Energy 244 (2022) 122635

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Comparing the effects of Juliflora biodiesel doped with nano-additives on the performance of a compression ignition (CI) engine: Part A

Babalola Aisosa Oni [a, *], Samuel Eshorame Sanni [b], David Oyinkepreye Orodu [c], Temitope Fred Ogunkunle [c]

[a] Chemical Engineering Department, China University of Petroleum, Changping, Beijing City, PR China
[b] Department of Chemical Engineering, Covenant University, KM 10 Idiroko Road, PMB, 1023, Ota, Nigeria
[c] Department of Petroleum Engineering, Covenant University, KM 10 Idiroko Road, PMB, 1023, Ota, Nigeria

ARTICLE INFO

Article history:
Received 30 May 2021
Received in revised form
15 September 2021
Accepted 14 November 2021
Available online 17 November 2021

Keywords:
Additives
Diesel engine
Juliflora biodiesel
Metal oxides
Nano-doped biodiesel

ABSTRACT

In lieu of the fact that modern-day research is saddled with the responsibility of replacing/supplementing fossil fuels with biodiesel for use in diesel engines, the challenge still remains the need to improve the properties of biofuels towards stimulating high engine compatibility and performance. Despite the advances made in improving biofuels such as those sourced from Juliflora with additives, none seems to have addressed the potentials that underly the use of hybrid nano-particles as property-improvers of Juliflora-biofuel for use in diesel engines. This then led to the need to harness the potential use of hybrid CeO_2:CuO, MnO_2:Al_2O_3, ZnO:TiO_2, and TiO_2:Al_2O_3 in different ratios as a means of determining the best combination for improved fuel properties, high engine performance and reduced emissions. The nanoparticles were produced via sol-gel method and ultrasonicated with the biofuel before being characterized using scanning electron microscopy/atomic force microscopy. Based on the engine-test results, the brake thermal efficiency (BTE) increased from 1.11 to 2.21% for the biodiesel mixed with nanoparticles. Furthermore, the Nitrogen oxide (NO_x), hydrocarbon (HC) and carbon monoxide (CO) emissions for the admixed biofuels decreased by 16.29–23.76%, 14.07–17.32% and 5.51–8.27% respectively compared to conventional diesel, thus reducing environmental pollution.

1. Introduction

Fossil fuel depletion, stringent emission norms and the high demand for energy have spurred the urge in researchers to seek for alternative fuels for use in diesel engines, thus bridging the gap between demand and supply of energy, especially for the automotive industry [1]. Biodiesels can be obtained from non-edible plants, edible plants, animal fats and algae, which can be employed in diesel engines with little or no modifications. In this work, Juliflora biodiesel was chosen due to its physicochemical properties which are close to those of conventional diesel fuel. Biodiesel as an alternative source of fuel, releases less gaseous emissions (i.e., CO, NO_x, SO_x and unburned hydrocarbons) relative to conventional diesel fuel. As a promising alternative fuel, it is sustainable and renewable [2]. Biodiesel contains extra oxygen atoms in its molecular structure, which contributes the required oxygen that assists in enhancing fuel combustion. Nonetheless, certain disadvantages are associated with the fuel despite its numerous advantages such as high viscosity, poor cold flow properties and lower heating value [3]. There are also several literature where biodiesel such as Cymbopogon flexuosus [1], eucalyptus oil, pine oil, and turpentine oil were used for diesel engine application [2,3]. These raw oils also resulted in higher emission levels and hence, the modern-day biodiesel research is focused on the addition of additives to biodiesel to reduce emissions and enhance engine performance [3].

Modification of fuel properties has been generally accepted by research scholars in the field as a means of improving the performance of diesel engines, attain specific fuel properties as well as reduce/control the exhaust emissions exiting the engine.

Asokan et al. [4] conducted an experiment on a single cylinder diesel engine with several proportions of conventional diesel mixed with Juliflora biodiesel blends. The results of the blended fuels indicated that the blended fuels gave comparative performance relative to that of the diesel fuel. However, the B100 Juliflora

* Corresponding author.
E-mail address: babalola.oni@covenantuniversity.edu.ng (B.A. Oni).

https://doi.org/10.1016/j.energy.2021.122635
0360-5442/

Biodiesel gave a similar and close BTE of 31.11% to that of the conventional fuel at 100% load. CO, hydrocarbon and smoke emissions for the biodiesel and its blends were lower compared to those of the conventional diesel, although the NO_x emission at full load, was higher for the B100 fuel. Rajeshwaran et al. [5] carried out an experiment on Juliflora biodiesel, the result showed that there was a decrease in the BTE by 8.34% with an increase in HC, smoke, CO emission, unburnt hydrocarbon (HC) and smoke by 16%, 11% and 10.7% with higher NOx emission of 10.71%, and low heat release rate (HRR) when compared to the conventional diesel at full load condition.

Soudagar et al. [6] itemized some limitations associated with the use of biodiesel fuels in diesel engines and they include high NO_x, cold weather conditions, high viscosity, low cetane number, and consistent replacement of engine parts/fuel lines, fuel tanks, clogged fuel filters and low BTE. According to them, nanoparticle addition as fuel additives may improve the properties of biodiesel fuels.

Currently, a procedure has been developed to improve the properties of the fuel through the addition of fuel additives [7]. The use of alcohol-based additives in biodiesel fuel blends have increased over the last decade, thus supplying more O_2 in the combustion chamber which will lead to efficient combustion and emission reduction. However, the formation of a lean mixture lowers the calorific value of biofuel, which, when combined with higher auto ignition temperatures and lower lubrication properties, results in reduced performance characteristics and engine deterioration [8–10], hence, researchers have explored the potential of nanoparticle- additives.

Following the recent advancements made in the use of fuel additives to modify the properties of biodiesels, the use of nanotechnology stands a promising approach in achieving this great stride which helps to greatly improve the fuel's quality thereby increasing the performance and combustion properties of the engine as well as reduce exhaust emissions [11].

Nano-additives and their effects are known to improve the performance of diesel engines as asserted by some investigators [12–14]; when added to fuels, these nanoparticles help to reduce NO_x emissions from the fuels when they undergo combustion [15,16]. Optimization of engine parameters such as injection timing, compression ratio (CR), and load have succeeded in reducing exhaust-emissions as well as improve the injection pressure [17], as well as combustion and performance characteristics of a diesel engine operating on different blends of biodiesel [18]. Dreizin [19] demonstrated that nanoparticles dispersed in test-fuels infused better thermo-physical characteristics in the fuels as a result of the high surface area to volume ratio of the nanoparticles; there was also high NO_x emission owing to the high oxygen content of the fuel. Kenneth et al. [20] also demonstrated the ability of nanoparticles to increase the rate of heat transfer as induced by the high specific surface areas of the nanoparticles. Idriss [3] observed the effect of a promoter on CeO_2-nanoparticles with CH_3COOH. The results showed that the nanoparticles can act as good fuel additive in HC liquid-fuels. Farfaletti et al. [21] also adopted the same additive/CeO_2-nanoparticles in diesel emulsion fuel, however, they obtained a drastic reduction in CO, particulate matter (PM) and unburnt HC emissions. Sajith et al. [8] carried out a study on the effect of CeO_2 nanoparticle dispersed in 30–70 ppm Jatropha methyl esters in a 4- stroke, naturally aspirated, single cylinder, CI engine. There was a significant reduction in the NO_x and HC emissions by 30 and 40% respectively, with 1.5% increase in the BTE compared to that of diesel fuel. Karthikeyan and Prathima [22] blended a hybrid-catalyst of 50 and 100 ppm (having CeO_2 on a multiwalled carbon nanotube) in Juliflora methyl esters, for use in a diesel engine with the aim of reducing the engine emissions. The results showed that the high surface area of the NPs and their proper distribution along with catalytic oxidation reaction resulted in significant reductions in the HC, NO_x and CO emissions. Ghafoori et al. [23] carried out a similar study on the use of biofuel (0.40 and 0.80% vol) mixed with magnetic nanoparticles as additives in diesel fuel in order to examine their effects on the emission and performance characteristics of a diesel engine. The addition of the nanoparticles gave a significant increase in the engine's performance and combustion characteristics as well as reduced the NO_x and SO_2 emissions.

The advantages of nano-additives in biodiesel is to upgrade the performance of the diesel engine and to dilute the emissions from the exhaust tailpipes accordingly. This can be attributed to the fuel's reducing and oxidizing catalytic activity on some hybrid nano-additives (CeO_2: CuO, MnO_2:Al_2O_3, ZnO: TiO_2, and TiO_2:Al_2O_3) in Juliflora biodiesel powered by direct injection in the CI engine.

Based on several consultations with related articles on the subject, several metal oxide additives such as CeO_2, Al_2O_3, ZnO and TiO_2 doped with diesel and biodiesel have been adopted as fuel all aimed at improving engine performance, combustion and reduced emissions. This then suggests that the addition of lone/nonhybrid nanoparticles as additives for biodiesel fuels serves as a promising measure for improving the properties of the fuels used in compression ignition engines alongside their service-lives. However, based on the extensive literature search conducted, it was observed that, till date, none of the related studies considers the adoption of hybrid nano-oxides of aluminum, cerium, titanium and zinc which are emulsified with sodium dodecyl sulfate (SDS) surfactant as potential property improvers of Juliflora biodiesel for use in CI engines.

In this study, Juliflora is the parent biomass from which the biodiesel was produced. The nanoparticles considered in this study are eco-friendly, which help to improve biodiesel quality. They are non-toxic with the potential to reduce fuel consumption with reduced emissions. Hence, the objective of this current research is to investigate the combined effect of the aforementioned nano-additives (CeO_2, Al_2O_3, ZnO and TiO_2 in different ratios) in Juliflora biodiesel fuel used to power a Kirloskar AV1 diesel engine as compared to using lone/nonhybrid nanoparticles as additives in the biodiesel. This is aimed at determining the best nanoparticle-fuel blend with optimum performance, minimal emission and better combustion characteristics for application in an unmodified compression ignition engine. The various parameters tested for the nano-oxide fuel blends were compared with those of conventional diesel fuel. Furthermore, this study also facilitates and proposes a future direction for the application of hybrid nano-additives in biodiesel for use in CI engines. Table 1 shows a list of some selected related works on the subject.

