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Chemical and quality performance of biodiesel and petrol blends

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A R T I C L E I N F O

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A B S T R A C T

The development of an appropriate fuel to run on a petrol compression ignition engine conceptualises a low-temperature combustion strategy, which faces challenges. With the high intake temperatures, low lubricity and need for a high compression ratio for this engine, the use of a petrol-biodiesel blend as a fuel addresses such issues. This study evaluates the characteristics of fuel quality and performance of blended fuels with biodiesel additives (5%, 15%, and 25%) to petrol (95%, 85%, and 75%) compared to 100% petrol and biodiesel. Biodiesel was produced from waste sunflower and palm oils. The fuel properties of the blends were assessed with respect to acid number, density, distillation, cetane number, metal contents, oxidation stability, viscosity, and water content. Results showed that the blended fuels met standard specifications and possessed improved fuel quality compared to pure petrol. Comparing the biodiesel-petrol blends with pure biodiesel, the values of these fuel properties were lowered except for oxidation stability which was enhanced. The two types of biodiesel fuel blends portrayed different fuel qualities, where sunflower biodiesel-petrol blends had more energy content and lower acid number, while palm biodiesel-petrol blends had exceptional thermal stability and characteristics of a better cold start. The high degree of unsaturation characterising sunflower biodiesel resulted in increased carbon residues, reduced cetane number and subsequent poor cold start. An increase in petrol percentage in the blends reduced concentrations of calcium and magnesium significantly and hindered the absorption of moisture content.

Introduction

The Paris Climate Accord COP21 which aimed at reducing the 21st-century global rise in temperature below 2 °C was signed by many countries, with a commitment that by 2030 the greenhouse gases (GHG) should be below 40% [1]. The feasibility of such a goal would require huge changes in the traditional way of energy production since most of the world's energy comes from fossil fuels [2]. Generally, the world's primary energy consumption mainly originates from fossil fuel (88%), while nuclear and renewable energy accounts for 7% and 5% respectively [3], and the transportation sector holds the highest share releasing about 23% of CO_2 and 14% of greenhouse gases (GHG) discharges.

Transport is mainly power-driven by the internal combustion engines using petrodiesel and petrol (>99.9 %). While the global demand for transport fuel continues to rise with an expected annual growth of 1%, there is a need for 4.9 billion litres of petrol and 1.3 billion litres of jet fuel daily. Also, the demand for vehicles is expected to grow mostly in non-Organization for Economic Co-operation and Development (OECD) nations such as India and China [4], owing to the population and prosperity growth. Perhaps, the rise in fuel prices is understandable [5]. Additionally, fossil fuels are finite and have inordinate damage to the earth's biodiversity [6,7], leading to a serious global warming phenomenon [8]. Therefore, the need to look for other ways of generating energy is necessary even if energy demand in 2020 declined by 4% and the use of the transportation sector went down by 14% as a result of less mobility and restrictions set, in preventing the spread of covid-19 pandemic [9]. We need energy security, control GHG released and enhance the community air quality in reaction to consumers' desires and demands [4,10].

In combating this, greener fuels which are renewable energy are being developed, to solve the issue of global climate change. With that, fascinating fuels such as biodiesel are being produced with the capacity of preserving the environment, bringing a feasible economy and creating social sustainability [11]. Besides this, the development of new engine

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combustion systems that can produce fewer emissions while maintaining high efficiency is underway [12]. Petrodiesel has traditionally been used to power compression ignition (CI) engines which produce high thermal efficiencies but use high combustion temperatures and limited fuel/air mixtures, resulting in a huge amount of emissions [13,14]. Nevertheless, using biodiesel or its blends in CI engines has proven to possess good combustion performance similar to petrodiesel with significantly reduced emissions of carbon monoxide (CO), and unburned hydrocarbon (HC), but has an increased amount of nitrogen oxide (NOx) emissions [15–17].

Additionally, in the combustion chamber of the petrodiesel CI engine, fuel injection is greatly affected by the viscosity of the fuel, and biodiesel is significantly less viscous than petrodiesel and more than vegetable oil [18], and according to the study by Nair [6], the use of 100% biodiesel (B100) would result in maintenance and performance issues. Furthermore, Sharma et al., [19], concluded that as the blending ratio of biodiesel increased, there is a decrease in engine efficiency, all carbon-based and smoke emissions but an increase in NOx emissions.

Contrary to diesel, petrol is a low reactivity fuel which is used to power spark-ignition engines that operate at low compression ratios and produce low engine efficiencies but extremely low emissions. Therefore, to produce high efficiency and low emissions, different combustion methods are proposed, by reducing combustion temperatures and improving fuel–air mixing [20]. Using petrol, which has high volatility and poor self-ignition, the air–fuel mixing is increased thereby creating a more volatile petrol-like fuel with a low cetane number (CN), which can be the solution for CI engines [21]. These engines rely on the concept of using low-temperature combustion strategies such as gasoline compression ignition (GCI), partially pre-mixed compression ignition (PPCI), homogenous charge compression ignition (HCCI) and reactivity controlled compression ignition (RCCI) [12]. Amongst these combustion strategies, GCI has proven to show more advantageous compared to others [22]. However, ignition at low-temperature conditions is a challenge for GCI [23], and by adding biodiesel, ignition will be enhanced [24]. Therefore, studies were conducted to improve the ignition characteristics of petrol, after their observations by Adam et al. [23], Putrasari & Lim [25], Das et al. [21], and Thongchai & Lim [26], reported that blending biodiesel with petrol improved thermal efficiency, reduced ignition delay and emissions significantly. They also added that 20% of biodiesel blended with 80% petrol (PB20) shows similarities to pure petrodiesel. High oxygen content, cetane number and viscosity of biodiesel improve air–fuel mixture, spray, fuel injection system and auto-ignition [25,27], while the low-cetane number of petrol helps in reducing intake temperature [23]. The qualities of these fuels are put together to render the blended fuel with superior auto-ignition characteristics and fewer combustion emissions [28,29]. Additionally, blending biodiesel with petrol will achieve enhanced fuel properties needed for GCI, in solving emission issues as compared to using pure petrodiesel [23,26,30].

Although certain studies have been conducted on the performances, emission and combustion characteristics of petrol-alcohol blends, petrol-diesel blends and petrol-biodiesel blends to be used in petrodiesel engines [27,31–35], there is a dearth of literature on blending biodiesel with petrol and the properties of these blends [21,25,26,29]. Also, no research has been recorded in evaluating numerous physical and chemical fuel properties of biodiesel-petrol blended fuel. The current study presents blending biodiesels produced from waste sunflower and waste palm oils with commercial petrol and evaluates the properties of the blended fuels to assess how their chemical and physical properties will be affected in relation to the fuel quality, performance, and unwanted metals in the petrodiesel engine. Elemental analysis and other tests were performed according to ASTM D6751 and EN 14,214 specifications. The D974 for acid number, D979 and D4737 for cetane number, EN ISO 3675 for density, D86 for distillation, EN 14,112 for oxidation stability, D445 for viscosity and D6304 for moisture content.

Materials and methods

Materials

Mineral acids and oxidising agents (57.2% nitric acid and 98.08% sulphuric acids) were purchased from KIMIX Chemical Lab Supplies South Africa. 35% hydrogen peroxide was purchased from Labchem South Africa, while biodiesel and deionised water of 18.2 MΩcm (Milli-Q) were obtained from Chemical Engineering Oil and Gas Laboratory Cape Peninsula University of Technology (CPUT) Bellville, South Africa. Petrol was purchased from Sasol fuel garage, South Africa.

