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Experimental investigation on the influence of H_2 on diesel engine fueled with Afzelia Africana biofuel – Titanium oxide nanoparticle blends

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ABSTRACT

Diesel engines are a major source of air pollution, which is increasingly endangering both the natural and built environments. The use of H_2-enrichment with nano-fuel was adopted in this research. The TiO_2-nanoparticles-Afzelia-Africana biodiesel was blended with H_2 for use in diesel engine. 25 ppm of TiO_2 nanoparticles was admixed with the biofuel and ultrasonicated. After that, H_2 was introduced through the intake air at different flowrates. The ratio of H_2 to the blended fuels (BNH) is (15:85 vol/vol%). The effects of the blends with H_2 on emission/performance characteristics were investigated by evaluating NO_x, CO, and HC emissions and brake thermal efficiency-(BTE). Higher BTE blends with hydrogen flowrate of 3 LPM improved the engine performance with lesser emissions. Sample blend with hydrogen flowrates of 3LPM gave the best performance/BTE of 39.4 %. The nano-fuel BN@25 + H_2 (3 LPM) recorded the lowest emissions (81, 0.33 and 5 g/kWh) at full load when compared with the diesel (129, 0.63 and 20 g/kWh) in terms of NO_x, CO, and HC. The in-cylinder pressure and heat release rates of the biodiesel significantly improved H_2 addition to TiO_2 -NPs by 10 and 14 % relative to diesel. Therefore, the H_2-enrichment with the nano-fuel displayed a positive effect on the engine without further modifications.

Introduction

Presently, diesel alone meets approximately 73 percent of transportation fuel demand, with petrol accounting for 22 percent, with alternative fuels such as CNG and LPG accounting for the remainder [1–3]. The rapid depletion of fossil fuels, rising fuel prices, and severe pollution regulations around the world have prompted experts to look for alternate energy sources [4]. In the past few decades, biodiesel has been sought as a possible replacement for conventional diesel fuel in internal combustion engines (ICE). Biodiesel is sulfur-free, renewable, biodegradable, and non-toxic [5]. In most cases, biodiesel emits fewer emissions and is deemed an alternative fuel sourced from renewable sources such as animal fats and plants. Biodiesel has benefits over fossil fuels, in that, it has the ability to replace diesel fuel in a sustainable manner without the need for engine modifications [6].

Igwenyi et al. [7] produced Afzelia Africana biodiesel via transesterification and found out that the crude biodiesel contains about 19 % lipid content with high amount of fatty acids. Further investigation showed that the biodiesel had a cetane number of 53 which showed that burning the biodiesel in a diesel engine will yield an average value of about 9209.45 cal./g. Montcho et al. [8] further demonstrated that the density and kinematic viscosity of the neat Afzelia Africana biodiesel blends met the ASTM D6751 and EN 14214 standards for use in diesel engines as a substitute for fossil fuels, however, till date, works on the use of neat Afzelia Africana biodiesel for use in diesel engine have not been reported.

Furthermore, there are many concerns about the impact of long-term biodiesel use on engine performance and longevity. Engine power, fuel efficiency [1], stability [9], cold weather performance, and clogging [10] among other issues, are known to limit biodiesel's use as a suitable replacement for conventional fuel. However, neat biodiesel tends to enhance NO_x emissions, making it just as dangerous as other hazardous pollutants including acid rain, severe air pollutants, and terminal

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Nomenclature

BTE	Brake thermal efficiency
LPM	Liter per minute
EGR	Exhaust gas recirculation
HRR	Heat release rate
BNH	Biodiesel-nano-additive-hydrogen
CO	Carbon monoxide
HC	Hydrocarbon
NOx	Oxides of Nitrogen
TiO_2	Titanium oxide
ASTM	American society of testing and materials
DI	Direct injection
SDS	sodium dodecyl sulfate
ICE	Internal combustion engine
CNG	Compressed natural gas

disease causative [12]. As a result, NO_x reduction is critical when using biodiesel in diesel engines. Supplementary section 1 (S1) presents some drawbacks on the use of biodiesel fuel.

Previous findings have shown that an intensive study is required to address the undesirable issues associated with biodiesel [10,12]. Researchers suggested that improving the combustion properties and fuel efficiency of neat biodiesel in ICE may be accomplished by changing the design of the engine or using fuel additives [13,14].

The reformulation of fuel is one cheaper and easier technique, which is most preferred, compared to modifying the engines [15]. Applying the principles of fuel reformulation reduces the emissions and thus improves the combustion as well as performance of the DI engines with efficient fuel economy [16]. Nevertheless, modification of the engine will require higher maintenance and manufacturing costs which may lead to the replacement of old engine vehicles. Due to such problems/difficulties, it is less preferable to consider engine modification as a reliable option [8,14]. To remedy these challenges associated with neat biodiesel, it is important to introduce a suitable nano-additive into the neat biodiesel so as to improve the fuel's performance/combustion and thus minimize emissions. These nano-additives act as catalysts and by acting as catalysts, metal-based nanoparticles improve the performance, and combustion of an engine with less production of noxious substances [6]. The nanoparticles' surface-area to volume ratio is a major cause of low emissions in diesel engines. Combustion is improved by increasing the surface area to volume ratio, which in turn improves the contact between the fuel and the oxidizer [2]. The ignition delay and evaporation rate may also be reduced [3]. In addition, nanoparticles can be used as a secondary carriers to enhance combustion and engine performance [4].

MgO, ZnO, CNT, Al_2O_3, Fe_2O_3, CuO, CeO_2, and MgO have recently been investigated as suitable nanoparticles for improving combustion while lowering the resulting emissions. Leo et al. [6] demonstrated that the introduction of nanoparticles to biodiesel improves the engine performance, raises the energy density of the liquid fuel, thus resulting in better combustion [6]. Also, the stability and preparation technique of the materials have an impact on the nanoparticles' effectiveness. To achieve high nanoparticle stability with uniform dispersion in biodiesel, two approaches are usually involved (stirring and the use of tiny nanoparticles). Fine nanoparticles may be disseminated quickly and effectively by using a method that is far less complicated than stirring. Ultrasonic, manual, and magnetic stirring are the most common methods [2]. According to Nithya et al. [15], long stirring time/duration leads to increased nanoparticle stability. Although, stability improves over time, it deteriorates beyond an optimum time [16]. Chemical procedures have also been used to stabilize the fuel, despite the existence of physical techniques [10]. The effects of TiO_2 nanoparticles admixed with diesel fuel have been studied in several works. Fangsuwannarak and Triratanasirichai [17] and Verma et al., [18] investigated the impact of performance and emission parameters on CI engines using TiO_2 nanoparticles in palm biodiesel at maximum load conditions. In comparison to other fuel blends, the results demonstrated an increase in BTE for the TiO_2 nanoparticles blended biodiesel fuel. With TiO_2 nanoparticles blended in mustard oil biodiesel, Yuvarajan et al. [19] examined the effects of its emission characteristics on a CI engine. The results showed that using TiO_2 nanoparticles in biodiesel reduced HC and CO emissions while increasing NOx emissions at full load compared to regular diesel. Khond and Kriplani [20] studied the emission and performance characteristics of a single cylinder diesel engine under various load circumstances using TiO_2 nanoparticle as an additive for diesel-biodiesel blends. Two TiO_2 nanoparticle combination of 250 and 500 ppm were mixed with a 20 percent biodiesel-diesel blend (B20). When comparing B20 blends to other tested fuels at 100 percent load, the results showed an increased BTE with lower smoke, CO and HC emissions, but a slight increase in NOx emissions for 250 ppm nanoparticle concentration. Venu et al. [21] used TiO_2 nanoparticles (25 and 50 mg/L) as additions to a diesel-biodiesel-alcohol (J50D10-Bu) blend to increase diesel engine performance. They concluded that the HRR and peak pressure increased, whereas, CO and HC emissions reduced with an increase in NOx emissions. Although nanoparticles are known to improve combustion and thus lower emissions, due to the low viscosity of biodiesel blends, the reduction in NOx is not usually very compelling. The addition of hydrogen to a diesel engine improves the A/F mixing time. As a result, enhanced combustion is achievable with less soot generated [9,17].

