

Characterization of biodiesel from waste cooking oil and conventional diesel blends: Effect of blending ratio

Abstract

Human civilization basically depends on the utilization of energy which plays a big role in socio-economic development by improving the standard of living. Fast growing population and increase in production processes have led to rapid rise in energy demand. In this study, Biodiesel was produced from waste cooking oil and the effect of blending ratios on the properties of conventional or fossil diesel and biodiesel produced from waste cooking oil was investigated in this study. Conventional diesel to biodiesel blends were prepared at the ratios of 90:10, 80:20, 70:30, 60:40, 50:50. Characterization analyses were performed on the blended biodiesel and fossil diesel mixtures for specific gravity, cetane number, flash point and pour point. Gas Chromatography with Flame Ionization Detection (GC-FID) analysis was conducted to identify and quantify the chemical compositions in the blends. Results from GC-FID analysis revealed varying compositions in different blends, with hydrocarbons of different carbon chain lengths, as well as specific chemicals like phytane, pristane, and *o*-terphenyl. The characterization analysis showed that the specific gravity of 100% biodiesel was higher than that of 100% fossil diesel and the blend ratios of 80:20 and 90:10 also exhibited higher specific gravity values. Cetane numbers were found to be lower in 100% biodiesel compared to 100% fossil diesel and certain blend ratios such as 50:50 and 60:40 showed improved cetane numbers compared to 100% Biodiesel. The pour point of 100% biodiesel was lower in both diesel fuels. Generally, it was observed that the diesel/BD blends demonstrated lower pour points than NNPC 100% Diesel. Based on the results, the diesel/BD 70:30 blend exhibited favorable properties in terms of cetane number, flash point, and pour point, suggesting potential benefits in terms of combustion efficiency and low-temperature operability.

Keywords: biodiesel, waste cooking oil, cetane number, pour point, flash point, specific gravity

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Introduction

There has been a dramatic increase in energy consumption due to the fast-growing population and the expansion of manufacturing operations. Energy consumption is foundational to human society; it elevates people's living conditions and contributes significantly to economic growth.¹ Access to affordable energy is critical to every nation's economic growth, but developing reliable energy infrastructure is no picnic. Furthermore, the extensive use of fossil fuels in vehicle engines and cars in particular has contributed to environmental pollution issues brought about by the high demand in both the industrialized world and the home sector.²

Worldwide, there are now an estimated 1.2 billion private autos and 380 million commercial vehicles, and these numbers are expected to grow substantially in the coming years. The use of fossil fuels to power internal combustion engines (IC) in all these cars accounts for 25% of global energy production and 10% of greenhouse gas emissions.³ The International Energy Agency (IEA) predicts that by 2030, almost all passenger cars and light-duty vehicles will be powered by gasoline or diesel engines. By 2050, 58% of passenger cars will still be powered by internal combustion engines (IC), with hybrid versions providing an essential backup.⁴

In light of the fact that fossil fuels are contributing significantly to environmental deterioration and the fact that the world's energy reserves are steadily dwindling, biodiesel has emerged as a potential

game-changer in the quest for sustainable transportation.⁵ One way to lessen the negative effects on the environment, such as pollution and reliance on fossil fuels, is to use alternative fuels made from vegetable oils and animal fats instead of diesel. Biodiesel, made from vegetable oils, is one of these fuels that has been getting a lot of attention lately because of its renewability, which might lead to a decrease in emissions of greenhouse gases and soot.⁶

It would seem that most cities in underdeveloped nations, including Nigeria, just dispose of their used cooking oil (WCO) in the trash. Because of this, people's health, the economy, society, and the environment are all negatively impacted. A higher concentration of organic contaminants may be achieved by the incorrect or inadequate discharge of WCO into bodies of water. As a result, fish populations, aquatic life, and the local community are all negatively impacted by the water's diminished quality. By reusing waste cooking oil (WCO) and turning it into sustainable energy with less pollution, biodiesel manufacturing is good for the environment. It reduces the expense of waste management while partially replacing the import of petrochemical oil.⁷