Biodiesel and petrol blends preparation

For this study, the method of transesterification reaction using methanol and the bifunctional catalyst was employed for palm and sunflower biodiesels production as described in the work of Simbi et al., [36], through. Apart from the economic advantages and availability of these waste oils [37], They possess varying fatty acids compositions allowing them to differ in their fuel properties [38], i.e., palm biodiesel has excellent engine performance, high specific fuel consumption, shorter ignition delay and high viscosity [39,40]. The biodiesels produced were mixed with commercial petrol in three different proportions of PB5, PB15, and PB25, which were made on a volume basis of (5% biodiesel, 95% petrol), (15% biodiesel, 85% petrol), and (25% biodiesel, 75% petrol) respectively. Where P stands for petrol, B stands for biodiesel, and the numeric value stands for the percentage of biodiesel content. Splash blending [41], was used for blending since it is an effective and accurate technique. This was conducted at constant temperatures of 22 to 24 °C with continuous stirring using 400 rpm for a minimum time of 30 min, using an overhead stirrer (Scientech inc, Boulder, US) to ensure homogeneity [27,42–44].

Characterisation of biodiesel and petrol blends

To check the quality of the biodiesel and its blends various tests were conducted at Oilwatch laboratories in South Africa, while oxidation stability and elemental analysis were done at Food Science and Technology and Analytical Chemistry laboratories at the Cape Peninsula University of Technology, Bellville, South Africa.

Measurement of acid value

The acid number test used colour indicator non-aqueous titration as detailed in ASTM D974 [45]. The petrol and biodiesel blends with acid levels ranging from 0.1 to 0.55 mg KOH/g were examined by adding 10 mL isopropanol into a 1 mg sample, then adding 2 to 3 drops of phenolphthalein and neutralising the solution with 0.1 M of KOH. Calculation of acid number was done using equation (1):

$$\text{Acid value}\,(\text{mg KOH/g}) = (56.1\ \times\ 0.1\,\text{M x V})/\text{g} \tag{1}$$

where 56.1 = constant molecular mass for KOH, 0.1 M = concentration of KOH, V = volume of final value - volume of initial value and g = weight of sample in grams.

Measurement of density

The density of the fuel was measured by using the modern high-precision density meter DMA40 (Anton Paar GmbH, Graz, Austria) operating at 15 °C according to EN 14,214 [45]. 2 mL of sample was injected into the measuring cell and each sample measurement was repeated three times to ensure accuracy and the average value was recorded. The density of a material is determined by the mass per volume measures compactness within a substance [46] i.e.:

$$\text{Density} = \text{Mass}/(\text{Volume}) = \text{kg/m}^3 = \text{g/cm}^3 \tag{2}$$

Calculation of cetane number

The calculated cetane index (CCI) was calculated by using of density reported in equation (2) with recovery temperature at 50% distillation (T50) according to ASTM D979-91 in equation (3) [47], or using distillation temperatures of 10%, 50% and 90% (T10, T50, T90) according to D4737-09 in equation (4) [48] as follows:

$$Cetane\ Index = 454.74 - 1641.416\ \rho + 774.74 \times \rho^2 - 0.554\ T_{50} + 97.803\ (log\ T_{50})^2 \quad (3)$$

where ρ = Density in g/cm^3 at 15 °C, T_{50} = Mid boiling point temperature in °C (the temperature at which 50% of the sample by volume has evaporated).

CCI = 45.2 + 0.0892 T_{10N} + [0.131 + 0.901B] T_{50N} + [0.0523 – 0.420B] T_{90N} + 0.00049 [(T_{10N})2 – $(T_{90N})^2$ + 107.

$$B + 60\ B^2 \quad (4)$$

where CCI = Calculated Cetane Index, D = Density in g/cm^3 at 15 °C, DN = D – 0.85, B = $e^{(-3.5)\ (DN)) - 1}$, T_{10} = Distillation temperature at 10% distillates (°C), T_{10N} = T10 – 215, T_{50} = Distillation temperature at 50% distillates (°C, T_{50N} = T50 – 260, T_{90} = Distillation temperature at 90% distillates (°C), and T_{90N} = T90 – 310.

$$CN = CCI - 2 \quad (5)$$

where CN = Cetane Number and CCI = Calculated Cetane Index.

Measurement of elemental content

Standards preparation

All glassware used was soaked in 10% volume per volume (v/v) nitric acid overnight and was rinsed with deionised water before usage. Multielement standard solutions containing (calcium-Ca, tin-Sn, arsenic-As, chromium-Cr, manganese-Mn, lead-Pb, phosphorus-P, aluminium-Al, nickel-Ni, cadmium-Cd, selenium-Se, antimony-Sb, zinc-Zn, copper-Cu, cobalt-Co, potassium-K, barium-Ba, magnesium-Mg, iron-Fe, sodium-Na, silicon-Si) were prepared in concentrations of 0.05, 0.01, 0.5, 0.1, 1, 5, 10, and 20 ppm, in 8 volumetric flasks of 100 mL using dilution method by decreasing concentration from 1000 mg/L stock solution using deionised water.

Sample digestion

Biodiesel has a high viscosity and therefore requires dilution before elemental analysis is carried out. An open system with conventional heating was used for digesting the samples by first weighing 1 g of 100% biodiesel (B100) or petrol-biodiesel blend (PBXX) sample into a borosilicate tube. 5 mL of HNO_3, 2 mL of H_2SO_4 and 1 mL of H_2O_2 were added and heated on a hot plate which was set at 90 ^{0}C for 2 h. Thereafter, 3 mL of HNO_3 and 1 mL of H_2O_2 were measured and transferred into the beaker holding the sample, and the hot plate temperature was subsequently adjusted to 220 °C and left for 40 min. Then 2 mL HNO_3 and 4 mL H_2O_2 were added to the beaker, when the sample colour did not turn colourless by this step, the procedures were repeated (from the first step) until the solution turned colourless. Finally, the sample was diluted to a volume of 10 mL with deionised water. The accuracy was checked by spiking the blank sample with the same digestion procedure [49].

ICP-OES sample procedure. An inductively coupled plasma optical emission spectrometer (ICP-OES) ARCOS HFS12 (Ametek Inc., Pennsylvania, United States) was used to measure elemental content and argon (Afrox Ltd., Gauteng, South Africa) was used as a plasma gas. Wavelengths were selected to measure emission intensities of analytes were 324.745 nm for Cu, 396.847 nm for Ca, 167.078 nm for Al, 259.941 nm for Fe, 766.491 nm for K, 279.553 nm for Mg, 589.592 nm for Na, 213.856 nm for Zn, and 177.495 nm for P.

The smart analyser vision was initialised after switching on the auto sampler on the computer connected to the ICP and the extractor fan on ICP switched on. Argon gas in the non-flammable gas room was allowed to flow while the system was flushed twice. The plasma was left to stabilise for 20 to 30 min while the needle in the auto sampler was in its original position. Thereafter, calibration was conducted three times before standards containing organometallic standard solutions of 0.05, 0.01, 0.5, 0.1, 1, 5, 10, and 20 ppm could be run through the ICP. After generating calibration curves for the analytes, organic samples were continuously introduced into the ICP through the nozzle and allowed to be analysed on the computer. 5% nitric acid was used in flushing the nozzle in between each sample.

Measurement of water content

The water content was measured using the Karl Fischer Titration method according to the most reliable D6304 technique [50,51]. An appropriate amount of sample was weighed, poured into a vial, sealed, and heated under a vacuum in an oven to evaporate water. The vaporised water was carried into a conditioned titration cell (hydranal Coulomat-AG) which was titrated with Karl Fischer reagent until the endpoint was reached.