2. Materials and method

2.1. Extraction of Juliflora oil

The seeds from Juliflora plant were harvested and rinsed with clean water so as to remove sand and other particles. The seeds were sun-dried for one week and manually separated from their fruits (Fig. 1a, b and 1c). The dried seeds were then transferred to an oven for further drying at 60 °C for 12 h. After complete drying, the seeds were crushed mechanically into small particles. The extraction process was done with a Soxhlet extractor. The sample prepared was introduced in a thimble of thick cotton, loaded in the Soxhlet's main chamber; hexane was used as the solvent for the extraction process. The Soxhlet extractor is also equipped with a condenser. Vapor from its heated section rose up into the thimble housing chamber where the seeds were placed. The chamber

Table 1
Review of some selected studies.

Ref.	Specification of the engine	Compression ratio and Engine Speed	Bio-diesel Blend	Nanoparticles and particle size.	Dosage of Nanoparticles and surfactant type	Nanofluid preparation	Performance compared to diesel fuel	Emission compared to diesel fuel
[24]	AV1-Kirloskar, four -Stroke, single cylinder, 230 BTDC, 210 bars	1500, 16.5:1	Pongamia methyl ester	Al_2O_3; 100 nm	50/100 ppm; $(CH_3)_3$. NH_4	2-step	BTE ↑	CO↑NOx ↓, HC ↑,
[25]	Kirloskar, Single cylinder, four -stroke, AC,	1500 rpm; 17.5:1	Jojoba methyl ester	Al_2O_3; CeO_2	Al_2O_3, 51 nm and CeO_2, 32 nm; Al_2O_3+CeO_2, 30 ppm,	2-step	BTE ↑	NOx ↓, HC ↓, CO↓, soot ↓
[26]	DEUTZ F1L511, 1-cylinder, four -stroke, DI, AC, 24 °C. A, BTDC; 175 bars	1500 rpm; 17.5:1	Egyptian Jojoba oil	Al_2O_3, 50–100 nm	20/30 mg/L	2 -step	BTE ↑	NOx ↓, HC ↓, CO↓, soot ↓
[27]	Kirloskar oil engines, single cylinder, 240, 4-stroke, 220 bars	1500 rpm; 16:1	Canola Oil methyl ester	Acetylferrocene, AcCp2Fe and palladium (II), PdL	25 ppm	2-step	BTE ↑	CO↓ NOx ↓, HC ↓,
[28]	Kirloskar, Single cylinder, four -stroke, DI engine, 23°BTDC, 220 bars	1500 rpm; 17:1	*Calophyllum inophyllum* methyl ester	TiO_2; 30–40 nm	40 ppm TiO_2; $(CH_3)_3{\cdot}NH_4$	2-step	BTE ↑	NOx ↓, HC ↓, CO↓, soot ↓
[29]	Single-cylinder, four -stroke, WC, 23°BTDC, 205 bars	1500 rpm; 17:1	Simarouba methyl ester (SME)	Graphene Oxide; 22.5 nm–26 nm	20–60 ppm GO; SDS	2-step	BTE ↑	NOx ↓, HC ↓, CO↓,
[30]	Kirloskar (TV1), 4-Stroke, single cylinder, WC, 23°BTDC, 250 bar (modified)	1500 rpm; 17:1	*Calophyllum inophyllum* methyl ester	CeO_2; 25 nm	40-ppm	2-step	BTE ↑	NOx ↓, HC ↓, CO↓, soot ↓
[31]	Kirloskar, 4- stroke, single cylinder, DI diesel engine, 23, 27, and 19°BTDC	1500 rpm; 17:1	Jojoba methyl ester B20 and ethanol 10%-BDE	Al_2O_3; 28–30 nm	25 ppm Al_2O_3 in BDE	2-step	BTE ↑	CO↓ NOx ↓, HC ↓,
This work	Kirloskar AV1), 4-Stroke, single cylinder, WC, 23°BTDC, 220 bar	1500 rpm; 17:1	Juliflora methyl ester	hybrid CeO_2:CuO; MnO_2:Al_2O_3; ZnO:TiO_2; and TiO_2:Al_2O_3	2:1; 1:1, 1:2 and 1:3	2-step	BTE ↑	CO↓ NOx ↓, HC ↓

(a) Juliflora Plant [32] (b) Juliflora seeds [33] (c) Dried Juliflora seeds[34]

Fig. 1. Juliflora plant and seeds [32–34].

where the crushed pieces of Juliflora were contained was gently filled with hexane. When the Soxhlet channel was nearly full, a siphon side arm automatically emptied its contents, thus sending back the solvent down to the distillation flask. The desired compound was concentrated in the distillation flask after several cycles. The obtained Juliflora oil is of low volatility and high viscousity. The extracted oil was then stored in a 2000 mL flask for further analysis.

Biodiesel from Juliflora oil was produced via transesterification, which helps to separate glycerin from the Juliflora oil methyl ester. Standard ASTM test procedures were used to determine the basic thermophysical properties (i.e., acid value, carbon residue, viscosity, density, calorific value, flash point, carbon residue content, iodine value, sulphur content, oxidation stability, cetane number, sulphated ash content, carbon residue content, iodine value, oxidation stability and sulphur contents) of the biofuel. The obtained Juliflora biodiesel had high density, flash point, cetane number, viscosity as well as lower sulphur content compared to those of the standard diesel.

2.2. Preparation of the nanofluids

Nanoparticles have higher surface energies as a result of their high surface areas. As a result, they appear to clump together to form microparticles and begin to settle when dispersed in a fluid, hence, the stability of the suspension is extremely critical for maximizing the mixture's properties. At 105 °C, the nanoparticle precursor was heated in an oven for 20 h. After drying, the particle was pulverized into fine powder and immediately transferred into a muffle furnace at 650 °C for 5 h. The required nanometal oxide was prepared. A known amount (see section 2.3) of nanoparticle with the biodiesel fuel was dissolved to attain gel solution. Based on the concentration of metal additive required, a metal-based reactive nanomaterial mixture was prepared. During nanofluid formation, a dispersant was typically employed as a means of preventing particle agglomeration. In the present study, six different nanoparticles were used namely, copper oxide (CuO), zinc oxide (ZnO), aluminum oxide (Al_2O_3), cerium oxide (CeO_2), manganese oxide (MnO_2) and titanium dioxides (TiO_2). The nanoparticles of different ratios were sonicated and used individually and in combined ratios, while several trial runs were conducted for the nanofluids in order to ascertain the nano-fuel with optimum performance or highest fuel-quality as well as reduced emissions. The different particle blends i.e., TiO_2–Al_2O_3, CeO_2–CuO, MnO_2–Al_2O_3, and ZnO–TiO_2 were used to form the nano-emulsions and their effects were experimented in a CI engine.

2.3. Preparation of all oxides using the sol-gel method

The preparation of all the metal oxides was carried out following different preparation methods as stated in Table 2: For the methods of preparation, please see references.

In the present work, the nanofluids were prepared using the sol-gel method which lasted 32 h. The nanoparticles were isolated and treated with deionized water. With the help of a sonicator (Anbull 6.5L Professional Ultrasonic Cleaner Machine with 304 Stainless Steel and Digital Timer Heater for Jewelry Watch Coin Glass Circuit Board Dentures Small Parts sonics VCX 750 model), and following the two-step method was used to ensure proper mixing of the hydrated salt of the metal oxides with the biofuel for a period of 2 h. Ultrasonication helps to homogeneously disperse the nanoparticles in the deionized water as well as the oil in order to form the desired emulsions at 50–60 kHz for 40 min. Hong et al. [39] demonstrated that the nanofluid stability can be improved at longer sonication times. Their results showed that, prolonged sonication time invariably reduces and prevents the particles from agglomerating. Amrollahi et al. [40] also made similar observations in their experiments. Both works are in agreement that longer sonication time helps to enhance nanoparticle-stability. Ruan and Jacobi [41] further stated that ultrasonication can break down/prevent particle-agglomeration thereby promoting better and stable distribution of nanoparticles in the base fluids. Sodium dodecyl sulfate (SDS) of analytical grade surfactant was added to the nanoparticles for surface modifications and stabilization, to reduce the possibility of coagulation and coalescence, as well as surface tension.

The Ultraviolet spectrophotometer (Jenway 6850/230V Double Beam Spectrophotometer) was used in the assessment of dispersion stability of the NPs and maintained within a wavelength range of 200 nm–1200 nm since the absorption band falls within the range. The van der Waals interactions are responsible for the surfactant tail group to adsorb onto the surface of the NPs [42]. Also, the stability of the nano-fuel blends was observed for three (3) months and 7 days (13 weeks) from the date in which the preparation was carried out.

2.4. The nano-doped fluids

200 mg of each nanoparticle additive prepared in section 2.3 was doped with 1000 mL of biodiesel fuel. In order to ensure a homogeneous mixing of the nano-powder and the biofuel, the mix was sonicated. The changes recorded in the properties of the biodiesel imposed by the introduction of the nanoparticle-additive were examined. The properties of the biodiesel fuel doped with nanoparticle and the characteristics of the diesel, biodiesel and nanoparticle-doped-biofuel are also discussed in the result section.

For clarity, the authors adopted the acronym as follows for all tested fuels.

A - Juliflora biodiesel addition to additive (CeO_2: CuO) with mixing ratio 2:1); B - Juliflora biodiesel addition to additive (MnO_2: Al_2O_3), with mixing ratio 1:1); C - Juliflora biodiesel addition to additive (ZnO: TiO_2) with mixing ratio 1:2); D - Juliflora biodiesel addition to additive (TiO_2: Al_2O_3), with mixing ratio 1:3).