Dimitriou and Tsujimura [22] conducted a thorough examination on the use of H_2 in DI engine. H_2 injection into DI engines reduces CO_2, HC, and CO emissions considerably. Because hydrogen is a carbon-free gas, it can be used as fuel in a diesel engine without constraint. When the H_2 ratio in the diesel engine increases, it also increases the HRR and cylinder pressure, which in turn increases the NO_x emission. However, moderate H_2 flow rate tends to decrease the NOx emission. A diesel engine operating on H_2-diesel in dual fuel mode was studied by Manigandan et al. [23]. The H_2 flow from the engine to the inlet manifold was at a lower pressure of 130 bar to 2 bar with flow rates of 4, 6, and 8 LPM. At 6 LMP, the flow rate of hydrogen imposed a higher BTE with the least amount of CO and HC emissions. Furthermore, at the same H_2 – flow rate, there was an increase in the NOx emissions, in-cylinder pressure and HRR.

Due to the depletion of fossil fuel and high NO_x emissions associated with it, which may pose environmental threats, there is need to look for an alternative fuel that possesses better fuel quality than fossil fuel, has the potential for improved performance with better combustion and lesser emissions from the diesel engine, hence the admixing of H_2 with Afzelia Africana biodiesel- TiO_2 blends in diesel engine became necessary as presented in this work.

Reports have shown that most hydrogen enriched nanofuels give high NO_x emissions [24 –25]. Other studies have shown that hydrogen admixed biodiesel as fuel in diesel engines, may produce high NOx emission with minimal improvement in combustion rate, which may likely occur due to the physicochemical properties of the biodiesel, which may in turn affect the fuel's property, thus leading to longer ignition delays [26,28]. Furthermore, refs. [29 –31] suggest that the hydrogen flow rate should be controlled, as high flow rates may lead to high NO_x emissions; they added that the size of nanoparticles should be less than 10 nm to avoid blockage of the tubes in the diesel engine.

Thus, using TiO_2 nanoparticles admixed with H_2 at a moderate flow rate to reduce NO_x emission with Afzelia Africana biodiesel is considered to remedy the challenges confronting the quality of the neat fuel in diesel engines. At greater loads, increasing the hydrogen mixture causes an advanced combustion phase, which results in an increased thermal efficiency with residual HC emission [8,11]. On the other hand, since NO_x emissions increase as the H_2 proportion grows, TiO_2 nanoparticles must be used as a result of their surface area, which improves the fuels physicochemical and combustion properties, alongside BTE with lesser emissions. Due to the fact that H_2 and nanoparticles reduce emissions at the engine's best performance, ascertaining the best circumstances for efficient fuel economy is necessary for a wide range of operations. Despite the vast volume of works on the use of H_2 enriched TiO_2 nanoparticle admixed biodiesel fuel in diesel engines, there is no existing literature that bothers on the use of H_2 -enriched TiO_2-Afzelia Africana biodiesel as fuel blends for Mitsubishi Centre (Test Engine) diesel engines; this aspect of research has not been given full attention by other published literature, which then led to the motivation for this study. As a result, the goal of this research is to examine the combustion, performance, and emission characteristics of an unmodified diesel engine fueled with hydrogen-enriched Afzelia Africana biodiesel-TiO_2 blends. The neat fuel's properties and those of its blends were determined as well.

Materials and method

The qualities of the fuels were determined in a research laboratory. Thus, the fuels flash points were measured using a PC-102 Cleveland Open Cup Flash Point Tester. The densities of the test-fuels were measured using a Kyoto Electronics DA-130 with a resolution of 0.001 g/cm^3. The Cetane number was determined using Zeltex ZX440. The Saybolt Universal Viscosimeter was used to determine the viscosity of the test-fuels.

Production of Afzelia Africana biodiesel

The Afzelia Africana seed was obtained from Auchi, south – south Nigeria. Thereafter, Afzelia Africana oil was extracted from the Afzelia Africana seed plant by means of a mechanical press. The Afzelia Africana seed oil was then heated at 55 °C while CH_3OH and NaOH were combined in a separate conical flask until the NaOH was dissolved in the CH_3OH so as to allow for transesterification to take place. The uniform mixture was then poured into the hot oil-containing flask. For 1.5 h, the mixture was stirred and thereafter, poured into the separating funnel after the transesterification step; this is so as to separate the biodiesel from glycerin. After separation, the biodiesel was obtained.

Synthesis of the TiO_2 nanoparticle

TiO_2 nanoparticles were synthesized via the sol-gel method using titanium *iso*-propoxide of 97 % purity as precursor which is in accordance with the method adopted in ref. [10].

Preparation of TiO_2 nanoparticle-biofuel blends

The preparation of the nanofluids lasted for 24 h, after which, they were treated with deionized water. The sonicated nanoparticles were mixed with biofuel for 2 h using a Sonics VCX 750 type sonicator. Ultrasonication assisted in the homogenous dispersion of the nanoparticles in the deionized water and oil which in turn generated the desired emulsions. Longer sonication periods can improve nanofluid stability [23]. The stability of TiO_2 nanoparticle is vital since it prevents nozzle blockage in diesel engines. As a result, a longer sonication duration prevents and decreases particle agglomeration. According to Chandrasekaran et al. [24], ultrasonication can inhibit particle agglomeration, resulting in stable nanoparticle distribution in the base fluids. The addition of sodium dodecyl sulfate (SDS) to the nanofuel in different proportions increases the surface modifications and stability of the nanofuels, thus reducing the potential for probable coagulation, surface tension and coalescence. The deionized water was used to calibrate the sonicator. The experiment was performed in triplicates and their average values were reported. The sonication speed, time and frequency adopted are 150 rpm, 60 min and 50 Hz respectively. A Jenway 6305 UV/Vis Spec with a 220 V AC input and frequency range of 50–60 Hz was used to determine the absorbance. The scanning electron microscope was used to determine the surface morphologies of the TiO_2 nanoparticles (Thermofisher scientific Prisma E-SEM 7350). The 300 mg TiO_2 nanoparticles were mixed with 1000 mL biodiesel fuel and sonicated. The impact of TiO_2 nanoparticle admixed with biodiesel on the diesel engine was examined (Table 3).

Properties of hydrogen

The H_2 gas of 99.8 % purity was bought from BOC company Limited, Lagos, Nigeria. The characteristics of hydrogen used are presented in Supplementary section 2 (S2).

