperatures. Deterioration in oil is considered to be low if peroxide value is between 1.0 and 5.0 meq O_2 kg^{-1} of oil; moderate when value is between 5.0 and 10.0 meq O_2 kg^{-1} of oil and high if the IP is greater than 10 meq O_2 kg^{-1} of oil [35,36]. In this work, peroxide value obtained for palm kernel shell oil is 0.87 meq/kg.

Acid value is also a major oil quality parameter that indicates a sample ease for use in biodiesel production. High acid value is an indication of high free fatty acid in the oil. Free fatty acids in oil can be elevated as a result of exposure to high temperatures, when the oil is fried, or oxidation that can occur in the presence of peroxides or light [37]. Acid value

of 0.50 mgKOH/kg obtained for palm kernel shell oil is low enough for use in biodiesel production. Acid value higher than 3.4 mgKOH/kg could reduce methyl ester yield considerably.

Saponification analysis involves the complete hydrolysis of the triglyceride (oil) in the presence of ethanolic alkaline solution. Values obtained for saponification and acid value are essential in quantifying the oil ester percentage and molecular weight. Ester percentage is the potential at which triglyceride can be converted to methyl ester, while molecular weight is essential in calculating quantity of methanol required for transesterification. Saponification value for the PKSO is 220.10 mgKOH/kg.

3.2. Catalyst characterization

Characterization of the catalyst is important because it help predict the actual condition of the oil. This will thus help to determine if the said catalyst is good for use as a material for biodiesel production. Table 2 presents the results obtained for the characterization the egg shell.

Table 2 Catalyst characterization

Parameter	Egg shell
Moisture (%)	0.04
Bulk Density (g cm-3)	0.688
pH	5.70
Surface Area (m2 g-1)	655
Organic Carbon (%)	2.96
Organic Matter (%)	8.78
Volatile matter (%)	9.84
Particle Density (g cm-3)	1.37
Total porosity (%)	50.97

3.3. Effects of process parameters on the biodiesel yield using egg shell as catalyst

3.3.1. Effect of Reaction Time on Biodiesel Yield
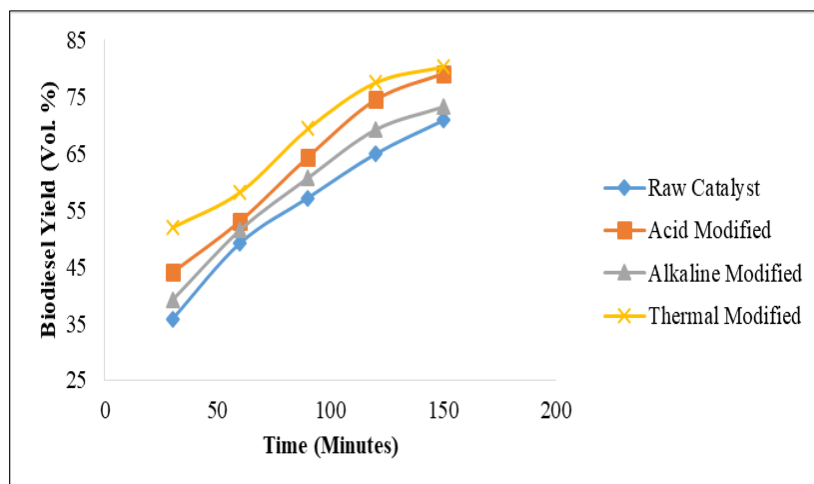
Figure 1 Effect of reaction time on biodiesel yield

Fig. 1 is a graphical presentation of the effect of reaction time on biodiesel production using the egg shell. Reaction time for the production were monitored for thirty to one hundred and fifty minutes at regular intervals. Egg shell catalysts

had its maximum biodiesel yield at 79.53% vol. During the reaction period, other process effects such as temperature, catalyst concentration, methanol and sample mole ratio, and agitation speed all remained constant.

