Journal of Newviews in Engineering & Technology
Faculty of Engineering
Rivers State University, Port Harcourt, Nigeria.
ISSN: 2795-2215
Email: rsujnet@gmail.com | Homepage: www.rsujnet.org

Characterization of Blends of Diesel Fuel #2 and Biodiesel Synthesized from Used Vegetable Oil

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ARTICLE INFO

Article History

Received: 22 February 2024
Received in revised form: 8 October 2024
Accepted: 9 October 2024
Available online: 20 July 2025

Keywords

Biofuel; Cetane Number; Combustion Efficiency; Fossil Fuel; Flash Point; Pour Point

ABSTRACT

In this study, the production of biodiesel from used vegetable oil was carried out using the base-transesterification process. Blends of the biodiesel (BD) and diesel fuel #2 (Chemical Abstract Service [CAS] No. 68476-34-6) – here referred to simply as diesel (D) were prepared in percentages of 50D:50BD, 60D:40BD, 70D:30BD, 80D:20BD, and 90D:10BD; and characterized using Gas Chromatography-Flame Ionization Detection (GC-FID). Results showed varying compositions of hydrocarbons of various carbon chain lengths and other specific organic compounds including phytane, pristine, and o-terphenyl in the blends. Additionally, the blends 80D:20BD and 90D:10BD exhibited higher specific gravity values while the blends 50D:50BD and 60B:40BD showed improved cetane numbers when compared with 100% biodiesel. It was also observed that the D/BD blends demonstrated lower pour points than 100% diesel. Overall, the 70D:30BD blend exhibited favourable cetane number, flash point, and pour point, suggesting potential benefits in terms of combustion efficiency and low-temperature operability.

1. Introduction

The economic operations and reliable performance of diesel engines have made them a dominant power source for various applications, including ships, construction machinery, heavy trucks, and automobiles (Gopal *et al*., 2014). This dominance is reflected in the vast global fleet, estimated at 1.2 billion private automobiles and 380 million commercial vehicles, with projections for significant growth. These vehicles primarily utilize internal combustion (IC) engines, which, according to Dahham *et al.* (2022), are responsible for 25% of the world's energy output and 10% of greenhouse gas emissions. Consequently, the International Energy Agency (IEA) predicts a rise in energy consumption to approximately 53% by 2030 (Chrysikou *et al*., 2019). This trajectory initiated a rapid move away from conventional fuels to renewable resource solutions (Demirbas, 2009; Gopal *et al*., 2014).

Car exhaust and fuel emissions are significant contributors to air pollution, with petroleum diesel combustion releasing many harmful pollutants, including CO_2, CO, NO_x, SO_x, PAHs, and particulate matter, which pose respiratory and health complications (Demirbas, 2009). Given the detrimental long-term effects of diesel emissions on the environment, the potential for a significant reduction in air pollution by biodiesel fuels strengthens its appeal as a viable alternative fuel for diesel engines (Quah *et al*., 2019; Dahham *et al*., 2020).

Biodiesel, produced through ester exchange reactions from animal and vegetable oils, including used cooking oil, offers a promising alternative due to its combustion characteristics comparable to petroleum diesel, along with its environmentally friendly and renewable nature, as well as several other advantages (Guimarães *et al.,* 2021; Hussein *et al*., 2021). Biodiesel, comprised of mono-alkyl esters derived from vegetable oils, is synthesized through a reaction with alcohol and a catalyst, yielding glycerin and methyl esters. This oxygenated fuel possesses several favourable properties, including superior lubricity, high levels of biodegradability, high combustion efficiency, and low toxicity compared to other conventional fuels. These attributes collectively position biodiesel as a strong candidate for substituting fossil diesel (Rosa *et al*., 2020; Grinsven *et al*., 2020).

