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PROCESS EVALUATION FOR PRODUCTION OF BIODIESEL USING COOKING OIL

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ABSTRACT

In this study, the fuel qualities of biodiesel made from leftover cooking oil are assessed and contrasted with those of traditional diesel. The waste cooking oil was characterized for moisture, density, acid value, free fatty acid, saponification value while the fuel properties of the biodiesel produced like flash point, cloud point, kinematic viscosity were characterized. Biodiesel was produced using waste cooking oil with the aim of investigating the effect of temperature on the optimal yield 55^0C*,* 60^0C*,* 65^0C *and* 70^0C *at a constant reaction time of 30 min using methanol as solvent was evaluated. The ratio of waste cooking oil to methanol was 4:1. The results obtained revealed that the highest yield of 88.94% was obtained at* 55^0C*. The biodiesel yield decreased with an increase in temperature beyond* 55^0C*. The characterization results of the waste cooking oil revealed pH (2.29), moisture content (0.25%), density (0.912 g/cm*^{3}*), acid value (2.86 mgKOH/g), free fatty acid (1.43 %), and saponification value (164.64 mgKOH/g).Flash point (178°C), cloud point (-12°C), kinematic viscosity (2.19 mm²/s), specific gravity (0.88), cetane number (42), calorific value (43 MJ/kg), and ash content (0.01%) are among the important metrics that were examined. The findings show that the biodiesel has good cold flow qualities, a low ash percentage for cleaner burning, and a high flash point for safe handling. The biodiesel exhibits compatibility with diesel engines and satisfies statutory standards for use, while having a little lower cetane number and calorific value than conventional diesel.*

Keywords: biodiesel, cooking oil, and methanol

INTRODUCTION

Waste cooking oil refers to the used vegetable oil obtained from cooking food. Repeated frying for preparation of food makes the edible vegetable oil no longer suitable for consumption due to high free fatty acid (FFA) content (Mohammed &Bhargavi, 2015). Waste oil has many disposal problems like water and soil pollution, human health concern and disturbance to the aquatic ecosystem. Rather than disposing it and harming the environment, it can be used as an effective and cost-efficient feedstock for biodiesel production as it is readily available (Javidialesaadi&Raeissi, 2013). Biodiesel is an alternative diesel fuel produced from biological sources such as vegetable oils. The first alkyl ester from palm oil ethyl esters was used in diesel engine in 1937, as reported in a Belgian patent but the low price of petroleum interrupted the use of vegetable oil (Van et al., 2004). The main parameters affecting the transesterification reaction are molar ratio of vegetable oil to alcohol, catalyst type and amount, reaction time, reaction temperature, the contents of free fatty acids (FFAs) and water in substrate oil and the intensity of mixing during the chemical reaction (Pahola&Urmila, 2012). Mathiyazhagan et al. (2011) found that higher reaction temperature increased reaction rate and shortened reaction time due to the reduction in viscosity of oils. However, Eevera et al. (2009) discovered that increase in reaction temperature beyond the optimal level led to decrease of biodiesel yield because higher reaction temperature accelerated the Saponification of the triglycerides. Except for the reaction temperature, other reaction parameters in transesterification of methyl esters have been optimized by various studies (Krishnakumar et al., 2008).Biodiesel is commercially made by reacting vegetable oil or animal fat or a combination of oils and fats with alcohol, usually nearly pure methanol, denatured ethanol or ethanol. The mixture is then combined with a catalyst, an alkaline chemical such as potassium hydroxide or sodium hydroxide (Obi, 2016; Obi & Agha, 2016). The combination of the alcohol and catalyst, commonly termed as methoxide, is a base. This chemical reaction breaks the fat molecules into an ester, which is the biodiesel fuel, and glycerol, a by-product which is eventually removed (Raafat, 2010).The focal point of this study is to evaluate the effect of temperature on the production yield of biodiesel obtained using waste cooking oil and methanol.