3.3.2. Effect of Temperature on Biodiesel Yield

Fig 2 is a graphical representation on the effect of temperature on the biodiesel yield, temperature was varied from 35 ^{0}C to 70 ^{0}C at five regular intervals. All other parameters were kept constant as follows; methanol and oil mole ratio is 10:1, catalyst concentration is 3 % wt., agitation speed is 250 rpm and time is 150 minutes. The time chosen is the maximum reaction time from figure 1. Results obtained from this work indicate that at temperatures as low as 35 ^{0}C, biodiesel can actually be produced, however, not optimal quantity. Maximum biodiesel yield by volume from palm kernel shell oil for the egg shell 79.53%. For all the catalyst forms, optimal temperature for biodiesel yield is 65 ^{0}C. At a temperature of 75 ^{0}C, they were a visible reduction in the biodiesel yield. This can be attributed to the fact that methanol which reacts with the sample to cause saponification, hence transesterification, boils at 65 ^{0}C. Thus, at 65 ^{0}C the maximum activation energy has been achieved. Higher temperatures can cause boiling and evaporation of methanol
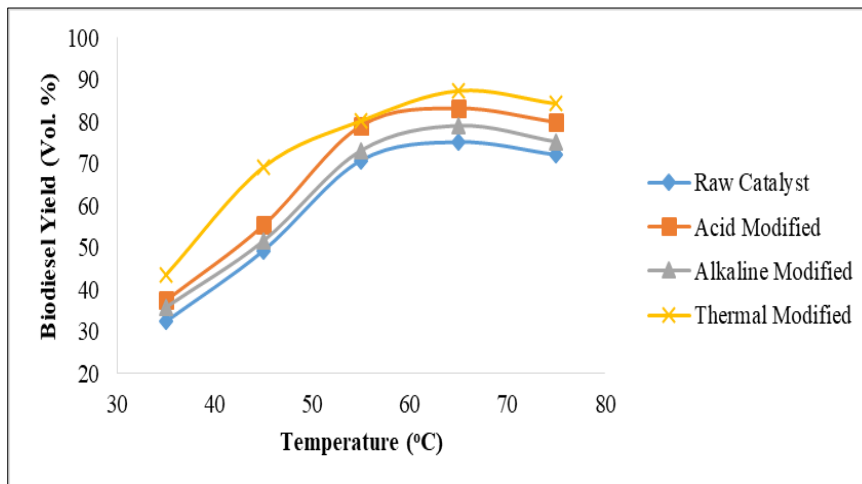
Figure 2 Effect of temperature (^{o}C) on biodiesel yield

3.3.3. Effect of Methanol/Oil Molal Ratio on Biodiesel Yield
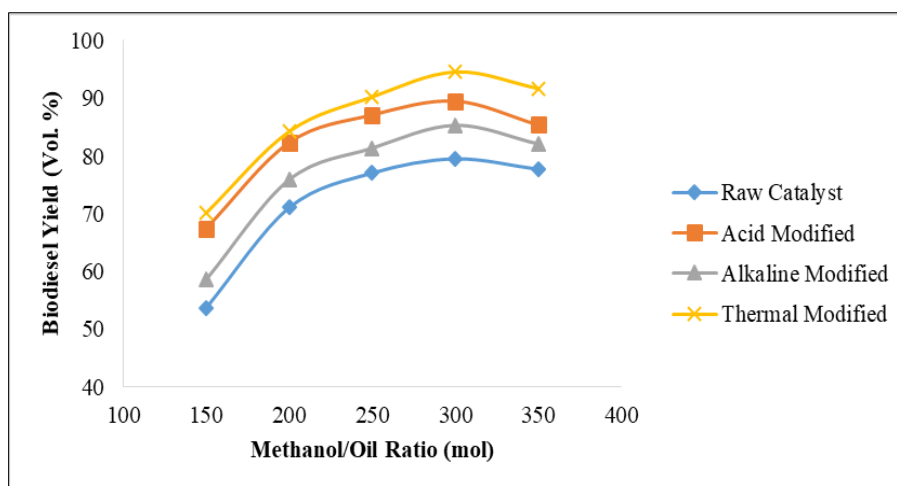

Figure 3 Effects of methanol/oil ratio (mol) on biodiesel yield

The effect of methanol and oil molal ratio on the yield of biodiesel is one that cannot be over emphasized as shown in Fig 3. Methanol to oil mole ratio was varied at five different study points (4:1, 6:1, 8:1, 10:1 and 12:1), while other study parameters were kept constant. Study time and temperature were held constant at their observed optimal conditions of 150 minutes and 65 ^{0}C. Researchers have reported optimal methanol to oil mole ratio at 6:1 [28]. However, majority of the research were done using egg shell. The catalysts (egg shell) had a maximum yield volume of 79.53 %. Methanol and oil molar ratio which gave this maximum yield was 12:1. Other factors that could affect biodiesel yield in respect to

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alcohol and sample mole ratio could also be fatty acid composition and moisture content of the oil, and also the nature of method of modification of the catalyst. Methanol and oil when placed in the reactor do not form a homogeneous mixture. Oil being denser, settles below while methanol stays afloat.