Extensive research has been carried out on the production of biodiesel from used cooking oil and the formulation of various blends of biodiesel and fossil diesel. For instance, Abed *et al*. (2019) evaluated the effects of various blending ratios (5, 20, and 50% biodiesel) on a marine diesel engine. The findings showed a significant soot emission reduction of up to 74% compared with pure diesel. Vara and Navdeep (2023) prepared and characterized biodiesel derived from Jatropha seed, blends of the biodiesel and fossil diesel were prepared in proportions of B20, B30, B40, and B50 blends. The authors observed fewer harmful emissions. Also, Mahmoud *et al*. (2021) investigated the effects of blending biodiesel from *mazut* seed and fossil diesel on the properties of residual fuels. After the blending process, the calorific value decreased. Furthermore, Ahmed et al. (2021) demonstrated an impressive 85% reduction in emissions like hydrocarbons, SO_2, CO, and smoke when utilizing used cooking oil biodiesel in combustion engines. Jati and Bhikuning (2021) investigated the impact of blending used cooking oil-derived biodiesel with kerosene on diesel engine performance. The study involved introducing kerosene and gasoline additives to biodiesel at concentrations of 5 and 10% by volume and testing the resulting fuel mixture in a diesel engine. The findings indicated a reduction in emissions compared to standard diesel fuel. Again, Gad and Ismail (2021) conducted a comparative analysis of kerosene-blended biodiesel and fossil diesel. The study, which examined fuel mixtures across the range of 5 to 95% volume ratios, showed that the A95-BS blend, composed primarily of biodiesel and diesel, exhibited suboptimal performance.

Clearly, previous studies have shown that utilizing various blends of biodiesel and diesel fuel can significantly improve combustion efficiency. However, limited studies have been carried out on blending of biodiesel from used cooking oil with diesel fuel #2 (CAS No. 68476-34-6) in Rivers State, Niger Delta region of Nigeria. Rivers State, as an industrial city, generates lots of used cooking oil from restaurants, homes, and other roadside cooking outfits. These used cooking oils are discarded most of the time in drains causing pollution in the waterways. Biodiesel-to-diesel fuel blends have key benefits, including economic (waste to wealth) and environmental (waste reduction). Hence, there is a need for further studies on blending biodiesel synthesized from used cooking oil with diesel fuel #2.

The objectives of this study were to synthesize biodiesel from used cooking oil, prepare various blends of the biodiesel with diesel fuel #2, and characterize the various blends by examining their acid value, specific gravity, cetane number, and flash point (among others). Also, this study compared the results of the various blends with those of unblended diesel fuel #2 as control. This study is significant as it aligns with the Sustainable Development Goals of the United Nations, particularly on Affordable and Clean Energy as well as Climate Change Action.

2. Materials and Methods

2.1 Materials

Materials for this study include (but not limited to) the following: used vegetable oil, methanol, distilled water, H_2SO_4, NaOH, and diesel fuel #2 (CAS No. 68476-34-6). For simplicity, diesel fuel #2 would be referred to as diesel from now on.

2.2 Methods

2.2.1 Production of biodiesel

Biodiesel was synthesized from used cooking oil employing a base transesterification process, adhering to established protocols (Attia & Hassaneen, 2016; Nurull *et al*., 2014; Quah *et al*., 2019; Zhang *et al*., 2020). A conical flask equipped with a reflux condenser, thermometer, and magnetic stirrer was utilized. used cooking oil was preheated to 65°C before the addition of 1% (w/w) sodium hydroxide (NaOH) catalyst dissolved in a 6:1 methanol-to-used cooking oil molar ratio solution. The reaction mixture was stirred for 2 hours, followed by phase separation in a separating funnel to isolate biodiesel from glycerol. The biodiesel was subsequently washed three times with warm water containing 5% acid and then with distilled water heated to 70°C. This washing process was repeated until the separated water layer was clear, ensuring complete removal of caustic substances and methanol. The purified biodiesel was then transferred to a storage container (Figure 1).

Figure 1: Samples of 100% diesel and biodiesel. Biodiesel was synthesized from used cooking oil.

Thereafter, the biodiesel (BD) was blended with diesel (D) following the procedures adopted by Gad and Ismail (2021), Jati and Bhikuning (2021). The mix ratios used were 50D:50BD, 60D:40BD, 70D:30BD, 80D:20BD, and 90D:10BD to obtain the various blends (Figure 2).

Figure 2: Blends of diesel and biodiesel. The biodiesel was synthesized from used cooking oil.

