Microscopic Characteristics of Biodiesel – Graphene Oxide Nanoparticle Blends and their Utilisation in a Compression Ignition Engine

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Abstract

Use of nano-additives in biofuels is an important R&D topic for achieving optimum engine performance with reduced emissions. In this study, rice bran oil was converted into biodiesel and graphene oxide (GO) nanoparticles were infused into biodiesel-diesel blends. Two blends containing (i) 5% biodiesel, 95% diesel and 30 ppm GO (B5D95GO30) and (ii) 15% biodiesel, 85% diesel and 30 ppm GO (B15D85GO30) were prepared. The fuel properties like heating value, kinematic viscosity, cetane number, etc. of the nanoadditives–biodiesel-diesel blends (NBDB) were measured. Effects of injection timing (IT) on the performance, combustion and emission characteristics were studied. It was observed that both B15D85GO30 and B5D95GO30 blends at IT23° gave up to 13.5% reduction in specific fuel consumption. Compared to diesel, the brake thermal efficiency was increased by 7.62% for B15D85GO30 at IT23° and IT25°. An increase in IT from 23° to 25° deteriorated the indicated thermal efficiency by 6.68% for B15D85GO30. At maximum load condition, the peak heat release rates of NBDB were found to be lower than the pure diesel at both IT. The CO, CO_2 & NOx emissions were reduced by 2-8%. The study concluded that B15D85GO30 at IT23° gave optimum results in terms of performance, combustion and emission characteristics.

Keywords

Combustion; Emission; Graphene oxide; Injection timing; Performance; Rice bran biodiesel

Nomenclature

B0	Pure diesel (0% biodiesel)
B15D85GO30	15% biodiesel, 85% diesel and 20 ppm GO
B5D95GO30	5% biodiesel, 95% diesel and 30 ppm GO
BDB	Bio-diesel blends
BSFC	Brake specific fuel consumption
bTDC	Before top dead centre
BTE	Brake thermal efficiency
CNT	Carbon nanotubes
CA	Crank angle
CI	Compression ignition
COOH	Carboxylic acid
CR	Compression ratio
E5	Engine test express software
EG	Exhaust gas
EGT	Exhaust gas temperature
GNP	Graphene nano-platelets
GO	Graphene oxide
GO-BDB	Graphene oxide biodiesel blends
GONP	Graphene oxide nanoparticle
HRR	Heat release rate
IMEP	Indicated mean effective pressure
IT	Injection timings
ITE	Indicated thermal efficiency
JCPDS	Joint committee on powder diffraction standards
MWCNT	Multiwalled carbon nanotubes
NBDB	Nano additives – biodiesel - diesel blends
NP	Nano-particles
OH	Hydroxyl group
PM	Particulate matter
PME	Pongamia methyl ester
SEM	Scanning electron microscope
TEM	Transmission electron microscope
UHC	Unburnt hydrocarbon
VCR	Variable compression ratio
XRD	X-ray diffraction

1. Introduction

Biodiesel is considered to be a suitable replacement for pure diesel for using in the compression ignition (CI) engines. This biodiesel can be extracted from various feedstock such as vegetable oil, animal fats, non-edible oils [1]. Used cooking oil is one of the commonly used feedstocks which can be converted into high-quality biodiesel [2]. The use of non-waste based feedstock such as blends of hazelnut oil and rapeseed oil biodiesels were also investigated by the researcher [3]. However, the biodiesel application in compression ignition (CI) engines is hindered by some drawbacks such as higher viscosity, higher density, lower cloud point, inefficient fuel atomization, and higher NOx emissions [1,4,5]. To overcome these drawbacks, some of the techniques investigated by the researchers are (i) use of fuel additives, (ii) use of hybrid fuels, and (iii) engine parameters modifications. One such technique is the inclusion of nano-particles additives with bio-diesel blends (BDB) [2]. Literature reported that nano-additives improved thermo-physical properties, performance characteristics (specific fuel consumption, brake power, etc.) [6], and combustion characteristics such as heat release rate (HRR) [7–10] of the pure diesel fuel. The performance and emission characteristic of the engine depends on the type and amount of nano-additives, and engine parameters (injection timing, injection pressure, compression ratio, etc.) [11–14]. The following literature investigated the behavioural variations of commonly used nano-particles (aluminium oxide, iron, and cerium oxide) and recently evolved nano-particles like graphene oxides and carbon nanotubes (CNT) when added to biofuels.

Adding the metal oxides of aluminium, titanium, silicon, etc. with biodiesel increases the thermo-physical properties (viscosity, cetane number and heating value) and helps in augmenting the thermal efficiency with the reduction in brake specific fuel consumption (BSFC) as compared to the fossil diesel fuel [15,16]. The Al_2O_3 nanoparticles mixed with water (nano-fluids) was added to fossil diesel and tested in a diesel engine [14]. The authors reported that the additives improved the brake thermal efficiency (BTE) by 5.5% with a significant reduction in exhaust gas emissions [17]. Another study reported that Al_2O_3 nanoparticle mixed with honge oil methyl ester improved the BTE by 10% with 11% reduction in BSFC. Also, the HC and CO emissions were dwindled by 26% and 43% respectively [18]. Also, it is inferred from the same study that increasing the blending ratio of nanoparticles more than 60 ppm reduces the fuel stability of the NBDB [18]. The aluminium oxide, boron oxide and iron nano-additives were added separately to diesel fuel; the study found that at higher loads, the peak combustion pressure and BSFC were reduced when compared to the pure diesel operation [19]. An increase in BTE was observed when aluminium oxide nano-particles were added with Mahua BDB [20,21]. An improvement in the HRR was reported when Al_2O_3 nanoparticles were added in biodiesel-diesel blends [7]. Compared to pure diesel operation, a notable enhancement in the BTE (about 12%) was reported when aluminium oxide and cerium oxide nanoparticles were added with biodiesel-diesel blends [20]. The authors have reported that nano-additives gave up to 30% and 38% decrease in the CO and HC gas emissions as compared to pure diesel. They recommended that the effects of other engine parameters like ignition timing, injection pressure should be investigated in the near future with various nanoparticles-biodiesel blends [20].