2.5. Characterization of the nanoparticles

The surface morphologies of the admixed nanoparticles were analyzed by scanning electron microscopy (SEM) (Thermofisher scientific Prisma E SEM GX 7330) and the Atomic Force Microscopy (AFM AA2000, Angstrom advanced) for the blended nanoparticles in vertical and horizontal views (i.e., 20 nm and 2 μm).

2.6. Testing of fuels in engine

Kirloskar AV1 was the diesel engine used for the experiment, the engine specification and schematic are illustrated in Table 3 and Fig. 2 respectively. The engine was first run with diesel fuel for 2 h, after which the nano-fuels each, (A, B, C, D) were introduced into the engine and allowed to run for 2 h; this was also done for the Juliflora biodiesel fuel (alone). This process was repeated for all fuels and the engine was operated at several bmep (brake mean effective pressure) based on the SAE J1515 MAR88 standard procedure on engine emission and performance. The Kirloskar AV1 engine test conditions were checked with the REO-DCA controller which was connected through a computer to the engine. For emission levels, the Gas analyzer QRO-402 was used to record the emission properties. The accuracy, range, and levels of uncertainties of the instrument are illustrated in Table 4.

2.7. Estimation of heat release rate (HRR)

For closed systems, the heat released from the chamber follows the first law of thermodynamics, which can be expressed as:

$$\frac{dQ}{dt} = \frac{\gamma}{\gamma - 1} P \frac{dV}{d\theta} + \frac{1}{\gamma - 1} V \frac{dP}{d\theta} \qquad (1)$$

$\frac{dQ}{dt}$ = ΔHRR with time; $\gamma = \frac{Cp}{Cv}$ = (ratio of specific heat capacity at constant pressure to constant volume, approximately = 1.4), V = volume of fuel, P = in-cylinder pressure.

Table 2
Nanoparticle prepared by sol-gel method.

S/N	Nanoparticle	Materials used/Precursor	Grades of chemical	Ref.
1.	TiO_2	The precursor used has 97% purity of Titanium isopropoxide (TTIP, Ti [$OCH(CH_3)_2]_4$) and 99.99% glacial Acetic acid (CH_3COOH) as catalyst all without further purification	Titanium isopropoxide (Sigma-Aldrich); Glacial Acetic acid (SDfine)	[11]
2.	Al_2O_3	24 g of $AlCl_3 \cdot 6H_2O$, 100 mL ethanol, 10.5 mL acetylacetone	Analytical grade	[35]
3	CeO_2	5.0 g of Poly (allylamine) (PAA), 20.0 g of cerium nitrate hexahydrate, distilled water, Glacial acetic acid, 1 M ammonium hydroxide		[7]
4.	MnO_2	$KMnO_4$, (0.25 M) with fumaric acid, 2 mL aqueous solution of NaCl		[36]
5	CuO	Aqueous solution of $CuCl_2 \cdot 6H_2O$ (0.2 M); glacial acetic Acid, 8 M NaOH,	All chemical used are from (Sigma-Aldrich)	[37]
6.	ZnO	Zinc chloride ($ZnCl_2$), distilled water, zinc nitrate ($Zn(NO_3)_2$) and sodium hydroxide (NaOH),	Analytical grade	[38]

Table 3
Specification of the test engine.

Type Kirloskar AV1	Kirloskar, single cylinder CI diesel engine, four stroke, air cooled
Nozzle spray hole diameter	0.3 mm
Injection timing	23 °C bTDC
Bore and stroke	87.5 mm × 110 mm
Angle of fuel spray (cone angle)	120°
Compression ratio	17.5:1
Rated output	5.2 Kw at 1500 rpm
Piston geometry	Hemispherical
Capacity	661 cc
Inlet valve open bTDC	4.5°
Exhaust valve open bBDC	35.5°
Inlet valve close aBDC	35.5°
Exhaust valve close aTDC	4.5°
Load indicator	Digital, range 0–40 kg, supply 220V AC

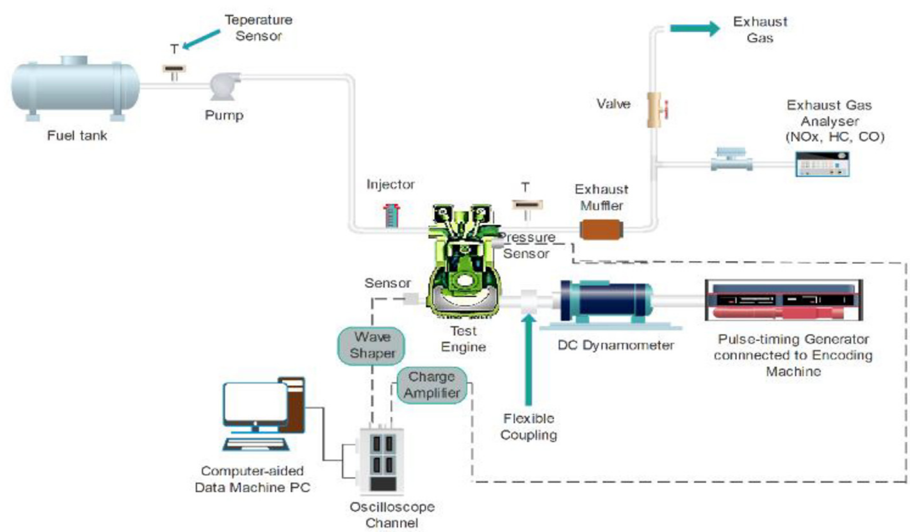

Fig. 2. Schematic of experimental engine test setup.

Table 4
Level of uncertainties, range and accuracy of the instrument.

Specification	Accuracy	Range	Uncertainties
Gas analyzer QRO-402			
Hydrocarbon (HC)	±20 ppm	(0–10,000) ppm	±0.2
Carbon (II) Oxide (CO)	±0.02%	(0–9.99) vol %	±0.2
Oxides of Nitrogen (NO_x)	±10 ppm	(0–5000) ppm	±0.2
Fuel flow meter	±0.1 cc	1–30 cc	±1
Pressure transducer	±0.1 MPa	0–10 MPa	±0.1
Crank angle encoder	0.2 °CA bTDC	0–720 °CA	±0.2
Eddy current dynamometer.	15W	200–8000 W	±0.3

3. Results and discussion

All physicochemical parameters were determined based on ASTM standard procedures as stated in Table 5.

3.1. Properties of the nanoparticles

The HMK-22 Fisher Sub Sieve Sizer/Average Particle Size Analyzer (Fisher Model 95 (Model 14–311A) was used to determine the average particle size of all nanoparticles used. Percentage purity of all oxides (nanoparticles) were analyzed using the HPLC- mass spectrometry. The surface area was analyzed using the Brunauer–Emmett–Teller (BET) (Horiba SA-9600 multipoint surface area analyzer, HORIBA Scientific). BET analysis gives detailed specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyzer. It describes the adsorption of gas molecules on a solid surface. Furthermore, the nanoparticle densities were determined in terms of mass per unit volume. The results are illustrated in Table 6.

Table 7 compares the properties of the Juliflora biodiesel with the Juliflora-nanoparticle blends. The results show that the Juliflora biodiesel possesses a high density, kinematic viscosity, low calorific value and cetane number relative to the nano-additive biofuel. The properties of Juliflora biodiesel lead to poor atomization, longer ignition delay, incomplete combustion, poor mixing with air and low peak pressure. However, the addition of nano-additives improved the biofuel properties. The performance characteristics of the fuel properties given in Table 6 can be found in the supplementary section A-1. The results from BTE obtained by blending the respective Juliflora biodiesel with the nanoparticle is quite lower than the BTE obtained from the diesel fuel, hence, there is need to optimize the fuels to further improve its quality in terms of its performance, combustion and emission properties in the CI engine. Having taken a closer look at the properties (densities, kinematic viscosities, cetane number, flash points and calorific values) of the fuels, several trials of different ratios such as 1:2,1:3,1:4,1:5, 2:1,2:2,2:3,2:4,3:1,3:2 etc., were tested so as to

Table 5
Characteristics of diesel and Juliflora biodiesel.

Parameter	ASTM standard	Crude Juliflora	Diesel	Juliflora biodiesel
Density (kg/m^3)	ASTM D1298	998	838	881
Sulphated ash, mass %	ASTM D874	–	0.001	0.002
Flash point (°C)	ASTM D93	157	68	125
Cetane number	ASTM D976	–	46	53
Kinematic viscosity @ 40 °C, mm^2/s	ASTM D445	4.3	2.31	4.03
Oxidation stability @ 110 °C hr.	ASTM D7545	–	–	9.32
Carbon residue, mass%	ASTM D4530	0.05	0.11	0.003
Latent heat of vaporization kJ/kg	ASTM E2071	–	233	200
Acid value mg KOH/g	ASTM D664	3.13	0.11	0.31
Sulphur value mg/kg	ASTM D4294	low	23	Very low
Calorific value kJ/kg	ASTM D240	38,018	44,960	39,974
Pour point	ASTM D97 -05	–	0	−4
Cloud point	ASTM D2500 -05	−3	3	−1

Table 6
Properties of the nanoparticles.

S/N	Parameter	ZnO	MnO_2	CeO_2	Al_2O_3	CuO	TiO_2
1	Molecular weight g/mol	81.39	70.93	172.115	101.96	79.545	79.87
2	Average particle size (nm)	12	10	11	11	10	13
3	Percentage purity	99.9	98.9	97.9	99.6	99.9	99.5
4	Color	Off-white	Brown black	pale yellow-white	White	black	white
5	Form	conforms	powder	Powder	Powder	powder	powder
6	Chemical abstract service number	1314-132-2	1344-43-0	1306-38-3	1344-28-1	1317-38-0	12,188-41-9
7.	Surface area, m^2/g	88.89	127	200	224.55	99.67	174.5
8.	Density, kg/m^3	561	543	722	395	631	432

Table 7
Properties of Juliflora biodiesel and Juliflora Juliflora-blended nanoparticle additive.