2.2.2 Hydrocarbon Analysis

Hydrocarbon analysis was performed using an Agilent 6890A gas chromatograph coupled to a flame ionization detector (FID) (Agilent Tech., Inc., USA). Built-in ChemStation software was used to process the GC-FID data. The method of analysis followed the standards of ASTM (1996) method D2887B for n-alkane determination. Separation was achieved on an HP-5 capillary column (30m × 320µm × 0.25µm). Split injection (20:1 ratio) was performed at 250°C with nitrogen as carrier gas. The oven programme initiated at 40°C (2min hold), ramped at 15°C/min to 300°C (10min hold) for a total run time of 30 minutes. The FID was operated at 330°C with hydrogen at 40.0 psi and compressed air at 400.0 psi. This configuration provided optimal sensitivity and flame stability for hydrocarbon quantitation, which was done using the external standard method. The instrument was calibrated with alkane calibration solution mix, which was made up with AccuStandard alkane standard solution (C_{10}-C_{40}), surrogate standard solution mix of 1-Chlorooctadecane, and dichloromethane. Solvent blank and method blank were also analyzed as quality control measures.

2.2.3 Determination of Specific Gravity of Samples

The hydrometer's accuracy was verified using distilled water heated to a temperature specified by ASTM (1996) method D4052. The sample was subsequently warmed to 15°C and transferred to a clean, dry hydrometer jar. Meticulous care was taken to prevent the formation of air bubbles within the container during the hydrometer insertion. The hydrometer reading was recorded after stabilization, and the calibrated instrument was used to determine the sample's specific gravity, accounting for temperature-related adjustments (Bose, 2017).

2.2.4 Determination of Flash Point of Samples

The flash point of the samples was determined according to ASTM (1996) method D93. The apparatus was assembled according to the manufacturer's specifications and calibrated with a certified reference material. After securing the lid, a portion of the diesel was introduced into the device. The temperature of the sample was gradually increased while a low-intensity flame was intermittently applied (Prashant et al., 2023).

2.2.5 Determination of Pour Point of Samples

The pour point of the sample was determined according to the standard of ASTM (1996) method D97. A clean, dry jar was filled with the sample and submerged in a cooling bath. The jar was periodically inverted to facilitate cooling until it reached the pour point. The temperature at which the gasoline ceased to flow when the jar was tilted to a specific angle was recorded (Udoezika *et al.,* 2020).

2.2.6 Determination of Cetane Number of Samples

The cetane number of samples was determined using ASTM (1996) method D613. The cetane engine was prepared following the manufacturer's guidelines. The sample fuel and a reference fuel with a known cetane number were blended in a specific ratio. The mixture was injected into the cetane engine, and combustion characteristics were observed. The ignition delay of the sample fuel was compared to that of the reference fuel to calculate the sample's cetane number (Odii *et al*., 2023).

3. Results and Discussion

3.1 Hydrocarbon Composition of the Fuel Blends

Figure 3 shows the total ion chromatograms of the hydrocarbon fingerprints of the various fuel blends identified by the GC-FID while Table 1 shows the identity of the hydrocarbon compounds. Figure 3 and Table 1 show a complex hydrocarbon composition, characterized by the presence of aliphatic chains ranging from nC_8 to nC_{34}. Aromatic compounds, including o-terphenyl and pristine were also identified. While pure diesel (D100) exhibited a broader range of carbon chain lengths, clean biodiesel (BD100) displayed a more concentrated distribution primarily within the nC_8 to nC_{21} and nC_{24} to nC_{39} ranges.

The 50D:50BD blend demonstrated a balanced composition, incorporating components from both diesel and biodiesel. Notably, the absence of o-terphenyl in this blend suggests potential interactions or synergistic effects between the fuel components. Conversely, the 60D:40BD blend, with its higher diesel content, retained certain characteristics of diesel while incorporating beneficial attributes of biodiesel. The 70D:30BD, 80D:20BD, and 90D:10BD blends demonstrated a progressive increase in diesel content, with corresponding shifts in hydrocarbon composition. While all blends contained aliphatic chains ranging from nC_8 to nC_{35}, the higher diesel proportions resulted in a narrower distribution of carbon chain lengths.

The presence of pristine, phytane, and o-terphenyl compounds remained consistent across these blends, suggesting their retention even at elevated diesel concentrations (Figures 3e – g). These findings highlight the potential of tailoring fuel blends to achieve specific performance objectives while incorporating varying levels of biodiesel as reported in the literature (Nurrel *et al*., 2014; Attia and Hassaneen, 2016; Dahham *et al*., 2022). The hydrocarbon composition of diesel fuel significantly influences its combustion characteristics and performance. Shorter chain aliphatic hydrocarbons generally exhibit lower boiling points, leading to improved cold-start properties and enhanced combustion efficiency (Gopal *et al.,* 2014).