The injection timings and injection pressure play an essential role in determining the combustion characteristics of the NBDB [22]. The performance characteristic of a diesel engine was improved by adding pentanol and titanium oxides nano-additives individually with corn biodiesel. The effect of injection pressure was investigated and it was inferred that the additives improved the BTE to the engine and reduced the CO_2 and NOx emissions [23]. However, the effects of injection timings were not investigated by the authors. Three different nanoparticles titanium dioxide, copper nitrate and cerium acetate were added separately to pure diesel and their combustion and emission characteristics were analysed [24]. The authors found that there was a reduction in the sound level of the engine block leading to the effective control of vibration [24]. Cerium oxide (CeO_2) was added with pongamia methyl ester (PME), it was inferred that the CeO_2 expedites the procedure of burning because of its high surface: volume ratio [8]. Another study reported that compared to CeO_2 nanoparticles, cerium composite oxide ($Ce_{0.5}Co_{0.5}$) reduced a higher amount of CO, NOx and UBHC emissions when blended with waste cooking oil [25]. Titanium oxide nanoparticles were diffused with palm oil biodiesel-diesel blends to reduce the BSFC and downturn the exhaust gas emissions like HC and CO. The study found that at part-load conditions, the nitrates of oxygen can be significantly decreased with the use of exhaust gas recirculation [26].

Recently, studies investigated the effect of various injection timing in nanoparticle enhanced BDB [9]. Nickel oxide was chosen as the nanoparticle and the effect of three injection timings (23°bTDC, 19°bTDC and 27°bTDC) on the behavioral characteristics were investigated. The authors reported that advancing the injection timing (to IT27°) improved the HRR and BTE of the engine. From the above literature review, it can be summarised that the traditional nanoparticle impregnation with biodiesel improves the combustion and performance characteristics with a considerable curtailment in the exhaust emissions. Recently, nano-additives such as graphene, carbon nanotubes are being investigated by the researchers due to their better physicochemical properties. However, hardly any literature was available pertaining to GO and CNT impregnation with biodiesel.

The effects of GO enhancement with dairy scum oil in the concentration of 20-60 ppm revealed that the BTE was improved by 12%; BSFC, UBHC emission, smoke emission and CO were reduced by 9%, 21%, 24%, and 39% respectively. Better HRR and peak in-cylinder pressures were achieved for the nanoparticle-biodiesel blends as compared to pure biodiesel [10]. Graphene quantum dots increased the torque and power output of the engine by 12% and 28% respectively when fueled with ethanol-biodiesel blends, with a considerable reduction (about 14%) in BSFC. The authors observed a significant reduction (about 30%) in the CO and HC emissions as compared to pure diesel operation [27]. Multi-walled carbon nanotube was mixed with jatropha biodiesel in various concentrations between 10-50 mg/l, a 16% improvement in BTE and 15% reduction in BSFC were observed for blended biodiesel as compared to pure biodiesel operation. Furthermore, the authors reported that approximately 50% reduction in the CO and UBHC were observed for the CNT blended biodiesel when compared to virgin biodiesel [28]. Another literature reported that as compared to neat biodiesel, the brake power was considerably increased when graphene oxide and CNT were impregnated in camelina oil biodiesel [29]. They reported that the UHC and CO emissions were significantly reduced, NO_x emission was slightly increased [29]. Compared to neat biodiesel operation, the BTE was increased by 17% when graphene oxide was added to jatropha methyl ester [30]. The HRR and in-cylinder pressure were increased by 6% and 8% respectively. The authors reported that compared to neat biodiesel operation, the nano-additive blends gave reduced CO, UHC and NO_x emissions by 60%, 50% and 15% respectively [30]. Another study carried out by the same authors reported that the graphene nanoparticles' impregnation in jatropha methyl ester reduced BSFC by 20% as compared to neat biodiesel [31].

The BSFC was decreased by 35% when a nano-additive fuel blend was used in the diesel engine consisting a mixture of GO, multi-walled carbon nanotubes (MWCNTs), n-butanol and jatropha methyl ester [32]. The CO, NOx and UBHC emissions were reduced by 55%, 50% and 45% respectively [32]. The GO was impregnated with Ailanthus altissima biodiesel blends at various concentrations (30 ppm, 90 ppm); the authors have inferred that the BP and EGT were considerably increased, whereas BSFC and oxides of carbon and nitrogen were significantly decreased [33]. Table 1 shows a summary of various nano-additives used with biodiesel. The GO and CNT nano-additives blended with biodiesel gave a better performance with a minimum emission as compared to unblended biodiesel (Table 1). However, researchers have used mostly Jatropha oil as a major biodiesel source for nano-additive blends with biodiesel. Nevertheless, recently evolved biodiesel such as rice bran biodiesel, leaf (veronica fordii) biodiesel, yolk biodiesel were not being investigated with GO and CNT nano-additives yet. In addition, researchers suggested that in terms of the biodiesel yield quantity, rice bran and leaf oil has better potential when compared to jatropha oil [34–36].

Table 1. Summary of the previous research work on nano-additives - biodiesel blends

Reference	**Nanoparticles added with BDB**	**Inference**
[7]	Aluminium oxide	BTE and heat release rate increased.
[9]	Nickel oxide	HRR and BTE improved. BSFC decreased.
[10]	Graphene oxide	BTE improved by 12%. BSFC reduced by 9%.
[15]	Aluminium oxide, titanium oxide and silicon oxide	BTE increased and BSFC decreased. CO emission reduced.
[18]	Aluminium oxide	BTE increased by 10%. BSFC, HC emissions, CO emissions reduced by 11%, 26% and 43% respectively.
[19]	Aluminium oxide, boron oxide and iron	Peak in-cylinder pressure and SFC deteriorated at high loads.
[20]	Aluminium oxide and cerium oxide nanoparticles	BTE improved by 12%. NO, CO, HC and smoke emissions decreased by 30%, 60%, 44% and 38%.
[21]	Aluminium oxide and cerium Oxide	BTE improved by 3% NOx emission reduced by 4%
[23]	Pentanol and titanium oxides	BTE improved CO_2 and NOx emissions decreased.