S/N	Parameter	Juliflora biodiesel	Juliflora biodiesel/(CuO), blend	Juliflora biodiesel/(ZnO) blend	Juliflora biodiesel/(Al_2O_3), blend	Juliflora biodiesel/(CeO_2), blend	Juliflora biodiesel/(MnO_2) blend	Juliflora biodiesel/(TiO_2) blend
1	Density (kg/m^3)	881	863	840	867	869	871	835
2	Pour point (°C)	−4	−3	−1	−3	−2	0	0
3	Kinematic viscosity mm^2/s	4.03	2.84	2.37	2.88	2.90	3.00	2.62
4	Flash point (°C)	121	93	88	101	83	90	76
5.	Cetane number	41	40	43	42	42	43	44
6.	Calorific value MJ/kg	40	41	43	42	43	44	44
7	Cloud point (°C)	−1	0	−1	−2	0	−3	−1

obtain the best performance for improved BTE. The Juliflora-nanoparticle blends were seen to have good spray atomization, low viscosity, faster fuel vaporization, improved air – fuel ratio, better combustion, increased peak HRR and low emissions compared to those of the conventional diesel fuel. The results from blended nano-additives on Juliflora biodiesel as demonstrated in Table 8, greatly improved the fuel properties.

3.2. Uncertainty analysis

All used apparatuses are of standard types, and measurements were conducted based on standard procedures. Uncertainties are fundamental in both measurement processes and apparatuses. Several possible sources of uncertainty were observed in the measurements including: (1) imperfect measurement of the properties/characteristics of the fuel and its blends as stated in Table 4. The uncertainty in the results are majorly from equipment

Table 8
Properties of diesel. Juliflora biodiesel and Juliflora biodiesel/additives.

S/N	Parameter	Diesel	Juliflora biodiesel	Juliflora biodiesel + CeO_2:CuO (2:1)	Juliflora biodiesel + MnO_2:Al_2O_3 (1:1)	Juliflora biodiesel + ZnO:TiO_2 (1:2)	Juliflora biodiesel + TiO_2:Al_2O_3 (1:3)
1	Density (kg/m^3)	838	881	841	847	837	844
2	Pour point (°C)	0	−4	−1	−2	0	−2
3	Kinematic viscosity mm^2/s	2.31	4.03	2.91	2.37	2.30	2.34
4	Flash point (°C)	62	121	79	83	72	88
5.	Cetane number	46	53	50	49	46	47
6.	Calorific value MJ/kg	45	40	44	43	45	44
7	Cloud point (°C)	3	−1	2	1	2	1

calibration conditions, sensor selection, observation and test procedure. Based on the uncertainties in the main experiment, the uncertainty of the experimental result should be considered. The result R is a function of independent variable X_1, X_2, X_3 ,… … … … … … … …. .. X_n .

Thus R= (X_1, X_2 , X_3 ,… … … … … … … …. .. X_n). Let E_R be the uncertainty in the result

and e_1 , e_2 , e_3 , …,… …. .. and e_n , be the uncertainties in the independent variables.

The uncertainty was expressed as follows:

$$(\frac{\partial R}{\partial X_1})e_1])(\frac{\partial R}{\partial X_1})e_1]^2 + (\frac{\partial R}{\partial X_2})e_2])(\frac{\partial R}{\partial X_2})e_2]^2 + \ldots + (\frac{\partial R}{\partial X_n})e_n])(\frac{\partial R}{\partial X_2})e_2])(\frac{\partial R}{\partial X_2})e_2]^2 + \ldots + (\frac{\partial R}{\partial X_n})e_n])(\frac{\partial R}{\partial X_2})e_2])(\frac{\partial R}{\partial X_2})e_2]^2 + \ldots + (\frac{\partial R}{\partial X_n})e_n]^2\}^{\frac{1}{2}} \quad (2)$$

The measurements were evaluated with the uncertainty analysis. The average of the measured value is given by ($\overline{X}$):

$$\overline{X} = \frac{\sum X_m}{n} \quad (3)$$

where: n represents the measurement number, and Xm gives the measured value. Thus the standard deviation (SD) is defined as:

$$SD = \sqrt{\sum_{m-1}^{n} (X - X_m)^2} \quad (4)$$

where the uncertainty "U" can be determined from the standard deviation as follows:

$$U = \frac{SD}{\sqrt{n}} \quad (5)$$

The results of all uncertainty based on the experiments conducted are presented in section **A-2**, supplementary file.

Fig. 3(a–d) are the SEM images of the blended nanoparticles.

The surface morphology of the prepared nanoparticles showing the textural and the pore size arrangement of the nanoparticles were observed to determine the porous structures of the nanoparticles. The microstructures of the nanoparticles were determined from the micrographs obtained from SEM. In order to determine the rate of diffusion within the pores and on the surface of the nanoparticles, the images of the nanoparticles were obtained. The morphology shows the particle size distribution of the blended nanoparticle samples. Fig. 3 a, b, c and d shows the nanodispersed form of the blended nanoparticles. The particles are seen to agglomerate. Although nanomaterials always stick together and exist as agglomerates (unless properly treated). In Fig. 3c and d, there are protrusions which are quite prevalent in the nanomaterial. Furthermore, higher levels of blunted sponge-like protrusions were seen in Fig. 3c and d which might be a probable reason for the compatibility of the nanoparticles in the Juliflora biodiesel. In order to have deep insight of the surface morphology of the blended nanoparticles, the atomic force microscopy (AFM) of the nanoparticles was carried out.

Fig. 4(a–d) are the Atomic Force Microscopy (AFM AA2000, Angstrom advanced) and image-surface roughness in vertical and horizontal views (i.e., 20 nm and 2 μm). The sizes of the nanoparticles are far less than the nozzle diameter (i.e., 28 nm) (see Table 3) of the fuel injector, thus indicating that the nanoparticles will not obstruct the flow of biodiesel as well as cause any damage when the mix flows through the nozzle.

Fig. 5 shows the stability of the nanoparticle-surfactant blends with the possibility of reducing coagulation and coalescence, and surface tension. At the end of each week, the absorbance reduces with an increase in time duration as shown for all blended nanoparticles with SDS at different ratios. The ratios of the blended nanoparticles to SDS are in 1:1, 1:2, 1:3 and 1:4 respectively as illustrated in Fig. 5a, b, c and d, showing the absorbance-concentration plot obtained from the UV-V spectrophotometry. The nanofluid blends were kept in static conditions, at the end of every week, hence the absorbance was measured. There was drastic reduction in the absorbance at the thirteenth week. Thus, it is recommended that nanoparticles should be used early after their initial date of blending to prevent agglomeration.

3.3. Emission properties of the fuels and fuel/additive blend

The emission parameters considered in this research include those of nitrogen oxide, hydrocarbons (HC), carbon (II) oxide (CO), and smoke emissions. The emissions were measure in g/kW h.

3.3.1. The hydrocarbon emission

The release of HC emissions is known to be caused by incomplete combustion. Based on the results obtained, for all the test-fuels, at full load condition, the hydrocarbon emissions increased with increased bmep as illustrated in Fig. 6. However, Higher emissions of Unburnt HC is associated with higher viscosities, poor combustion and poor atomization. The unburnt HC emissions are comparatively lower for the biodiesel-nanoparticle mixed fuels relative to the diesel and Juliflora biofuel. There lower HC emissions at varying bmeps for the biodiesel-nanoparticle mixtures are due to lower viscosities, good atomization as well as complete combustion. From the present study, the findings show that the combustion of samples A-D resulted in lower hydrocarbon emissions at full load compared to those of the diesel and undoped biofuel. This shows that samples A -D were effectively combusted at full load, thus leading to good air–fuel ratio in the combustion chamber, with resultant reductions in the expected HC emissions. This is in line with the findings of other studies [15,18,29]. When titanium oxide nano-additives were blended with biodiesel, the best reduction in HC emissions was obtained for all the biodiesel-diesel blends studied. Such HC reduction may be due to the catalytic activity of the metal oxide-based additive during the combustion process [11,17]. This report is also similar to that reported by Ganesh and Gowrishankar [43] on the addition of magnalium (Mg–Al) and cobalt oxide (Co_3O_4)) in biodiesel which helped to substantially reduce the HC emissions. Harveer et al. [44] also obtained lower HC emissions for CeO_2 doped biodiesel-ethanol-diesel blends. Basha and Anand [45] combined water and Al nanoparticle in a bid to improve the combustion characteristics of diesel and biodiesel fuels. Their results showed that water in both diesel and biodiesel had negative effects on HC emissions, however, upon adding the metal oxide-based additives in both fuels, there was a decrease in the resulting HC emissions from the diesel and biodiesel. In the

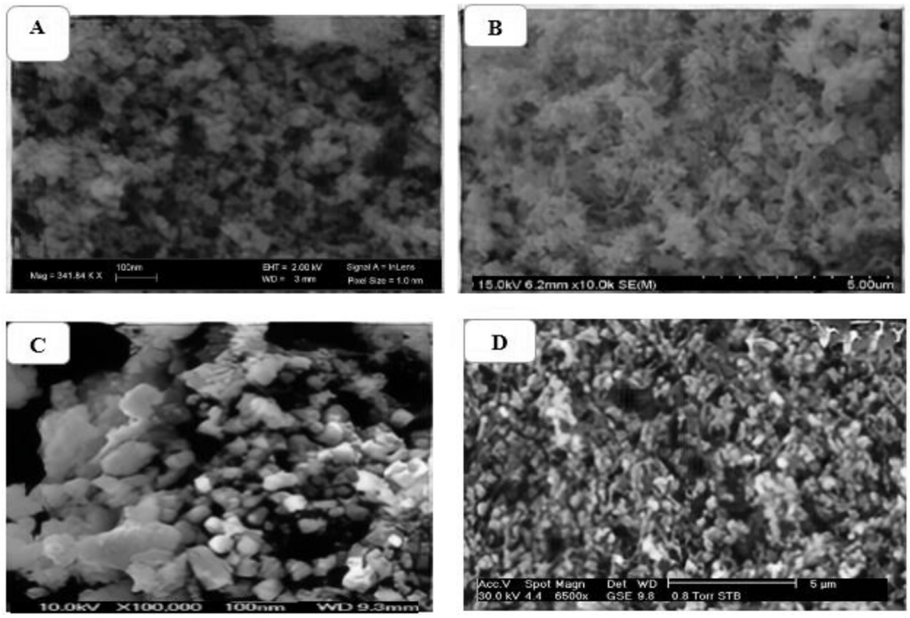

Fig. 3. SEM images of (a) (CeO_2: CuO); (b) (MnO_2: Al_2O_3); (c) (ZnO: TiO_2) (d) (TiO_2: Al_2O_3).