Results and discussions

Effect on acid number

As observed in Fig. 1, Petrol (P100) had an acid number value of 0.1 mg KOH/g and an increase in the blending percentage of biodiesel increased the total acid number (TAN) from 0.23 mg KOH/g and 0.28 mg KOH/g in 5% biodiesel-95% petrol blend (PB5) of sunflower and palm biodiesel blends (S-PB5 & P-PB5) to 0.46 and 0.55 mg KOH/g in pure sunflower biodiesel and palm biodiesel (S-B100 and P-B100) respectively (Fig. 1). Also, the figure illustrates a higher acid value for palm biodiesel as compared to sunflower biodiesel, with a decrease in the TAN as the percentage of petrol added in blends increases which were comparable to a conclusion drawn by Jain & Sharma [52], when petrodiesel and biodiesel were blended. According to Phan & Phan, [53] and Gopinath et al., [54], these acid values were indicative of fatty acid or acid moieties content in the fuel, which were found to fall within set limits of ASTM D974 and EN 14,104 standards with a maximum limit of 0.8 mg KOH/g and 0.5 mg KOH/g respectively [55,56]. Except for a slight deviation of 0.05 mg KOH/g in palm biodiesel which was above the EN specification. Similarly, close values were reported by Hossain & Boyce [57], after producing biodiesel from waste sunflower oil and the TAN obtained was 0.44 mg KOH/g while 0.43 mg KOH/g was found for waste cooking oils by Phan & Phan [53]. Also, in a study conducted by Saydut et al. [58], when comparing biodiesel fuel quality produced from

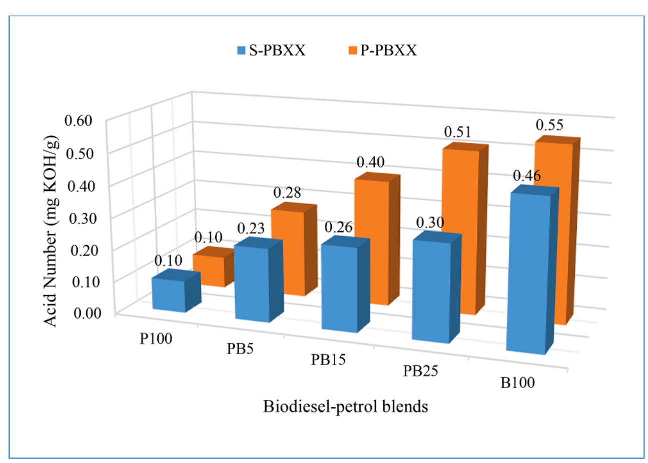

Fig. 1. Acid values in palm and sunflower biodiesel-petrol blends.

different oil sources, acid values reported were in the range of 0.50–0.52 mg KOH/g for refined sunflower oil and 0.56–0.57 mg KOH/g for waste cooking oil. Comparing those studies with the current study, an improvement in the acid value was obtained.

On other hand, according to ASTM D467-08, a maximum limit of 0.3 mg KOH/g was set for biodiesel blends of 6% biodiesel 94% petrodiesel to 20% biodiesel 80% petrodiesel (B6-B20) [59]. Therefore, all the sunflower biodiesel-petrol blends (S-PBXX) had values that met the specification set for a blended fuel, while in palm biodiesel-petrol blends (P-PBXX), only P-PB5 met the specification. The high acid value is problematic with regard to the fuel supply to the engine [60], which would result in the increased viscosity, and cloud point [61], (Fig. 1 and Fig. 9), and would subsequently lead to the corrosion of rubber parts within the engine, causing deposits. These insoluble impurities are created by heavy molecular weight as reported by Kumar [62], and Kumar et al. [63]. Also, a study by Matějovský et al [64], further concluded that an increase in corrosion rate was greatly affected by increased TAN of the fuels. Additionally, the value of the acid number indicates the degree of degradation upon storage in time [65]. Therefore, it is clear that in sunflower biodiesel-petrol blends, the acid value is lower than the palm biodiesel-petrol blends. All sunflower biodiesel-petrol blends (S-PB5, S-PB15, S-PB25) could be considered for use in compression ignition engines without modification, since their acid number values for S-PB5, S-PB15, S-PB25 were 0.23 mg KOH/g, 0.26 mg KOH/g and 0.30 mg KOH/g respectively. However, in palm biodiesel-petrol blends (P-PB5, P-PB15, P-PB25) only P-PB5 qualifies for use.

Effect on density

Fig. 2 illustrates the density of palm and sunflower biodiesel-petrol blends ranging from 762-763 kg/m^3 to 887.1–882 kg/m^3 for 5% biodiesel-petrol blend (PB5) to 100% biodiesel of sunflower and palm (S-B100, P-B100) respectively. It was observed from these results, that the obtained densities did not surpass the ASTM and EN specifications standard limits set in the range 860–900 kg/m^3 in biodiesel, petrodiesel in the range between 815–840 kg/m^3 and petrol range between 715–780 kg/m^3 [38,66]. Previous studies by Borugadda et al. [5]; Ilkilic & Öner [67]; and Phan & Phan [53] reported high densities from biodiesel synthesised from waste oils, Even biodiesel produced from neat sunflower oil possessed higher density than the waste palm oil as reported by Alptekin & Canakci, [68], obtaining 884.5 kg/m^3 and 874.6 kg/m^3 respectively. In the study of Hoekman et al., [59], it was reported that the increase in density was caused by the high degree of unsaturated alkyl esters which is indicated by the presence of double bonds. Also, Folayan et al. [69], reported a decrease in the density due to the presence of a longer chain length. This is in agreement with the previous results obtained by Simbi et al., [36], where there were fewer linoleic (polyunsaturated) acids but more palmic and oleic acids in the palm waste oil, while in sunflower waste oils more linoleic acids were observed. Also, since high density increases nitrogen oxide (NOx) emissions [70,71], causing poor vaporisation which leads to incomplete combustion [72], this was evidenced in Table 1 where the highest carbon residue was in S-B100. Blending biodiesel with petrol will produce a fuel that has a reduced density as shown in Fig. 2 since petrol has a low density of 739.2 kg/m^3. Considering the low density of petrol, it varies around also 712.7 kg/m^3, 737 kg/m^3 and 762 kg/m^3 and this is supported by literature by Agarwal, [73]; Putrasari & Lim, [44]; Thongchai & Lim, [74]; Zhong, [30].

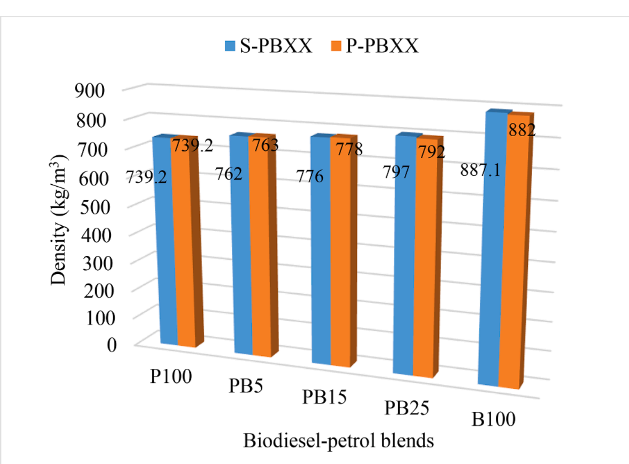

Fig. 2. The density of palm and sunflower biodiesel-petrol blends.

When petrol was blended with biodiesel, enhancement in density of blended fuel in comparison with the original density of pure petrol was achieved. This affects the amount of fuel injected, with more biodiesel per volume pumped into the engine [75], which influences the air–fuel ratio and energy content in combustion chambers [8], and consequently relates to the performance characteristics [76]. Moreover, Das et al [21], and Thongchai & Lim [74], reported that density relates to spray mass flow rate, and since biodiesel-petrol blends have low density than petrodiesel, but higher than pure petrol the characteristics of spray combustion will differ. Consequently, more energy is released by S-B100 and S-PB25 as compared to P-B100 and P-PB25, while lower biodiesel-petrol blends of PB5 and PB15 palm biodiesel-petrol blends are characterised by more energy than sunflower biodiesel-petrol blends.

Effect on distillation

Distillation or volatility of the fuel can be determined by the use of the D86 method with an advanced distillation curve, which measures the percentage of the fuel vaporized as temperature increases [77]. This property relates to combustion processes and engine emissions and therefore will influence the performance, safety and long-term usage of the fuel [15,78]. Furthermore, Knothe, [45], recognised a great correlation of volatility with other properties such as viscosity, heating value and average molecular weight. Therefore, interpreting various points obtained on the curve will provide information on the behaviour of individual fuels and conclusions drawn from it [78,79].