[24]	Titanium dioxide, copper nitrate and cerium acetate nano-additives used separately	CO and HC emissions reduced. Cerium acetate gave better results than other nano-additives.
[25]	CeO_2 and $Ce_{0.5}Co_{0.5}$	CO emission reduced by 39%. UBHC reduced by 40%
[26]	Titanium oxide	CO emission decreased by 46%. NOx reduced by 20% when EGR was used.
[27]	Graphene quantum dot	Power increased by 28%. CO and HC emissions reduced by 30%.
[29]	Graphene oxide and CNT	Brake power and BSFC increased. HC, CO emissions decreased, NO increased.
[30]	Graphene oxide	BTE, HRR and in-cylinder pressure increased by 17%, 6% and 8% respectively.
[31]	Graphene oxide	BSFC decreased by 20%; CO, NO decreased by 40%.
[32]	Graphene oxide, MWCNTs	Peak in-cylinder pressure increased by 6%. BSFC decreased by 35%.
[33]	Graphene oxide	Brake power increased. BSFC decreased. CO, NO gas emissions decreased.

Furthermore, it is construed from the literature review that none of the studies investigated the effects of injection timing on the GO nanoparticle enhanced BDB. To bridge the above research gap, the present research focusses on incorporating recently evolved nanoparticles i.e. GO with rice bran biodiesel-diesel blends and investigate the performance, combustion and emission characteristics of the engine. The eminent combination at optimum injection timing of nano additives-biodiesel blends has a higher aptitude to become a potential substitute for fossil diesel. The objectives of the current study are: (i) to investigate the microscopic characteristics of the rice bran biodiesel-diesel-nanoparticle blends, (ii) To optimize the injection timing with the best combination of nano additives – biodiesel - diesel blends (NBDB), (iii) To reduce the exhaust emission level and improve the combustion and performance characteristics of NBDB, and (iv) comparison of the combustion and exhaust emission results with and without nano additives.

2. Materials and Methods

2.1. Production of biodiesel

The unprocessed rice bran oil was stirred at 1000 rpm and heated up to 70°C. Then, KOH and methanol were mixed and the raw heated oil was added to the mixture. Rice bran oil, methanol, and KOH were mixed at the ratio of 1000ml: 250ml: 5g respectively [13,37]. Due to the density variations, methyl ester was settled at the top of the mixture and separated. The biodiesel was then washed with preheated water and filtered [38]. This distillation process was repeated until the desired purity of the biodiesel was obtained.

2.2. Preparation of GO enhanced biodiesel-diesel blends

Graphene oxide was purchased from SRL, India with the specified purity of about 99.7%, the GO was added to the prepared BDB following the procedure adopted in the literature [39]. The particle size, surface area and thermal conductivity of the GO nanoparticle are 22.5-26 nm, 492 m^2/g, and 3000 W/mK respectively. Various combinations of nanoparticle-diesel-biodiesel blends (B5D95GO30 – 5% biodiesel, 95% diesel and 30 ppm GO; B15D85GO30 - 15% biodiesel, 85% diesel and 30 ppm GO) were prepared using an ultrasonic shaker for homogeneous dispersion of nano-additives. The main challenge faced during the preparation of GO enhanced biodiesel-diesel blend was maintaining the stability of the nanocomposite blend. The stability of the nanocomposites is influenced by agglomeration and clogging of nanoparticle in the base fluid due to Vander walls interactions [40,41]. The stability of NDBDs was ensured by adopting the two-step stability process suggested in the literature [42–44], they include (i) choosing the small particle size with less weight in the colloidal solution which reduces the possibility of getting agglomerated over the base fluid, and followed by (ii) continuous agitation (in an ultrasonic shaker) with the addition of surfactant [Sodium Dodecyl Benzene Sulfonate (SDBS)] which reduces the probability of nanoparticles getting coagulated over the base material. The above two steps were followed in the present research to ensure the stability of the nanocomposites thus reassuring the homogeneous dispersion of nanoparticles on the biodiesel blends. Once the NBDBs were prepared, their properties were measured. The technical details of the engine, instrumentations and various equipment used for measuring fuel properties are shown in Tables 2 and Table 3.

2.3. Experimental setup

The engine test was conducted using a single-cylinder, four-stroke diesel engine. The rated power output of the engine is 3.7 kW, the engine was operated at constant speed mode with varying injection timing (23º & 25º bTDC) and load (0 - 100 Nm). At first, the engine was started with pure diesel (B0) and then switched to GO-BDB fuels (B5D95GO30 and B15D85GO30). The detailed specification of the engine is given in Table 4. Fig. 1 presents schematic of the test rigs showing two fuel tanks (one for GO-BDB fuels and one for diesel fuel), air box, manometer, fuel measuring unit, transmitters for air and fuel flow measurements, process indicator and engine indicator. Eddy current dynamometer to apply and vary the load on the engine. NETEL gas analyser was used to measure the concentration of CO, HC, CO_2, NO_x gases in the exhaust stream.

Table 2. Technical details and measurement accuracies of the instruments

Equipment	**Make & Model**	**Range and Accuracy**	**Parameter**
CI Engine	Kirloskar, TV1, CVCR03-OECU	CR range: 12 to 20, CR accuracy: ±0.1mm	Performance, Combustion
Crank Angle sensor	Kubler (Germany), Model - 8.3700.1321.0360	Resolution: 1 degree, 2048 steps (11-Bit)	Crank angle position
Air intake measurement	DP sensor with inline transmitter	Pressure Transmitter Range: 250 mmwc (millimeter water column)	Air intake flow
Fuel meter	Yokogawa, Model - EJA110-EMS-5A-92NN	Calibration range:0-500 mm H_2O	Fuel flow
Load indicator	Selectron, Model-PIC 152-B2, 85 to 270 VAC	Re-transmission output 4-20 mA	Engine load
Eddy current dynamometer	Saj Test Plant Ltd., AG 10		
Load cell	Sensortronics 60001	Zero Balance ± 0.1 mV/V Non linearity < ± 0.025% Hysteresis < ± 0.020% Non-repeatability < ± 0.010%	
Temperature sensor	Wika, Model: T19.10.3K0-4NK-Z, K type Thermocouple, Output 4-20 mA, Supply 24 VDC	Calibrated for range 0 - 1200°C	Temperature
Pressure sensor	PCB Piezotronics, M111A22 Piezo-electric: 0-100 bar	Resolution: 0.1 psi Sensitivity: 1 mV/psi Low Frequency Response (5%): 0.001 Hz Linearity: 2% (Best Straight Line)	In-cylinder pressure
Rotameter	Eureka, PG 6, Range: 40-400 LPH	Accuracy: ±2% of Full Flow Standard	Water flow