3.3.4. Effect of Catalyst Concentration on Biodiesel Yield

The effect of catalyst, a character that enhances the rate of chemical, is part of the crucial parameters studied. For this study, concentration of the egg shell and other catalyst modified forms were varied at 1 %, 2 %, 3 %, 4 % and 5 % weight. Other parameters remained constant. Conditions observed to be optimal for temperature, time and methanol and oil mole ratio which have been studied were used. For the four catalyst forms used, catalyst concentration of 3 % weight gave the highest yield of biodiesel. The highest yield of biodiesel obtained was 79.53 % by volume. From catalyst concentrations of 1 % to 4 %, there was gradual increase in the yield of biodiesel as concentration increases as seen in Fig. 4. However, at 5% concentration, there was reduction in the yield of biodiesel. This was as a result of absorption of the product by the excess catalyst following increase in concentration.
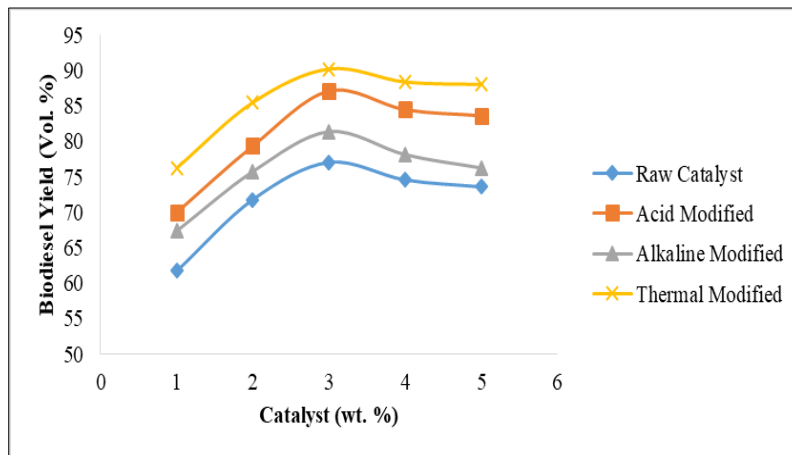
Figure 4 Effects of catalyst concentration (wt %) on biodiesel yield

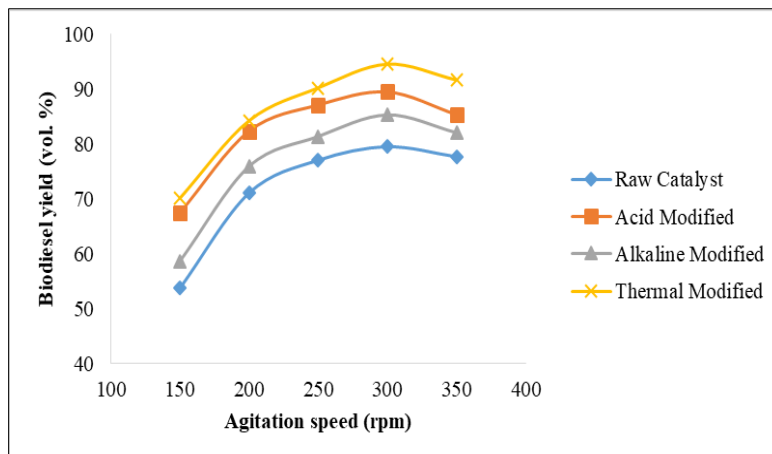### 3.3.5. Effect of Agitation Speed on Biodiesel Yield

Figure 5 Effects of agitation speed on biodiesel yield

Agitation is an effective method which ensures that non homogeneous phases are mixed. Agitation or stirring speed is therefore an effect that permits effective homogenization of the reacting components (methanol and oil) and the catalyst. The study of the effect of reactants agitation was clearly seen in Fig. 5. The agitation speed was at five equal intervals namely; 150 rpm, 200 rpm, 250 rpm, 300 rpm and 350 rpm (revolution per minute). Optimal conditions from other parameters (time, temperature, catalyst concentration, and methanol and oil mole ratio) were kept constant. Optimal yield for the egg shell catalyst were obtained at agitation speed of 300 rpm. Maximum yield was obtained at

79.53 % by volume. At 400 rpm, biodiesel yield reduced. This reduction in yield is as a result of dissolution of the catalyst (solute) into the solution following excessive stirring.

3.4. Characterization of the biodiesel (blends) and diesel

The biodiesel produced from the palm kernel shell oil into different blends (B_5, B_{10}, B_{20}, B_{30}, B_{40} and B_{100}) including the diesel (D_{100}) were characterized to ascertain their oil properties.