Hydrogen flow rate relative to that of the sonicated biodiesel- TiO_2 nanoparticle blend

Mass flow rates (3 and 4) LPM (liter per minute) of H_2 were employed in enriching the air inlet. Equal volume of hydrogen in the inducted air was kept constant at 15 vol/vol for all the hydrogen induced fuel mixtures. Due to H_2 enrichment of the intake air, the volume of consumed methyl ester (biodiesel) was constant at different flow rates. The proportions of Afzelia Africana methyl esters -TiO_2 nanoparticle admixed with H_2-air mix at the intake manifold are given in S3.

Experimental procedure

Fig. 1 is an illustration of the experimental flow-process. The H_2 flow line consists of a pressure regulator, cylinder, flame trapper and flow meter. The H_2 supplied was under high pressure in a cylinder and released at an exit pressure of 2 bar with the aid of a regulator. S4 presents the property of the test engine. The air-hydrogen flow rates of 3 and 4 LPM were delivered at high pressures to provide 15 % vol/vol each to 85 % Afzelia Africana methyl esters -TiO_2 nanoparticle mix. The nanofuels produced with H_2 were homogenized and agitated at 1500 rpm before being introduced in the test-engine. Fig. 2 represents the pictorial form of the test engine.

Uncertainty measurements

Errors may occur during the process of obtaining measurements as a result of incorrect calibration of any measuring devices. Uncertainties are majorly determined by the measure of repeatability obtained in three measurements with a low level of insignificant magnitude of standard deviation. The uncertainty Eqs. (1) to (3) were adopted in calculating the percentage uncertainties of all the measured parameters (S5).

$$\Delta R = [(\frac{\partial P}{\partial v_1}\Delta v_1)^2 + (\frac{\partial P}{\partial v_2}\Delta v_2)^2 + \ldots + (\frac{\partial P}{\partial v_n}\Delta v_n)^2]^{\frac{1}{2}} \quad (1)$$

Where ΔR represent the total uncertainty.

P – is a function of the independent variables of v_1, v_2 …………v_n, $\Delta v_1, \Delta v_2 \cdots\cdots\cdots \Delta v_n aretheindependentvariableuncertainties.$

Thus, the percentage overall uncertainty is ±0.59%

Results and discussion

Properties of crude Afzelia Africana oil and Afzelia Africana biodiesel

S6 contains the physicochemical properties of the crude Afzelia Africana oil and biodiesel. The density and kinematic viscosity of the biodiesel are lower than that of the crude Afzelia oil as a result of the nature of its methyl esters. Other properties of the oil that were determined include cetane number, calorific value and flash point.

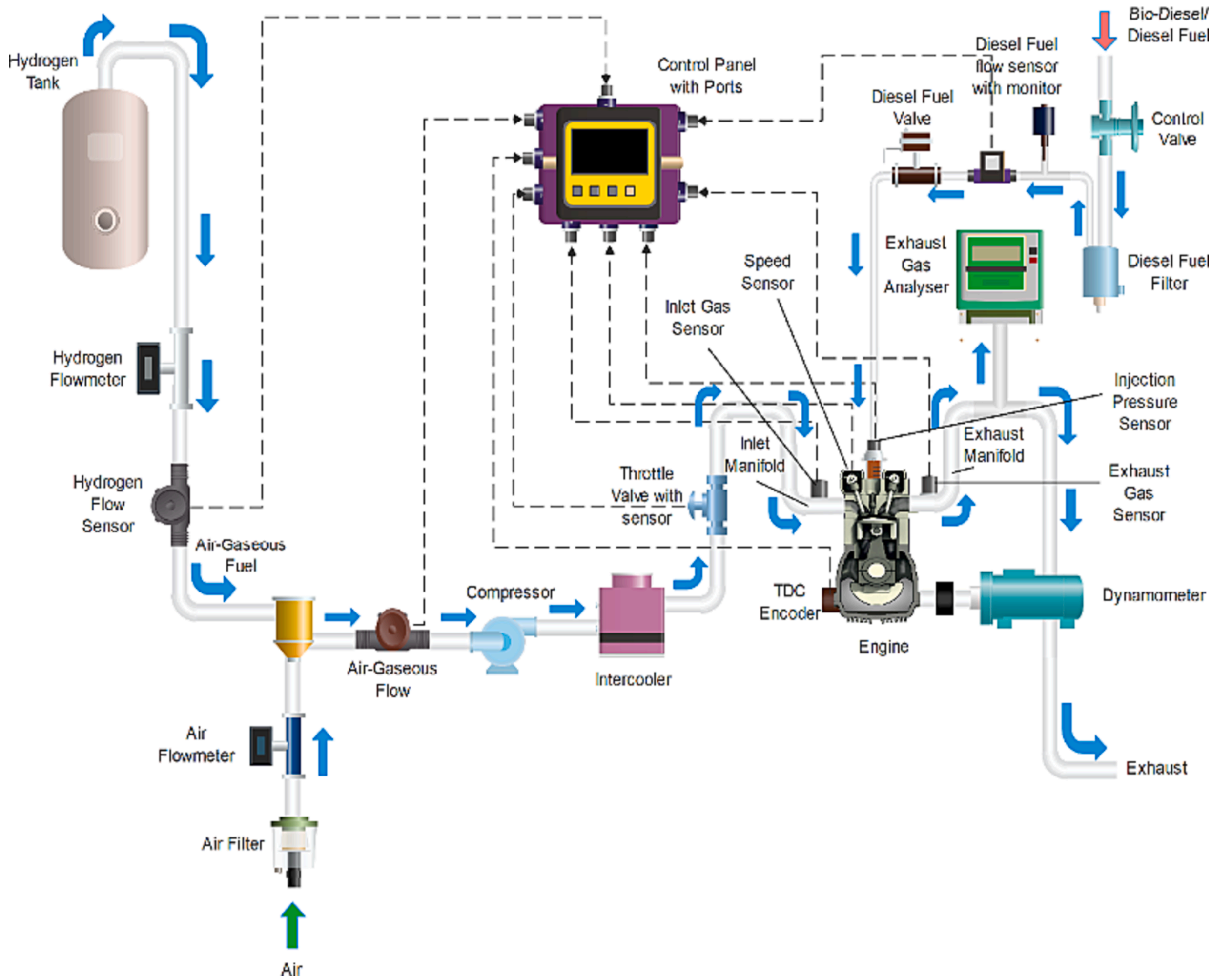

Fig. 1. Schematic of the test engine.

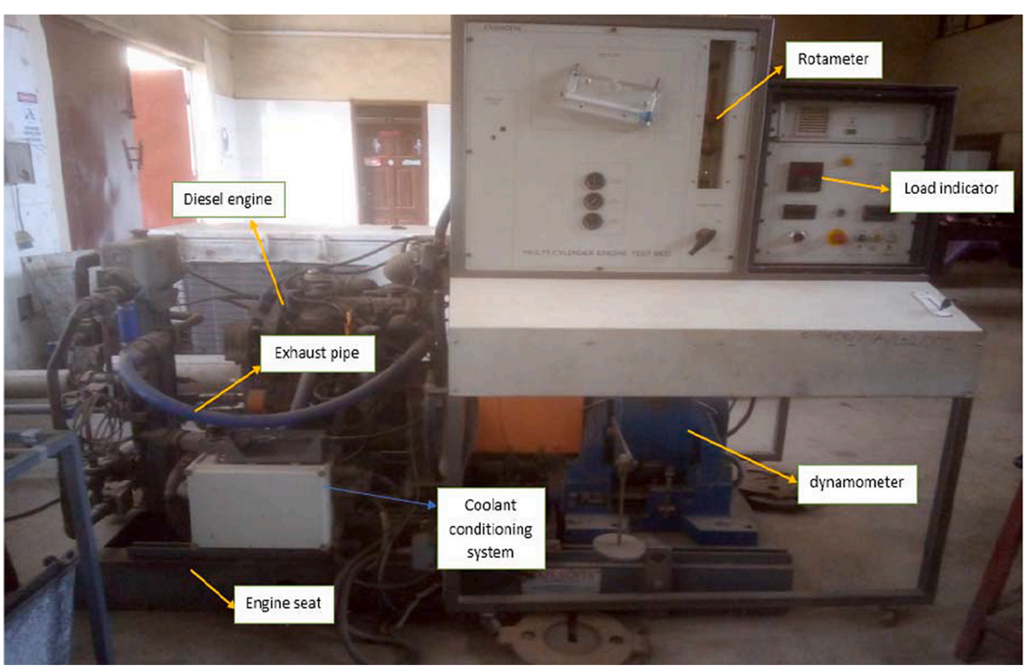

Fig. 2. Pictorial representation of the test engine.