Table 3. Technical details of the equipment used for fuel preparation and properties

Name of the apparatus	Model	Accuracy	Parameter
Ultrasonic m/c	Johnson Plastosonic, ULP-3000	±0.01°	Preparation of nano-additive blends
Kinematic viscometer	Biolab Model – Viscol 10a	Range: 0.5 - 25000 cSt, Accuracy: ±0.02cSt	Kinematic viscosity
Hydrometer	Thomas scientific Model – 6025C47	Range: 0.790-0.900 g/cm^3 Accuracy: ± 0.001	Density
Bomb Calorimeter	Orbit Technologies, Model – 6100	Precision: 0.1 - 0.2% Temp resolution: 0.0001˚C	Heating value
Pensky-Martens flash point tester	Pensky-Martens, Model - PMA 500	Range: 20 - 410 °C Heating rate: 0.5 to 12 °C/min.	Flash and fire point

The specification of the gas analyser is shown in Table 5. Combustion analysis was done by a transducer (quartz piezoelectric pressure transducer) placed on the cylinder head and a crank angle encoder fixed on the output shaft of the engine. Combustion parameters such as in-cylinder pressure, occurrences of peak in-cylinder pressures, ignition delay and heat release rate were obtained and analysed using LabVIEW based software and engine test express (E5) software. The E5 software was developed by Legion Brothers exclusively to investigate the characteristics variation of an engine.

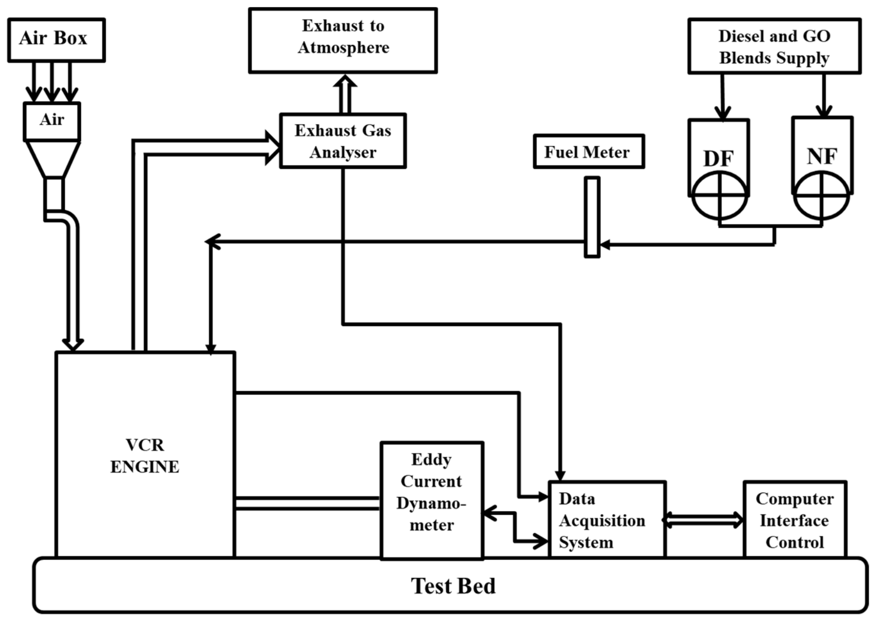


Fig. 1. Schematic diagram of the experimental setup

Table 4. Specification of the experimental engine

Manufacturer and Type	Kirloskar, single-cylinder, water-cooled
No. of strokes	Four
Rated Power	3.7 KW
Bore/Stroke	87.5 mm / 110 mm
Rated RPM	1500
Compression Ratio	17.5 (standard)
Injection Timing	21 to 25 ° bTDC
Type of ignition	Compression Ignition
Injection opening pressure	201 bar

Table 5. Technical details of the NETEL (NPM-MGA-2) gas analyser

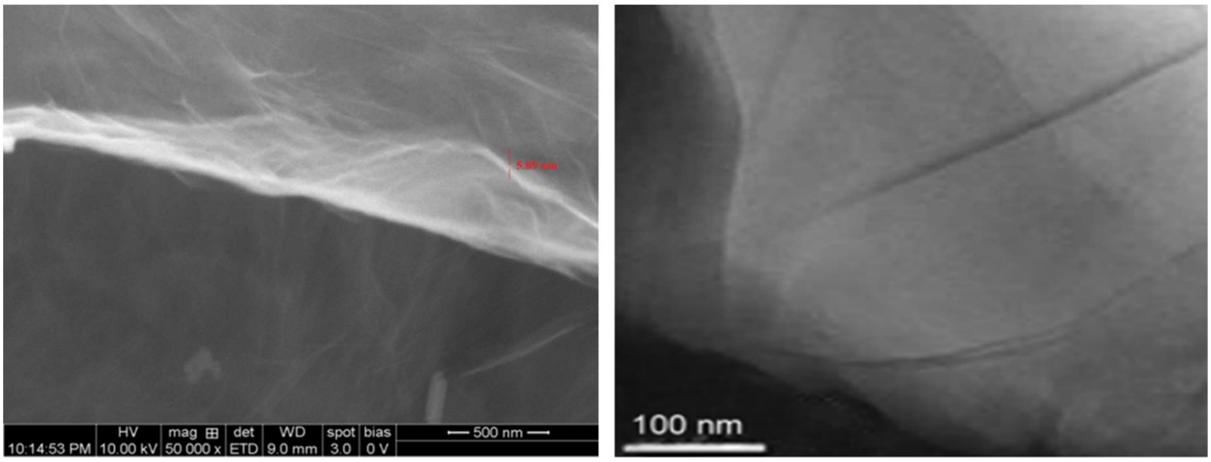
Gas	Range	Resolution
CO	0-10 %	0.01%
CO_2	0-20 %	0.1%
HC	0-2000 ppm	1 ppm
O_2	0-25%	0.01%
NOx	0-10000 ppm	1 ppm