Blending biodiesel with fossil diesel may lower the expense and environmental effect of burning 100 percent fossil diesel. Biodiesel is a replacement for diesel fuel made from WCO, which was formerly used for frying in restaurants and hotels but is no longer in use. Because of the higher oxygen concentration in biodiesel, experimental studies have shown that it reduces emissions of unburned hydrocarbons,

carbon monoxide, and particles when blended with diesel.^{8,9} There are a number of environmental and public health issues associated with using fossil diesel fuel, and these issues have far-reaching, perhaps permanent effects on global warming. There are three potential benefits of blending biodiesel with fossil diesel: financial, ecological, and waste management-related.¹⁰

This has led to a plethora of research on combustion engine performance and biodiesel/conventional fuel mix characteristics. Parameters from diesel fuel, kerosene, and biodiesel blends were studied in.¹¹ The study, which included a volume range of 5% to 95% biodiesel and diesel, found that the A95-BS model combination performed poorly. On the other hand, the A80-BS and A85-BS models, with 375 values and 2.456 cSt kg/m viscosities, respectively, performed very well for two mixtures, and the A80-S model, with 357 values and 2,378 cSt kg/m viscosities, performed very well for a single mixture.

Also,³ investigated the properties of biodiesel produced from Mazout. It was observed that the blending method is a very effective method to reduce the percentages of harmful compounds such as sulfur, and the compound percentages that occupy volumetric proportions of fuel such as water content. Once again, researchers looked at how diesel engines ran, how fuel burned, and how much pollution was produced while using biodiesel made from recycled cooking oil in combination with gasoline and kerosene.¹² Due to its improved performance parameters, combustion characteristics, and emissions reduction, WCO biodiesel combined with gasoline or kerosene may be seen as a viable alternative to diesel engine fuels.

Similarly,¹³ investigated the feasibility of biodiesel, a sustainable fuel made from used cooking oil, for use in internal combustion engines. In order to preserve the environment, WCO biodiesel efficiently lowers emissions by 85% owing to a drop in hydrocarbon, SO₂, CO, and smoke emissions in the exhaust. Additionally, brake-specific fuel consumption rises while brake-specific energy consumption, braking power, and torque decrease. In 2018, Abed et al. mixed biodiesel with fossil fuels at varying ratios and found that the resulting mixtures have physical and chemical properties similar to conventional fossil fuel.

¹⁴According to waste cooking oil (WVO) direct usage in energy conversion systems reduces the effect, economically, energetically, and environmentally, compared to biodiesel production. Also, Giancarlo investigated the impact of waste cooking oil percentage in blends with fossil diesel on its performance and emission characteristics in automobiles. It was observed that engine performance was quite similar for B20 and diesel oil. A reduction in CO and HC was obtained with biodiesel blends along with an increase in NO_x. Particulate emissions were also reduced for biodiesel blends.

Apparently, meeting the world's energy needs in a sustainable way is one of the biggest challenges facing humanity. Therefore, the aim of this study is to produce biodiesel from waste cooking oil using base trans esterification method and to investigate the effect of blending ratios on the properties of conventional or fossil diesel and biodiesel in order to contribute to the understanding of how blending ratios impact the properties of biodiesel blends and provides insights into selecting optimal blend ratios for enhanced fuel performance.

Materials and methodology

Specific Gravity, Flash Point, Pour Point, and Cetane Number are some of the parameters that were investigated in this study using the under listed materials. The methods were compliant with ASTM standards, which ensured that the measurements were precise and standardized.

Materials

- i. Waste Cooking Oil (vegetable oil)
- ii. Methanol
- iii. Water
- iv. H₂SO₄
- v. Measuring cylinder
- vi. Funnel
- vii. AGILENT 6890A Powered with ChemStation Software
- viii. Fossil diesel
- ix. ASTM-compliant measurement instruments:
 - a. Hydrometer for Specific Gravity (ASTM D4052)
 - b. Closed-cup apparatus for Flash Point (ASTM D93)
 - c. Cooling bath and apparatus for Pour Point (ASTM D97)
 - d. Cetane engine or instrument for Cetane Number (ASTM D613)

Methodology

Oil sample preparation: The waste cooking oil (WCO) collected from an offshore facility was allowed to settle for 5 days to allow any residential solid and water to settle at the bottom. The WCO was filtered through different sieves of 400 and 200 microns to ensure all particles were screened off.