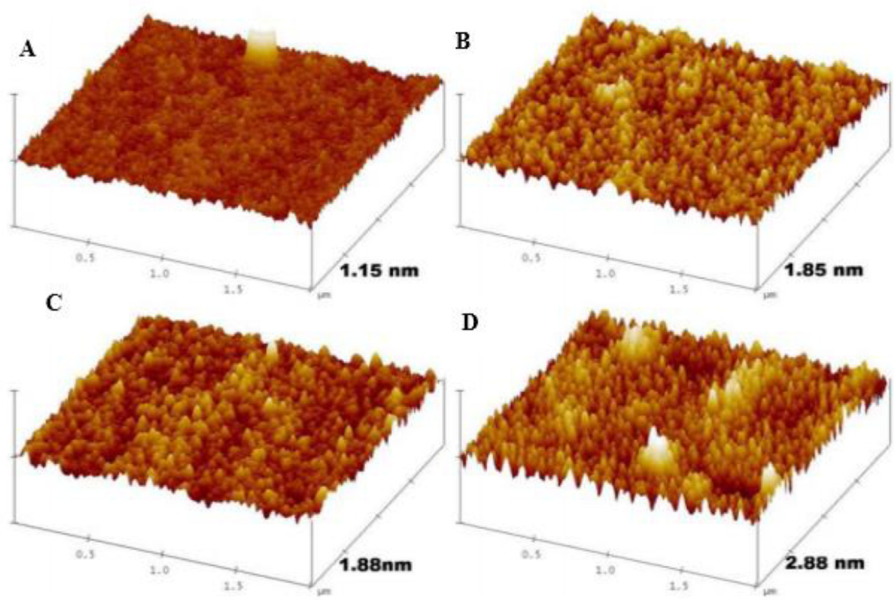

Fig. 4. 3D AFM Image-surface roughness of the blended nanoparticles in vertical and horizontal range (20 nm and 2 μm): (A) CeO_2: CuO, (B) MnO_2: Al_2O_3, (C) TiO_2: Al_2O_3 (d) ZnO: TiO_2.

current study, the HC emission for the neat biodiesel is 0.33 g/kW-hr, while that of the biodiesel-nanoparticle mix are approximately 0.20, 0.21, 0.18, and 0.22 g/kW-hr, respectively, all of which are quite lower than that of the diesel fuel whose HC emission is 0.39 g/kW-hr. However, it can be seen that fuel sample “C” gave the lowest HC emissions for all the analyzed fuels.

3.3.2. Carbon monoxide emission

CO is a colorless, and harmful gas that exits the exhaust of an engine as a result of incomplete combustion of fuel [4]. At high bmeps, due to richer air-fuel ratios, the carbon confined in the injected fuel is not adequately exposed to oxygen for its complete oxidation to carbon dioxide. Alternatively, leaner air-fuel mixtures may lead to a reduction in cylinder temperatures, thus preventing the conversion of carbon monoxide to carbon dioxide [10]. Hence, high carbon monoxide in the chamber may occur as a result of limited amount of O_2 and low cylinder temperature throughout the combustion process. The variation in CO emissions for all the test-fuels was in the range of 3.2–8.9 g/Kw. hr. From the results contained in Fig. 7, the emitted CO decreased with increase in bmep for all the fuels. This may be attributed to increase in fuel injection rate which led to incomplete combustion. From the engine tests conducted, the CO emission is higher at full load condition for the diesel fuel compared to those of the neat biodiesel and biodiesel-

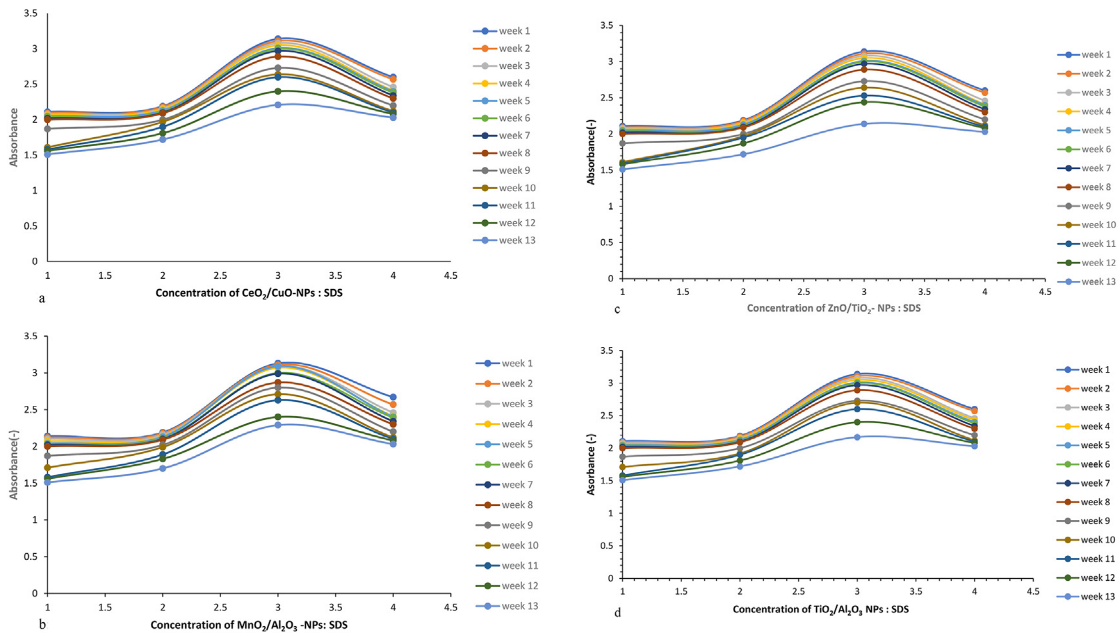

Fig. 5. a) Absorbance vs concentration of CeO_2/CuO NPs: SDS (1:1, 1:2; 1:3, 1:4). b) Absorbance vs concentration of MnO_2/Al_2O_3 NPs: SDS (1:1, 1:2; 1:3, 1:4). c) Absorbance vs concentration of ZnO/TiO_2 NPs: SDS (1:1, 1:2; 1:3, 1:4). d) Absorbance vs concentration of TiO_2/Al_2O_3 NPs: SDS (1:1, 1:2; 1:3, 1:4).

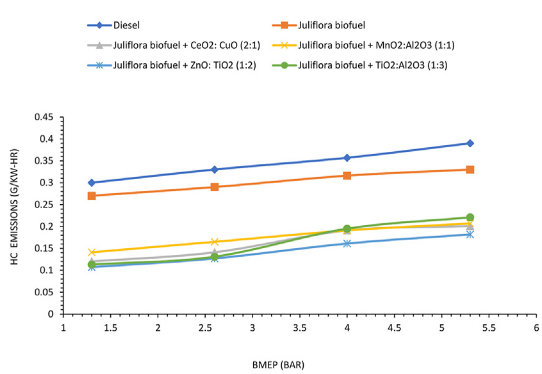

Fig. 6. Variations of Hydrocarbon emissions of different fuels.

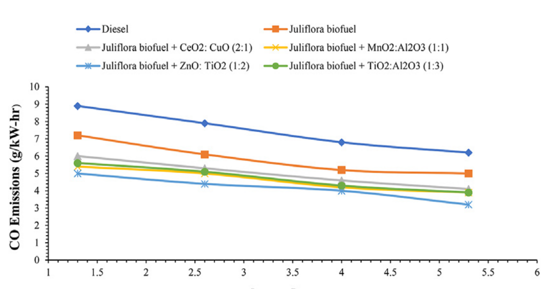

Fig. 7. Variations of carbon monoxide emissions of different fuels.

nanoparticle mixtures [18–20]. According to Oni et al. [46], oil droplets/pockets in a diesel engine, or insufficient turbulence or swirls created in the combustion chamber can result in high CO emissions from diesel fuels. The introduction of biodiesel in diesel engines reduces CO emissions, due to the higher O_2-contents of biodiesel fuels which aids complete combustion in the cylinder with evidential reduction in CO emissions; this also allows for carbon molecules to burn faster. To complement that assertion, the CI engine operated with Juliflora biodiesel-nano-additives produced lower CO emissions compared to those of the standard diesel and Juliflora biodiesel fuels owing to the higher O_2 contents of the nano-doped fuel samples A, B, C and D. These nano-metal oxide additives act as agents of oxidation that aid the higher/complete combustion of the biofuels, thus converting carbon monoxide to carbon dioxide in the process. The emission results from CO are 8.9 and 7.2g/kW-hr for the diesel and Juliflora biodiesel Juliflora biodiesel fuels, while those of the nano additive-biodiesel fuels are A (6 g/kW-hr), B (5.4 g/kW-hr), C (5 g/kW-hr) and D (5.6 g/kW-hr) (Fig. 7). These results corroborate the results presented by other authors [5,9,16,22]. The above-mentioned results indicate that ZnO: TiO_2, in the ratio 1:2 gave the lowest CO emissions and thus the best result for all the test-fuels analyzed; the results are also similar to the reports of refs. [24,29] in which TiO_2 nanoparticles were dispersed in 80 mg/L diesel fuel; they recorded 25% decrease in carbon monoxide emission for the nano-doped biofuel relative to that of the diesel fuel.