3. Results and discussion

3.1. Characterisation of GO-BDB fuel

The size and range of the nanoparticles are important parameters that affect the dispersion efficiency and agglomeration in the derived nano-composites. The surface morphology of GO was measured using Carl Zeiss MA15/EVO18 scanning electron microscope and CM-120-Philip transmission electron microscope to authenticate the procured GO is in the correct nano range. This will aid in the improvement factor of the combustion, performance and emission characteristics of blended NBDB as compared to virgin biodiesel owing to the quantum effects, expanded surface area and tenability [45–47]. The resolution and magnification of the SEM were 3.0 nm and 50-100 K respectively. The operating voltage and temperature of TEM lie between 20-100 kV and -100 to 450 °C respectively. The SEM and

TEM images of the GO nanoparticles are depicted in figures Fig. 2 (a) and Fig. 2 (b) respectively. The size of the nanoparticle was measured using point to point inbuilt measuring tool and found to be approximately 5.8 nm. The TEM image confirmed a higher surface to volume ratio which governs the variation in thermal conductivity of the nanoparticles when dispersed in biodiesel-diesel blends. The phase composition and crystal structure of the nanoparticle are examined using X-Ray diffraction. Shimatzu diffractometer (XRD 6000, Japan) with the scattering angle and minimum step angle of about 20 to 80° and 0.002° respectively was used for experimentation. Fig. 3. depicts the XRD pattern of the graphene oxide nanoparticles.



a. SEM image of GO nanoparticles **b. TEM image of GO nanoparticles**

Fig. 2. Surface morphology of GO nanoparticle

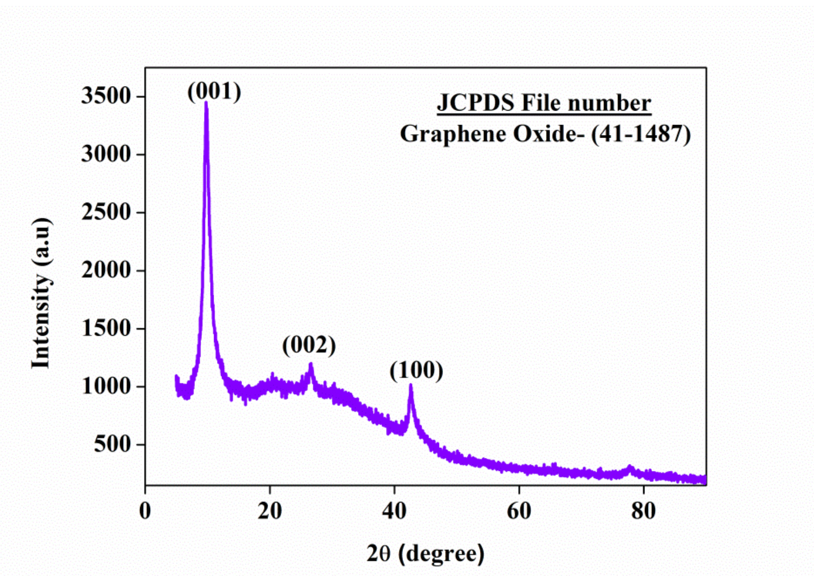


Fig. 3. Diffraction pattern confirming the presence of GO

The intensive peak (2θ) at 11.7° (hkl plane: 002) is due to the formation of -OH and -COOH groups. Due to this character, lattice plane distance decreased and as a result, sp^2 carbon (C=C i.e. a carbon atom bonded with two atomic orbital) is re-established. The peak corresponding to 2θ = 42.6° [(hkl plane: 100), JCPDS fl.no: 41-1487] confirms the withholding of graphite structure after the reduction process [48].

3.2. Properties of GO-BDBs

The properties such as cetane number, heating value, kinematic viscosity and flash point temperatures of the B5D95GO30 and B15D85GO30 blends were measured and compared with the fossil diesel and neat biodiesel properties (Table 6). The flash points of pure diesel, B5D95GO30 and B15D85GO30 are 56°C, 160°C and 158°C respectively (Table 6). At 40^0C, the kinematic viscosity of pure diesel was 2.8 cSt; on the other hand, the kinematics viscosity of the nano-additive blends was 3.8 cSt. Compared to pure diesel, the heating values of the blends were decreased by about 21% (Table 6). The density of the B5D95GO30 and B15D85GO30 blends was increased by 6.5% and 7% respectively when compared to the density of the pure diesel. The cetane number was measured using the ASTM D613 standard. Base fuels (n-hexadecane and 1-methylnaphthalene) were used to calculate the cetane number through standard cetane number scale. The required cetane number was calculated using the empirical inverse relationship [cetane number = % cetane + 0.15 (% hepta-methylnonane)]. The cetane numbers of the GO-BDB were found to be lessened as against fossil diesel. The cetane numbers of pure diesel, B5D95GO30 and B15D85GO30 were 46, 42 and 43 respectively (Table 6).

Table 6. Characterisation of GO-BDB fuels

Properties	Measurement Standards	Pure diesel (B0)	Rice-bran biodiesel (B100)	B5D95GO30	B15D85GO30
Flash point temp (°C)	D93	56	170	160	158
Kinematic viscosity (cSt) @ 40°C	D445	2.8	5.6	3.8	3.8
Lower heating value (MJ/kg)	D4809	46	35	36.23	36.76
Density (kg/m^3)	D1298	840	880	865	871
Cetane number	D613 & D976-80	46	42	38	38

3.3. Performance characteristics

The effects of GO-BDBs on engine performance characteristics such as BSFC, BTE, IMEP and ITE will be discussed in the following sections:

3.3.1. Brake Specific Fuel Consumption (BSFC)

The BSFC of various fuels with engine load is depicted in Fig. 4. In general, the BSFC of the B5D95GO30 & B15D85GO30 blends were found to be lower than pure diesel. At IT23°, the BSFC of the B5D95GO30 fuel was observed to be 11% to 13.5% lower than that of B0 fuel; whereas, at IT25º the BSFC of the same nano-additive blend was decreased by 3-6% when compared to B0 fuel (Fig. 4). This proved that advancing injection timing improved BSFC value in NBDBs. This may be due to the optimistic calorific value, density and viscosity of GONP; moreover, it acts as an oxygen supporter for biodiesel to yield high pressure and temperature inside the engine cylinder [7,49].