Characterization of TiO_2 nanoparticle

A previous study by the authors [10] details on the characteristics of TiO_2 nanoparticles. The SEM image of the prepared nanoparticle is as shown in S7. The nanoparticles' surface morphologies which revealed their pore size arrangements and textural outlooks, were used to determine the porous architectures of the NPs. The morphologies of the NPs were determined from the micrographs received from the scanning electron microscope (SEM). Fig. 2 reveals that the nano-dispersed NPs are spherical in nature; the particles appear clumped/agglomerated.

Stability of the nanoparticle

Weekly stability evaluations of titanium oxide-surfactant blends (TiO_2: SDS) with the potential to reduce coagulation, surface tension and coalescence, are shown in S8. According to the data collected from UV–Vis spec, the absorbance of all nanoparticles admixed with SDS decreased with time. The nanofluids were held under static conditions. Furthermore, absorbance measurements were taken at the end of each week, and the result shows that the absorbance curve became flat at the end of the 11th week. The prepared nanoparticles were employed right away in order to avoid further agglomeration.

Improving the volumetric efficiency of the engine at different hydrogen doses

A number of factors were considered in other to maintain a constant engine volumetric efficiency (VE) and some of which include the intake and exhaust restrictions, cylinder sealing, valve timing, rpm, gas inertia etc., all these factors influence the VE of the engine, when using different hydrogen flowrates as discussed. VE depends on inlet pressure and temperature, thus, an increase in any one of them will lead to enhanced combustion efficiency or combustion temperature. VE can be improved in a number of ways, most effectively this can be achieved by compressing the induction charge (forced induction) in naturally aspirated engines, for example in racing applications. The VE of an engine depends on the geometry of the intake manifold, the intake mass flow rate (based on the engine speed), the intake air temperature and pressure.

Physicochemical properties of diesel and hydrogen- enriched nanofuel

The physicochemical properties of the test-fuels and those of conventional diesel are shown in Table 1. The fuel's properties have very close similarities with those of diesel fuel. However, the blended fuels' density and kinematic viscosity are lower than those of diesel fuel, which indicates good mixing property and better atomization. Higher cetane number and good calorific value of the fuel, are indicative of the fuel's short ignition delay period and good combustion properties in terms of heat release rate (HRR). Table 2 shows data of some previous works on hydrogen enriched nano-blended fuels in diesel engines.

Table 1
Physicochemical properties of the test fuel.

Parameter/ Fuel type	Diesel	Biodiesel/ nano-additive at 25 ppm	blend with hydrogen flowrate of 3 LPM	blend with hydrogen flowrate of 4 LPM
Kinematic viscosity @ 40 °C	3.23	3.49	2.99	3.11
Cetane number	44.7	45.7	46.2	46.0
Density (Kg/ m^3)	868	874	856	862
Calorific value (MJ/kg)	47.2	45.2	47.2	47.0
Flash Point (°C)	76	89	80	84
Pour point (°C)	2	−1	1	2

Brake thermal efficiency (BTE)

The ability of the engine to convert chemical energy into useful work is determined by the BTE. Fig. 3 illustrates the variations of BTE versus engine load for all the tested fuels at full load. The engine load increased with increase in BTE. The highest BTE was recorded for the blend with hydrogen flowrates of 3 LPM as 39.4 %, while that of diesel and neat biodiesel are 29 and 21 % respectively, which is in line with the works of refs [8,17]. Poor/lower BTEs can occur as a result of poor atomization/ spray characteristics of the fuels. The high performance of the H_2 enriched fuel- blends with hydrogen flowrates of 3 and 4 LPM is as a result of lower fuel consumption and the better heating values of the fuels. The lower BTEs of the neat biodiesel are as a result of the high premixing of the fuel. The H_2 enrichment with nanofuel increases the BTE as a result of the synergistic effect both components have on the blends for an increase in the engine load. Additionally, the addition of H_2 increases the cetane number of the blends with hydrogen flowrates of 3 and 4 LPM, thus increasing the efficiency and performance of the test-fuels. Cetane number is accountable for improved fuel ignition and ignition delay. A positive effect was observed (at 5 kW) as the load increased (Fig. 3). Due to the reduced viscosity and specific fuel usage, the aforementioned is possible. The BTE can be enhanced at higher speeds by reducing the mass of fuel that transports into the combustion chamber [5].

Wall temperature

S9 profiles the variation of wall temperature at various engine loads. An increase in the engine load causes an increase in the wall temperature of the cylinder. At 1 kW, a smooth growth was observed in the wall temperature. There was nearly up to 2.31 % increase in the wall temperature for the hydrogen enriched- nanofuel above that of the diesel fuel at full load condition within constant oscillation. At a higher speed of 5 kW, the fuels maximum temperature was achieved. The nanofuels gave higher temperature values compared to those of the conventional diesel due to their higher heating rates (i.e., 19 % and 16 %) imposed by the blends with hydrogen flowrates of 3 and 4 LPM; this justifies the results presented in ref. [22].

Combustion properties

Heat release rate (HRR)

At 100 percent load, Fig. 4 demonstrates the difference in rate of heat release in relation to the crank angle for the various fuel blends. The sooner the fuels diffuse rather than go through a lengthier pre-mix combustion phase, the greater the cetane number of the fuel blends [11,30]. The HRR profiles of the blends show a similar trend to that of diesel, which is due to the shorter ignition delay of the fuel blends, which in turn influences the pre-mix burning peak phase pressure and HRR. Due to heat-absorption from the compressed hot air, negative HRRs were attained for all the test-fuels throughout the delay period. Due to uncontrolled combustion, the HRR reached its peak after the delay period ended. After the TDC, the value of the HRR peaked at a few crank angle degrees. Due to the obvious premixed combustion, there was an additional release of heat at the second stage. The occurrence of H_2/nanoparticle in the biodiesel fuel made the fuels accumulate in the chamber at the premixed combustion phase, thus increasing the HRR of the fuel blends [6,7,25]. At stage 2, a combined effect of diffused and premixed combustion of blend with hydrogen flowrates of 3 LPM, led to a high heat release rate compared to that of diesel, biodiesel/nano-additive at 25 ppm, and that of the blend with hydrogen flowrate of 4 LPM. It can be observed that the maximum HRR was 74.1 J/°CA which

Table 2
Compared data from other works with those of this study.