Oil titration

Isopropyl Alcohol 98% purity (BDH), phenolphthalein indicator, 20mL vials, Caustic Soda anhydrous 98% Purity (BDH), Distilled water, WCO and syringes were used for oil titration process for three different samples using a standard solution of caustic soda. The average value from the titration process of the 3 readings was recorded. This determined the amount of the catalyst (amount of Catalyst – 7.0 + titre average) used in the main Base Trans esterification process. Thereafter, Methoxide was prepared using methanol 98% purity (Analar grade). The Methoxide was added into the oil and mixed by shaking 50 times. The mixture was then kept in hot water bath and allowed to heat for 2hrs with continuous stirring. The mixture was removed from water bath and given another shake for 50times and poured in separating funnel. It was then allowed to stand for 10hrs. The glycerol was at the bottom and very dark in colour, while the biodiesel was at the top and dark Amber in colour.

Separation

The glycerol at the bottom of the separation funnel was drained into a container in a controlled manner until no trace of glycerol could be seen.

Washing of biodiesel

Distilled water was heated to 70°C and used to wash the biodiesel and was used in washing and draining until a clear water was observed at the bottom of the separating funnel. This was to ensure no caustic and methanol mix were left in the biodiesel. This was then poured into a storage container.

Quick quality assurance test

- 1. 327 test** - 3mLs of Biodiesel was taken and 27mL of methanol was added. It was shaken 10 times and allowed to stand for 1 hour. Once there was no oil separation at the bottom, it was an indication that all the oil reacted and is a good product.
- 2. Soap test** – A known volume of the biodiesel was collected, and water added to it. The mixture was shaken 10 times and allowed to stand. Once clear separation after settling, it was an indication that there was no soap left in the Biodiesel.

Biodiesel and convectional diesel blending

The following process was applied in blending the convectional diesel and biodiesel:

- Selection basis for measurement: 500ml
- Measurement of 500ml convectional diesel and 500ml bio diesel
- Blending of convectional diesel and biodiesel (90:10)

Step 1: Calculate 90% of 500ml of diesel:

$$90\% \text{ of } 500\text{ml} = 0.90 * 500\text{ml} = 450\text{ml of diesel}$$

Step 2: Calculate 10% of 500ml of biodiesel:

$$10\% \text{ of } 500\text{ml} = 0.10 * 500\text{ml} = 50\text{ml of biodiesel}$$

Step 3: Combining the results from Step 1 and Step 2 to get the total fuel mixture:

$$\text{Total fuel mixture} = 450\text{ml of diesel} + 50\text{ml of biodiesel} = 500\text{ml}$$

Now, by mathematical linear expression:

Let D represent the volume of convectional diesel (in ml).

Let B represent the volume of biodiesel (in ml).

The equation for the calculation is:

$$0.90D + 0.10B = 500 \quad (2.1)$$

The equation represents the mixture of 90% convectional diesel and 10% biodiesel, resulting in a total volume of 500ml. The approach above was used also for other blends such 80:20, 70:30, 60:40, and 50:50.

For 80:20,

$$0.80D + 0.2B \quad (2.2)$$

For 70:30

$$0.60D + 0.4B \quad (2.3)$$

For 60:40

$$0.60D + 0.4B \quad (2.4)$$

For 50:50

$$0.50D + 0.5B \quad (2.5)$$

GC FID analysis

ASTM D2887 Procedure B was followed to test for the biodiesel mixture, aliquots of the samples were dried using sodium Sulphate and injected whole into the GC-FID at Split ratio 20:1 under the following conditions (Table 1).

Table 1 GC-FID conditions and method

GC	AGILENT 6890A Powered with ChemStation Software
Injection temperature	250°C
Split ratio	20:1
Carrier gas	Nitrogen
Inlet temperature	250°C
Column type	HP 5
Column dimension	30m x 320µm x 0.25µm
Oven program	Initial temperature at 40°C, hold for 2mins. Ramp at 15°C/min hold for 10 min (30min total run time) Final Temperature 300°C,
Detector	FID
Detector temperature	330°C
Hydrogen pressure	40.0psi
Compressed air	400.0psi
Target compounds	n-alkanes
Method	ASTM D2887 B