As shown in Fig. 3 and Fig. 4, distillation curves for sunflower (S) and palm (P) biodiesel-petrol blends (PBXX) are shown in Figs. 3 and 4, where XX indicates the percentage of biodiesel content. Typically, the initial boiling point (IBP) of biodiesel from distillation is higher than petrodiesel [80,81], and certainly much higher than petrol [82]. IBP for pure biodiesel (B100) of sunflower and palm obtained were 299 °C and 238 °C respectively, indicative of the purity of biodiesel while the blended fuels had extremely low IBP as compared to pure biodiesel.

Similarly, studies by Benjumea et al. [83] and Phan & Phan [53], reported temperatures of 300 °C and 213 °C as IBP of biodiesel produced from palm and waste cooking oils respectively. The difference found in their boiling points was attributed to their fatty methyl esters [84,85]. Graboski & Mccormick [86], suggested that a low IBP in biodiesel could have resulted from methanol and glycerol left in biodiesel after the transesterification process. Normally, according to ASTM D6751, the

Table 1
Residue of distillation.

PBXX	Carbon Residue % (m/m) (In 10% distillation residue)	Recovery rate (%)
S-B100	25	70
S-PB5	0.5	95
S-PB15	20	70
S-PB25	9.2	90.4
P-B100	4	92
P-PB5	0.5	96
P-PB15	< 0.5	96
P-PB25	0.5	80

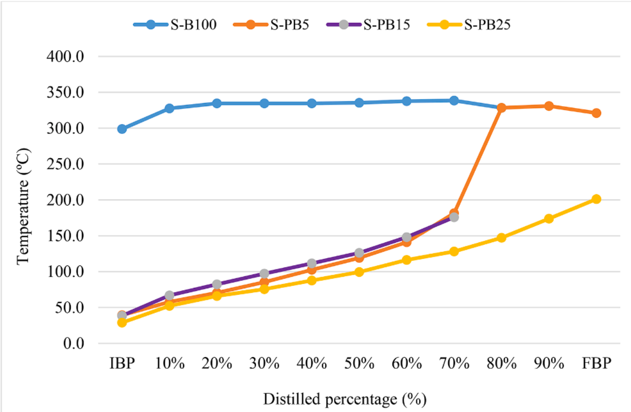

Fig. 3. Distillation curves for sunflower biodiesel and petrol blends.

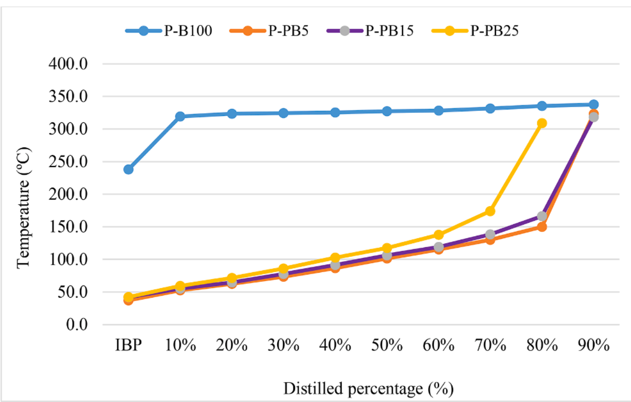

Fig. 4. Distillation curves for palm biodiesel and petrol blends.

temperature of B100 at 90 percent distilled volume per volume (90% v/v) should not exceed 360 ℃ [87]. This is necessary for the prevention of deposits in combustion chambers and spark plugs [88], therefore biodiesel produced met the standard specified since at 90% v/v of palm biodiesel (P-B100) approximately 338 °C was obtained. This is fairly close to 340 °C, the maximum limit set for petrodiesel [66]. Initial points on the curve are crucial, lower temperatures of IBP and 10% v/v would allow for the easy start of an engine while a lower temperature at 50% v/v would allow for faster warm-up [89]. Temperatures obtained at 10% and 50% v/v for S-B100 were 327.4 ℃ and 335.5 ℃ while P-B100 had 319.3 ℃ and 327.4 ℃ respectively. Also, the high density of sunflower biodiesel seen in Fig. 2, due to a higher degree of unsaturation played a role in increased temperatures of distillation. This results is also supported in a study conducted by Benjumea et al. [90], where high temperatures at 50% and 90% v/v correlate to a high density found in fuel. A further observation was noticed when a high temperature is obtained at 90% v/v, emissions of total hydrocarbon (THC) will increase [90].

Overall, distillation temperatures across boiling points had a narrow range with a boiling point difference of 7.1 ℃ – 11.1 ℃ as observed in S-B100 and P-B100 from 20% v/v to 70% v/v. The occurrence of such a narrow range was majorly influenced by closeness in the boiling points of alkyl esters [15,53,78]. However, a gradual decrease was obtained for S-B100 at 80% v/v, which thereafter was depleted. While in P-B100 a constant increase was observed from the IBP and a subsequent depletion at 80 % v/v. The depletion could be caused by the presence of high unsaturated esters i.e. methyl linoleate [77,81], which was expected in sunflower biodiesel for this current study as seen in Fig. 3. Considering IBP, 10% and 50% points, P-B100 showed a better ignition characteristic in terms of cold start and warm-up since obtained results were lower than S-B100.

On the other hand, distillation temperatures of petrol were 50% lower than petrodiesel [21,91]. In sunflower blended biodiesel (S-PBXX), the IBP obtained for 5% biodiesel 95% petrol (PB5), 15% biodiesel 85% petrol (PB15) and 25% biodiesel 75% petrol (PB25) were 39.4 ℃, 38.4 °C and 29 °C while 37.2 ℃, 41.2 ℃ and 42.3 °C were obtained for palm blended biodiesel (P-PBXX). The low IBP reported in blended fuel was due to the use of high volatile fuel petrol (P100), which normally has an IBP value ranging between 25 °C and 30 °C and a final boiling point (FBP) of approximately 210 ℃ [33,79,82,92]. Therefore, temperatures at IBP in blended fuels will have lower values that are closer to that of petrol [79,81]. In blends of S-PB5, S-PB15 and S-PB25 at 10% v/v, temperatures of 57.7 °C, 66.9 °C, and 52.3 °C were obtained in P-PB5, P-PB15 and P-PB25 corresponding temperatures of 52.5 °C, 55.1 °C, and 59.2 °C were found. Meanwhile, temperatures obtained at 50 % v/v for S-PB5, S-PB15 and S-PB25, were 119.2 °C, 126 °C, 99.4 °C and for P- PB5, P-PB15 and P-PB25, temperatures obtained were 101.5 °C, 106.4 °C and 117.6 °C respectively.

In a study by de Coro et al., [79], for petrol fuel to have a good cold-start at 20% v/v the fuel must have vaporised below 70 °C. Therefore, in the distillation curves below, at 20% v/v P-PB5, P-PB15 and P-PB25 had 62.7 °C, 64.9 °C and 71.5 °C. While S-PB5, S-PB15 and S-PB25 had values of 70.4 °C, 82.2 °C and 65.9 °C respectively. This shows that palm blended fuels have the potential for a better cold start. Overall, broader boiling point ranges were observed for blended fuels with a sharp increase in temperatures from 70% v/v onwards approaching that of biodiesel. This occurred as a result of the presence of ester quantity in the biodiesel according to Aleme & Barbeira [81]. An increase in biodiesel percentage within the blends increased the distillation temperatures from 10% v/v to FBP, with more effect observed from middle and final distillation points as clearly shown in Fig. 3 and Fig. 4. This was also reported by Paulauskiene et al. [93].