Conversely, longer-chain hydrocarbons possess higher boiling points, potentially resulting in increased energy density but also compromising low-temperature operability and contributing to particulate emissions. The presence of pristine, a specific hydrocarbon component, exerts a notable influence on cetane number, a critical parameter governing fuel ignition. Fuels with higher cetane numbers demonstrate superior ignitability, leading to smoother engine operation and reduced emissions (Abed *et al.,* 2018). Phytane, another hydrocarbon constituent of diesel fuel, can also influence cetane number and combustion characteristics. Pristine and phytane share similarities in their effects, the presence of o-terphenyl imparts distinct properties, enhancing fuel stability and mitigating deposit formation. The intricate interplay of these components significantly impacts the overall performance of diesel fuel, which is meticulously formulated to optimize combustion efficiency, minimize emissions, and maximize engine performance (Nwafor, 2004).

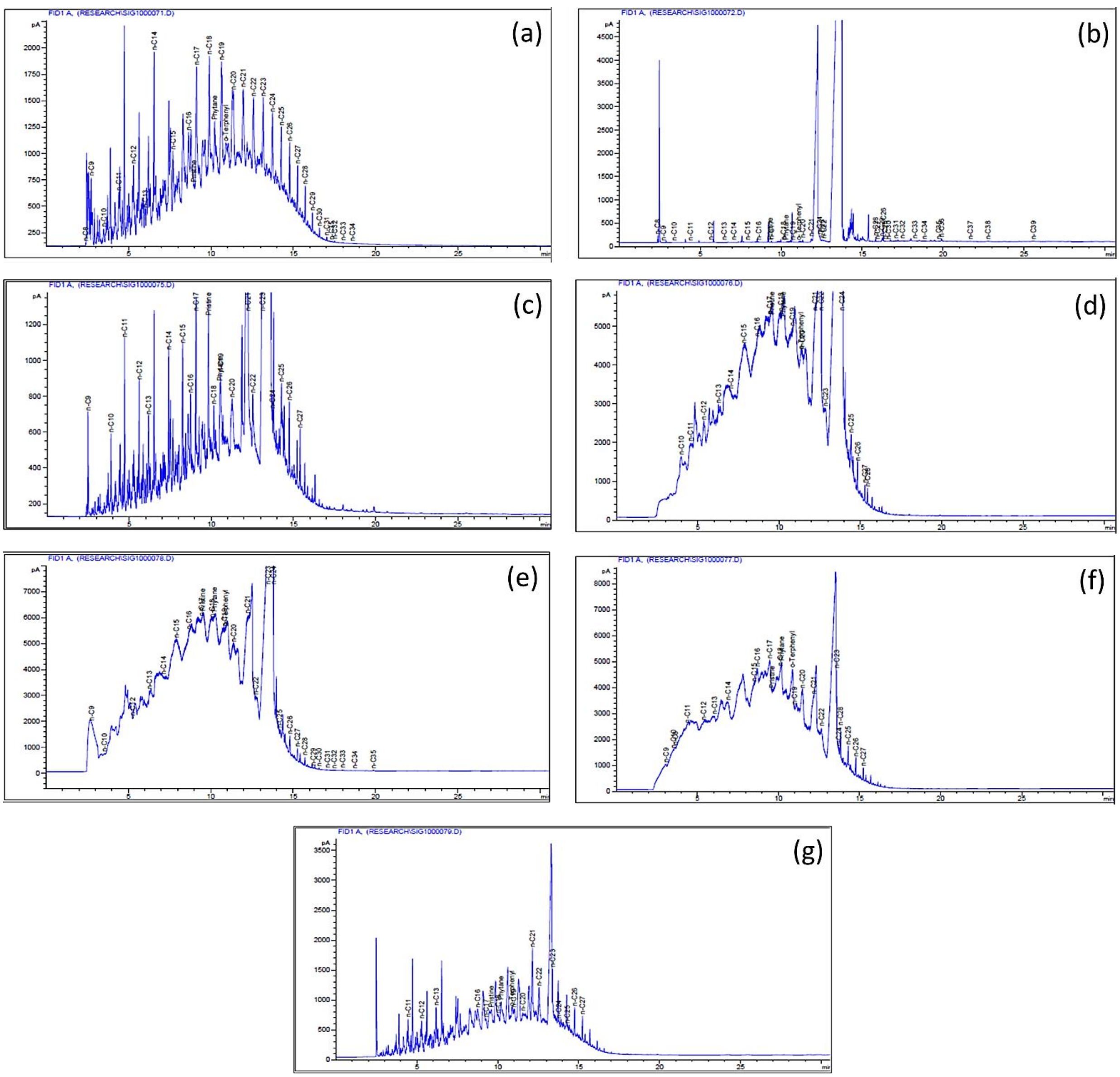

Figure 3: Total Ion Chromatogram for (a) 100% Diesel [D] sample, (b) 100% Biodiesel [BD] sample, (c) 50D:50BD blend, (d) 60D:40BD blend, (e) 70D:30BD blend, (f) 80D:20BD blend, and (g) 90D:10BD blend.

Table 1: Hydrocarbon Composition of the Various Fuel Blends identified by GC- FID.

Sample	Components identified in blends
100% D	$nC_8 - C_{34}$ (Total Petroleum Hydrocarbons), Pristine, Phytane, o–Terphenyl
100% BD	$nC_8 - C_{21}$ (Diesel Fuels), $nC_{24} - C_{39}$ (Lubricating Oil), Pristine, Phytane, o–Terphenyl
50D:50BD	$nC_{13} - C_{27}$ (Kerosene), Pristine, Phytane
60D:40BD	$nC_{10} - C_{28}$ (Diesel Range Organics), Pristine, Phytane, o–Terphenyl
70D:30BD	$nC_9 - C_{35}$ (Aliphatics), Pristine, Phytane, o–Terphenyl
80D:20BD	$nC_8 - C_{27}$, Pristine, Phytane, o–Terphenyl
90D:10BD	$nC_{11} - nC_{13}$, $nC_{16} - nC_{27}$, Pristine, Phytane, o–Terphenyl

D, Diesel; BD, Biodiesel

3.2 Characteristics of the Fuel Blends

3.2.1 Flash Point