According to statistics on world leading biodiesel producers, biodiesel is produced from transesterification of refined vegetable oils, including canola, palm, sunflower and soybean with methanol. Production of biodiesel from other oils such as coconut, cottonseed, olive, and rapeseed has also been reported (El-Diwani et al., 2009). Literature reports have shown that the yields of oil expressed or extracted from different seed plants vary (Melo et al., 2022). Production of biodiesel from populous seed oils, such as palm oil, groundnut oil, soy oil, *Pongamiapinnata*and*Jatrophacurcas*, have been investigated in several literatures under different applied reaction variables like molar ratio of alcohol to oil, temperature, catalyst amount/concentration, and time (Qiu et al., 2011). The use of biodiesel in combustion ignition engines currently is promising based on the associated performance and emissions characteristics (Adebayo et al.,2021). Biodiesel production from waste cooking oil (WCO) is environmentally friendly as it recycles waste cooking oil and gives renewable energy with lower pollution (Tadesse et al., 2019). It substitutes some amount of petrochemical oil import and lowers the cost of waste management ((Tadesse et al., 2019).). Biodiesel production from waste cooking oil has three solutions - economic, environmental and waste management (Mohammed et al., 2015).

Reaction Mechanism in Biodiesel Production

The method usually used in the production of biodiesel is base catalysis method. The reaction is called transesterification, and the process takes place in four steps. The first step is to mix the alcohol for reaction with the catalyst, typically a strong base such as NaOH or KOH. The alcohol/catalyst is then reacted with the fatty acid so that the transesterification reaction takes place (Van et al., 2004). Figure 1 shows the formation of methoxide.

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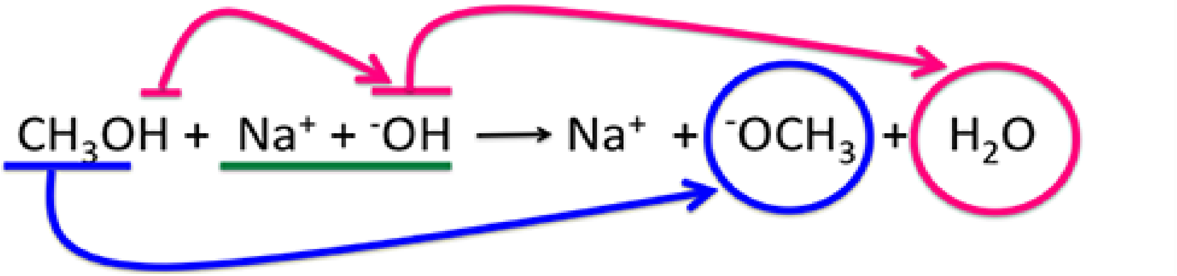

Figure 1: Formation of methoxide(Van et al., 2004)

The catalyst is prepared by mixing methanol and a strong base such as sodium hydroxide or potassium hydroxide. During the preparation, the NaOH breaks into ions of Na^+ and OH^-. The OH^- abstracts the hydrogen from methanol to form water and leaves the CH_3O^- available for reaction. When the OH^- ion reacts with H^+ ion, it reacts to form water. Water will increase the possibility of a side reaction with free fatty acids (fatty acids that are not triglycerides) to form soap, an unwanted reaction. Enzymatic processes can also be used (called lipases); alcohol is still needed and only replaces the catalyst. Lipases are slower than chemical catalysts, high in cost, and produce low yields (Romano et al., 2006).

Once the catalyst is prepared, the triglyceride will react with 3mols of methanol, so excess methanol must be used in the reaction to ensure complete reaction. The three attached carbons with hydrogen react with OH^- ions and form glycerin, while the CH_3 group reacts with the free fatty acid to form the fatty acid methyl ester, the biodiesel (Meher et al., 2006). Figure 2 shows the chemistry of biodiesel production:

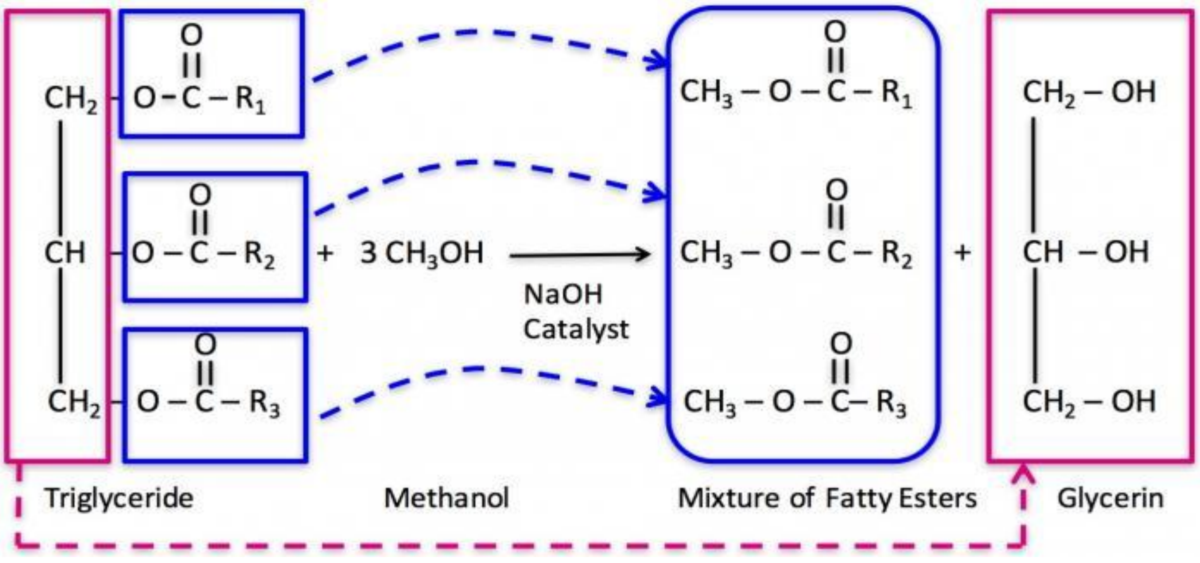

Figure 2: The Chemistry of biodiesel production

(Meher et al., 2006)

MATERIALS AND METHOD

Sample Preparation

The waste cooking oil was obtained from fast food vendors within Port Harcourt, Nigeria. The collected waste cooking oil was put in plastic bottles and sent to the laboratory for further analysis. The samples were filtered using a filter paper to remove unwanted food chunks and placed in beakers.

Characterization of Waste Cooking Oil

Determination of Density

A clean dry measuring cylinder was placed on a weighing balance and the weighing balance was tared to zero. Waste cooking oil was gently poured into the measuring cylinder until the 5cm^3 mark was reached. The corresponding weight at the mark was noted. The density was calculated using Equation 1.

$$Density(g/cm^3) = \frac{Mass(g)}{Volome(cm^3)} \quad (1)$$

Determination of Moisture Content

A clean dry empty beaker was weighed and about 5ml of waste cooking oil was placed in it and weighed. The beaker was then placed in a drying oven at 105^{0}C till constant was obtained. The moisture content was determined using equation 2.

$$Moisture\ \ Content\ (\%) = \frac{m_2 - m_1}{m_3 - m_1} \times 100 \quad (2)$$

Where

m_1= weight of empty beaker (g)

m_2= weight of empty beaker and oil before drying in grams

m_3 = weight of empty beaker and oil after drying in grams

Determination of Acid Value

Ten grams of waste cooking oil sample was measured using a weighing balance and placed in a conical flask, to which 100ml of ethanol was added and swirled gently till complete mixing. Then, 10 drops of phenolphthalein were added, and the solution was titrated with 0.1N KOH until light pink colour was obtained that persisted for about 30s. The acid value was calculated using equation 3

$$AV = \frac{V \times N \times m_w}{m_s} \quad (3)$$

Where

AV = acid value (mg KOH/g)

V = volume of titrant (ml)

N = Normality of KOH = 0.1N

m_w = molecular weight of KOH

m_s= weight of sample (g)

Determination of Free Fatty Acid Value

The free fatty acid value was obtained from the determined acid value as given in equation 4.

$$FFA(\%) = \frac{AV}{2} \quad (4)$$

Where

FFA (%) = free fatty acid

AV (mg KOH/g) = acid value

A dry empty conical flask was weighed to which 5g of waste cooking oil was added. Then, 50ml of ethanol was added to it and swirled gently to ensure proper dissolution. Afterwards, 2 drops of phenolphthalein indicator were added to the solution and was titrated with 0.5N KOH until a pink colour that persisted for 30s was achieved. A blank solution was prepared using ethanol and the procedure performed. The saponification value was calculated using Equation 5 below.

$$S = \frac{(V_1 - V_0) \times N \times m_w}{w_s} \quad (5)$$

Where

SV = saponification value (mg KOH/g oil)

V_1= Volume of KOH solution used for the oil sample in ml

V_0 = Volume of KOH solution used for the blank in ml

N = Normality of KOH solution (usually 0.5 N)

W_s = Weight of Oil Sample in grams

Biodiesel Production Process

The waste cooking oil was pretreated before it was used for biodiesel production.200ml of waste cooking oil was put in a 250ml conical flask and warmed gently to a temperature of about 50^{0}C. About 4.27g of KOH was properly dissolved in 50ml methanol and gently poured into the warmed waste cooking oil and set at 55^0C. It was mixed using a magnetic stirrer. The reaction proceeded for 30min after which the produced biodiesel was washed by spraying warm water over it to remove unreacted methanol and residual catalysts which may corrode engine components. The procedure was repeated at 60^0C, 65^0C and 70^0C.