Table 1 shows the carbon residues and recovery rate percentages for S-B100, P-B100 and the blended fuels (PBXX). Carbon residues obtained for S-B100 and P-B100 were 25% and 4% respectively, while S-PB5, S-PB15 and S-PB25 had carbon residues values of 0.5, 20, and 9.2%, and P-PB5, P-PB15 and P-PB25 had carbon residue values of 0.5, < 0.5 and 0.5%. Standardisation by ASTM D6751 and EN 14,213 specify the level of carbon residue in biodiesel at 10% distillate should not exceed 0.05% and 0.30% respectively, while in blends of B5-B20, ASTM D6751 and EN 14,213 standardisation allow 0.35 maximum for ASTM D524 [56,94]. Therefore, results show that palm biodiesel-petrol blended fuels are to be used in the engine and thermal conditions are applied, there will be less tendency for the formation of carbonaceous deposits as a result of a low % of carbon residue. On other hand, sunflower biodiesel-petrol blended fuels will have carbon residue increasing and worsening as the content of biodiesel increases in the blends [53,95], as a result of degradation of glycerides/polymerisation of unsaturated fatty acids at high temperatures which will cause engine problems [96,97]. For this study, the produced S-B100 had more unsaturated fatty acids in the parental oil than P-B100 [36], However, blending S-B100 and P-B100 with petrol reduced the carbon residue significantly, with a better recovery rate shown in palm biodiesel and its biodiesel-petrol blends.

Effect on cetane number

Cetane number (CN) is a fuel property that indicates ignition characteristics [83], and fuel's aromaticity [86]. A very low CN will reduce thermal performance [98], as a result of longer ignition delay which causes knocking and subsequently incomplete combustion and increased particular exhaust emission (PM) [99]. Conversely, a higher cetane number makes combustion easier [93], thereby reducing the release of hydrocarbons, carbon monoxide (CO), nitrogen oxides (NOx), and sulfur oxides (SOx), which play a role in pollution reduction [48,100]. Measuring CN can be expensive to conduct since Cooperative Fuel Research (CFR) engine, ignition Quality Tester (IQT) or Fuel Ignition Tester (FIT) would be required [47,101]. Therefore, a simple and reliable method using distillation temperatures and density was utilised [48]. Such methods use equations 3 or 4 to obtain the Calculated Cetane Index (CCI) as shown in Table 2.

S-B100 and P-B100 had CCI of 46.35 and 46.98 according to the ASTM D976 method in equation (3) which considers the middle distillation temperatures at 50% v/v and density. Therefore, the predicted CN were 44.35 and 44.98 for S-B100 and P-B100 respectively. When the ASTM D4737 method was presented in equation (4), and the distillation temperatures at 10% v/v and 90% v/v were used, the obtained CCI and CN for P-B100 were 53.87 and 51.87. As seen in Fig. 3, there was a depletion of S-B100 at 90% v/v, therefore CCI and CN for S-B100 could not be calculated. The D4737 method showed more reliable values for S-B100 and P-B100 since more temperature points of distillation curves were considered which were relatable to the values reported [58,63,83,102]. However, Hoekman et al., [59], argued that no valid computerized method for reliable correlation between cetane index to CN was found. Nevertheless, engine fuels such as biodiesel need to auto-ignite alone otherwise they will have poor running and difficulty starting [77]. For this reason, biodiesel normally has a good cetane number which is above 40 [59,102,103], and according to American and European standards, the minimum CN should be 47 and 51 respectively [45,54,58,71].

In the current study, produced biodiesel (P-B100) met the requirements set for CN according to the ASTM D4737 method rather than the D976 method. Some errors were encountered when calculating the CN for the blended fuels using the D976 method, while in pure biodiesel this method gave the same CN values as petrodiesel fuel (40–55) [55]. For this reason, the D4737 technique was a preferred method of predicting CN through CCI and was also found to be a reliable analysis technique by Benjumea et al. [83]. In pure esters, it is expected that a high degree of unsaturated esters such as linoleic acid will reduce the CN while longer chains will increase the CN [75]. Therefore, palm biodiesel or methyl palmitate was expected to have a higher cetane number due to more carbon chain in fuel [84,104], while sunflower biodiesel with more methyl linoleate will have a lower CN [69,77,105]. This was confirmed in Table 2 where CN obtained from either D976 or D4737 methods were higher in palm biodiesel than sunflower biodiesel. Furthermore, biodiesel is composed of longer chained hydrocarbons (C14-C24) allowing the CN of biodiesel to be higher than petroleum fuels, which has shorter hydrocarbons i.e. petrol (C4-C12) [8,33].

Considering a study conducted by Zhong, et al. [12], reported the CN for petrol to be 14 while hydrogenated catalytic biodiesel CN was 103.3. Adding petrol to biodiesel, with such high volatile fuel will reduce the CN in biodiesel-petrol blends. Normally, blends of biodiesel and petrodiesel up to B20 need to meet the minimum cetane index or CN of 40 according to ASTM 7467 [106,107]. However, since petrol was blended with biodiesel as a new alternative fuel for petrol compression ignition engines, all blended fuels had values below the standard set for biodiesel and petrodiesel blends. Although these values obtained were low, they were still higher than that of pure petrol for instance, in P-PB5 and P-PB15 CN, the CN were 14.39 and 16.67 respectively. Also, the CN increased as the percentage of biodiesel added to the blends increased. Although CN calculations can be carried out using the methods mentioned above, Valente et al. [80], suggested that a further investigation on the method of calculating cetane index in biodiesel blends would be needed since ASTM D4737 was established for petrodiesel. Moreover, a recommendation was given by Chaichan [20], to use a CN ignition improver to enhance the CN in the petrodiesel-biodiesel blends, since petrodiesel has a CN of 17. Overall, P-B100 will ignite quicker and easier than S-B100 as a result of higher CN seen in Table 2, and the lower CN in S-B100 will cause higher carbon residue due to incomplete combustion and could lead to possible exhaust emissions, which are evident in Table 1.

Presence of elemental contents

Evaluation of the analytical figures of merit is shown in Table 3, indicating a good correlation coefficient value (R^2) for all elements for the set of standard solutions which are in the range of 0–24 mg/L used. The R^2 for all analytes were above 0.99 while Zn had 0.97. The high coefficient of determination (R^2) represented good linearity [108]. This confirms that analytical calibration curves correlate the measured emission signal with the concentration of analytes standards [109]. Also, a good R^2 show satisfactory standard calibration curves for analysing the digested samples [110].

Presence of group i metal

The concentrations of sodium in S-B100, P-B100 and P100 were 0.372 mg/kg, 0.430 mg/kg, and 0.392 mg/kg respectively, while potassium (K) was absent in all samples as shown in Table 4. An increase in the concentration of Na in biodiesel-petrol blends (PBXX) was noticed with 0.800 mg/kg, 1.057 mg/kg, and 0.804 mg/kg in S-PB5, S-PB15, and S-PB25 respectively. The concentration of Na in palm biodiesel-petrol blends (PBXX) in P-PB5, P-PB15, P-PB25 was also determined to be and 0.917 mg/kg, 0.784 mg/kg, and 1.224 mg/kg respectively. According to standards set by ASTM D6751 and EN 14214, a maximum set limit for Na + K and Ca + Mg is 5 mg/kg [59]. All biodiesel and the blended fuels in this study met the Na + K specification. With an increase in biodiesel content, the concentrations of Na were observed to increase in all blends, having a concave downward shape for S-PBXX and a concave upwards shape for P-PBXX. According to Table 4, Na was present in both biodiesel and petrol. Studies by de Jesus et al. [111], and Avila Orozco et al. [109], reported that Na, K, Ca, and Mg will appear in the biodiesel during the production phase. It was evident that blending increased the concentration of Na. These metals need to be kept below standards set for biodiesel and its blends since a high concentration of these metals can result in the formation of deposits within the engine which is undesirable [110].