3.3.3. NO_X emission

Fig. 8 shows the variation in NO_x emissions with bmep. The NO_x emissions were lower for the biofuels doped with the different nanoparticles compared to those of the standard diesel fuel at constant engine load as observed in Ref. [17]. High temperature during combustion leads to increased NO_x emissions. Two factors that determine the rate of NO_x emissions are the in-cylinder pressure and air–fuel ratio. The formation of NO_x is a function of the temperature-concentration of air in the combustion chamber [22]. The production of NO_x emissions is a function of the extreme temperature in air concentrations/cylinder, as well as the residence time. When the piston is still near the top of the stroke, NO_x emission is established in the chamber. Furthermore, this emission is formed all through the diffusion-controlled combustion phase on the weak side of the reaction zone. Factors such as combustion duration, air-fuel ratio, cylinder temperature and cylinder pressure can influence NO_x emissions [5,28]. During combustion, oxygen and nitrogen react thus giving rise to NO_x emissions at high temperatures. The maximum NO_x emission for the neat biodiesel

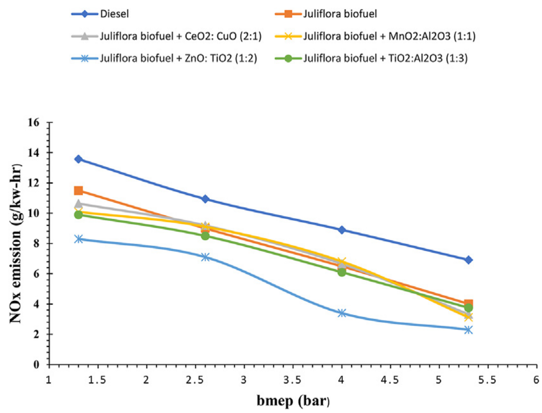

Fig. 8. Variations of NO_x emissions.

recorded for this study is 13.57 g/kW-hr, while those of the biodiesel-additive fuel systems are 11, 11.07, 8.3, 9.9 g/kW-hr compared to the value (11.5 g/kW-hr) obtained for the diesel fuel. Several researchers have also demonstrated similar results; for instance, the work of Koc and Abdullah [47] recorded 8% NO_x emission-reduction for the biodiesel-water-diesel emulsion system adopted. Hence, in the current study, the addition of the nanoparticles into the biofuel led to reductions in NO_x emissions compared with those of the neat biodiesel and diesel fuels. Fuel-samples A, B, C and D gave marginal reductions in NO_x emission during combustion; and this may be due to the catalyzing effect of the metal oxide-based nanoparticle additives which increased the power utility per hour and cylinder temperature that resulted in less fuel consumption at constant power. The increasing impact of the metal oxide-based additives on the cetane number of the biofuel is another factor to be put into consideration for possible NO_x reduction, which may in turn improve the combustion potential of the fuel [7,19,41]. There were reductions in the NO_x emissions as observed for the nanoparticle-biodiesel fuel mixtures and this is in line with the results obtained in Refs. [9,11,17]. Some researchers have also reported the effectiveness/engine-performance of some nanoparticles (Al–Mg) and cobalt oxide (Co_3O_4) in biodiesel [12,19,20], $FeCl_2$ in neat biodiesel and neat diesel [10,21] when used in CI engines. Reports also have it that NO_x can be reduced to N_2 and O_2, as a result of high thermal degradation of the nanoparticles which result in significant reduction/breakdown of NO_x emissions.

3.4. Brake thermal efficiency (BTE)

The engine's performance depends on its BTE, which shows how

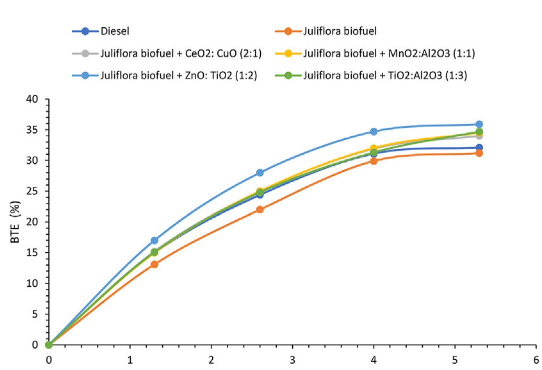

Fig. 9. Variations of BTE.

efficiently the fuel's energy is transformed into mechanical output. Fig. 9 illustrates the variation in BTE of the diesel fuel, biodiesel fuel and biodiesel fuel -additive. The BTEs of all the fuels increased with increase in bmep. However, it can be seen that the biodiesel fuel additive systems gave improved BTEs over the pristine and standard diesel fuel. The observed BTEs for all the test-fuels at full load condition are 32.1, 31.2, 34.0, 34.5, 35.9, and 34.7% for the diesel, Juliflora biodiesel, samples A, B, C and D respectively. These results are in line with the findings of refs. [5,11,19,20]. The BTE improvements for the nanoparticle- Juliflora biodiesel system is as a result of the improved atomization, rapid evaporation and combustion of the nano-doped biofuels relative to the standard and undoped biofuel; this is due to the inducement of better air-fuel mixing, thus providing a higher interfacial area for the surface molecules of the nano-fuel system to react with O_2. It was also noticed that fuel C-(ZnO: TiO_2) with mixing ratio 1:2, gave the highest BTE compared to all other fuels. According to Oni et al. [46], low air-fuel mixing and higher viscosity can give rise to poor atomization, high molecular weight and lower calorific value of any fuel, which can also result in low BTEs. Furthermore, the fuel having higher molecular weight requires more energy and time to degrade, thus increasing the ignition delay period. So, the time needed for combustion is reduced and this may possibly reduce the combustion efficiency. The pure biodiesel's BTE is lowest and those of the standard diesel and nano-doped biofuels are higher due to the higher heating values imposed by the nanoparticles/additives. However, higher BTEs are associated with the inclusion of biodiesel-additives owing to the improvement in combustion properties, high calorific value, cetane number as well as low viscosity, and micro explosion [6–8,28,29].

3.5. Combustion characteristics

The combustion characteristics of the diesel engine fueled with diesel, Juliflora biodiesel and Juliflora biodiesel nano-additives are discussed with highlights on the effects of the in-cylinder gas pressure and heat release rate (HRR) on the performance of the compression ignition engine.

3.5.1. Cylinder-pressure variation

The in-cylinder pressure is an important parameter in diesel engines which converts heat energy to useful work in accordance with the first law of thermodynamics [48]. Data generated from this can be useful for HRR and cumulative HRR calculations. The variation in in-cylinder gas pressure is related to the crank angle (CA) for all the test-fuels at 100% load (Fig. 10). As the engine load increased, there was also an increase in the in-cylinder gas pressure due to more fuel being consumed. Notably, the in-cylinder gas pressure variation with crank angle demonstrated similar drifts for all the tested fuels. The diesel engine operated with the biodiesel nano additive biofuel mix gave higher in-cylinder peak pressures compared to the Juliflora biodiesel and diesel fuel; this was caused by the higher calorific value of the nano-biodiesel fuels that resulted in higher peak cylinder gas pressures. The maximum peak cylinder pressure was obtained for the nano-additive biofuel mixtures and the recorded in-cylinder pressures are A (81 bar), B (81.6 bar), C (82 bar) and D (81.7 bar), whereas for diesel and Juliflora biodiesel, their pressures are 80.2 and 74.2 bar respectively. These results corroborate the findings of refs. [12,16,19–21]. It can also be seen that combustion starts earlier for the undoped-biodiesel than for other fuels at full load (Fig. 10). According to some researchers, high cetane number and O_2 content of pure biodiesel advances the fuel evaporation and atomization process, thus reducing the delay period and thus results in low peak cylinder pressures [4,43]. The nano additive-biodiesel fuels gave

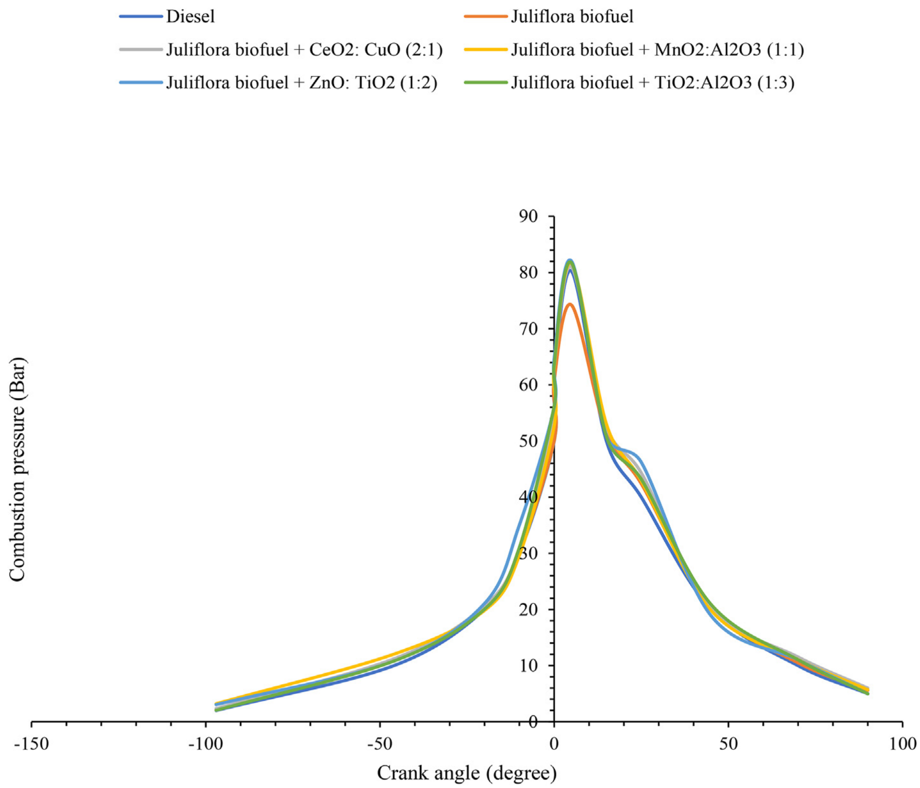

Fig. 10. Variation of In-cylinder pressure with crank angle.