3.4.1. Kinematic Viscosity

Kinematic viscosity is a term that describes how a liquid reacts to shear stress in terms of flowing from one location to the other. In terms of energy utilization, a less viscous biodiesel tends to burn more efficiently when compared to a more viscous biodiesel. Apart from poor combustion, fuel whose viscosity is wildly beyond the viscosity limit could pose a higher risk of environmental pollution in terms of exhaust emission, filter damage and much pump resistance [38].
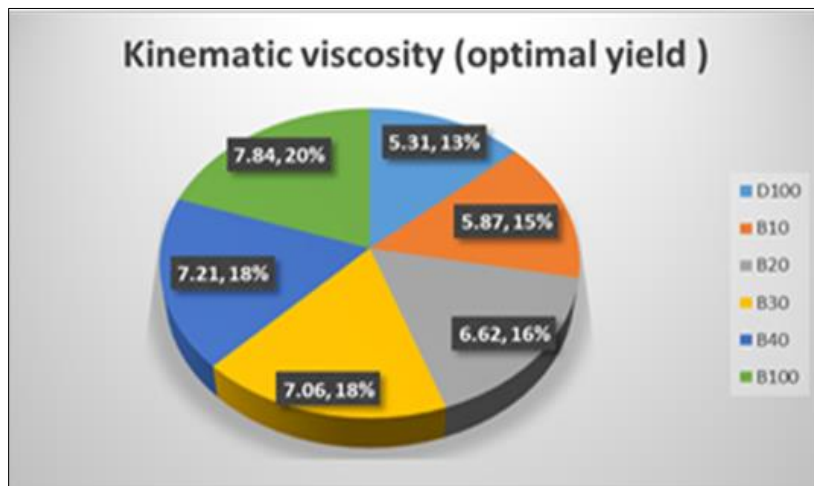
Figure 6 Optimal yield on kinematic viscosity of the biodiesel (blends) and diesel

The kinematic viscosity reported for samples as shown in Fig. 6, from this work range of 5.31 mm^2s^{-1} to 7.84 mm^2s^{-1}. National Agency for Petroleum, Natural Gas, and Biofuels (ANP) resolution specified limit for kinematic viscosity is 6.00 mm^2s^{-1}. Samples that passed within this range are D_{100} and B_{10}. Though others such as B_{20}, B_{30}, B_{40} and B_{100} weren't within the specified range however, they weren't completed far off. Fuel atomization is a function of viscosity; lesser viscosity enhances fuel atomization.
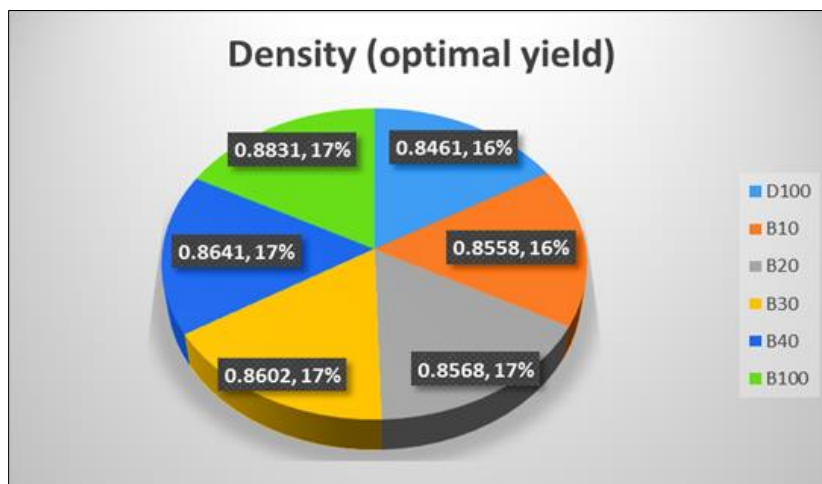
3.4.2. Density

Figure 7 Optimal yield on density of the biodiesel (blends) and diesel

The density of the petroleum diesel is lower than the blends and the pure biodiesel from palm kernel shell oil. This is consistent with the study carried out by [26].

Densities as shown in Fig. 7, recorded a range from 0.8461 kg m^{-3} to 0.8831 kg m^{-3}. They were gradual increase in densities from the Petro-diesel through the blends and pure biodiesel from which the blends were made. Higher density which characterizes the pure biodiesel and the blends confers an advantage on their when compared to petroleum diesel; it is called being 'chemically advanced' as it affects injection time [39]. This phenomenon means that the time required for biodiesel and its blends to travel from the injection pump to the injector is considerably shorter when compared to the petroleum diesel. This in effect compensates for lesser energy value of biodiesel [28]. Densities obtained in this work is within EN approved range which is 0.860-0.900 kg m^{-3}.