Presence of group II metal

The Concentrations of calcium (Ca) and magnesium (Mg) in S-B100 and P-B100, were observed to be 31.357 mg/kg and 26.683 mg/kg respectively as presented in Table 5. For the blended fuels, a linear increase in the concentrations of Ca was observed as biodiesel content increased in S-PB5, S-PB15, and S-PB25 with values of 23.178 mg/kg, 27.491 mg/kg, and 34.657 mg/kg. While P-PB5, P-PB15 and P-PB25 had

Table 2
Calculated cetane index and predicted cetane number for biodiesel blends.

	ASTM D976-91		ASTM D4737-09	
BXX	CCI	CN-Predicted	CCI	CN-Predicted
S-B100	46.35	44.35	–	–
S-PB5	9.41	7.41	23.22	21.22
S-PB15	9.19	7.19	–	–
S-PB25	−26.22	−28.22	12.87	10.87
P-B100	46.98	44.98	53.87	51.87
P-PB5	−9.12	−11.12	16.39	14.39
P-PB15	−10.47	−12.47	18.67	16.67
P-PB25	−5.20	−7.20	–	–

Table 3
Analytical figures of merit for determination of elements by ICP-OES.

Analytes	Line range (mg/L)	Std.Error (mg/L)	Correlation Coefficient
Al	0–24	0.169	0.99961
Ca		0.375	0.99809
Cu		0.0797	0.99991
Fe		0.374	0.99821
K		0.184	0.99954
Mg		0.139	0.99974
Na		0.184	0.99954
Zn	0.00288–24	1.43	0.97194

Table 4
K and Na concentrations in biodiesel and biodiesel-petrol blends.

Elements	Sunflower biodiesel-petrol blends S-B100	S-PB5	S-PB15	S-PB25	Palm biodiesel-petrol blends P-B100	P-PB5	P-PB15	P-PB25	Petrol P100
K (mg/kg)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na (mg/kg)	0.372	0.800	1.057	0.803	0.430	0.917	0.784	1.224	0.392
K + Na (mg/kg)	0.372	0.800	1.057	0.803	0.430	0.917	0.784	1.224	0.392

Table 5
Ca and Mg concentrations in biodiesel and biodiesel-petrol blends.

Elements	Sunflower biodiesel-petrol blends S-B100	S-PB5	S-PB15	S-PB25	Palm biodiesel-petrol blends P-B100	P-PB5	P-PB15	P-PB25	Petrol P100
Ca (mg/kg)	31.216	23.178	27.491	34.657	26.683	33.309	35.571	34.314	0.000
Mg (mg/kg)	0.141	0.019	0.063	0.132	0.302	0.043	0.199	0.247	0.000
Ca + Mg (mg/kg)	31.357	23.197	27.554	34.789	26.985	33.352	35.770	34.561	0.000

a linear increase in the Ca concentration with increased biodiesel content of 33.309 mg/kg, 35.571 mg/kg, and 34.314 mg/kg. This linear increase was also obtained for Mg across all biodiesel-petrol blends. The presence of these metals did not occur in petrol, it was therefore evident that blending petrol with biodiesel led to a significant reduction in both Ca and Mg concentrations for S-PB5 and S-PB15 while in P-PBXX the inverse was evident. The limits set for Ca and K concentration in biodiesel was 5 mg/kg, and as observed in Table 5, all PBXX were above the specified limit set by EN 14,213 and ASTM D6751 [56,112]. This could have been attributed to the (CaO/Al_2O_3) catalyst used in the synthesis of biodiesel or some left during the purification stage and hence, having an increase in Ca and Mg concentrations in the biodiesel and the blended fuels [113]. Also, Ca and Mg could have been absorbed during the cleaning process [114]. A high concentration of Ca causes pollution in the air once combusted [115], which then may form undesirable compounds leading to engine malfunctioning and reducing fuel stability [109].

Presence of Phosphorus

Phosphorus (P) concentrations in S-B100, P-B100 and petrol (P100), were 9.29 mg/kg, 10.10 mg/kg and 9.75 mg/kg respectively as shown in Fig. 5. The EN 14,107 and ASTM D4951 set the P limit in biodiesel to be 10 mg/kg [45,107], S-B100 passed the test while P-B100 was slightly above the specified limit. In biodiesel-petrol blends, the lower value was only noticed in SB25, while in other blends there was an increase in P concentration as the biodiesel content was increased. Since there was P present in P100 and B100, blending these two fuels resulted in an increased concentration of P in the blended fuels. The P level amongst blended fuels of PB5 and PB15 did not change much except in PB25, this can be supported by a conclusion drawn by research of Southwest Research Institute which reported that no significant change was found in P for biodiesel blends [96]. Nevertheless, it was reported by Iqbal et al., [110], that the presence of P was due to its initial feedstock, which showed that waste palm oil had more P concentration than waste sunflower oil [36]. The high presence of P has a negative impact on the engine, and it can cause the formation of deposits within the engine which can damage the ability of after-treatment systems [116]. Further, studies by Iqbal et al., [110] and Korn et al., [49], reported that the presence of high P can be poisonous to catalytic converters of petrodiesel engines, which will emit a high level of CO, CO_2 and SO_2.

Presence of sulphur

Sulphur (S) concentrations found in S-B100 and P-B100 were 4 mg/kg and 6 mg/kg, while in S-PB5, S-PB15, and S-PB25, concentrations of 14.50 mg/kg, 18.70 mg/kg and 20.90 mg/kg were obtained respectively as shown in Fig. 6. In P-PB5, P-PB15, and P-PB25, had S concentrations of 18.60 mg/kg, 34.30 mg/kg, and 17.90 mg/kg. Also, a decrease in the S concentration was observed in P-PBXX as the biodiesel content was increased in P-PB5 to P-B100 except in P-PB15. On other hand, in S-PBXX, S concentration increased linearly from in S-PB5, S-PB15, and S-PB25, with a subsequent decrease in S-B100. Typically, in biodiesel-petrodiesel blends, S content decrease with an increase in biodiesel content [78]. This was achieved in P-PBXX with a slight deviation in P-PB15. In biodiesel, a maximum limit set for sulphur was 10 mg/kg according to EN ISO 20,884 and ASTM D5453 [45,117], while for biodiesel-petrodiesel blends, up to 20% of biodiesel (B20) a maximum of 15 mg/kg of S was allowed c.

Both biodiesels met the standard specifications with low S content obtained, and in PBXX, only S-PB5 met the specification set for blended biodiesel while other blends failed this test because of higher concentration of S in petrol as compared to biodiesel. Even though, S found in

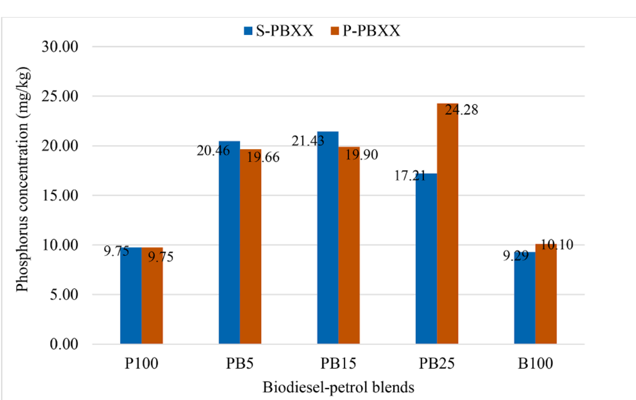

Fig. 5. Phosphorus concentration in biodiesel and petrol blends.