3.3.2. Brake Thermal Efficiency (BTE)

Fig. 5 depicts the variation of BTE with engine load for various GO-BDBs at IT23º & IT25º. It is inferred from the graph that BTE behaved harmoniously with load from 25 N to 100 N. In all load conditions, the B15D85GO30 fuel at IT23° gave the highest BTE results as compared to other fuels. The maximum BTE of about 28.73% was achieved by the blend B15D85GO30 at IT23º; whereas, for B5D95GO30 and B0 fuels, the BTE was found to be 27.29% and 21.11% respectively at the same injection timing (Fig. 5). At IT25º, the BTE of B5D95GO30, B15D85GO30 & B0 was found to be 27.61%, 27.45% and 23.31% respectively. The reason behind the enhancement of BTE was due to the homogenous combination of the air-fuel which directly resulted in more heat release during combustion. Also, prolonged mixing time causes slow combustion [50–52]. Summarily, GO-BDBs gave better BTE results as compared to B0 at IT23º and IT25º.

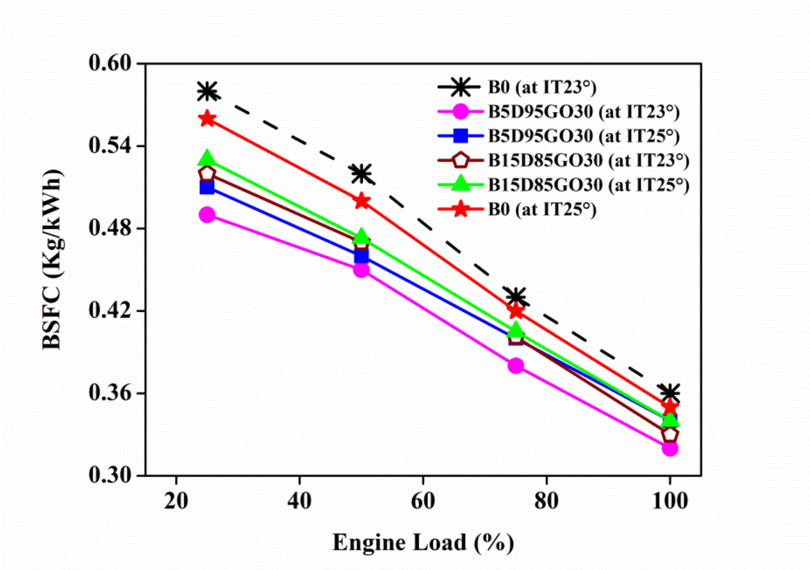


Fig. 4. BSFC vs. engine load at various injection timings

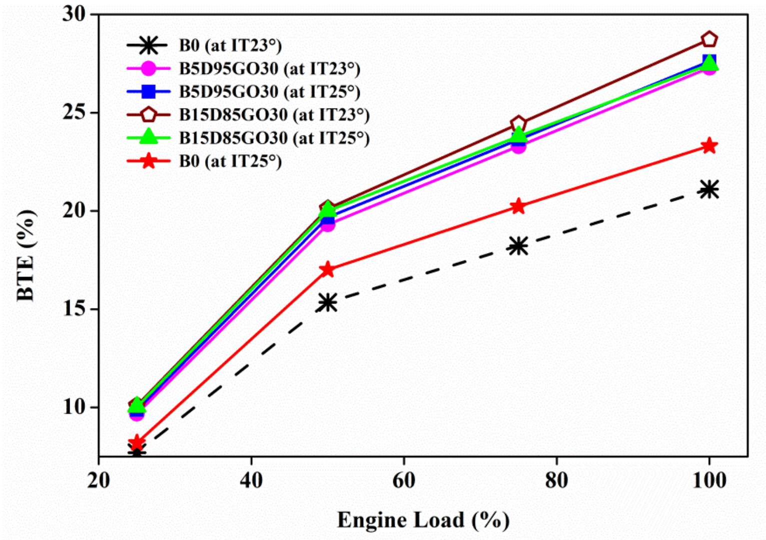


Fig. 5. BTE as a function of the injection timing at various loads

3.3.3. Indicated Mean Effective Pressure (IMEP)

The IMEP of the blend B15D85GO30 was observed to be low at both injection timings (Fig. 6). At partial load condition, the blend B15D85GO30 showed lower IMEP than other fuels. The B15D95GO30 had 9.5% lower IMEP at IT25° & 6.4% lower at IT23° as compared to the fossil diesel at maximum load. On the other hand, at IT23°, the IMEP of B5D95GO30 and B15D85GO30 were 4.6% and 6.3% lower than pure diesel (B0) at full load condition; whereas, at IT25°, they were decreased by 7.5% and 8.7% respectively.

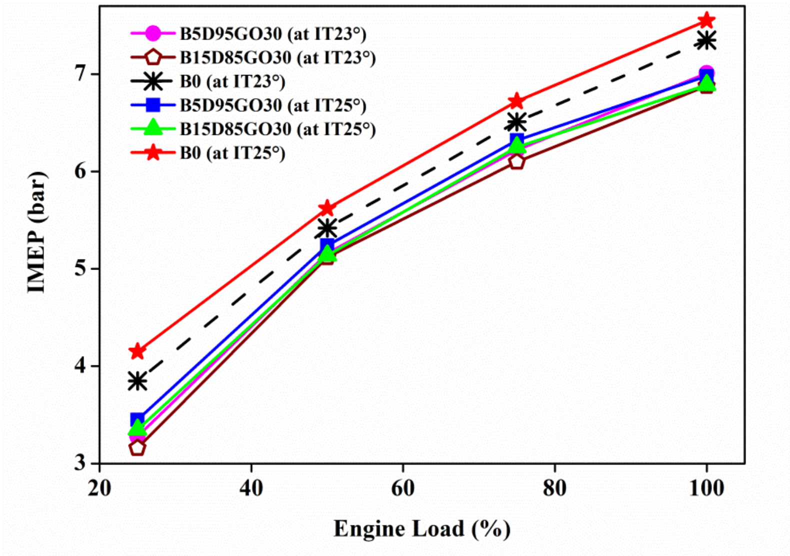


Fig. 6. IMEP as a function of the injection timing

Thus, it is summarized that an increase in engine load led to an increase in IMEP for all GO-BDBs and pure diesel at both injection timings. Also, it was inferred that at both injection timings (IT23° and IT25°), the IMEP of GO-BDBs was lower than pure diesel.

