Waste Frying Oil as a Feedstock for Biodiesel Production

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Abstract

This study was initiated to blend the biodiesel produced from waste frying oil (WFO) with petroleum diesel in three different proportions (B20, B50 and B80), and the dual fuels were tested on compression ignition engine to evaluate their emission characteristics. The biodiesel produced from WFO was achieved via heterogeneous catalyzed transesterification using anthill-eggshell-Ni-Co mixed oxide composite catalyst at reaction temperature of 70°C, reaction time of 2 h, catalyst loading of 3 wt% and methanol to oil molar ratio of 12:1. Various analyses carried out on the prepared WFO-based biodiesel confirmed that it is of good quality and also meet the ASTM standard. The blended fuel containing 20% by volume biodiesel content (B20) emitted 1050 and 14,000 ppm of CO and CO₂, respectively, which were lower than those emitted by B0, B50 and B80. It can be concluded that blending the diesel with appropriate volume of biodiesel not only improves its quality but also lowers greenhouse gases emission.

Keywords: biodiesel, catalyst, diesel, transesterification, diesel engine, waste frying oil

1. Introduction

The basic concept of biodiesel synthesis was invented by Rudolf Diesel in the 1890s, and the diesel engine had become the device of choice for power reliability and high fuel economy globally. He envisaged that pure vegetable oil could be used on compression ignition engine as fuel [1]. After it was used, it became obvious that it was not suitable to power diesel engine due to some limitations associated with its use. Those limitations include carbon deposition in heating chamber, sticking of piston ring, injection tip coking and partial combustion [2–4].
However, modern biodiesel fuel has its basis in research conducted in Belgium [5], but biodiesel production plant was not set up in any of the European countries until the late 1980s [4]. Continents in the other parts of the world including Africa also witness the local production of biodiesel starting up. Today, there are many countries with commercial biodiesel projects [6]. Renewable and alternative fuel such as biodiesel is capable of solving associated problems with fossil hydrocarbon fuel. Greenhouse gas emissions arising as a result of fossil hydrocarbon fuel burning in vehicular or compression ignition (CI) engine have been identified as the main problem confronting the entire world nowadays [7]. Recently, interest in non-toxic, renewable, biodegradable, alternative fuel such as biodiesel and bio-hydrogen, with their unique applications in powering vehicular and CI engines, is ongoing. However, the problems related to sticking of piston ring and injector tip coking do occur in long run usage of biofuel without necessarily adjusting fuel consumption and engine performance [8]. Since carbons present in biodiesel are biodegradable, it contributes less to carbon cycle. Besides, the qualities of petrol-diesel get improved and the emissions of sulphur and nitrogen oxides get reduced when biodiesel is blended with appropriate quantity of diesel [9].

Standard specifications for biodiesel have been adopted by most countries, for instance, America and Europe use ASTM D6751 and EN 14212, respectively. Generally, a code consisting of a number that indicates the biodiesel content in percentage is employed, for example, B100 is purely 100% biodiesel while B40 simply means a mixture containing 40% biodiesel and 60% petrol-diesel. In some part of the Europe, Sweden in particular, a dual fuel containing 5% biodiesel (B5) is often used [10]. Recently in Nigeria, the Nigerian National Petroleum Corporation (NNPC) adopted B20 as standard specification for biodiesel-fossil diesel blend. This according to the corporation would require 80 volumes of petrol-diesel to be blended with 20 volumes of biodiesel.

Generally, any material that contains triglyceride can be used to produce biodiesel [11]; however, a choice of feedstock to be used should be carefully made. At present, it is usually made from edible and non-edible plant oils obtained from palm kernel seed [12–14], soybean [15–18], rapeseed [19–22], coconut oil [23], sunflower oil [24–30], Tiger nut [31, 32] (Cyperus esculentus), cotton seed [33] and Sorghum [34]. The use of oil from algae [35], fish [36], Karanja [37], Jatropha curcas seed [38–41], yellow horn corn oil [42] and Chinese tallow seed oil [43] for the synthesis of biodiesel had also been reported. It has also been reported that biodiesel can be conveniently synthesized from waste vegetable oils [10].