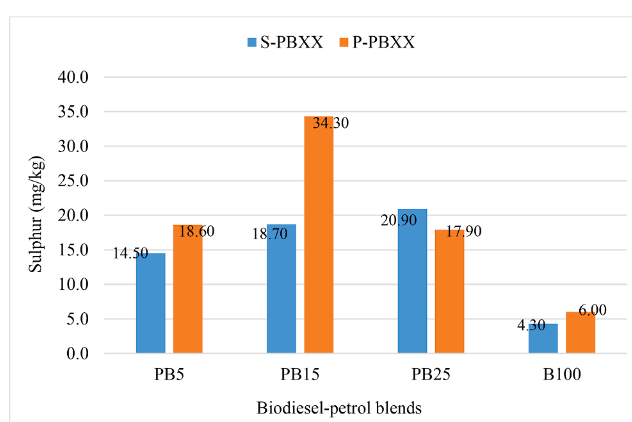

Fig. 6. Sulfur concentration in biodiesel and petrol blends.

petrol was below 10 mg/kg which was supported by a similar finding by Han et al. [118], and in the study by Zhong [119], they reported increased S content in blended fuels. However, these blended fuels showed characteristics of fuels needed for ultra-low emission vehicles (ULEV) and low emission vehicles (LEV) which are under category 3 of petrol and petrodiesel. The specification for this category is a maximum S concentration of 50 mg/kg and 30 mg/kg for petrol and petrodiesel respectively [66]. High S content can negatively affect emission-control system performance and the environment [120]. Therefore, the low S content in the biodiesel helps in reducing engine wear and exhaust emissions [80].

Presence of minor elements (Al, Cu, Fe and Zn)

Copper (Cu) was absent in all B100 and PBXX, with 0.212 mg/kg of Cu measured in PB25 as observed in Fig. 7. Also, it was noticed that the concentration of Fe in the PBXX was the highest among other elements followed by Zn then finally Al as depicted in Fig. 7. Although, all these minor concentrations were below the standard limit allowed in biodiesel, blending increased the elemental content. Metals in fuel can lead to mechanical problems within the engine due to deposits caused by corrosion [121], and they can result in environmental pollution [122]. Moreover, it was reported that the oxidation stability of alkyl esters was reduced by the increase in Cu, Fe, Ni, and Sn, with Fe being a very effective hydroperoxides decomposer [123]. This can be explained by the catalytic effects of these metals in the auto-oxidation of oils as a result of rancidity [124]. As observed in Fig. 7 the Fe concentration was higher in P-PBXX as compared to S-PBXX which explains a greater reduction in induction period seen in Fig. 8 and a subsequently higher rate of reduction in oxidation stability for P-PBXX.

Effect of oxidation stability

The oxidation stability (OS) of B100 and PBXX as indicated by the induction period (IP) in an hour (h) is presented in Fig. 8. The IP values for S-PB5, S-PB15, S-PB25 and S-B100 were observed to be 7.19 h, 6.5 h, 3.98 h and 4.2 h respectively. While in P-PB5, P-PB15, P-PB25 and P-B100, the IP values of 24.09 h, 21.45 h, 17.22 h and 17.43 h were obtained. An increase in biodiesel content within blended biodiesels resulted in decreased IP which indicated a drop in OS and by increasing petrol content, OS was enhanced. Low OS in biodiesel is caused by the presence of unsaturated fatty acids found in biodiesel as compared to petrodiesel. These acids facilitate the increased chance of the fuel reacting with air, temperature, and metal ions. Furthermore, the storage time and exposure to ultraviolet or visible light in biodiesel can increase the oxidation [31,125,126]. Also, natural antioxidants found in vegetable oils play a role in varying OS of different oils [94]

Karavalakis et al. [127], reported a decrease in OS with an increase

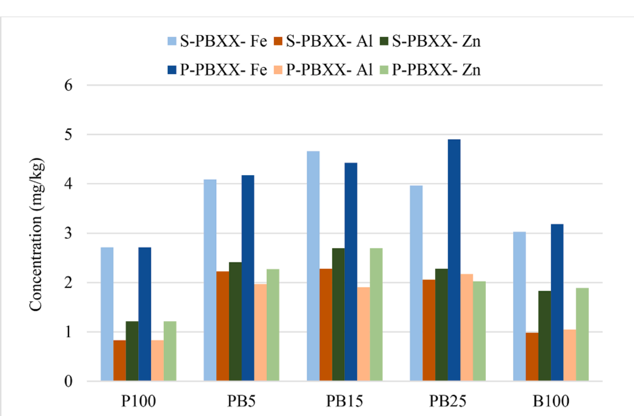

Fig. 7. Minor elements in biodiesel and petrol blends.

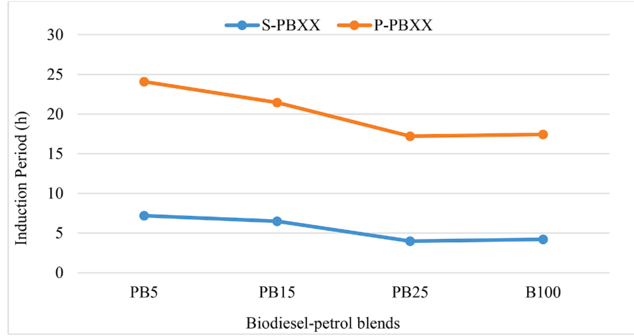

Fig. 8. Change in oxidation stability in biodiesel and petrol blends.

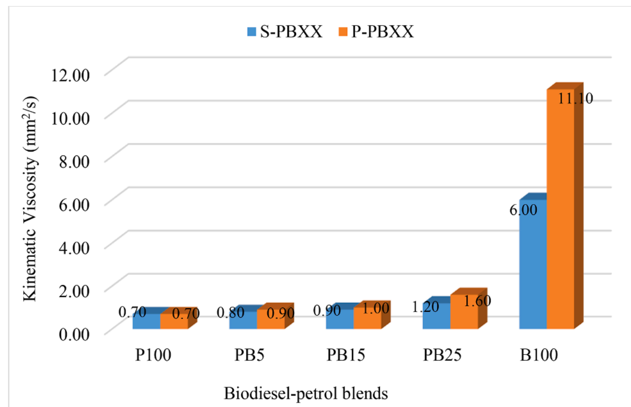

Fig. 9. Viscosity at 40 °C of biodiesel and petrol blends.

in biodiesel blends. because of the increased presence of linolenic and linoleic acids. In the current study, both biodiesels met the 3 h minimum requirement set by the ASTM D5761, with P-B100 exceptionally surpassing the 6 h minimum set by EN 14,112 [98,120,127]. In the study conducted by de Goede et al. [117], they reported that the number of double bonds and the position influence the rate of oxidation, with OS decreasing in order of oleic > linoleic > linolenic. This was the reason palm biodiesel was highly saturated with more OS than sunflower biodiesel which has more double bonds. This was also confirmed by Simbi et al. [36], with an expected superior OS of methyl esters in palm biodiesel [75]. Similarly, the reports by Benjumea et al. [90] and Baena & Calderón [128], noticed higher oxidation stability of 12.83 h in palm biodiesel in their various studies. Also, Sarin et al. [129], reported oxidation stability of 18 h in palm biodiesel when Rancimat equipment was used with heating to a temperature of 100 °C and with a further increase in the temperature to 110 °C, a decrease in OS was obtained at 13.37 h with palm biodiesel from 18 h. According to ASTM D525, a minimum OS of 8 h must be met for petrol [66]. Therefore, by adding biodiesel to petrol, an increment in OS of biodiesel-petrol blends was observed. Since oxidation is inversely proportional to an increase in the percentage of biodiesel [52], due to the presence of high unsaturated fatty acids [130]. A minimum of 20 h OS was required according to IS 15,607 D590 for biodiesel blends [131,132], while in EN14112 specification 6 h minimum is required in biodiesel blended fuels [59,72]. Therefore, biodiesel-petrol blends of S-PB5 and S-PB15 met the EN 14,112 standardisation, while all P-PBXX met the EN 14112, with P-PB5 and P-PB15 passing the IS 15,607 standard for blended fuels.