Engine specification	Nanoparticle/dosage	Flowrate of hydrogen (LPM)	Biodiesel blend	Performance of compared to diesel	Emission properties compared to diesel	Refs.
Mitsubishi Canter- Direct Injection- in-line 4. naturally aspirated, 4-stroke, 4 cylinder DI diesel engine	Al_2O_3 – 50 ppm	5	soybean biodiesel	BTE ↑	NOx ↑, CO ↓, HC ↓	[29]
Modified CI engine.	Al_2O_3 – 50 ppm	5	Eucalyptus biodiesel	BTE ↑	NOx ↑, CO ↓, HC ↓	[30]
Kirloskar, AV1, Single-cylinder, Four-stroke, Direct Injection, Water-cooled CI Engine	ZnO- 100 ppm	1.5	Jatropha biodiesel	BTE ↑	NOx ↑, CO ↓, HC ↓	[31]
Simpson 217 Modified dual injection, water cooled, Vertical, inline, four-stroke diesel engine	ZnO- 100 ppm ZnO- 100 ppm	4	Corn blend biodiesel	BTE ↑	NOx ↓, CO ↓, HC ↓	[14]
Kirloskar, India; Water-cooled engine; Four-stroke, CI engine.	graphite oxide nanoparticle – 50 ppm	3	**Microalgae -Euglena Sanguinea**	BTE ↑	NOx ↓, CO ↓, HC ↓	[32]
Mitsubishi Centre (Test Engine)- DI engine	TiO_2 – 25 ppm	3	Afzelia Africana biodiesel	BTE ↑	NOx ↓, CO ↓, HC ↓	This study

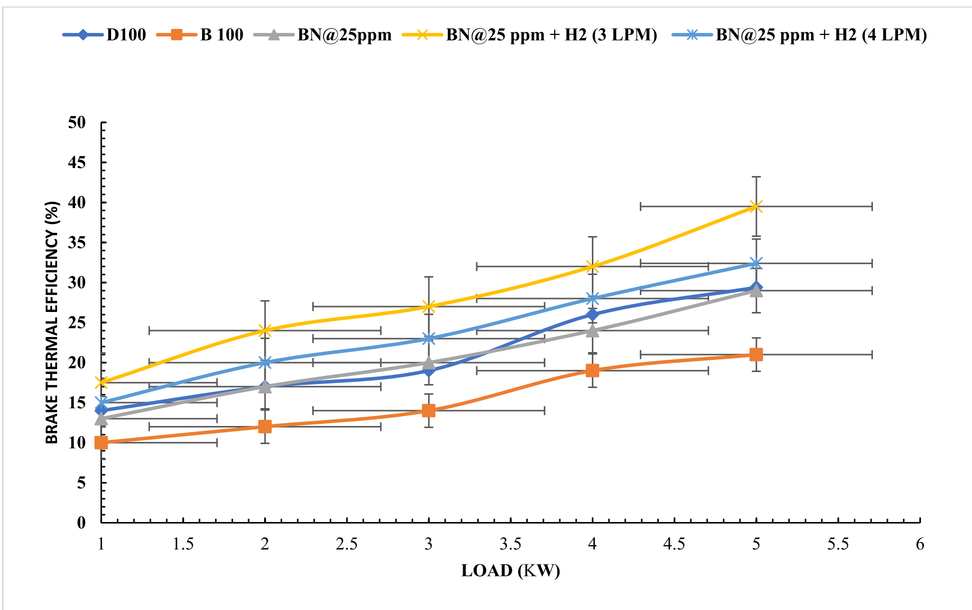

Fig. 3. Variation of BTE vs engine loads.

was recorded for the blend with hydrogen flowrate of 3 LPM compared to that of the biodiesel/nano-additive blend at 25 ppm with 64 J/°CA HRR, and that of the blend with hydrogen flowrate of 4 LPM which is 70 J/°CA, while that of the diesel fuel was lowest amongst them with a HRR/crank angle of 60 J/°CA.

In-cylinder pressure variation

The in-cylinder pressure variation with crank angle at full engine-load is as illustrated in Fig. 5. Factors such as delay period, fuel quality/type, and operating conditions contribute to changes in in-cylinder gas pressure [26 –28]. Considering the DI-engine, the amount of fuel burnt all through the premixed combustion phase, mainly impacts the peak pressure and combustion rate at the initiation step. As the engine load increases, the quantity of fuel that is burnt also increases, thus aggravating the pressure inside the cylinder in a gradual manner. According to some researchers, high peak cylinder pressures in the case of hydrogen-enriched biodiesel is vital in DI engines as a way of enhancing their ignition delays and exhaust gas temperatures [2,7,11,15]. When H_2 is used to enhance the performance of biodiesel fuels, it raises the possibility of a high peak pressure compared to other modes of fuel enhancements, owing to the reduction in delay period and combustion. TiO_2 nanoparticle blended with Afzelia biodiesel was admixed with hydrogen at different flow rates, which thus improved the ignition delay period of the fuel-blends. Fuel-characteristics, such as higher volatility, low viscosity, quenching distance and higher flammability are usually associated with hydrogen, which makes it a suitable blend for the nano fuels. These properties help to achieve complete combustion via rapid vaporization of the fuel mixtures [8,17,19,22]. Therefore, higher cylinder pressures were recorded for the biodiesel/nano-additive @ 25 ppm, and for the blends with hydrogen flowrates of 3 and 4 LPM fuels but were more predominant for the blend with hydrogen flowrate of 3 LPM fuel due to the nanoparticle-hydrogen incursion in the biodiesel alongside variation in H_2-flowrate. The maximum in-cylinder pressure of 75.2 bar was obtained for the blend with hydrogen flowrate of 3 LPM, while for the blend with hydrogen flowrate of 4 LPM, the measured pressure was 74.7 bar. Further increase in the flowrate and volume of hydrogen, reduced the calorific value of the fuel-blends, which resulted in a reduction of the in-cylinder pressure of the engine.

Exhaust emissions

NOx, HC, and CO emissions are usually influenced by engine design, durability, fuel quality, fuel/air ratio, operating pressure, and operating conditions.