3.4.3. Flash Point

Flash point and fire point are fuel heat properties which determines the highest safe temperature a fuel can be exposed such that it will not combust when a light source is placed closed to it. These properties can also be described as fuel storage properties.
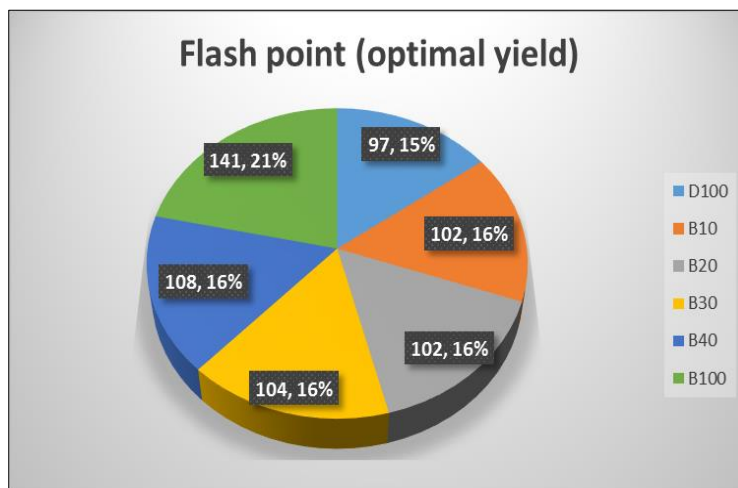

Figure 8 Optimal yield on flash point of the biodiesel (blends) and diesel

Flash point is the least temperature at which a fuel (biodiesel) will ignite for a short while when a light source is placed close to it, while fire point is the least temperature required for a fuel to combust continuously when a light source is brought close to it. In this research section on the fuel properties of biodiesel from palm kernel shell oil, flash point values are in the range of 97 ^{0}C to 141 ^{0}C as seen in Fig. 8. This is within the ANP resolution and EN standard.
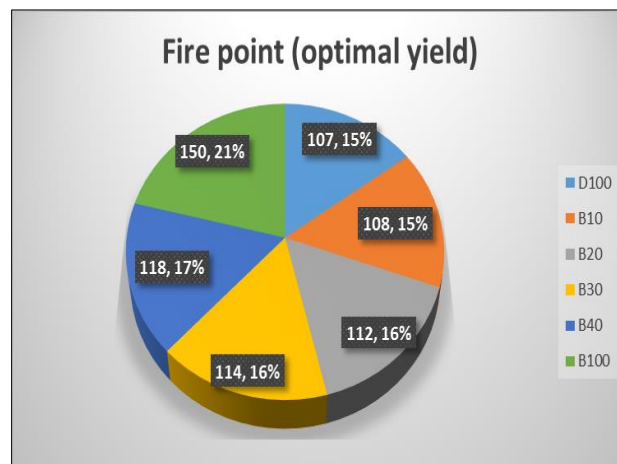
3.4.4. Fire Point

Figure 9 Optimal yield on fire point of the biodiesel (blends) and diesel

Fig. 9 shows that the fire point values are in the range of 107 °C to 150 °C. Petro-diesel has the least flash point and fire point values. Subsequently, flash point and fire point increases as blend ratio increases. The pure biodiesel has the highest flash point and fire point value of 141 °C and 150 °C respectively. According to EN standard, minimum flash point value for unblended biodiesel is 120 °C. Flash point values are lesser than fire point values.

3.4.5. Cloud Point

Cloud point and pour point are fuel cold flow properties which is used to determine how viscous the liquid fuel could be at cold temperatures. These fuel properties, even as flash point and fire point, are also storage properties. At very cold conditions which could confer higher viscosity on the fuel (biodiesel), it will be almost impossible to move the diesel engine or vehicle at such condition. There fuel cloud point is the lowest temperature at which the heavier molecules become more viscous, thus conferring higher viscosity on the sample ranging from 4.14 – 6.5 °C as shown in Fig. 10.
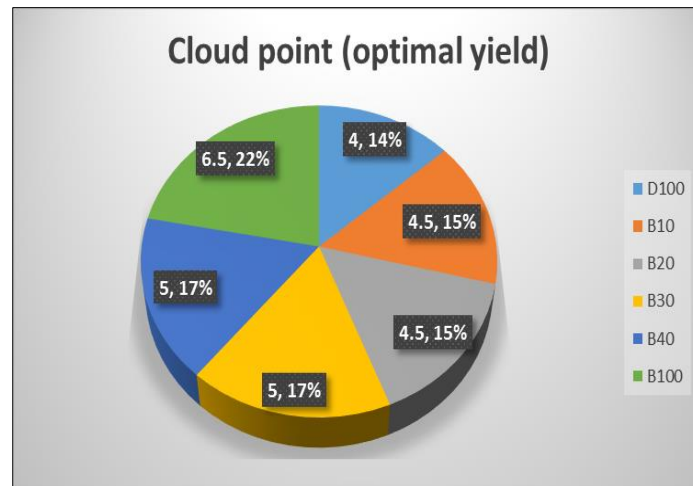