1.1. Waste frying oil as economic feedstock for biodiesel synthesis

Waste frying oil (WFO) is regarded as spent oil which has been employed for deep frying and is no more viable for further consumption. WFO is made up of saturated and unsaturated monocarboxylic acids with the trihydric alcohol glyceride saturated and unsaturated monocarboxylic acids [44]. During frying, the physical, chemical and organoleptic features of the plant oil change [45]. More so, free fatty acids content are enhanced in the oil by hydrolysis of reactive components as a result of water from food during heating. High cost of biodiesel has been identified as the major reason why its production has not been widely commercialized.
One of the ways in which this could be addressed is to develop a holistic method to minimize the biodiesel cost [46, 47]. Those options include biodiesel synthesis from spent frying oil and also minimize its processing cost through the optimization of process parameters that have influence on its yield and quality [48].

Oils which contain high free fatty acids (FFAs) such as waste cooking oil are now being used for biodiesel synthesis, because they are less expensive than refined oil [49, 50]. More so, it offers significant advantages which include reduction in environmental problem and the production cost [51]. WFO is available in large amount, and its management constitutes a serious disposal problem. In most of the developed countries, spent frying oil is being used as raw material for making soap [52].

According to United States Energy Information Administration Agency, several gallons of used cooking oil are collected daily in United States of America [52], where close to 9 pounds of used cooking oil are produced per person each year [53]. In Europe, about 0.49–0.7 million gallons per day of waste frying oil are collected [54]. In Nigeria, WFO is one of the major wastes generated in hotel, restaurants and eateries [55]. However, since no strict and more stringent environmental legislations on WFO discharge, those organizations mentioned earlier discharge WFO indiscriminately into water bodies and on land, thus leading to environmental degradation [52]. More so, there is no Information Administrative Agency that accounts for WFO generated in Nigeria. However, the operation of Students’ Cafetaria at Afe Babalola University (ABUAD), Ado-Ekiti, Nigeria, where the waste frying oil used in this study was collected, is being monitored by food scientist and nutritionist. They make sure that the used oil is not reused more than two times after initial frying to prevent the intake of free fatty acid and thus use the WFO as raw material for producing soap.

Table 1 shows the average fatty acid composition in waste frying oil [50]. However, low quality feedstock, which contains high concentration of free fatty acid (greater than 1%), cannot be

| Fatty acid (trivial/rational name) | Methyl ester (trivial/rational name) | Formula | Common acronym | Acid composition (%) |
|------------------------------------|-------------------------------------|---------|----------------|----------------------|
| Palmitic acid/hexadecanoic acid    | Methyl palmitate/methyl hexadecanoate | C_{16}H_{32}O_{2} | C16:0           | 15.86                |
| Stearic acid/octadecanoic acid     | Methyl stearate/methyl octadecanoate | C_{18}H_{36}O_{2} | C18:0           | 4.87                 |
| Oleic acid/9 (E)—octadecenoic acid | Methyl oleate/methyl 9 (E) octadecenoate | C_{18}H_{34}O_{2} | C18:1 (E)       | 29.83                |
| Linoleic acid/9 (Z), 12 (Z)—octadecadienoic acid | Methyl linoleate/methyl 9 (Z), 12 (Z) octadecadienoate | C_{18}H_{30}O_{2} | C18:2 (Z,Z)    | 28.85                |
| Linolenic acid/9 (Z), 12 (Z), 15 (Z)—octadecatrienoic acid | Methyl linoleate/methyl 9 (Z), 12 (Z), 15 (Z)—octadecadienoate | C_{18}H_{30}O_{2} | C18:3 (Z,Z,Z)  | 2.49                 |

Source: [50].

Table 1. Average fatty acid composition in waste frying oil.
easily transformed into biodiesel by alkali transesterification because it consumes the catalyst and reduces its performance leading to substantial yield losses [56, 57].

Acid-catalyzed transesterification remains the best means of converting oil with high FFA content to biodiesel, but due to the harsh reaction conditions and prolong time of reaction [42, 46, 58], it has been largely ignored. Talebian-Kiakalaieh et al. [51] investigated that heterogeneous transesterification of WFO rich in FFA with methanol using heteropoly acid (HPA) catalyst and 88.6% of biodiesel was obtained at optimum reaction conditions. Meanwhile, the authors only focused attention on the performance and reusability of the heterogeneous acid catalyst while process economy was not given attention.