3.3.4. Indicated Thermal Efficiency (ITE)

The variation of ITE at various injection timing for GO-BDBs is shown in Fig. 7. It was inferred that the ITE of B0 fuel gradually reduced for both injection timings. At higher load conditions, the ITE of B15D85GO30 at IT23° gave better results as compared to other fuels. The maximum ITE of 57.67% was achieved by the B15D85GO30 at IT23° (Fig. 7).

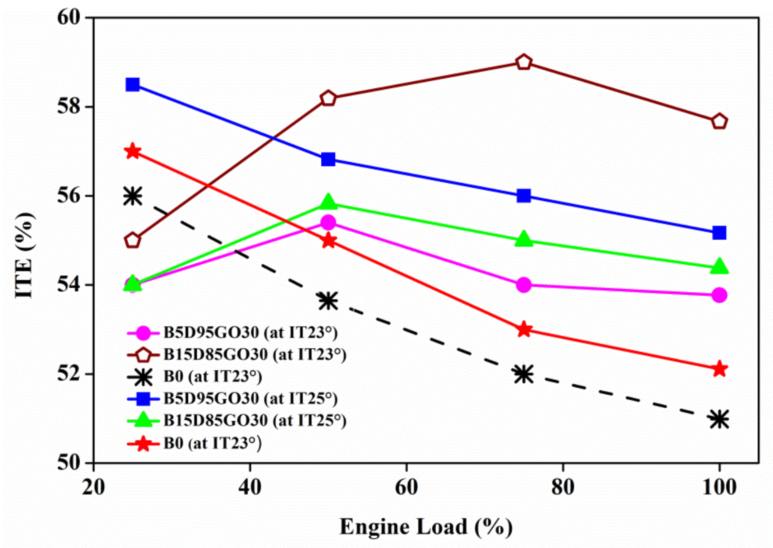


Fig. 7. ITE results as a function of engine load and injection timing

At IT23º, the maximum ITE of the B5D95GO30 and B0 fuels were found to be 53.77% and 50.99% respectively. Furthermore, at IT25º, the ITE of B5D95GO30, B15D85GO30 and B0 were found to be 55.17%, 54.38% and 52.11% respectively. The reason behind the ITE improvement was due to the properties such as density, viscosity and lower compressibility of GO-BDB's [53–55]. Summarily, the GO-BDBs gave better ITE results compared to pure diesel at both IT23º and IT25º.

3.4. Combustion characteristics of nano-additive blends

3.4.1. Heat release rate (HRR)

The variation in HRR of nanoparticle enhanced BDBs at IT23º and IT25º is depicted in Fig. 8. The peak HRRs of B15D85GO30 and B5D95GO30 fuels were found to be lower than that of B0 fuel for both injection timings. At IT23º, the peak HRRs of B5D95GO30 and B15D85GO30 fuels were 64 J/ºCA and 55 J/ºCA respectively. It was inferred that except B5D95GO30 (at IT25º) and B0 (at IT25º & IT23º) fuels; all the other fuels liberated approximately an equal amount of peak HRRs at both injection timings (Fig. 8). The start of the combustion was advanced for all the GO-BDBs at IT25º and IT23º due to rich mixture in the premixed ignition span and diffused combustion at the rest of the span [43,56].

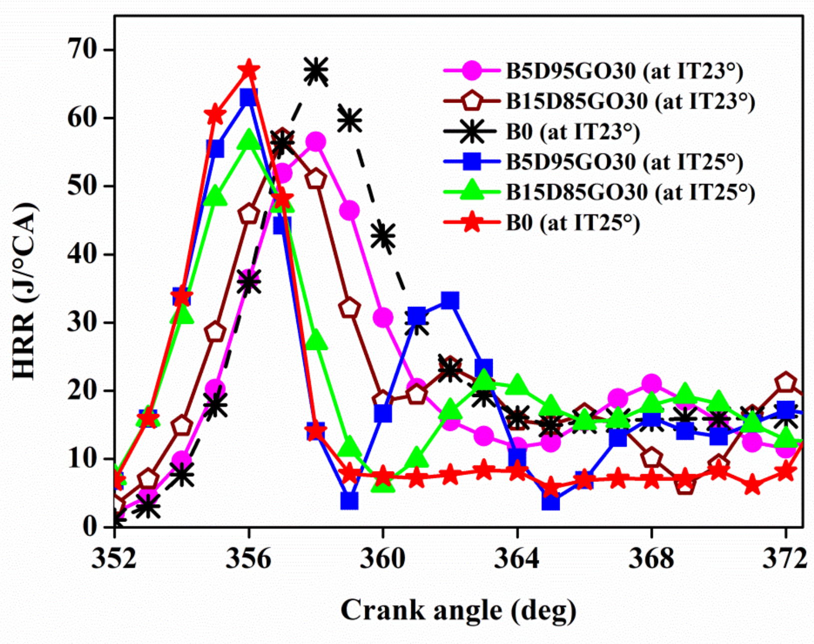


Fig. 8. The HRR at full load and at various injection timings

3.4.2. In-cylinder pressure

The in-cylinder pressures for GO-BDBs at full load (at IT23° and IT25°) is shown in Fig. 9. The peak in-cylinder pressure of B0, B5D85GO30 and B15D85GO30 was found to be 65 bar, 56 bar and 59 bar respectively at IT23º. On the other hand, at IT25°, the peak in-cylinder pressures for B5D85GO30, B15D85GO30 and B0 were found to be 61 bar, 58 bar and 63 bar respectively (Fig. 9). The reason behind this variation was believed to be increased specific gravity of the BDB's when enhanced with GO nano-additives. Also, advancing the injection timings shorten the ignition delay and increase in the rate of fuel burning in the diffusion combustion phase are the dominating reasons to achieve lower combustion in-cylinder pressure with less knocking [28,57–61].