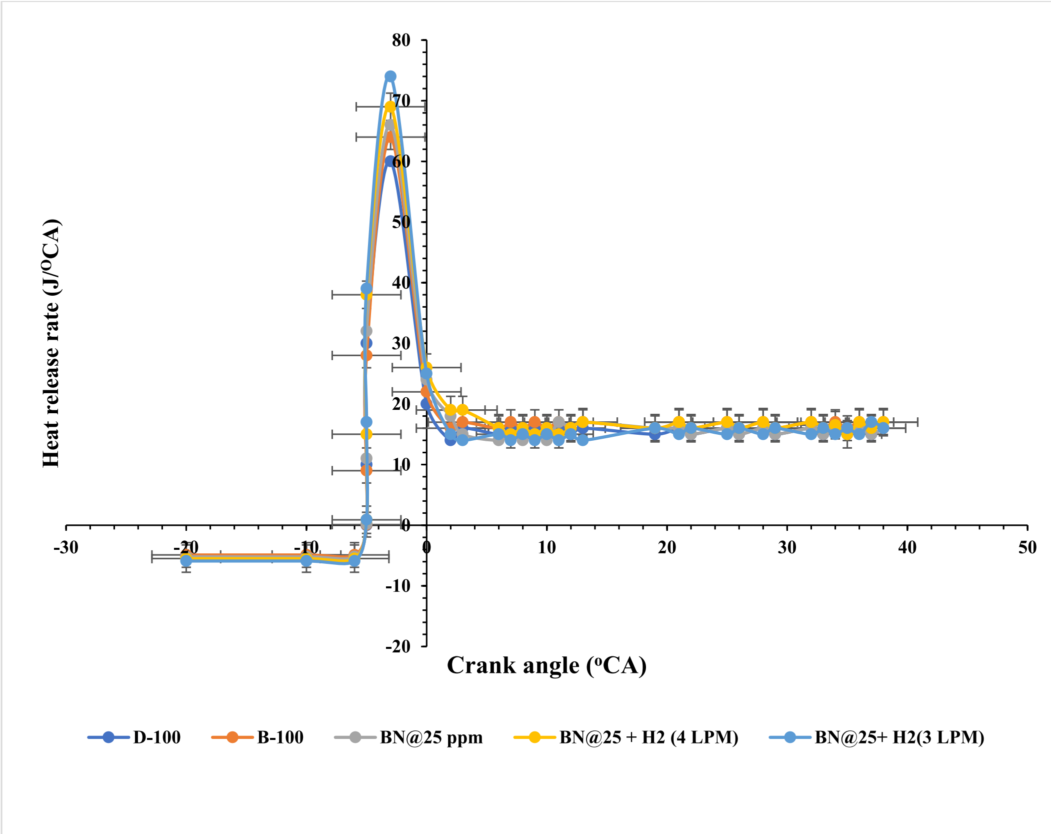

Fig. 4. Variation of HRR with the crank angle of the engine's shaft. *(J/°CA) – Joule per degree Crank Angle.

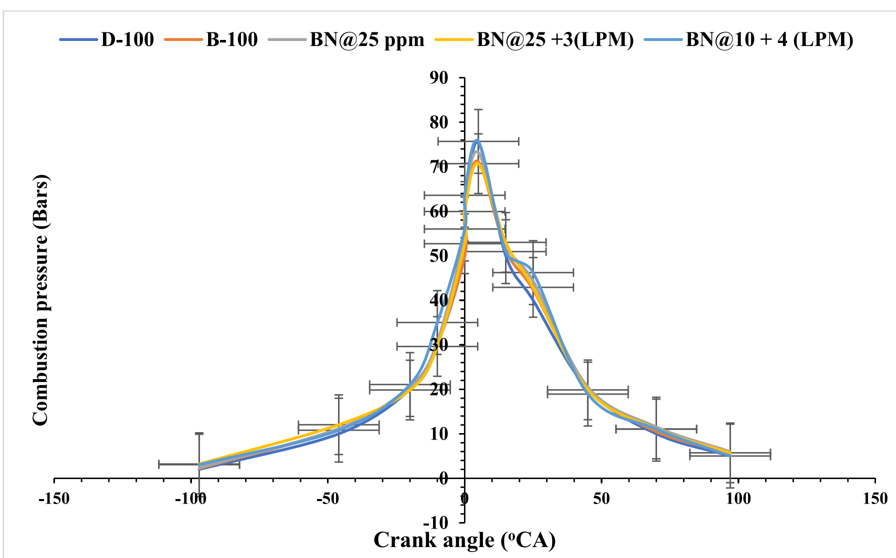

Fig. 5. Variation of combustion pressure with crank angle of the engine's shaft.

CO exhaust emissions

Fig. 6a depicts the recorded CO emissions of the tested fuels at 100 % load condition. The O_2 content of the biodiesel improved intensely as a result of hydrogen involvement in the fuel, thus lowering the emissions of CO. CO emissions, are alternatively higher in diesel due to incomplete fuel burning and inadequate mixing. The addition of H_2 to the nano-fuel increases the O_2 content, which in turn allows for complete burning of the fuel. Furthermore, a higher fraction of hydrogen in the diesel engine lowers the carbon content of the fuel, thereby reducing the CO emissions. Nanoparticles, on the other hand, have a significant influence on the amount of CO released after burning each fuel. The oxygen level in the fuel increases due to nanoparticle addition, which resulted in lean combustion [24]. In addition, factors such as pressure and injection timing reduce CO emissions. As a result, it is clear that biodiesel mixed with nanoparticles produce very little amount of CO. Because of the enhanced combustion rate, CO emissions decreased as the engine load

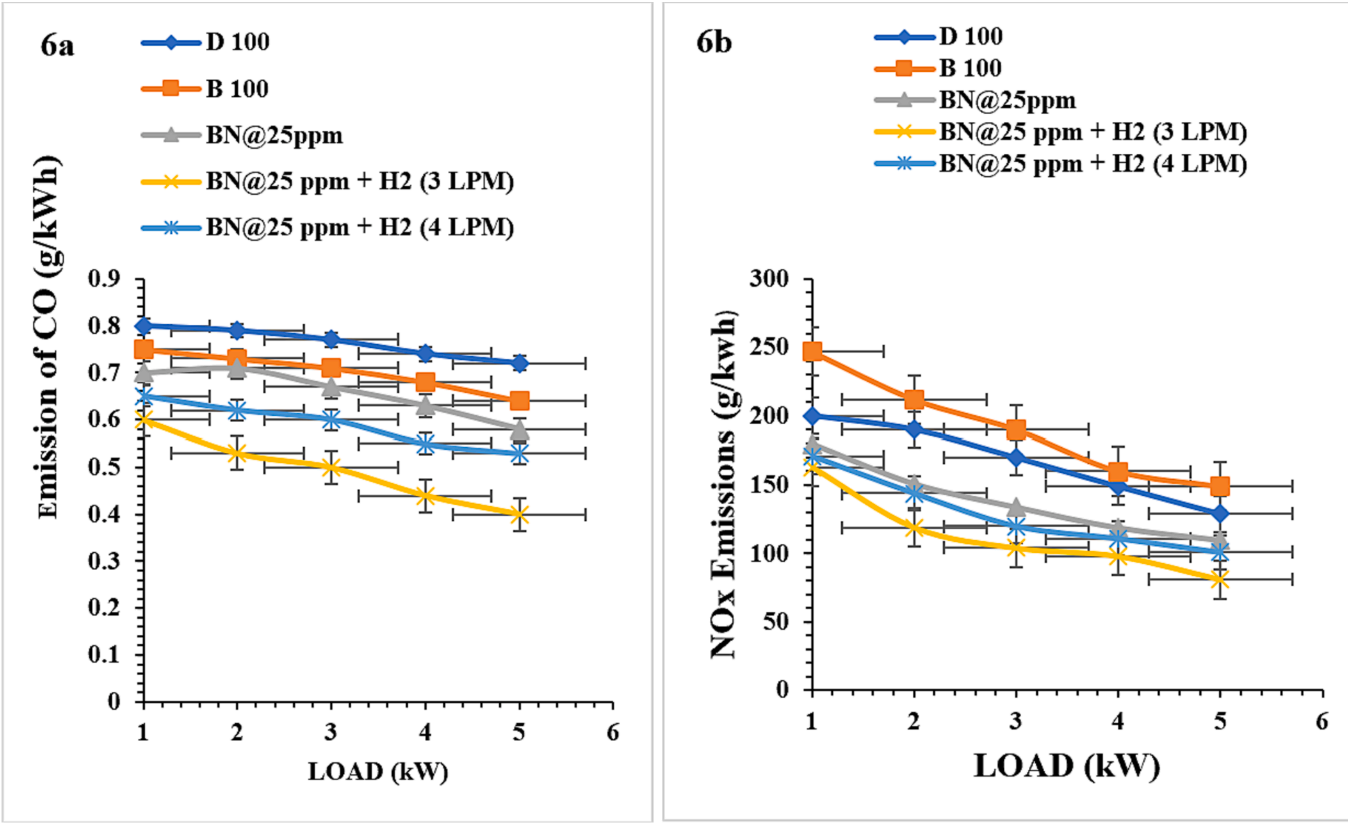

Fig. 6. (a) Variations of CO emissions vs engine load; (b) Variations of HC emissions vs engine load.