Since the transesterification of waste frying oil rich in FFA may not proceed using solid base catalyst, a two-step transesterification reaction is often employed [56, 59, 60]. The first step is the acid esterification process through which high FFA oils react with methanol using mineral acid usually concentrated tetraoxosulphate (VI) acid as catalyst to produce free fatty acid ester [44, 50, 61]. Followed by the basic transesterification process, whereby acid preheated waste frying oil reacts with methanol in the presence of base catalyst to form biodiesel and other products [52]. Therefore, a two-step transesterification process not only removes high free fatty acid content (FFA) but also improves the biodiesel yield [44]. The test of the waste frying oil-derived biodiesel on commercial diesel engines provides better performances and less gaseous pollutant is emitted apart from NO\textsubscript{X} [62].

2. Raw materials

Apart from the biodiesel feedstock, alcohol and catalyst also play important roles in biodiesel production. The required raw materials for the synthesis of biodiesel from WFO are explained as follows:

2.1. Alcohol

In biodiesel synthesis, monohydric alcohols, such as methanol, ethanol and butanol, are usually employed as co-reactant. Methanol is a basic monohydric alcohol used in excess for the production of biodiesel via catalyzed transesterification process. Methanol is light, volatile, poisonous and inflammable and contributes to ozone layer depletion. Biomass-derived fuel produced with methanol from natural gas or coal has approximately 94–96% biogenic content [63]. However, a 100% renewable biodiesel could be produced, if bioethanol is used as a substitute for methanol [64]. Ethanol is also a light alcohol, volatile, flammable, colourless and biodegradable. Among those aforementioned alcohols, methanol is mostly used for biodiesel production commercially, because it is relatively cheap, readily available and easier to separate glycerol from the product mixture [65]. The use of ethanol and other monohydric alcohols for biodiesel production has however all been reported [66].

2.2. Catalyst

Industrial production of biodiesel is frequently done via homogeneous catalyzed transesterification process, whereby the triglyceride contained in vegetable oil or animal fat reacts with
alcohol (methanol/ethanol) in the presence of liquid catalyst. Utilization of enzymes as biocatalyst for the transesterification of triglyceride to biodiesel has also been reported [67]. However, due to the problem associated with homogeneous catalysis (wastewater generation and difficulty in reusability) and enzymes (exorbitant cost and deactivation), there have been simulated researches in the field of heterogeneous catalysis for biodiesel production [68, 69]. The solid-based catalysts include pure metal oxides, mixed metal oxides, alumina, silica and zeolite-supported catalyst, sulphated metal oxide and those ones derived from waste and naturally occurring materials. Vujicic et al. [70] investigated the transesterification of sunflower oil using CaO catalyst. Apart from that, Wen et al. [43] studied the transesterification reaction between cotton seed oil and methanol using TiO-MgO as heterogeneous catalyst. Many more heterogeneous catalysts suitable for biodiesel production have been reported in literature [23, 71].

3. Materials and methods

3.1. Materials

The WFO after used for long frying was collected from students’ Cafeteria 1, Afe Babalola University, Ado-Ekiti, Nigeria. The chemicals/reagents used for waste frying oil characterization such as potassium hydroxide (KOH), ethanol (95%), hydrochloric acid (HCl), diethyl ether, phenolphthalein, diethyl ether, chloroform and acetic acid (BDH, England) were all obtained from Chemical Science Laboratory, ABUAD, Ado-Ekiti, while analytical grade methanol (JHD, AR China) was procured from Nizo Chemical Enterprise, Akure and was used as received. Distilled water was prepared in the laboratory. The heterogeneous catalyst used for this study was a self-synthesized, and it is known as anthill-eggshell-Ni-Co mixed oxide composite catalyst (AENiCo).