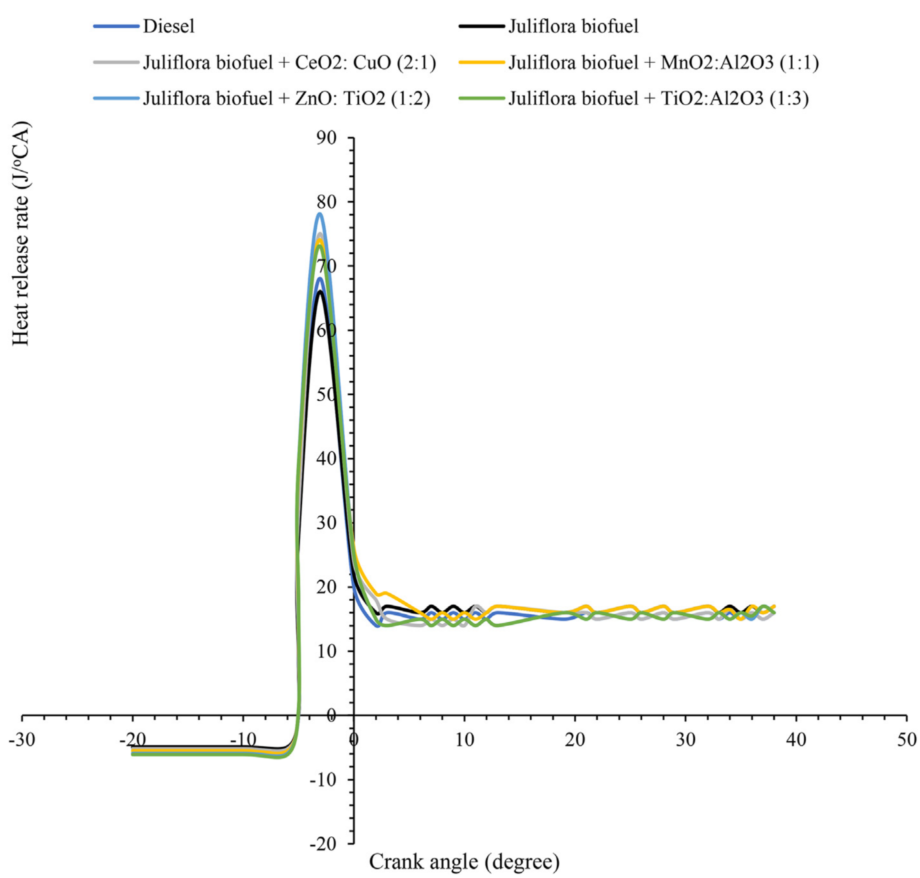

Fig. 11. Heat release rate versus Crank angle degree.

marginal high peak in-cylinder pressures as a result of the effects of the nanoparticles in the biofuel. Alternatively, the presence of nanoparticles in the Juliflora biodiesel fuel produced a catalytic effect during combustion, thus leading to shorter ignition delays and increased/improved cetane numbers, thus resulting in complete combustion of the nano-doped biofuels [2,16,20].

3.5.2. Heat release variation (HRR)

Fig. 11 shows the variation of HRR for all the test-fuels (diesel, Juliflora biodiesel and Juliflora biodiesel nano − additives (A-D)) with respect to crank angle. As observed, the HRRs of all the tested fuels followed the same pattern. As stated in a previous section, the combustion process started earlier for the Juliflora biodiesel. Furthermore, the lower HRR were seen for Juliflora biodiesel as well as the diesel fuel with respect to the Juliflora biodiesel + nano-additive fuels A, B, C and D. The addition of the nano-additives to the Juliflora biodiesel increased their HRRs relative to that of the diesel fuel due to the enshrined peak pressures and enhanced combustion obtained for the nano-additive fuel systems compared to the pure biodiesel and normal diesel fuel. It is also noted that the exhaust gas recirculation with respect to the biodiesel nano -additive systems increased their HRRs as a result of the availability of unburnt fuel in the air-fuel mixture which produces speedy combustion and improved HRR [20]. The peak HRR for the Juliflora biodiesel nano -additive fuels was higher compared to that of the diesel fuel as a result of improved combustion and shorter ignition delay period. The heat release rate chart describes the following stages; pre-mixed combustion, ignition delay, mixed controlled combustion and the late combustion phases. The maximum HRR at full load for diesel and Juliflora biodiesel fuels are 68 J/deg and 66 J/deg respectively, while those of the Juliflora biodiesel-nano additive fuels are 75, 74, 78, and 73 J/deg for fuels A, B, C and D, with fuel sample C giving the highest HRR. The net HRR is highest for the biofuel-nano -additive system “C”, as a result of the fuel experiencing a rapid pre-mixed combustion followed by diffusion and combustion, which corroborates the observations in Refs. [3,14]. The pre-mixed fuel burns rapidly and produces maximum heat accompanied by controlled heat-release. According to Amrollahi et al. [40], the addition of nanoparticle to biodiesel fuel increases its HRR, this is also in line with the findings in Refs. [5,9,17]. The main reason for high HHRs for the nano-additive fuel systems may be due to the fuel's spray characteristics followed by good fuel-air mixing and longer premixed combustion periods which result in higher residence times, thus indicative of the essence of the nanoparticles as HRR enhancer for Juliflora biofuel.

4. Conclusion

The impact of nanoparticle addition on Juliflora biodiesel fuel's physico-chemical properties, combustion, emission and performance characteristics were investigated. The study confirms the suitability of CeO_2: CuO, MnO_2:Al_2O_3, ZnO: TiO_2 and TiO_2:Al_2O_3 nanoparticles as improvers of the overall engine performance of diesel engine fueled with Juliflora biodiesel fuel. The observed improvements validate the potentials of the blended/added nano-additives to the Juliflora biodiesel which in turn minimize both environmental and energy associated problems with the use of pure Juliflora biodiesel. Thus, the conclusions from this study include:

1. The addition of nanoparticles in Juliflora biodiesel in specific amounts did not produce any problems in the physicochemical properties such as density, kinematic viscosity, distillation characteristics, sulphur, and CFFP, however, there were slight increases in the cetane number and flash point temperatures of the fuels.
2. There was a marginal increase in the engine performance for the nanodoped- Juliflora biodiesel with the ZnO−TiO_2 hybrid nanoparticles giving the best improved properties of the biofuel owing to the property-changes of the fuels aided by the particles which in turn gave improved BTEs, bmeps, in-cylinder peak pressures as well as CO, HC and NO_x emissions.
3. The NO_x, CO, and HC emissions were lower for the nano-doped fuels relative to the standard diesel and Juliflora biodiesel fuels.
4. The addition of nanoparticles in the biodiesel increased the peak HRR, reduced the ignition delay period and enhanced the initiation of combustion. Operating a CI engine with all the nano additive-fuel based systems gave similar HRR curves and in-cylinder gas pressures at full load condition for all the fuels as compared with that of standard diesel fuel. Nevertheless, the peak in-cylinder gas pressure increased considering the inclusion of the nanoparticles which offered synergistic effects in the final fuel's properties thus enhancing the engine's performance.

Limitations and future studies

One of the limitations to this work is funding, the project is capital intensive and very expensive.

Suggestions for future studies are stated in the recommendation section of the manuscript.

Recommendation

Investigations on the long-term effects on the engines life span/salvage value are required in order to properly evaluate the influence of these nanoparticles on engine wear. This is currently under investigation as Part B of this project.

Author statement

Babalola Aisosa Oni: Conceived the idea, carried out the experimentation, Made the first draft copy of the manuscript. Samuel Eshorame Sanni: Made useful contributions at different stages of the research, involved in recomposing key sections of the manuscript, results and discussion. Oyinkepreye D. Orodu: Result analyses. and general editing of manuscript. Temitope F. Ogunkunle: Data curation, Made very vital/useful observations at the experimental.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.energy.2021.122635.

References

[1] Arockiasamy P, Anand RB. Performance, combustion and emission characteristics of a D.I. diesel engine fuelled with nanoparticle blended jatropha biodiesel. Period Polytech - Mech Eng 2015;59(2):88−93.

[2] Khan H, Soudagar MEM, Kumar RH, Safaei MR, Farooq M, Khidmatgar A, Banapurmath NR, Farade RA, Abbas MM, Afzal A. Effect of nano-graphene oxide and n-butanol fuel additives blended with diesel—nigella sativa biodiesel fuel emulsion on diesel engine characteristics. Symmetry 2020;12:961.