increased. Furthermore, blends with hydrogen flowrates of 3 and 4 LPM gave 8 and 14 % less CO compared to the neat diesel, and this is due to the inclusion of hydrogen in the biodiesel since hydrogen fuel contains no carbon atom. Higher in-cylinder pressure due to higher flame propagation speed of the hydrogen fuel, results in complete combustion due to enhancement of the homogeneous mixture because of higher diffusivity of hydrogen, higher temperature kinetics due to hydrogen enrichment and availability of more oxygen in the biodiesel which in turn leads to reduced CO emissions [18,24,27]. The traces of CO emissions in the exhaust could be due to the possibility of lubricating oil combustion and also partial combustion of biodiesel. The addition of TiO_2 nanoparticles on the other hand reduces the resulting CO emissions compared to that which is released when diesel is used. The nanoparticles in the fuel increased the atomization rate and redox characteristics of the fuel at full load which then induced complete combustion [25,28]. The reduction of CO emission is mainly due to the catalytic nature and redox ability of TiO_2 nanoparticles, which can further oxidize CO to give CO_2 [16].

Hydrocarbon emissions (HC)

S10 shows the HC emissions at various engine loads. Due to the incomplete combustion process in the combustion chamber, HCs are emitted from the diesel engine. At low engine speeds, a larger compression ratio results which then reduces the resulting HC emissions dramatically. However, due to the increased power demand, all engines are run at higher speeds. Wall wetting and flame quenching are the most common causes of incomplete combustion. Interestingly, as engine load increases, HC emissions drop (S10). This is mostly due to the reduced evaporation of fuel droplets and poor mixing of the blends. Aside from the aforementioned factors, fuel quality, spray type, and operating conditions also contribute to greater HC emissions. Because the bulk of the fuel that was fed into the combustion chamber is considerable, HC emissions are reduced as the load increases. With the TiO_2- biodiesel blend however, the amount of HC produced is lower than that obtained for diesel fuel. Due to high oxygen content in the nanofuel admixed hydrogen fuels, they have the ability to effectively accelerate combustion, thus resulting in total combustion [25]. The diesel fuel emitted more than 39 % HCs at full load than those recorded for the blends with hydrogen flowrates of 3 and 4 LPM. Regardless of the load, the hydrogen enriched- nanofuel emitted lower HCs. Since nanoparticles operate as O_2 buffers, lower amount of HCs are produced compared to the case of diesel. Refs [10,26] described a similar pattern of activity. As a result, adding H_2 to the nanofuel in the diesel engine, can prevent flame quenching, which may give rise to lower HC emissions. Furthermore, adding TiO_2 nanoparticle to the biodiesel, improved the fuels' calorific values and combustion by acting as a catalyst [27]. Thus, hydrogen addition to nanofuel, lowers the latent heat of vaporization, thus resulting in a rich mixture of air and fuel. Also, by steadily increasing the amount of H_2 in the fuels, the viscosity of the admixed fuel drops. Hence, blends with hydrogen flowrates of 3 and 4 LPM marginally reduced the recorded HC emissions (S10).

NO_x emissions

During combustion, the engine produces hazardous NO_x emissions. Fig. 6b shows the NO_x emissions that were documented for all the tested fuels. Compared to diesel fuel, Afzelia Africana biodiesel generates a lot of NO_x as seen in Fig. 6b. This is usually caused by a high mass flow rate of fuel into the combustion chamber. Another fact is that high oxygen concentrations and bulk modulus of compressibility may also contribute to the increased NO_x emissions. Afzelia Africana biodiesel emits 18 % more NO_x than regular diesel. The addition of TiO_2 nanoparticles to the fuels, has some favorable impacts on the fuel's NO_x emissions. Due to lower heat of vaporization and density of the nanofuel, it emits less NO_x relative to diesel fuels. Biodiesel admixed with TiO_2 nanoparticles performs better than diesel fuel. For example, the influence of nanofuel is credited with a 10 % reduction in NO_x emissions. As a result, the nanofuelemissions are significantly lower than those of pure diesel due to their increased oxygen contents. Since the intrinsic oxygen concentration of nanoparticles in fuel allows for a high combustion rate at full load, the resulting NOx emissions are reduced significantly. Ref. [28] also observed a similar trend. The NO_x emission reduces further at moderate flow rates of hydrogen in the nanofuels [3,25]. Even at greater loads, lower NO_x production ensued for the blends with hydrogen flowrates of 3 and 4 LPM. Research has shown that B100 had low NO_x emission when the engine was operated at low load [4,19,26], however, with the use of Afzelia Africana biodiesel in the diesel engine, high NO_x emission was observed. This biodiesel type produces more NO_x because biodiesel contains oxygen within it. In addition, increase in NO_x emissions may persist for multiple reasons at low load; such reasons include (i) the feed stock, (ii) engine type/technology (iii) the operating conditions.

Implementation of NOx emission regulations

Several regulations have been adopted and applied by the automotive and petroleum industries to fuel and market vehicles as a means of reducing toxic emissions (primarily NOx and particulate matter in CI engines) [29]. To meet the increasingly stringent requirements of emission regulations , strict laws on engine and fuel design have been implemented [30,31]. In essence, it is generally stated that the only goal that engine manufacturers presently pursue is the reduction in emissions, as they undoubtedly penalize diesel engine power output and fuel economy so as to achieve a relatively large reduction in exhaust emissions by increasing the EGR ratios, including post-injections thus - retarding the main injection [30,32 –33].

Emphases on NOx emission reduction in diesel engines have been on, with the use of (i) an after-treatment device which comprises of a HC-selected catalytic reduction (HC-SCR) system, (ii) reformed EGR in addition to the fuel, that will enable the engine to run under dual fuel conditions, and (iii) an ultra-clean, designed diesel fuel (GTL fuel) from a Fischer–Tropsch process [9,31,34].

Different SCR catalyst (Ag, Pt, Cu.) types have previously been proposed with various types of pure HCs and fuels tested as reducers [22,30 –33]. The Pt over alumina catalyst has been shown to match those characteristics, though it is not without drawbacks (which include N_2O formation in some cases and a small temperature range of 200 to 300 °C which helps to attain maximum NOx conversion [34].