Determination of Yield

The amount of biodiesel produced was calculated as shown in Equation 6

$$Yeild\ (\%) = \frac{weight\ of\ biodiesel}{weight\ of\ waste\ cooking\ oil} \times 100 \quad (6)$$

Determination of Fuel Properties

Determination of Cloud Point

5ml of the sample were poured into a test tube, ice was scooped into a beaker, and the test tube containing the sample was placed in the beaker containing the ice. It was observed until wax crystals were noticed at the surface of the sample after which the temperature was recorded at this point.

Determination of Flash Point

The sample (biodiesel – 2.5 ml) was poured into a porcelain dish of a predetermined weight. The biodiesel sample was heated for some minutes and a piece of paper was lighted and was waved across the diesel being heated. The point at which the diesel became ignited was recorded as the flash point. When a flame was observed, the temperature was immediately recorded with the use of thermometer.

Determination of Kinematic Viscosity

50 ml of the sample (biodiesel) was poured into a beaker, viscometer spindle suitable for the quantity of biodiesel poured, was dipped into the sample until it covered a considerable amount of the spindle. The rotational rate was set at 30 rpm for 5min, and the reading was taken.

Determination of Specific Gravity

Five millimetres (5ml) of produced biodiesel sample was measured using a measuring cylinder and weighed. Also, five millimetres (5ml) of distilled water was weighed and the readings taken. The specific gravity of the sample was obtained by taking the ratio of the density of the sample to that of distilled water. The mathematical expression is shown in Equation 3.2 below.

$$s.g = \frac{\rho_U}{\rho_w} \quad (7)$$

where

$s.g$= specific gravity

ρ_u= density of produced biodiesel sample in g/ml

ρ_w = density of distilled water in g/ml

Determination of Calorific Value

The calorific value was determined using a bomb calorimeter. One gram (1g) of the biodiesel was weighed and placed in the calorimeter bomb which was then filled with pure oxygen. The sample was then electrically ignited to cause it to combust completely. The temperature increased in the water jacket surrounding the bomb was then measured.

Sample was observed and recorded as the pour point.

Determination of Ash Content

Five grams of biodiesel sample accurately weighed and put in a crucible in a muffle furnace at 450^0C until the combustible material was burned off. The crucible was allowed to cool, and the remaining ash residue weighed. The ash content was expressed as a percentage of the original sample weight.

Determination of Cetane Number

The cetane number of the produced distillate was determined using the ignition quality tester, IQT (ASTM D6890) standard. 20 ml of the produced distillate sample free from dirt and contaminants was injected into the ignition quality tester (IQT) chamber which is the cetane number determining equipment using a micropipette. The ignition quality tester chamber was closed, and the ignition cycle started. The cetane number was displayed on the ignition quality tester screen as the cetane number of the produced distillate sample.

RESULTS AND DISCUSSION

Results for Characterization of Waste Cooking Oil

Table 1: Characterization of Waste Cooking Oil.

S/No	Parameter	Value
1.	Moisture content (%)	0.25
2.	Density(g/cm^3)	0.91
3.	Acid Value (mg KOH/g)	2.86
4.	Free fatty acid value (%)	1.43
5.	Saponification Value (mg KOH/g oil)	164.64

Table 1 presents the results for characterization of waste cooking oil. The parameters evaluated include moisture content, density, acid value, free fatty acid value and saponification value. The values obtained were 0.25%, 0.912g/cm^3, 2.86mgKOH/g, 1.43% and 164.64mgKOH/g respectively.

The moisture content of 0.25% (vol.) in waste cooking oil (WCO) is significantly lower than the usually recommended threshold of 0.5-2% for biodiesel feedstock. This low moisture level offers considerable benefits for biodiesel production. Energy-intensive drying processes mightnot be required because the feedstock already has a low moisture content, increasing production efficiency overall.