Figure 10 Optimal yield on cloud point of the biodiesel (blends) and diesel

3.4.6. Pour Point

Pour point is the least temperature at which the liquid fuel forms an immobile mass. Petro-diesel has the lowest cloud point and pour point followed by B_{10}, B_{20}, B_{30}, B_{40} and B_{100}. ASTM standard range for pour point is -15 to 6 °C. Range of values obtained for pour point is 1.5 to 4.5 °C as seen in Fig. 11.
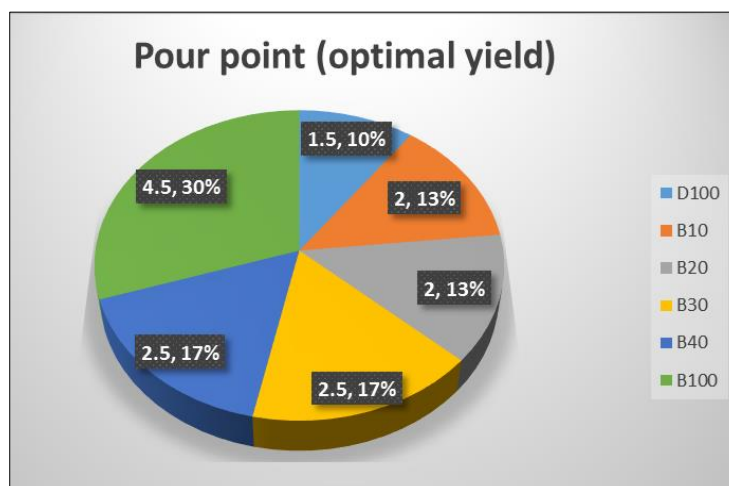

Figure 11 Optimal yield on Pour point of the biodiesel (blends) and diesel

3.4.7. Free Fatty Acid

Acid value is a storage property which determines the stability of a fuel (biodiesel). Fuel storage stability can be influenced by environmental oxidation of impurities in the fuel such as phosphates and metal fillings and or corrosion. The acid value of Petro-diesel is higher than the values obtained for the blends and the biodiesel. Value obtained for Petro-diesel (D_{100}) is 0.931 mgKOH/kg while value obtained for biodiesel (B_{100}) is 0.318 mgKOH/kg. In between the values for D_{100} and B_{100} are the values for blends which increased as biodiesel blends increased ($B_{10} < B_{20} < B_{30} < B_{40}$) as shown in Fig 12.
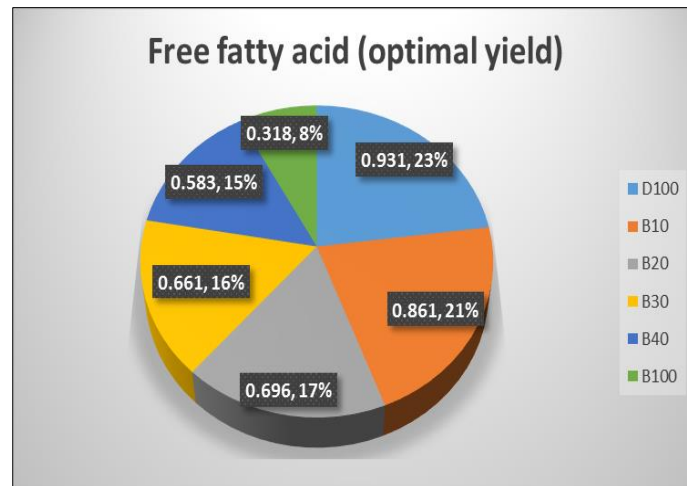

Figure 12 Optimal yield on free fatty acid of the biodiesel (blends) and diesel

3.4.8. Aniline Point

Aniline point of a fuel is the minimum temperature at which a product will become miscible with aniline. It is simply a test for aromaticity. The Petro-diesel has a higher aniline point than the biodiesel. Products with lesser aniline point has higher content of aromatic hydrocarbon. This is because aniline is an aromatic hydrocarbon ranging from $45 - 52\,^0C$ and would mix quicker with fuels with higher aromatic hydrocarbon content as seen in Fig. 13. Aniline point can also be applied in calculating the amount of carbon present in any given fuel [8].
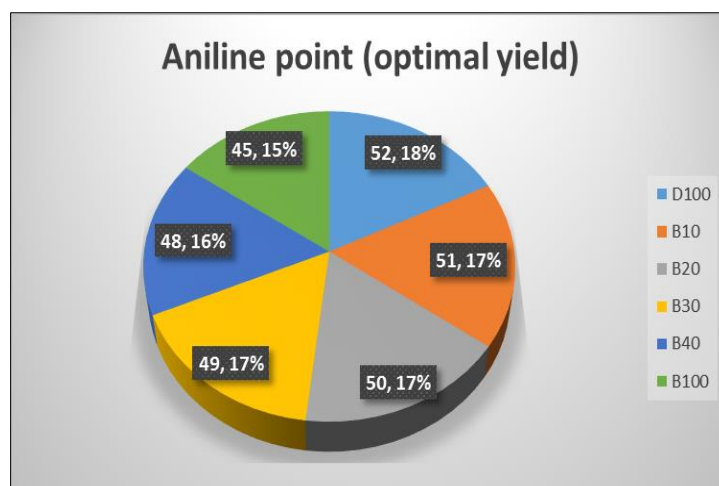