The flash point of a fuel represents the minimum temperature at which its vapours, when exposed to an ignition source, will ignite. This property serves as a critical safety index, with lower flash points indicating a heightened risk of fire due to the increased susceptibility of the fuel's vapours to ignition. Conversely, higher flash points correspond to reduced fire hazards (Demirbas, 2009). In Figure 4, the flash point analysis showed a notable difference between pure biodiesel (BD100) and pure diesel (D100), with BD100 exhibiting a significantly higher flash point, indicative of its greater resistance to ignition. The flash points of the diesel-biodiesel blends were generally intermediate, falling between those of the pure components. Importantly, all the blends had flash points well above the ASTM D93 safety standard for diesel fuels. These findings suggest that the incorporation of biodiesel into diesel fuel can elevate its flash point, potentially enhancing its safety during handling and storage, as previously reported in the literature (Ahmed *et al*., 2021; Yesilyurt, 2019; Dobroshi et al., 2019).

Biodiesel, derived from vegetable oils, exhibits a characteristically higher flash point compared with conventional diesel fuel. This elevated ignition temperature contributes to enhanced safety during handling and storage (Paul *et al*., 2021; Udoezika *et al*., 2020). The higher molecular-weight vegetable oils, relative to diesel hydrocarbons, play a pivotal role in determining the flash point. Moreover, the lower volatility of biodiesel, resulting from its molecular structure, further inhibits vapourization, reinforcing the higher flash point. This inherent property reduces the susceptibility of biodiesel to accidental ignition, thereby mitigating fire hazards associated with its handling, transportation, and storage (Omidvarborna *et al.,* 2015; Bose, 2017).

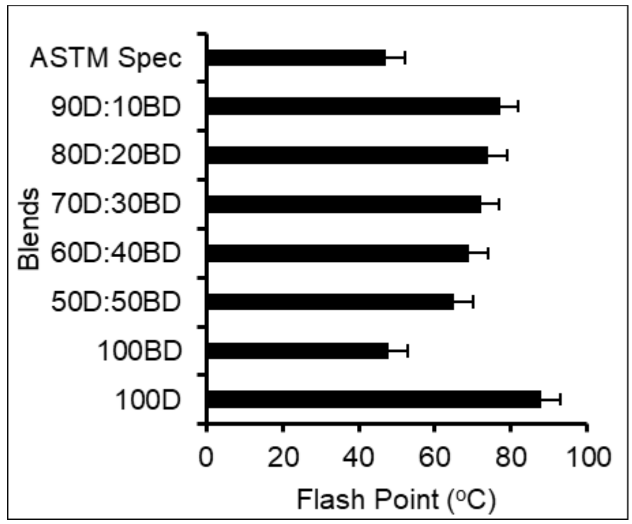

Figure 4: Flash Point of Diesel and Biodiesel Blends. [D = Diesel; BD = Biodiesel. Error bars on chart represent standard error]