Table 2 Summary of characterization of blends

Parameters	Sample Code		NNPC Diesel 100%	Biodiesel 100%	Diesel/BD 50:50	Diesel/BD60:40	Diesel/BD 70:30	Diesel/BD 80:20	Diesel/BD 90:10	ASTM Specification
	Unit	Test Method								
Specific Gravity @ 15/15oC	@ 15/15°C	ASTM D4052	0.848	0.883	0.865	0.86	0.86	0.855	0.851	0.83
Flash Point, min	°C	ASTM D93	87	165	107	95	93	92	90	93 mins
Pour Point	°C	ASTM D97	-17.5	-2.1	-6.2	-7.5	-8.3	-9.1	-11	Report
Cetane Number	mins	ASTM D613	85	48	65	69	72	74	77	47 mins

Characterization analysis

Specific gravity (ASTM D4052)

The accuracy of the hydrometer was checked using distilled water that was heated to a certain temperature. The sample was heated to 15 degrees Celsius and placed in a clean, dry hydrometer jar. When inserting the hydrometer into the sample, great care was taken to avoid creating any air bubbles in the container. After the reading on the hydrometer had become stable, it was recorded. After considering the effect of temperature on the calculation, the calibrated hydrometer was used to determine the specific gravity of the sample.

Flash point (ASTM D93)

The flash point apparatus was assembled and was calibrated with the help of a recognized reference diesel. After the lid was fastened in place, a portion of the diesel was transferred into the device. The temperature of the sample was raised at a steady but manageable pace while a low-powered flame was introduced at certain intervals. The temperature at which the sample began to flash was what was referred to as the flash point.

Pour point (ASTM D97)

The sample was placed inside of a jar that had been thoroughly cleaned and dried. The jar was submerged in a chilling bath and allowed to progressively cool while being inverted at regular intervals to determine when it had reached the pouring point. The temperature at which the gasoline in the jar stopped dripping when it was tilted to an angle was recorded as the pour point.

Cetane number (ASTM D613)

The preparation of the cetane engine was carried out in accordance with the instructions provided by the manufacturer. A fuel sample and a reference fuel with a known cetane number were combined in a certain proportion according to a predetermined ratio. After injecting the mixture into the cetane engine, observations were made on the combustion characteristics. The sample fuel's ignition delay was measured against that of the reference fuel, which allowed for the calculation of the fuel's cetane number.

Results and discussion

GC-FID (Gas Chromatography with Flame Ionization Detection) analysis is represented from (Figures 1–7) for the different blends.

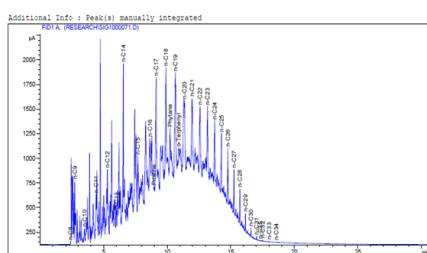


Figure 1 GC - FID Result for 100% diesel sample.

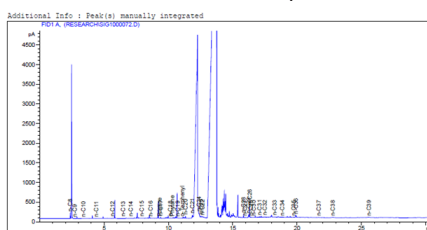


Figure 2 GC-FID Result for 100% biodiesel sample.

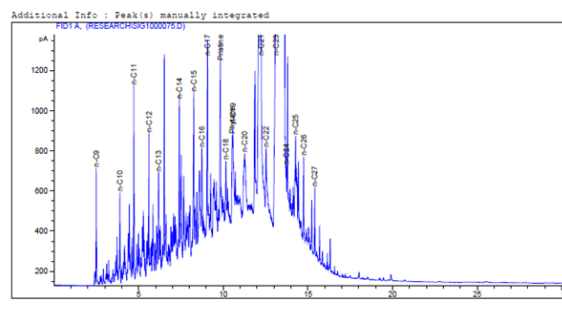


Figure 3 GC-FID Result for 50:50 blends of each sample.