Effect on viscosity

The viscosity of P-B100 was found to be 11.1 mm^2/s and S-B100 was 6 mm^2/s as shown in Fig. 9. The viscosity obtained for P-B100 was higher than 7.7 mm^2/s from the results of the study by Yogeeswara et al. [71], in biodiesel produced from waste frying palm oil, and with the 6.01 mm^2/s reported by Bukkarapu et al. [133], for biodiesel produced from neat palm oil. Nevertheless, there was an improvement in the viscosity of S-B100 in this study, when compared with the results reported by Hossain & Boyce [57], when biodiesel was produced from pure and waste sunflower oil having 5.8 mm^2/s and 9.5 mm^2/s respectively. Additionally, a study by Santos et al. [101], reported a high viscosity of 6.3 mm^2/s in sunflower methyl ester. Even though S-B100 did not meet the specification set for EN 14,214 as it is greater than the range of 3.5–5 mm^2/s, the obtained viscosity was in the range of 1.9–6 mm^2/s limit set in ASTM D7651 [134]. Also, Knothe [45], suggested that the maximum limit of 5 mm^2/s should exclude biodiesels produced from frying oils since they have a high amount of trans fatty acids, and which are less unsaturated. Hence, waste palm oil has more saturated fatty acids than waste sunflower oil [36], which justifies their high viscosity as seen in Fig. 9 and lower density in Fig. 1. There is a huge relationship between viscosity and density, as the viscosity increases with the increased volume fraction of biodiesel [100,135]. The relationship between density and viscosity was supported by Parikh [136], as palm biodiesel had a density of 0.876 g/cm^3 corresponding with 4.8 mm^2/s viscosity, and with a subsequent increase to 0.882 g/cm^3, the viscosity changed to 7.01 mm^2/s [137]. Also, problems such as cold start at lower temperature conditions can appear since it increases with a decrease in temperature [41,59].

In Fig. 9, it was observed that petrol had an extremely low viscosity of 0.7 mm^2/s as compared to biodiesel (Fig. 9). Similarly, Chaichan [20], reported the viscosity of petrol to be as low as 0.44 mm^2/s and Bao et al. [138], reported 0.735 mm^2/s as the viscosity of petrol. Therefore, with the blending of petrol and biodiesel, it is expected that the viscosity of the blends will be less than that of pure biodiesel. This is preferred in compression ignition engines since it renders easier fuel movements allowing faster atomisation and lower ignition delay [27,68,75]. According to D455 of ASTM D7467, the viscosity of biodiesel-petrol blends up to 20% biodiesel content should range between 1.9 and 4.1 mm^2/s [106], while no limit has been set for biodiesel-petrol blends of low viscosity, which is necessary for better atomization [139]. Viscosity values of PB5, PB15, and PB25 are in order of magnitude with increased viscosity than the original pure petrol. PB25 represents a better blend with 1.2 mm^2/s and 1.6 mm^2/s for S-PB25 and P-PB25 respectively which is close to the limit set in ASTM D7467 [106,132].

Effect of moisture content

Moisture content in S-B100 and P-B100 were 0.050 and 0.055 vol% respectively as shown in Fig. 10. Also, the determined moisture content for S-PBXX of S-PB5, S-PB15, and S-PB25 were 0.020, 0.030 and 0.040 vol% while in P-PBXX of P-PB5, P-PB15, and P-PB25, the moisture content observed were 0.031, 0.035 and 0.050 vol% respectively. According to EN 14,214 and ASTM D6751 standards, the maximum moisture limit for pure biodiesel is 500 mg/kg or 0.05 vol% [41,68,140], and in biodiesel blends, the limit is set at 0.05 vol% according to ASTM D7467 or EN ISO 12,937 standards [106]. Gumahin et al., [141], reported that the chances of biodiesel absorbing moisture are 6.5 times higher than petrodiesel even if there is constant relative humidity, this is due to the presence of ester bonds within biodiesel. Therefore, when comparing the moisture content of petrol and that of biodiesel in this study, it is clear that biodiesel moisture content was approximately 5.5 times higher than that of petrol. Another way to evaluate the presence of moisture content in biodiesel is the indication of its high acidity [142]. Observation of the high acidity in P-B100 and P-PBXX as shown in Fig. 1 corresponds with the higher moisture contents of P-PBXX as compared to S-PBXX in Fig. 10, which shows a correlation between moisture content and acidity and subsequential corrosion within the engine. In reducing the moisture content of biodiesel, blending it with petrol will reduce the hydrophilicity of biodiesel since petrol had a moisture content of 0.01 vol% [94]. Even though, P-B100 had a moisture content that was above the limit set for biodiesel, the addition of petrol led to a lowered moisture content, therefore improvement with the blended fuels was observed (P-PBXX and S-PBXX), meeting specifications set for blends. As reported by Baena & Calderón [128], blending created mixtures with lower absorption capacity. It is essential to evaluate moisture content within fuels to avoid microbial growth during storage as this enhances degradation [45], causing low heating value [140] and would result in re-processing of the fuel [143].

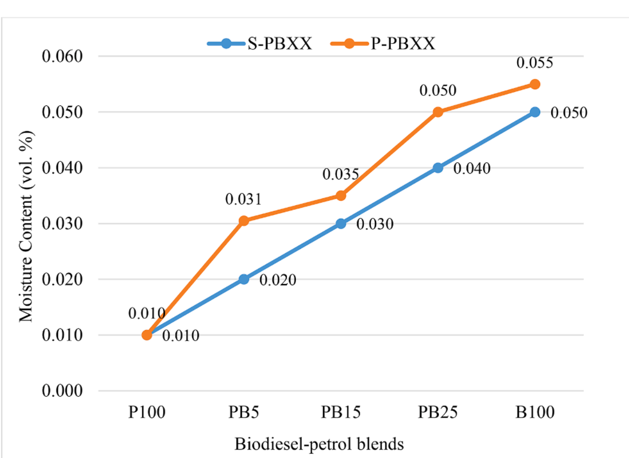

Fig. 10. Moisture content in biodiesel and petrol blends.

Conclusions

In conclusion, blending sunflower and palm biodiesel with petrol resulted in blended fuels that have improved characteristics compared to pure biodiesel or petrol. They met standard specifications set for biodiesel and petrodiesel blends. By adding petrol, the acid number, density, volatility, cetane number, viscosity, moisture content, carbon residue and harmful metals were lowered while oxidation stability was enhanced. S-PBXX showed a lower acid number and more energy due to higher density and were more viscous than P-PBXX. While these properties seemed to correlate with each other i.e., acidity and moisture content, density and viscosity, density and carbon residue, an increase in values was observed for these properties as the percentage of biodiesel content is elevated within the blends, owing to the structural properties of esters present. A high degree of unsaturation found in S-B100 resulted in more chances for the formation of total hydrocarbons, depletion at 80% v/v, with more carbon residues, and subsequently longer ignition delay for S-PBXX. On other hand, P-B100 portrayed a quicker and easier cold start and warm up after ASTM D4737-09 was found to be a reliable method for obtaining cetane numbers. Therefore, P-PBXX showed better performance with characteristics of a good cold start, with exceptional oxidation stability as compared to S-PBXX due to the longer chain length of esters in P-B100. However, higher impurities of Ca, Mg, P, and S were reported in P-PBXX as compared to S-PBXX. This will result in possible engine damage, and high emissions, while a high concentration of Fe leads to an increased rate of oxidation. The addition of petrol to biodiesel was noticed to increase the concentration of S, P, and some minor elements. Blending biodiesel with petrol, Ca + Mg metals decreased for S-PB5 and S-PB15 while moisture content was reduced significantly for both blends.

CRediT authorship contribution statement

Ines Simbi: Resources, Methodology, Formal analysis, Writing – original draft, Conceptualization, Writing – review & editing. **Uyiosa Osagie Aigbe:** Conceptualization, Writing – review & editing, Project administration, Supervision. **Oluwaseun Oyekanmi Oyekola:**

Conceptualization, Writing – review & editing, Project administration, Supervision, Funding acquisition. **Otolorin Adelaja Osibote:** Conceptualization, Writing – review & editing, Project administration, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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