3.2.2 Cetane Number

Cetane number, a critical parameter of diesel fuel, reflects its ignition quality. A higher cetane number facilitates cold starts by promoting rapid ignition and ensuring optimal ignition timing. This, in turn, leads to more complete fuel combustion, resulting in smoother engine operation and potentially enhanced fuel efficiency (Dahham, 2020). In Figure 5, cetane number analysis showed that pure biodiesel (BD100) exhibited a notably lower value compared with pure diesel (D100). However, blending diesel with biodiesel resulted in a significant enhancement of cetane number, particularly for the 50D:50BD and 60D:40BD blends. While a slight decrease in cetane number was observed for blends with higher diesel content (70D:30BD and above), these values remained within acceptable limits. A higher cetane number generally correlates with improved ignition quality and combustion efficiency, aligning with previous findings (Prashant *et al.,* 2023). The superior cetane number of biodiesels compared to diesel is attributed to the molecular structure of fatty acid methyl esters (FAMEs), which facilitate faster ignition than diesel hydrocarbons. This advantageous property of biodiesel can potentially contribute to enhanced engine performance and reduced emissions (Gad and Ismail, 2021). Overall, the higher cetane number of biodiesels is a positive attribute compared to diesel, potentially contributing to better engine performance and lower emissions.

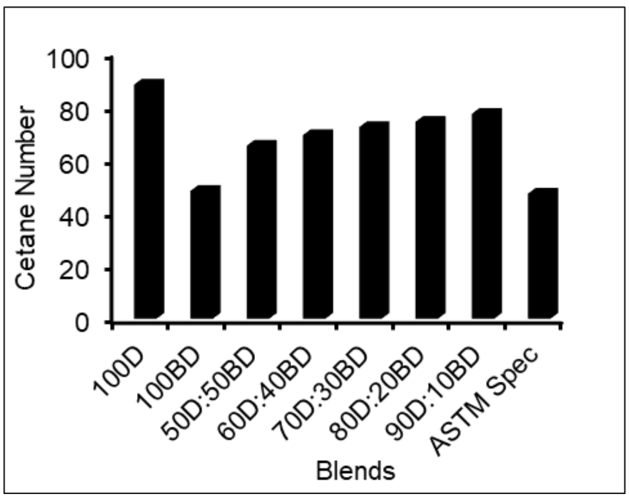

Figure 5: Cetane Numbers of Diesel Blends. [D = Diesel; BD = Biodiesel].

3.2.3 Specific Gravity at 15/15°C

This indicates how much heavier a substance is compared to the same volume of water. Specific gravity is relevant for various aspects of fuel handling and storage, including determining the mass of a specific volume of fuel, which is crucial for accurate inventory management and fuel delivery and for precise calculations when blending them in desired proportions (Bose, 2017).

The specific gravity of the fuel blends exhibited a direct correlation with biodiesel content, as illustrated in Figure 6. Pure biodiesel (BD100) demonstrated the highest specific gravity, reflecting its greater density compared to diesel. The 80D:20BD and 90D:10BD blends displayed reduced specific gravity values, suggesting a decrease in density attributable to the higher diesel component. These findings are consistent with the established understanding that biodiesel generally possesses a higher density than conventional diesel due to its distinct chemical composition (Udoezika *et al*., 2020; Paul *et al*., 2021).

The specific gravity values for both diesel and biodiesel can vary slightly depending on the specific source and production process. Blending biodiesel with diesel results in a specific gravity that falls between the values of the two pure fuels, proportional to the blending ratios. Specific gravity is a valuable property, although it is not the only factor considered for fuel compatibility. Other properties like viscosity and cetane number also play crucial roles (Dobroshi *et al*., 2019). Generally, the difference in specific gravity between biodiesel and diesel is relatively small and does not significantly impact their practical use in most situations.