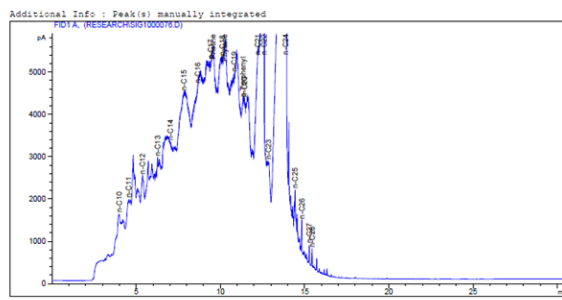


Figure 4 GC-FID Result for 60:40 blends of each sample.

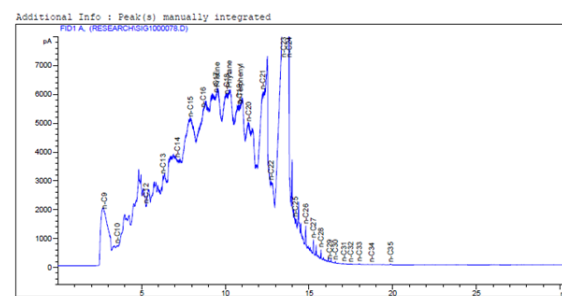


Figure 5 GC- FID Result for 70:30 blends of each sample.

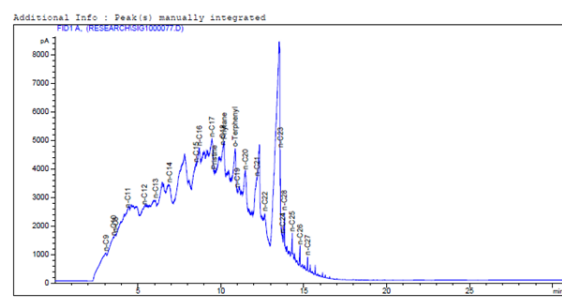


Figure 6 GC-FID Result for 80:20 blends of each sample.

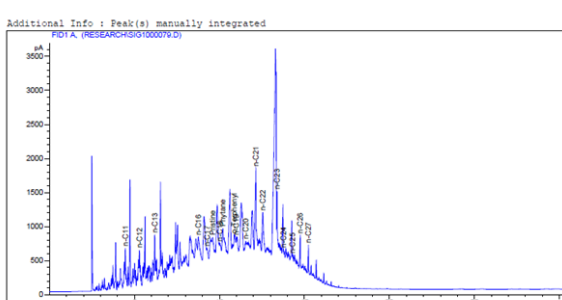


Figure 7 GC-FID Result for 90:10 blends of each sample.

D100 (Pure diesel)

The result (Figure 1) showed that carbon chains of lengths from nC_8 to nC_{34} are present. There are also o-terphenyl, phytane, and pristine chemicals. This is consistent with that reported by.¹⁴ It was reported in the study that convectional fossil diesel is a blend of several hydrocarbons, which has been confirmed by GC FID analysis in this study.

BD100 (Pure biodiesel)

Similarly, in figure 2, Carbon chains from nC_8 to nC_{21} and nC_{24} to nC_{39} are revealed by the analysis. Additionally, o-terphenyl, phytane, and pristine chemicals are reported. Biodiesel is a blend of several fatty acid methyl esters that is primarily produced from vegetable oils (FAMES).¹⁶ The presence of FAMES with a range of carbon chain lengths was confirmed in this sample by GC FID analysis.

D/BD 50:50 (50% Diesel and 50% biodiesel blend)

Again, figure 3 revealed that this blend contains carbon chains from nC_{13} to nC_{27} . Compounds of Pristine and Phytane have been discovered, however no o-Terphenyl compounds have been found. This findings is similar that that observed by.^{17,18} This mix contains Diesel and Biodiesel in equal quantities, which may create a balance between the qualities of both fuels.