Figure 13 Optimal aniline point of the biodiesel (blends) and diesel

3.4.9. Diesel Index

Diesel index is a measure of ignition quality of a fuel [8]. The Petro-diesel has higher ignition quality when compared to the biodiesel. In same effect, blends with lesser biodiesel mixtures have higher ignition quality or diesel index ranging from 31.83 – 41.17 as shown in Fig. 14.
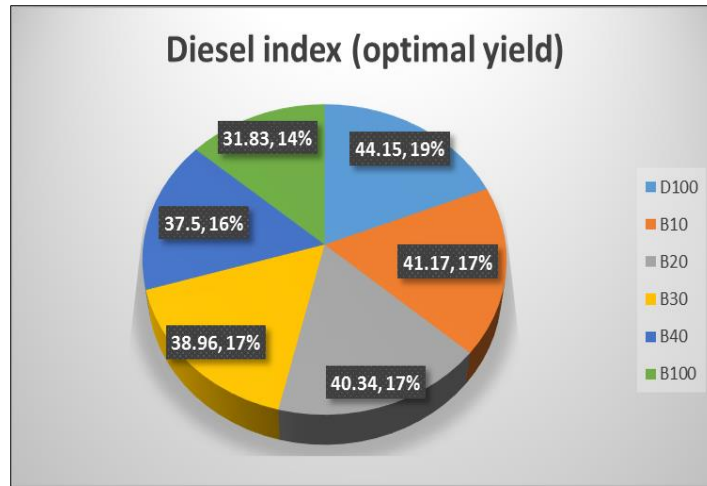
Figure 14 Optimal yield on diesel index of the biodiesel (blends) and diesel

3.4.10. America Petroleum Institute (API) Gravity

API gravity is a measure used to determine the weight of a fuel in relation to water, that is, how heavy or light a fuel could be. When the value is greater than 10, it implies it is lighter than water hence will float on it. When the value is less, it implies it is heavier and will sink. In effect, a sample with lower API gravity is heavier than one with higher API gravity. The API gravity ranges from 28.165 – 33.258 as seen in Fig. 15.
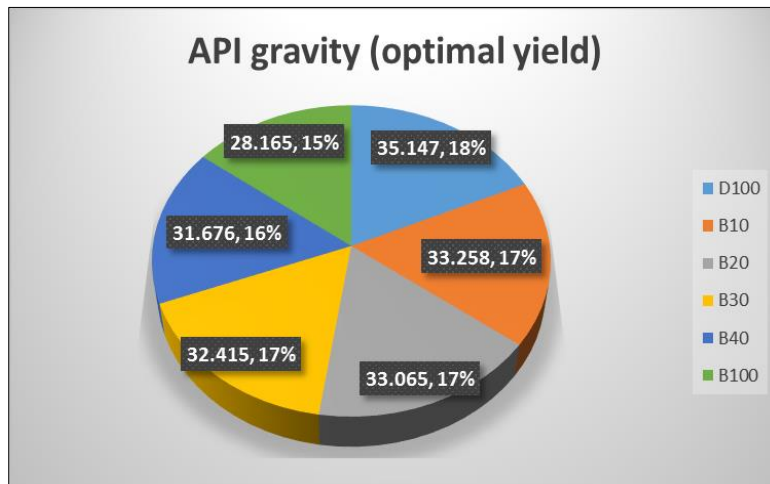