3.2. Characterization of waste frying oil

The WFO was first heated in a hot air oven at 120°C for 4 h and later filtered using a 120-μm sieve mesh to remove any non-oil components or bits of food residues. The basic physicochemical properties of the waste frying oil shown in Figure 1 are determined as follows:

3.2.1. Density

The empty density bottle was weighed and recorded as \( w_1 \). Prior to this, the temperature of the oil was taken with thermometer and obtained to be 23°C. The bottle was filled with distilled water, after which it was weighed and recorded as \( w_2 \). Furthermore, the bottle was emptied, cleaned with tissue paper and also filled with equal volume of waste frying oil. The weight of the bottle and waste frying oil was then measured and recorded as \( w_3 \). The density of the sample was thereby determined using Eqs. (1) and (2).

\[
R.D = \frac{w_0}{w_\nu} = \frac{w_3 - w_1}{w_2 - w_1}
\]

\[
\rho_{wfo} = R.D \times 1 \text{ g/cm}^3
\]
3.2.2. Kinematic viscosity

The essence of subjecting vegetable oil (edible and non-edible) to transesterification reaction process is to reduce its viscosity and density, because it cannot be used directly to power any diesel engine. This property needs to be determined before and after biodiesel synthesis from vegetable oil. In order to determine this property, a weighed quantity of oil was poured into a stainless cup of DV-III ultra programmable rheometer (Brookfield: model LVDV-III U) and preheated to a temperature of 60°C for 1 h. Thereafter, its spindle and cup containing heated oil were placed under the rheometer. The rotor and spindle were both immersed in the cup after the rheometer had been set to require speed (150 rpm). The value of dynamic viscosity was immediately taken when the temperature of the preheated oil dropped to 40°C. However, in order to determine the kinematic viscosity, the density of waste frying oil at 40°C was therefore determined using Eq. (3).

$$\mu_k = \frac{\mu_D}{\rho_{wco40}}$$  \hspace{1cm} (3)

3.2.3. Acid value

It is the number of milligram potassium hydroxide needed to neutralize the acid contained in 1 g of oil or fat sample. It measures the extent at which the glyceride contained in an oil sample decomposes by the activity of lipase or other actions. Acid value of the WFO was examined by titration method reported elsewhere [72].

In this method, 5.926 and 6.695 g of oil samples were weighed and poured into flasks A and B, respectively, and 25 mL each of diethyl ether and ethanol was added into flasks A and B and 2 drops of 1% phenolphthalein indicator solution were also added into each of the flasks. Thereafter, potassium hydroxide (KOH) solution was then titrated against dissolved oil-solvent mixture under constant agitation until the solution turned into pink as shown in Plate VI. The acid value (A.V) and free fatty acid content (% FFA) were thus calculated using Eqs. (4) and (5).
(A.V) in mgKOH/g = \frac{56.1 \times C_{KOH} \times V_{KOH}}{w_o} \quad (4)

\%FFA = \frac{AV}{2} \quad (5)

Where \( V_{KOH} \) is the volume of potassium hydroxide, \( C_{KOH} \) is the concentration of potassium hydroxide, \( w_o \) is the weight of oil used whose value must lie between 0 and 10 g, AV is acid value and \% FFA is the percentage of free fatty acid.

3.2.4. Saponification value

The saponification value of an oil or fat is the number of mg of potassium hydroxide required to neutralize the fatty acids resulting from the complete hydrolysis of 1 g of the sample. It helps in detecting oils and fats, which contain a high proportion of the lower fatty acids. The principle is that oil or fat undergoes saponification reaction with large volume of alcoholic potassium hydroxide, and the resulted product is subjected to titration process in order to determine the amount of potassium hydroxide remaining after saponification reaction.

In order to determine the saponification value of WFO, 8.221 g of KOH pellet was weighed and dissolved in 5 ml distilled water, after which 250 ml of 95%v/v ethanol was added and allowed to settle overnight. Decant of the clear solution of alcoholic potassium hydroxide was then obtained. Also, 1 g of phenolphthalein powder was dissolved in 100 ml ethanol to make phenolphthalein indicator solution.

About 2.030 g of oil was weighed into flat bottom flask A and 25 mL of alcoholic potassium hydroxide solution was added into the flask A. Another flat bottom flask B was also filled with 25 mL of alcoholic KOH without oil. The reflux condensers were attached to each of the flasks and heated on a boiling water bath for 1 h with occasional shaking. The flasks A and B were then removed from the water bath after 1 h and two drops of phenolphthalein indicator were added into each of the flasks. Both colours in flasks A and B changed to pink. While still hot, contents in flasks A and B were titrated with the standard 0.5 M hydrochloric acid with constant shaking until the solutions in flask A and B changed back to pale yellow and colourless, respectively. However, after the estimation of volume of acid consumed, the saponification value (SV) was then calculated using Eq. (6) [50].

\[ SV = \frac{(b - a) \times 28.05}{w_o} \text{(mgKOH/g)} \quad (6) \]

Where \( a \) and \( b \) are volumes of acid used against alcoholic KOH solution with oil and alcoholic KOH solution without oil, respectively. \( w_o \) is the volume of WFO used, while SV is the saponification value.