D/BD 60:40 (60% Diesel and 40% biodiesel blend)

Figure 4 showed that this blend consists of carbon chains from nC_{10} to nC_{28} . Pristine, Phytane, and o-Terphenyl compounds are present. This is in agreement with that reported by.¹⁵ The increased Diesel proportion in this mix preserve certain attributes of Diesel while combining the advantages of Biodiesel.^{18,19}

D/BD 70:30 (70% Diesel and 30% biodiesel blend)

The analysis indicated carbon chains from nC_9 to nC_{35} in this blend (Figure 5). Pristine, Phytane, and o-Terphenyl compounds were also observed. A larger amount of Diesel in the mix implies an intention to preserve Diesel's performance qualities while making use of Biodiesel's advantages.^{17,18}

D/BD 80:20 (80% Diesel and 20% biodiesel blend)

Figure 6 showed that this blend contains carbon chains from nC_8 to nC_{27} . Pristine, Phytane, and o-Terphenyl compounds were observed. Diesel makes up the bulk of the mix, with only 20% Biodiesel added.¹⁹

D/BD 90:10 (90% Diesel and 10% biodiesel blend)

Also Figure 7 showed that this blends contains carbon chains from nC_{11} to nC_{13} and nC_{16} to nC_{27} . Pristine, Phytane, and o - Terphenyl compounds were also identified. This blend has a significantly higher Diesel content and a minimal addition of Biodiesel (90%:10%).

In general, hydrocarbons with shorter carbon chain length (lower nC) have lower boiling temperatures and burn more quickly, which aids in better cold-start performance and increased combustion efficiency. Hydrocarbons with a longer carbon chain length (higher nC) have higher boiling temperatures, which may contribute to a larger energy content, but may also lead to decreased operability in cold conditions and increased particle emissions.^{20,21}

Pristine in particular is an hydrocarbon molecule that is often present in Diesel fuel. It affects the cetane rating, a measure of the fuel's ability to be ignited. It is common knowledge that engines run more smoothly and produce fewer pollutants when using fuels with

higher cetane levels because they ignite more readily and effectively. Diesel fuel also contains phytane, another kind of hydrocarbon. Like Pristine, it has the potential to alter the cetane rating and combustibility of the fuel.²²

The chemical stability and combustion properties of fuel can be affected by the presence of o-terphenyl. The production of deposits during combustion is mitigated and fuel stability is enhanced. The overall performance of Diesel fuel can be affected by the presence of many components. Diesel fuel is specifically formulated to improve combustion efficiency, limit emissions, and maximize engine performance.²⁰

Characterization of blends

Flash point

The flash point of 100% Biodiesel is 165 °C, this is considerably higher than that of NNPC 100% Diesel, indicating its higher ignition resistance. The flash points of the Diesel/BD blends in this study (90 – 165°C) are generally lower than that of 100% Biodiesel but higher than NNPC 100% Diesel. This is similar to that reported by,^{22,23} where 174.2°C and 171.3 ± 1.15°C were observed. However, in the [18], flash point for biodiesel produced from used vegetable from frying akara was reported to be 260 °C at 70 °C for 40 minutes. This may be as a result of difference in transesterification technique, temperature etc. From Figure 8, the flash points of the different blends are still well above the safety requirement (ASTM D93) for diesel fuels. This suggests that the addition of biodiesel to diesel fuel increases its flash point and may contribute to safer handling and transportation.¹³ The Flash Point is used in shipping and safety regulations to define flammable and combustible materials. The Flash Point is also used to ensure the residual methanol left in the fuel after biodiesel processing will not negatively affect combustion and other fuel system components.¹⁷ The more the flash point the safer the fuel and vice versa.

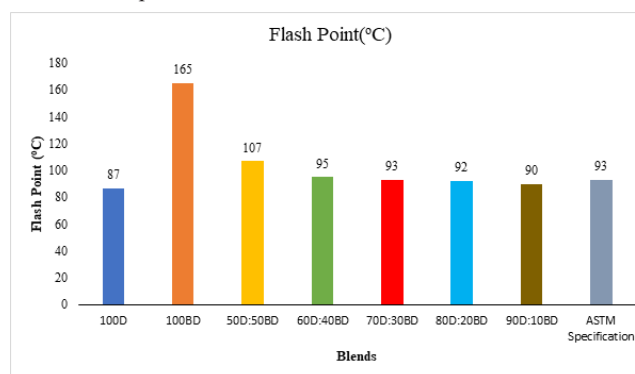


Figure 8 Flash point of diesel blends.