Reformed EGR has been tested recently [27,29 –33] and is a promising alternative for minimizing both NO_x and smoke emissions in some diesel engines operating at low loads. Reformed EGR is an H_2/CO-rich gas that can be produced on-board in a fuel reformer by reacting HC fuels and exhaust gas over a catalyst [35]. This gas is recycled into the combustion chamber with a reduction in the amount of liquid fuel injected into the cylinder while maintaining the same engine torque and speed. As a result, the engine runs in a partially premixed charge compression ignition (PPCCI) mode, which is a HCCI type of combustion [37]. Since the high self-ignition temperature of H_2 makes the compression temperature insufficient to initiate the combustion [15,24,30], a H_2-rich gas cannot be used as the sole fuel in a CI engine, so ignition is usually achieved through the injection of a liquid fuel [26]. This fuel can be fossil fuel or biodiesel. One disadvantage of the reformed EGR technique is an increase in H_2 emissions due to incomplete combustion [36]. However, the inclusion of a SCR catalyst in the vehicle exhaust pipe may allow the exhaled H_2 to be used by improving NO_x conversion in the catalyst, particularly at low temperatures, while also lowering the resulting HC and CO emissions [20,24]. In addition, the use of the admixed fuel not only helped to improve engine emissions and performance, but also served as a boost for fuel supply sustainability. According to Scarnegie et al. [38], new ultra-clean designed fuels, the use of reformed EGR, and a SCR catalyst as an after-treatment device may lead to about 90 % reduction in NOx emissions. Depending on the state of the engine, this reduction can increase up to about 95 % in some cases. Lou et al. [39] significantly reduced NO_x emissions by combining a diesel particulate filter and an EGR system, as well as a SCR and urea system.

EGR and SCR techniques have been proven to reduce NOx in exhaust gas. The SCR approach minimizes NO_x levels above 90 %. However, due to the negative effect on engine power, the percentage of EGR limits NO_x reduction [32,39]. SCR technology is not detrimental to engine life. However, the EGR technology is less expensive and lighter than the SCR method [33]. EGR has a negative impact on engine performance in terms of horsepower, oil contamination and fuel consumption. EGR is more effective in cars because the urea tank and injection system take up less packaging space [28,39]. SCR is more effective for long wheel-based applications. EGR is very efficient for low power engine applications and not for heavy duty engines as a result of its contamination effects [40]. EGR alone may not meet the Bharat Stage-VI level NO_x emissions due to limitation on the %EGR, however, SCR can. The cost of SCR becomes very high. Thus, combining SCR and EGR holds water for future consideration [41–42]. Table 3 Compares data from other works with those of this study.

Challenges and future recommendation

Challenges

Efforts were made to boost the BTE and lower the emissions of the other tested fuels besides the blend with hydrogen flowrate of 3 LPM by varying their concentrations in the biodiesel, however, there was no further increase in BTE/decrease in emission despite increasing/ decreasing their concentrations in the biodiesel. Thus, the blend with hydrogen flowrate of 3 LPM was the best nanofuel among others. Compared to nanofuels, neat biodiesel is not suitable in CI engines due to its poor performance, poor emissions, and poor physicochemical properties. It was discovered that the least performing nanofuel, BN@25 ppm, had weaker properties that negatively affected its flash point, cetane number, and viscosity with a longer ignition delay than those of the blend with hydrogen flowrate of 3 LPM fuel.

Future recommendation

One of the important key factors that affect fuel quality when admixed, is the type of (NPs) nanoparticles, their sizes, as well as their volume concentrations. More researches are required to counteract this disparity by taking into account the source of biodiesel, NP- type, as well as varying the NP dosage level.

Furthermore, several NPs have been discovered to have distinct features. More researches into the intermingling behaviour between NPs and biodiesel is required to optimize engine characteristics. New applications and improved performance may be possible by allowing two or more NPs to be blended together [18], however, the response mechanisms alongside their associated effects, are not completely understood. Also, a comprehensive analysis on the safety of NPs is required to avoid injury/damage to people and the environment. It is critical to verify their toxicities with particular emphasis on NP solubility and NP interaction [23]. To conduct a full analysis, the impact of NPs on lubrication mechanisms and tribological behavior in engine applications should be investigated. In addition, the physical properties of diesel engine fuels and oils are difficult and complicated; during engine combustion, the reactions involving NPs, oils and fuels appear to be poorly defined. Thus, blending different fuels with more than one NP should be looked into in the future. The use of this technique should be adopted in diesel engines which will in turn reduce the dependence on fossil fuel as well as the resulting exhaust emissions in our environment.

Conclusion

The production of different fuel blends using hydrogen enrichment admixed with TiO_2 nanoparticles on Afzelia Africana biodiesel blend at different flowrates were investigated in this study with the aim of achieving low emissions and high engine performance in a single-cylinder direct injection diesel engine. The proportion of hydrogen-enriched biogas with the nanofuel was maintained at 15:85 % vol/vol for all the tested fuels. H_2 plays a vital role in the future energy sector. The ASTM specification tests for the fuel quality measurements had been stated for the blended nanofuels and compared with the diesel fuel. The fuel blends description data showed some similarities with the diesel fuel. The experiments were conducted at several engine loads in order to determine the emission and performance characteristics of the test fuel in a DI engine. Other conclusions are as follows:

i. The nano-fuels demonstrated lower HC, CO, and NO_x emissions compared to those of the diesel and neat biodiesel fuels. The effect of H_2 on the air system is another mandatory cause for reduced emissions. CO, HC and NO_x emissions were lower for the blended fuels; at maximum load, BN@25 + H_2(3LPM) displayed the lowest CO gas emissions (i.e. 0.4 – 0.6 g/kWh). There were decreases by 28.7 % and 15.2 % for BN@25 + H_2(3LPM), BN@25 + H_2(4-LPM) and 9.5 % for BN@25 in CO emissions relative to those of diesel fuel. For HC emissions, BN@25 + H_2(3LPM) and BN@25 + H_2(4-LPM) emissions were 5 g/kWh and 11 g/kWh lower compared to that of diesel (21 g/kWh). The NO_x emissions of BN@25 + H_2(3LPM) and BN@25 + H_2(4-LPM) fell between 81 and 163 g/kWh and 101 – 171 g/kWh respectively, compared to that of the diesel fuel (149–247 g/kWh).

ii. The hydrogen enriched nanofuel blends gave higher BTEs for all the tested fuels. The synergetic effect of H_2 enriched nanofuels not only improved engine performance attributes but also significantly reduced fuel consumption and emissions. At full load condition, the BTEs of all the tested fuels were 39.5 %, 32.4 %, 29.4 %, 29 % and 21 % for BN@25 + H_2(3LPM), BN@25 + H_2(4LPM), diesel, BN@25 and biodiesel; this justifies the suitability of hydrogen as a viable additive for enhancing the BTE of the engine.

iii. TiO_2 nanoparticle addition to the biodiesel improved the physicochemical properties (density, flash point, cetane number, kinematic viscosity, cloud point and pour point) of the fuels.

iv. The H_2 enriched nanofuels were characterized by shorter ignition delay periods due to their HRRs and in-cylinder pressures. Due to their huge surface areas, TiO_2 nanoparticles increase combustion rates. Thus, the BN@25 + H_2(3LPM) and BN@25 + H_2(4LPM) displayed higher HRRs of 74.1 J/°CA and 70.0 J/°CA, compared to that of the diesel fuel (60 J/°CA).

v. The performances of the nano-fuels in the engine are in the following order of increased magnitude: the blend with hydrogen flowrate of 3 LPM > blend with hydrogen flowrate of 4 LPM > BN@25 ppm > Diesel- (neat diesel) > Biodiesel-(neat biodiesel), which is thus, indicative of the superiority of the hydrogen enriched nanofuel sample relative to other fuel samples in terms of the measured BTEs. Thus, TiO_2 nanoparticle plays a vital role in the fuel's emission and performance characteristics.

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.

Data availability

No data was used for the research described in the article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seta.2023.103495.

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