3.2.5. Average molecular weight

It is the weight in atomic mass units of all the atoms in a given formula. The determination of molecular weight of a substance is necessary in order to ascertain the number of grams
It is a function of saponification and acid values. Average molecular weight (AMV) of oil is determined using Eq. (7).

$$A.M.W = \frac{56.1 \times 1000 \times 3}{(S.V - A.V)}$$  \hspace{1cm} (7)

Where A.M.W is the average molecular weight. Saponification and acid values are denoted by S.V and A.V, respectively.

3.3. Biodiesel production from WFO

The transesterification of WFO to biodiesel using AENiCo catalyst was carried out in a batch reactor made up of a 250 mL one way round bottom flask fitted with a condenser and thermometer as shown in Figure 2. The reaction was performed at reaction conditions, considering catalyst loading of 3 wt%, reaction temperature of 70°C, reaction time of 2 h and methanol to WFO molar ratio of 12:1, while stirring rate was kept constant throughout the reaction. At the end of the reaction, the resulting mixture was filtered using white cloth in order to remove the spent catalyst, and the filtrate was then poured into a separating funnel and left there overnight to settle. During the process, two layers of liquid were observed, in which the upper layer was biodiesel and the lower layer indicated glycerol.

3.4. Preparation of different blends of biodiesel and petroleum diesel

In this study, waste frying oil-derived biodiesel was mixed with petroleum diesel and used on ignition engine to evaluate its performance and characterize the exhaust gas emission. The mixing of two different diesels (biodiesel of waste frying oil and fossil diesel) was made in plastic container coupled with electric mixing machine as shown in Figure 3. The blends were made at different proportions with 20% (B20), 50% (B50), 80% (B80) and 100% (B100) by volume of biodiesel. It was vigorously mixed with the help of agitator being driven by electric motor at room temperature with agitation speed of 400 rpm. The characteristic of the prepared biodiesel, biodiesel-diesel blend and diesel including specific gravity, kinetic viscosity, lower heating value (LHV) and flash point were determined. The LHV of the fuels was determined using Eq. (8) [73].

$$LHV = -0.167 \rho + 184.95$$  \hspace{1cm} (8)

3.5. Emission characterization of compression ignition engine

The method reported by Elsolh [74] was adopted for the performance evaluation of the engine. The gas emission of three different blends of biodiesel and diesel were measured and compared in a Yoshita S195NM ignition engine whose technical features are given in Table 2. The first blend used was B20, it was poured into the fuel tank of the ignition engine and the engine was immediately turned on by hand whirling. The probe of a gas analyzer was thereafter attached to exhaust pipe of the engine. The engine was left to work for almost 20 min in order to make it stabilize and allow the thick smoke to escape. The measurement was then taken.
by gas analyzer every 5 min for 20 min, and the values of the emission measurements were stored on an input computer program to determine the average values. The same procedure was used for other fuels (B50 and B80) (Figure 4).

Table 2. Ignition engine specification.

| Technical properties     | Values             |
|--------------------------|--------------------|
| Number of stroke         | 4                  |
| Number of cylinder       | 1                  |
| Declared speed           | 2000 rpm           |
| Compression ratio        | 20:1               |
| Rated power              | 3.32 kW            |
| Overall dimensions       | 900 × 440 × 760 mm |
| Bore and stroke          | 95 × 115 mm        |

Figure 2. (a) Experimental set, (b) raw materials and synthesized biodiesel and (c) biodiesel-glycerol mixture.