The energy content of produced biodiesel is influenced by the feedstock's density. Because it correlates with a suitable balance of fatty acid composition, a density of 0.91 g/cm^3 is advantageous because it guarantees a biodiesel product with competitive calorific values when compared to fossil diesel. Waste cooking oil-derived biodiesel frequently has a density between 0.86 and 0.90 g/cm^3, which satisfies international standards such as ASTM D6751 and EN 14214 that require biodiesel densities between 0.86 and 0.90 g/cm^3.

Waste cooking oil (WCO) with an acid value (AV) of 2.86 mg KOH/g has significant implications for the production of biodiesel. This number is slightly higher than the ideal threshold (≤2 mg KOH/g) for direct base-catalyzed transesterification, which is frequently used in the production of biodiesel. A modest FFA content (~1.43% FFA) is indicated by an AV of 2.86. This amount may result in soap production, which lowers the yield of biodiesel, decreases reaction efficiency, and makes product separation and purification more difficult. Degradation of oil is correlated with high acid readings. WCO with an AV of 2.86 mg KOH/g is still usable, but as the acid value increases, efficiency declines.

Waste cooking oil (WCO) with a free fatty acid (FFA) content of 1.43% has significant implications for the synthesis of biodiesel, especially with regard to the transesterification procedure. The production of biodiesel is impacted by the presence of FFAs, in the oil. When FFA levels are higher than 0.5–2%, transesterification usually needs to be preceded by an esterification reaction (with an acid catalyst, such as sulfuric acid) to lower the FFA content. If the right pretreatment is used, an FFA level of 1.43% is within a reasonable range for the production of biodiesel. The output of biodiesel may be decreased if pretreatment is not carried out, and the resulting biodiesel may contain contaminants, which could result in lower fuel quality and possible engine problems.

A significant amount of FFAs in WCO is indicated by a saponification value of 164.64 mg KOH/g, which, if not controlled, could result in soap formation and reduced biodiesel yields. To guarantee effective biodiesel production, pre-treatment to lower FFAs (such as acid esterification) is frequently necessary. Tolessen the impact of excessive FFAs, careful management of process parameters (such as base concentration and methanol-to-oil ratio) was implemented.

Results for Yield at Different Temperatures

Table 2 presents the biodiesel yield obtained at the reaction temperatures of 55^0C, 60^0C, 65^0C and 70^0C with values of 88.94%, 82.96%, 81.56%, and 80.5% respectively. The order of yield follows: 55^0C > 60^0C > 65^0C > 70^0C.

Table 2: Yields at Different Temperatures

S/No	Temperature (^{0}C)	Yield (%)
1.	55	88.94
2.	60	82.96
3.	65	81.56
4.	70	80.50

A distinct trend of declining yield with rising temperature can be seen in the biodiesel yield at reaction temperatures of 55°C, 60°C, 65°C, and 70°C. The equilibrium between reaction kinetics and reactant and intermediate stability is probably best achieved about 55°C. Without seriously degrading the feedstock or biodiesel product due to heat, this temperature may be perfect for promoting the transesterification process. The yield noticeably decreases as the temperature rises to 60°C. Higher temperatures may cause the biodiesel molecules to break down into smaller, less attractive chemicals, which could be the cause of this drop.

High temperatures can promote the production of undesirable byproducts like coke or gaseous hydrocarbons. At 65°C, as the temperature continues to rise, the trend continues. The biodiesel molecules degrades even further. The yield is lowest around 70°C. This is probably the result of serious deterioration. At such high temperatures, biodiesel molecules and precursors are extremely vulnerable to thermal breakdown. Predominance of unwanted responses. Side reactions that consume feedstock without aiding in the manufacture of biodiesel could be made worse by the increased energy input. According to the data, in order to optimize the production of biodiesel, reaction temperatures should be kept at or near 55°C.

Results for Fuel Properties of Produced Biodiesel

Table 3 presents some fuel properties of the produced biodiesel from waste cooking oil with respect to flash point, cloud point, kinematic viscosity, specific gravity,cetane number, calorific value, and ash content. The values obtained for each parameter were 178 ^{0}C, -12^{0}C, 2.19mm^2/s, 0.88, 42, 43 MJ/kg and 0.01 % respectively and was compared with conventional diesel standards.