[3] Idriss H. Ethanol reactions over the surface of noble metal/cerium oxide catalysts. Platin Met Rev 2004;48:105–15.
[4] Asokan Bade, Nekkanti PKK, Gopal Gutta VM Sri Sai. Performance, combustion and emission characteristics of Juliflora biodiesel fuelled DI diesel engine. Energy 2019;173:883–92.
[5] Rajeshwaran M, Marimuthub P, Mayilvelnathana V, Parthasarathic R. Studies on Prosopis juliflora methyl ester production and its effect on DI diesel engine. Indian J Geo Mar Sci 2020.
[6] Soudagar MEM, Nik-Ghazali N-N, Abul Kalam M, Badruddin IA, Banapurmath NR, Akram N. The effect of nano-additives in diesel-biodiesel fuel blends: a comprehensive review on stability, engine performance and emission characteristics. Energy Convers Manag 2018;178:146–77.
[7] Hosseini M1, Amjadi I, Mohajeri M, Mozafari M. Sol–gel synthesis, physico-chemical and biological characterization of cerium oxide/polyallylamine nanoparticles. Polymer 2020.
[8] Sajith V, Sobhan CB, Peterson GP. Experimental investigations on the effects of cerium oxide nanoparticle fuel additives on biodiesel. Adv Mech Eng 2010: 1–6 [ID 581407].
[9] Gavhane RS, Kate AM, Soudagar MEM, Wakchaure VD, Balgude S, Rizwanul Fattah IM, Nik-Ghazali N-N, Fayaz H, Khan TMY, Mujtaba MA, et al. Influence of silica nano-additives on performance and emission characteristics of soybean biodiesel fuelled diesel engine. Energies 2021;14:1489. https://doi.org/10.3390/en14051489.
[10] Venkatesan SP, Ganesan S, Joshua Prabhahar J, Venkateswara Rao Kaveti, Anoop Akhil, Andrew Aghil. Performance and emission test on diesel engine using Prosopis juliflora seed oil. Int J Ambient Energy 2020. https://doi.org/10.1080/01430750.2020.1719887.
[11] Dubey RS, Krishnamurthy KV, Singh S. Experimental studies of TiO2 nanoparticles synthesized by sol-gel and solvothermal routes for DSSCs application. Res Phy 2019;14:102390.
[12] Venkatesan SP, Kadiresh PN. Influence of an aqueous cerium oxide nanofluid fuel additive on performance and emission characteristics of a compression ignition engine. Int J Ambient Energy 2016;37(1):64–7. https://doi.org/10.1080/01430750.2014.882863.
[13] Milano J, Ong HC, Masjuki HH, Silitonga AS, Chen WeiHsin, Kusumo F, Dharma S, Sebayang AH. Optimization of biodiesel production by microwave irradiation-assisted transesterification for waste cooking oil- Calophyllum inophyllum oil via response surface methodology. Energy Convers Manag 2018;158:400–15.
[14] Kim HJ, Park SH, Lee CS. Impact of fuel spray angles and injection timing on the combustion and emission characteristics of a high-speed diesel engine. Energy 2016;107:572–9.
[15] Gowtham M, Prakash R. Control of regulated and unregulated emissions from a CI engine using reformulated nano fuel emulsions. Fuel 2020;271:117596.
[16] Datta MM, Mukherjee P, Ghosh B, Jha TB(. In vitro clonal propagation of biodiesel plant (Jatropha curcas L. Res Commun 2007.
[17] Yew Guo Yong, Lee Sze Ying, Show Pau Loke, Tao Yang, Law Chung Lim, Nguyen Thi Trung Chinh, Chang Jo-Shu. Recent advances in algae biodiesel production: from upstream cultivation to downstream processing. Bioresource Technology Reports; 2019. p. 100227. https://doi.org/10.1016/j.biteb.2019.100227.
[18] Dhinesh B, Annamalai M. A study on performance, combustion and emission behaviour of diesel engine powered by novel nano nerium oleander biofuel. J Clean Prod 2018. https://doi.org/10.1016/j.jclepro.2018.06.002 ( ), S0959652618316500.
[19] Dreizin EL. Phase changes in metal combustion. Prog Energy Combust Sci 2000;26:57–78.
[20] Kenneth KK, Risha GA, Evans BL, Boyer E. Potential usage of energetic nano-sized powders for combustion and rocket propulsion. Mater Res Soc Symp MRS Proc 2003;800:3–14.
[21] Farfaletti A, Astorg C, Martini G, Manfredi U, Mueller A, Rey M. Effect of water/fuel emulsions and a cerium-based combustion improver additive on HD and LD diesel exhaust emissions. Environ Sci Technol 2015;39:6792–9. 2005.
[22] Karthikeyan S, Prathima A. Emission analysis of the effect of doped nano-additives on biofuel in a diesel engine. Energy Sources, Part A Recovery, Util Environ Eff 2016;38(24):3702–8. https://doi.org/10.1080/15567036.2016.1166164.
[23] Ghafoori M, Ghobadian B, Najafi G, Layeghi M, Rashidi A, Mamat R. Effect of nano-particles on the performance and emission of a diesel engine using biodiesel-diesel blend. Int J Automot Mech Eng 2015;12:3097–108. https://doi.org/10.15282/ijame.12.2015.23.0258.
[24] Sivakumar M, Sundaram NS, Thasthagir MHS. Effect of aluminium oxide nanoparticles blended pongamia methyl ester on performance, combustion and emission characteristics of diesel engine. Renew Energy 2018;116: 518–26.
[25] Prabu A. Nanoparticles as additive in biodiesel on the working characteristics of a DI diesel engine. Ain Shams Eng J 2017.
[26] El-Seesy AI, Attia AM, El-Batsh HM. The effect of aluminum oxide nanoparticles addition with Jojoba methyl ester-diesel fuel blend on a diesel engine performance, combustion and emission characteristics. Fuel 2018;224: 147–66.
[27] Keskin A, Yaşar A, Yıldızhan Ş, Uludamar E, Emen FM, Kulcu N. Evaluation of diesel fuel-biodiesel blends with palladium and acetylferrocene based additives in a diesel engine. Fuel 2018;216:349–55.
[28] Praveen A, Lakshmi Narayana Rao G, Balakrishna B. Performance and emission characteristics of a diesel engine using *Calophyllum inophyllum* biodiesel blends with TiO2 nanoadditives and EGR. Egypt J Pet 2017. 11/10/2017.
[29] Paramashivaiah B, Banapurmath N, Rajashekhar C, Khandal S. Studies on effect of graphene nanoparticles addition in different levels with Simarouba biodiesel and diesel blends on performance, combustion and emission characteristics of CI engine. Arabian J Sci Eng 2018:1–9.
[30] Vairamuthu G, Sundarapandian S, Kailasanathan C, Thangagiri B. Experimental investigation on the effects of cerium oxide nanoparticle on *Calophyllum inophyllum* (Punnai) biodiesel blended with diesel fuel in DI diesel engine modified by nozzle geometry. J Energy Inst 2016;89(4):668–82.
[31] Venu H, Madhavan V. Effect of Al2O3 nanoparticles in biodiesel-diesel-ethanol blends at various injection strategies: performance, combustion and emission characteristics. Fuel 2016;186:176–89.
[32] http://tropical.theferns.info/image.php?id=Prosopis+juliflora.
[33] https://keys.lucidcentral.org/keys/v3/eafrinet/weeds/key/weeds/Media/Html/Prosopis_juliflora_(Prosopis_or_Mesquite).htm.
[34] https://www.indiamart.com/proddetail/prosopis-juliflora-tree-seed-14990421948.html.
[35] Basha SJ, Anand RB. An experimental investigation in a diesel engine using carbon nanotubes blended water–diesel emulsion fuel., proceedings of the institution of mechanical engineers, part A. J Power Energy 2011.
[36] Dubey RS, Krishnamurthy KV, Singh S. Experimental studies of TiO2 nanoparticles synthesized by sol-gel and solvothermal routes for DSSCs application. Res Phy 2019;14:102390.
[37] Ashrafi F, Babanejad SA, Ghasemi A. Synthesis of alumina nano powder using sol-gel method and chelate precursor. Asia Acad Res J Multidiscip 2015;2(Issue 2).
[38] Hosseini M1, Amjadi I, Mohajeri M, Mozafari M. Sol–gel synthesis, physico-chemical and biological characterization of cerium oxide/polyallylamine nanoparticles. Polymer 2020.
[39] Hong KS, Hong T, et al. Thermal conductivity of Fe nanofluids depending on the cluster size of nanoparticles. Appl Phys Lett 2006;88:031901.
[40] Amrollahi A, Hamidi AA, Rashidi AM. The effects of temperature, volume fraction and vibration time on the thermo-physical properties of a carbon nanotube suspension (carbon nanofluid). Nanotechnology Aug. 2008;19(31). Article 315701.
[41] Ruan B, Jacobi AM. Ultrasonication effects on thermal and rheological properties of carbon nanotube suspensions. Nanoscale Res. Lett. 2012;7(1):127.
[42] Nanthagopal K, Ashok B, Tamilarasu A, Johny A. Mohan A Influence on the effect of zinc oxide and titanium dioxide nanoparticles as an additive with Calophyllum inophyllum methyl ester in a CI engine. Energy Convers Manag 2017;146:8–19.
[43] Ganesh D, Gowrishankar G. Effect of Nano-fuel additive on emission reduction in a Biodiesel fuelled CI engine. IEEE 2011.
[44] Harveer PS, Kumar N, Alhassan Y. Performance and emission characteristics of an agricultural diesel engine fueled with blends of Sal methyl esters and diesel. Energy Convers Manag 2015;90:146–53.
[45] Basha SJ, Anand RB. An experimental investigation in a diesel engine using carbon nanotubes blended water–diesel emulsion fuel., proceedings of the institution of mechanical engineers, part A. J Power Energy 2011.
[46] Oni BA, Sanni SE, Daramola M, Olawepo AV. Effects of oxy-acetylation on performance, combustion and emission characteristics of Botryococcus braunii microalgae biodiesel-fuelled CI engines. Fuel 2021:296 120675.
[47] Koc AB, Abdullah M. Performance and NOx emissions of a diesel engine fueled with biodiesel-diesel-water nanoemulsions. Fuel Process Technol 2013;109: 70–7.
[48] Sanni SE, Ovie FS, Ajayi O, Agboola O, Adefila SS, Popoola P, Sadiku R. Effect of controlled pH and concentrations of copper sulphate and silver nitrate solutions during nanoparticles synthesis towards modifying compressor oil yield stress and lubricity for improved refrigeration. Heat Mass Tran 2020;56: 931–61. https://doi.org/10.1007/s00231-019-02746-3.