Figure 3. (a) Petroleum diesel and WFO-derived biodiesel, (b) blending of biodiesel and petroleum diesel and (c) blended fuels.
4. Results and analysis

4.1. Characterization of WFO

In this current study, WFO used as feedstock was characterized based on its physicochemical properties. The properties are summarized in Table 3. Its density at 25°C was determined to be 0.9147 g/cm³. The obtained value of density was slightly less than those ones recorded by Chhetri et al. [52] and Mahgoulb et al. [75] as 0.9216 and 0.9185 g/cm³ at 23°C, respectively. This difference is attributed to the fact that density is a function of temperature [52] and decreases as temperature increases [76]. The kinematic viscosity of waste frying oil was 9.36 cP.

More so, the acid value obtained was 3.945 mgKOH/g. The free fatty acid concentration in the used frying oil was equivalent to 1.973 wt%. Since the free fatty acid content is less than 3 wt%, it implies that the waste frying oil (WFO) could be directly converted into biodiesel via single-step transesterification process. The saponification value was determined to be 183.1 mgKOH/g. This value obtained was lower than that of waste frying oil collected in Malaysia by Tan et al. [44]. Meanwhile, it was approximately equivalent to the one reported by Buasri

| Property                  | Unit      | Value  |
|---------------------------|-----------|--------|
| Density at 25°C           | g/cm³     | 0.9147 |
| Viscosity at 40°C         | cP        | 9.36   |
| Acid value                | mgKOH/g   | 3.945  |
| Free fatty acid           | wt.%      | 1.973  |
| Saponification value      | mgKOH/g   | 183.1  |
| Average molecular         | g/gmol    | 939.41 |

Table 3. Physicochemical properties of waste frying oil (WFO).
et al. [77]. However, the average molecular weight of oil or fat, usually expressed in g/gmol, is a function of acid and saponification values of fat and oil [78]. Average molecular weight of waste frying oil obtained in this study was found to be 939.4 g/gmol, which was comparable to other sources, 942 and 928 g/gmol [75].

4.2. Comparison of physicochemical properties of biodiesel, diesel and their blends

The results of the measured properties of the WFO-derived biodiesel, petrol-diesel and biodiesel-diesel blends are presented in Table 4.

The physicochemical features of different biodiesel-fossil diesel mixtures as contained in Table 4 indicate that the specific gravities/densities of those blends and pure biodiesel vary in the range of 0.825–0.883. The densities of B20 and B80 samples showed conformance with the ASTM standard (0.86–090) while B50 did not. However, the kinematic viscosities as measured for the blends of biodiesel and conventional diesel samples on comparison with the ASTM standard for biodiesel meet the requirements as they fall within the range (1.9–6.0 mm²/s); this observation is attributed to homogenized mixture, which might have resulted from proper mixing of the two fuels. Meanwhile, these values as seen in Table 4 are higher than that of fossil diesel (2.03 mm²/s), indicating that biodiesel has large molecular mass [79]. However, the viscosity of pure biodiesel (3.76 mm²/s) was larger compared to those of three blends. This indicates that blending leads to reduction in viscosity. Hence, a complete combustion and reduction in emission of greenhouse gases are possible [80].

Energy content (calorific value) is a property that determines the fuel combustion quality. As can be seen in Table 4, biodiesel has lower energy content as compared to that of petrol-diesel. The main reason for this behaviour is due to the fact that biodiesel contains 11% oxygen by

| Parameter                      | Unit   | B0    | B20   | B50   | B80   | B100  |
|-------------------------------|--------|-------|-------|-------|-------|-------|
| Specific gravity              | —      | 0.809 | 0.866 | 0.825 | 0.872 | 0.883 |
| Kinematic viscosity           | mm²/s  | 2.03  | 3.31  | 2.27  | 2.23  | 3.76  |
| Lower heating value (LHV)     | MJ/kg  | 48.23 | 40.33 | 47.18 | 39.33 | 37.49 |
| Flash point                   | °C     | 84    | 130   | 79    | 124   | 162   |

Table 4. Physicochemical properties of WFO-derived biodiesel, petrol-diesel and their blends.

| Fuel type | CO (ppm) | CO₂ (ppm) | O₂ (ppm) |
|-----------|----------|-----------|----------|
| B0        | 2300     | 9500      | 98,750   |
| B20       | 1050     | 14,000    | 185,250  |
| B50       | 1055     | 19,000    | 173,450  |
| B80       | 1450     | 22,500    | 173,500  |

Table 5. Average values of exhaust emissions for every biodiesel blend.
weight [81, 82]. More so, it was revealed that B50 has the highest energy content (caloric value) compared among the three blended fuels, followed by B20. However, the lower heating values of those dual fuels (B20, B50 and B80) are higher than that of pure biodiesel but lower than that of petrol-diesel, thus indicating high specific fuel consumption. The same findings were also reported by Yoo and Lee [83] in the prediction models and LHV effect on the CI engine performance when fuelled with biodiesel blends.