Table 3: Fuel Properties of Produced Biodiesel compared to Conventional Diesel

S/no.	Parameter	Conventional diesel	Produced Biodiesel
1.	Flash point (^{0}C)	52 to 96	178
2.	Cloud point (^{0}C)	-15 to -5	-12
3.	Kinematic viscosity(mm^2/s)	2 to 4.5	2.19
4.	Specific gravity	0.82 to 0.88	0.88

5.	Cetane number	40 to 55	42
6.	Calorific value (MJ/Kg)	45	43
7.	Ash content (%)	<0.02	0.01

The temperature at which a fuel generates enough vapor to ignite is known as the flash point. It is an important safety factor. The biodiesel has a much higher flash point (178°C) than the conventional diesel (usually between 52 and 96°C), it will be safer to handle, store, and transport compared to the conventional diesel. This will lower the risk of a fire.

The temperature at which fuel starts to form wax crystals, which can block fuel filters, is known as the cloud point. In contrast to many other biodiesel samples, which typically have higher cloud points because of the feedstock utilized, this one has a favorable cloud point of -12°C. It is appropriate for usage in colder climates since it has good cold flow qualities.

Kinematic viscosity influences combustion, spray properties, and fuel atomization. The value of 2.19 mm²/s compares favorably to conventional diesel (usually 2–4.5 mm²/s) and falls within the permissible range for biodiesel (1.9–6.0 mm²/s). This guarantees appropriate fuel flow and compatibility with injection systems.

The fuel's density in relation to water is indicated by its specific gravity. It affects the combustion properties and energy content. With a specific gravity of 0.88, which is in close agreement with diesel standard (0.82–0.88), it is possible to use it in diesel engines without requiring major adjustments to engine calibration.

The fuel's ignition quality is gauged by its cetane number. Greater values guarantee less engine noise and improved combustion efficiency. Conventional diesel has a cetane number of 40–55, which is comparable to 42. It indicates smooth engine operation and good ignition quality, while slightly higher values are ideal for premium performance.

Fuel economy and power production are impacted by the fuel's calorific value, which indicates its energy content. Compared to regular diesel, which has a calorific value of 45 MJ/kg, this diesel has a slightly lower value of 43 MJ/kg. This suggests a little reduced energy content, but it is still sufficient for efficient engine operation.

The amount of inorganic residue that remains after burning is indicated by the ash content. Wear and deposits in engines might result from a high ash content. The ash concentration of 0.01% is equivalent to or better than that of standard diesel (usually <0.02%) and falls well below permissible bounds for biodiesel. This guarantees less engine fouling and cleaner combustion.

With a few small disadvantages (such as a slightly lower calorific value) and certain benefits (such as a higher flash point and reduced ash content), the biodiesel made from used cooking oil has characteristics that match or closely resemble those of conventional diesel. All things considered, it shows great promise as a sustainable substitute for fossil diesel, especially in situations where environmental advantages and safety are top priorities.

CONCLUSION

In this research, biodiesel was produced from waste cooking oil and the effect of reaction temperature ranging from 55 ^{0}C, 60 ^{0}C, 65 ^{0}C and 70 ^{0}C at a constant reaction time of 30 min using methanol as solvent on the yield was studied. It was found that the reaction temperature at 55°C gave the optimum yield of 88.94% waste cooking oil biodiesel. Comparing the fuel properties of the produced biodiesel with conventional diesel showed the suitability of waste cooking oil biodiesel. Also, the waste cooking oil was characterized with respect to moisture content, density, acid value, free fatty acid value and saponification value revealing values of 0.25%, 0.91 g/cm^3, 2.86 mgKOH/g, 1.43%, and 164.64 mgKOH/g respectively. Fuel properties such as flash point, cloud point, kinematic viscosity, specific gravity, cetane number, calorific value and ash value were analyzed giving values of 178^{0}C, -12^{0}C, 2.19mm^2/s, 0.88, 42, 43 MJ/kg, and 0.01 %respectively. The study remains relevant due to the decrease in oil reserves, environmental problems, and the high price of petroleum products in the international market.

Compared to traditional diesel, its high flash point (178°C) guarantees safe handling and storage. A low cloud point of (-12°C) indicates suitability for cold climates. It is compatible with diesel engines since its kinematic viscosity (2.19 mm²/s), specific gravity (0.88), and ash content (0.01%) closely match diesel specifications. Engine deposits and wear are decreased by a low ash concentration, which lowers residue. It has a slightly lower calorific value (43 MJ/kg) than regular diesel, which could have a modest impact on engine power output and fuel economy. Although adequate, its cetane number of 42, might be upgraded for better engine performance and ignition quality.

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