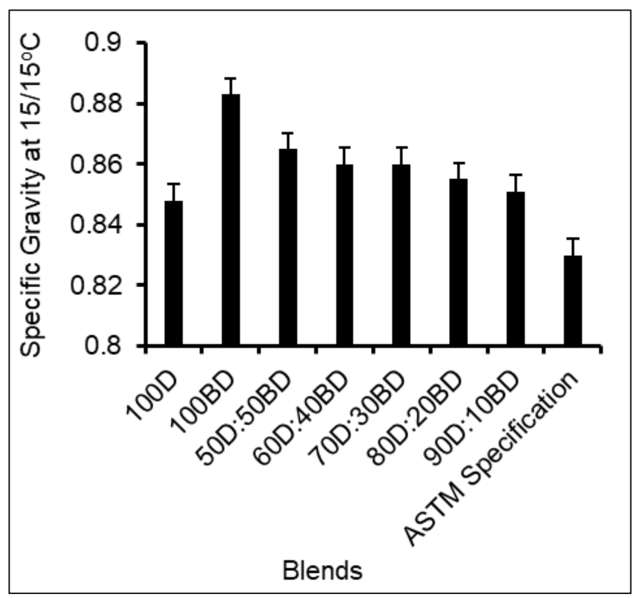

Figure 6: Specific Gravity at 15/15°C of Diesel Blends. [D = Diesel; BD = Biodiesel. Error bars on chart represent standard error].

3.2.4 Pour Point

The pour point of a fuel represents the minimum temperature at which it remains fluid. Below this temperature, the fuel thickens and becomes waxy, hindering its flow (Prashant *et al.,* 2023). If a fuel reaches its pour point, it can clog filters and impede engine startup. As depicted in Figure 7, biodiesel (BD100) exhibits the lowest pour point, indicating superior low-temperature flow properties compared to both diesel fuels and the blends. The diesel-biodiesel blends demonstrated lower pour points compared to pure diesel, suggesting potential enhancements in cold weather performance of pure diesel. These findings are consistent with the established understanding that biodiesel can improve the low-temperature properties of diesel fuel (Rosa *et al.*, 2020). Blending biodiesel with diesel in appropriate ratios is a common strategy to address cold flow issues while still benefiting from the environmental advantages of biodiesel.

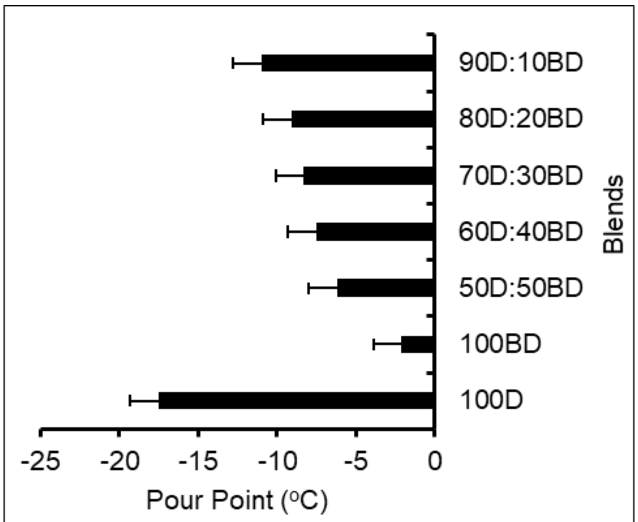

Figure 7: Pour Point of Diesel Blends. [D = Diesel; BD = Biodiesel. Error bars on chart represent standard error].

4.0 Conclusions

Biodiesel was synthesized from used vegetable oil and the properties of the biodiesel and its blends with diesel fuel were investigated in this study. The diesel blends were found to contain several hydrocarbons, including carbon chains from nC_8 – nC_{21} and nC_{24} – nC_{39} as well as o-terphenyl, phytane, and pristine. The findings of this study further showed that when the biodiesel content increased, the cetane number, flash point, and pour point reduced, as specific gravity increased. There is, therefore, promise that used vegetable oil is a veritable source of good quality biodiesel.

Declarations

Author Contribution

I. Altraide: Writing the original draft, methodology, investigations, conceptualization. **O. Akuma:** investigations, final analysis. **J.G. Akpa**: reviewing and editing. **T.N. Amadi**: reviewing and editing.

Funding

The authors received no funding from an external source.

Competing Interest

The authors declare no conflict of interest.

Acknowledgements

The authors appreciate the immense contributions and support of the second author during the synthesis and analysis of the various diesel and biodiesel blends.

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