The measure of flammability of the fuel is referred to as flash point [7]. The measured values of flash point obtained for the three blended fuels indicate a significant drop when compared to that of B100. This indicates an improvement in fuel qualities. As for diesel fuel (B0), it could be noticed that the results of the specific gravity, the kinematic viscosity, flash point and the lower heating value shown in Table 4 are very close to the DIN EN 590 standards of diesel and to the experimental results reported by Chopade et al. [84].

4.3. Performance and emission characteristics

In this aspect, the gas exhaust emissions are compared for different biodiesel blends, that is, B20, B50 and B80 and pure diesel (B0) at the engine speed of 2000 rpm. The gas emissions measured include carbon monoxide (CO) and carbon dioxide (CO₂). The gas analyzer used in this study could only measure those aforementioned gases. The mean values of the resulted emissions for each of the fuel are presented in Table 5.

As shown in Table 5, it was noticed that the average value of CO₂ rises as the volume of biodiesel increases in the mixture of biodiesel and conventional petrol-diesel. This trend may be due to the presence of oxygen in biodiesel [85].

4.3.1. Comparison of carbon monoxide (CO) emission

Higher percentage of CO was emitted when the diesel engine was fuelled with B80 fuel, followed by B50 which released 1055 ppm, and least CO was emitted from diesel engine when it was fuelled with B20 blended fuel as can be seen in Table 5. Although, the amount of CO emitted for every fuel biodiesel blend was found to be very small. There was no much difference among the three blended fuels. A similar observation was also recorded by Xue [86], who observed that the blends of biodiesel lowered CO emissions. Moreover, biodiesel, being an oxygenated fuel, enhances combustion and leads to reduction in CO emission. It is noticed that the three blended fuels have lower values of CO as compared to other gases emitted. This indicates that the combustion was almost completely done. However, the reported increase of CO emission with the use of pure diesel (B0) is due to the absence of oxygen in the fuel, thus leading to incomplete combustion [83].

4.3.2. Comparison of carbon dioxide (CO₂) emission

As shown in Table 5, it was noticed that B80 fuel emitted largest concentration of CO₂, followed by B50 fuel, and this indicates that CO₂ emission increases as the biodiesel content increases in the biodiesel-diesel blend. As reported in the literature, biodiesel provides a means of reusing
CO\textsubscript{2}, so there is no net increase in global warming [74]. Moreover, it is a known fact that complete combustion inside the combustion chamber of diesel engine promotes CO\textsubscript{2} [7]. Besides, it has been reported by many researchers that the presence of O\textsubscript{2} in biodiesel enhances better combustion [87, 88], which helps to convert CO and CO\textsubscript{2} and, therefore, increases CO\textsubscript{2} emission rate. This is attributed to why B80 fuel released large amount of CO\textsubscript{2} as compared to other blended fuels.

It is quite evident from Table 5 that the CO\textsubscript{2} emission of biodiesel-fossil fuel mixture is higher than that of pure diesel (B0) at all blends and a maximum increase is noted when compared to each of the blend. According to Datta and Mandal [7], the emission of CO\textsubscript{2} from ignition engine should increase with biodiesel addition to diesel fuel because of improved combustion due to the presence of oxygen in the molecular structure of biodiesel.

5. Conclusions

The major achievements in this research work are the production of biodiesel from WFO via heterogeneous catalyzed transesterification process and the performance of ignition engine fuelled with WFO-derived biodiesel-diesel blend. Various analyses carried out on the WFO-derived biodiesel confirmed that it is of good quality and also meet the ASTM standard. Moreover, the performance and emission evaluation conducted on existing diesel engine fuelled with biodiesel-diesel blend showed that the blend containing 20% biodiesel content (B20) emitted least CO and CO\textsubscript{2}, thus suggesting better dual fuel combination.

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