Figure 15 Optimal yield on API gravity of the biodiesel (blends) and diesel

3.4.11. Cetane Number

Cetane number is a dimensionless fuel quality parameter vital for determining its combustion suitability in a compression ignition engine [28]. A fuel (biodiesel) with a higher cetane number will give a better combustion. In this study, Petro-diesel (D_{100}) has a higher cetane number than the biodiesel (B_{100}). Values for the blends are in between as they decrease with increased volume of the biodiesel as shown in Fig 16.
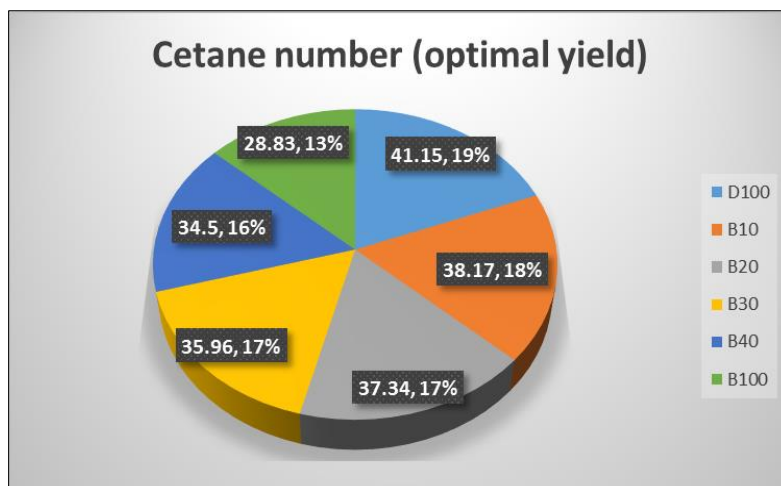
Figure 16 Optimal yield on cetane number of the biodiesel (blends) and diesel

3.4.12. Gross Calorific Value

Gross calorific value or high heating value is the amount of heat evolved when 1 mole biodiesel is burnt [8]. In this study, the biodiesel (B_{100}) was higher than the Petro-diesel (D_{100}) as shown in Fig 17.
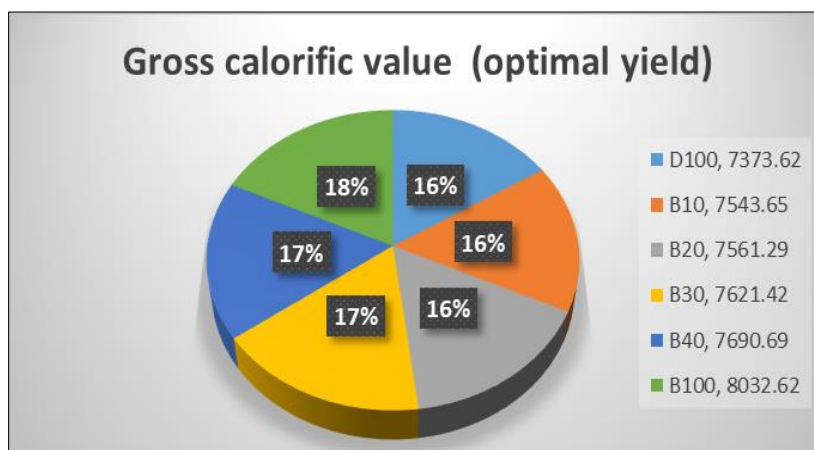

Figure 17 Optimal yield on gross calorific of the biodiesel (blends) and diesel

4. Conclusion

Production of biodiesel from PKSO using egg shell as catalysts has been carried out. The parameters that have an effect on the transesterification of methanol with PKSO and modified egg shell heterogenous catalyst were investigated to obtain the biodiesel yield. Process of transesterification of methanol with extracted PKSO and modified egg shell heterogenous catalyst was also examined. Produced biodiesel was characterized by the cloud and pour point, flash and fire point, anisidine point, fuel gravity, cetane index and cetane number respectively, according to National Agency of Petroleum, Natural Gas and Biofuels (ANP) specified limit, EN standards, and ASTM standard range for diesel fuels. Effect of process parameters (which includes; catalyst concentration, time, temperature, methanol/oil molal ratio, and agitation speed) on the produced biodiesel yield was also determined. The result showed significant effect of the catalyst on the biodiesel yield. Characterization of the various blends of produced biodiesel in comparison with petro-diesel was further carried out to ascertain their diesel fuel properties, as well as the biodiesel blend with the best properties according to ANP specified limit, EN standards, and ASTM standard range for diesel fuels. The biodiesel with the optimum diesel fuel properties was pure biodiesel (B_{100}) as compared to Petro-diesel (D_{100}), and other biodiesel blends studied (B_{10}, B_{20}, B_{30}, and B_{40}). Lastly, blends of biodiesel increased in cetane number, API gravity, diesel index, aniline point and acid value, with a decrease in blend volume. While, blends of biodiesel increased in calorific value, pour point, cloud point, fire point, flash point, density, and kinematic viscosity, with an increase in blend volume. The results have

demonstrated that biodiesel can be produced from PKSO, and egg shell can be used as a catalyst, owing to its characteristics and significant effect on the biodiesel yield.

Compliance with ethical standards

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