Cetane number

Cetane number is a measure of the quality or performance of diesel. The higher the number, the better the fuel burns within the engine of a vehicle. The minimum acceptable cetane for diesel is 44.¹⁵ From Figure 9, 100% Biodiesel has a significantly lower cetane number of 48 compared to NNPC 100% Diesel of 85 but slightly higher than the minimum acceptance index for diesel. Again, the cetane value for 100% Biodiesel in this study is slightly higher than the ASTM specification of 47. This is in agreement with that reported by.^{23,24} The blend ratios of Diesel/BD 50:50 and Diesel/BD 60:40 showed improved cetane numbers compared to Biodiesel 100%. A higher cetane number generally indicates better ignition quality and combustion efficiency.²⁵

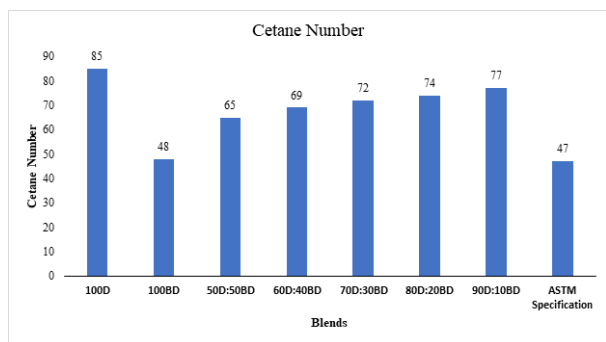


Figure 9 Cetane numbers of diesel blends.

Specific gravity @ 15/15oC

The specific gravity of the samples @ 15/15°C varies across the different blends is as shown in Figure 10. 100% Biodiesel has the highest specific gravity of 0.883 @ 15/15°C, indicating its density is higher than 100% NNPC Diesel. This is similar to that reported by²³ but deviated from that observed by²² where the specific gravity obtain for glycine max seed oil is 0.8969±0.0002. The difference may arise from the seed type and transesterification temperature. A decrease in specific gravity is observed as the percentage of convectional fossil diesel increased in the blends suggesting an increase in density due to the diesel component. This aligns with the general understanding that biodiesel tends to have a higher density than traditional diesel due to its different chemical composition.²⁶

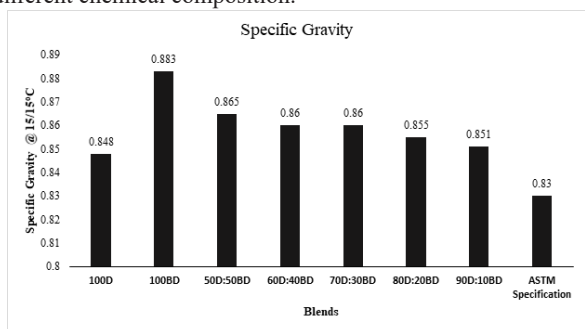


Figure 10 Specific gravity of diesel blends.

Pour point

Pour point is the temperature at which the liquid ceases to flow (Amir & Reza, 2019). In Figure 11, 100% Biodiesel has the lowest pour point of -2.1°C, the Diesel/BD blends generally show lower pour points than NNPC 100% Diesel of -17.5°C, indicating potential improvements in cold weather performance. This aligns with the general understanding that biodiesel can improve the low-temperature properties of diesel fuel.^{27,28}

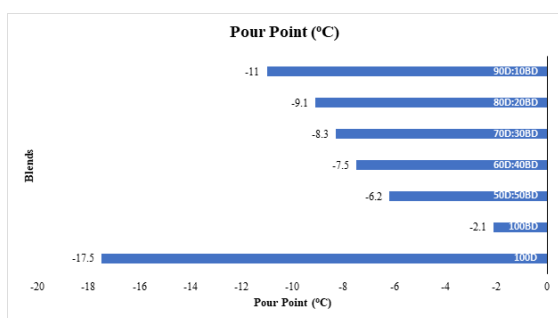


Figure 11 Pour point of diesel blends.

Conclusions and recommendation

This research found that while the cetane number decreased, the flash point, ignition quality, and low-temperature flow characteristics all improved as the biodiesel concentration increased. The Diesel/Biodiesel of 70:30 and 80:20 blends was observed to have characteristics closed to convectional fossil diesel. Consequently, it is recommended based on the findings from this study that engine performance testing using the different biodiesel-diesel blends should be carried out to assess their effects on engine efficiency, emissions, and overall performance. This will provide a more comprehensive understanding of the practical implications of using these blends.

Acknowledgments

None.

Conflicts of interest

Declare if any conflict of interest exists.

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