3.5. Exhaust gas emission characteristics

3.5.1. NOx gas emission

The NOx emission characteristics of the GO-BDBs at IT23° and IT25º are shown in Fig. 10. In general, NOx emission was found to be lower for nano-additive blends than pure diesel (Fig. 10). However, at maximum load with IT25º, the NOx emission of B15D85GO30 fuel was higher than fossil diesel.

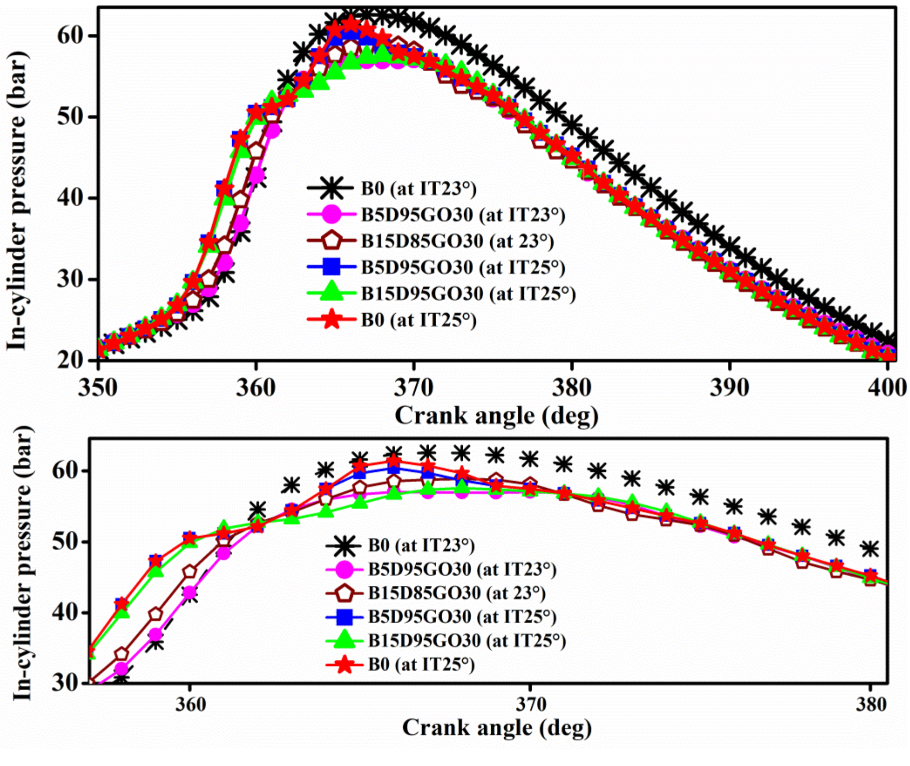


Fig. 9. In-cylinder pressure as a function of injection timing

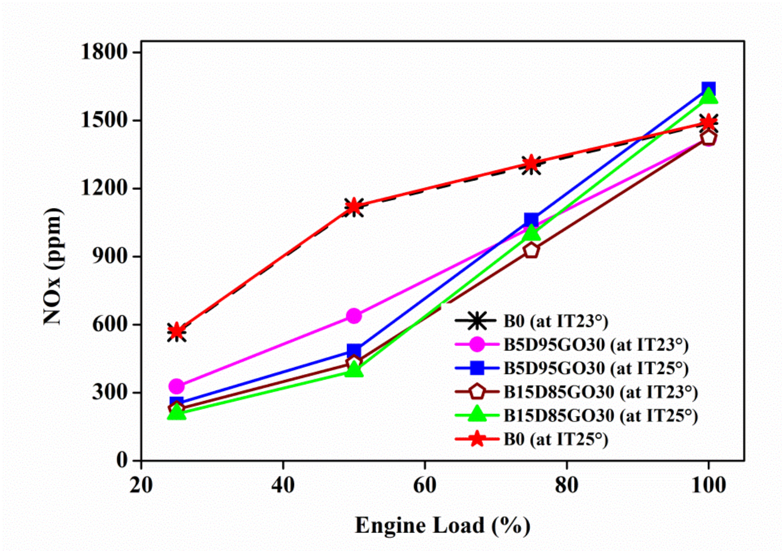


Fig. 10. NOx gas emission at various engine load and injection timing

At partial load condition and with IT23º, B5D95GO30 and B15D85GO30 blends emitted 42.8% and 61.4% lower NOx emission as compared to fossil diesel. Whereas, at peak load condition, the decrement percentage corresponds to 4.2% and 4.5% respectively for B5D95GO30 and B15D85GO30 blends as compared to diesel. Furthermore, it was observed that at part load condition, the NOx emissions of B5D95GO30 and B15D85GO30 blends were decreased by 56.8% and 64.7% respectively. The B5D95GO30 blend gave the lowest NOx gas emission both at IT23° and IT25° (Fig. 10). This NOx emission variation may be attributed due to premixed charge temperature during uncontrolled combustion zone and higher heat release rates [62–65]. Summarily, GO-BDBs gave lesser NOx emission as compared to pure diesel owing to the proper impregnation of GO additives.

3.5.2. Hydrocarbon (HC) emission

The HC emission of GO-BDBs at various injection timings is shown in Fig. 11. For pure diesel, at IT23º and IT25°, the rate of HC gas emission was increased as the engine load increased from 25% to 100% (Fig. 11). Furthermore, pure diesel emitted the same amount of HC at all loads at both injection timings, they were also higher than those obtained for nano-additive blends. Interestingly, the HC emission of GO-BDBs at IT23º was found to be lower as compared to the HC emission found at IT25°. At 50% load, and at IT25°, both GO-BDBs released almost the same amount of HC gas. It was also observed that at maximum load, the B15D85GO30 blend emitted about 50% lower HC emission when compared to the HC emission obtained for the pure diesel.

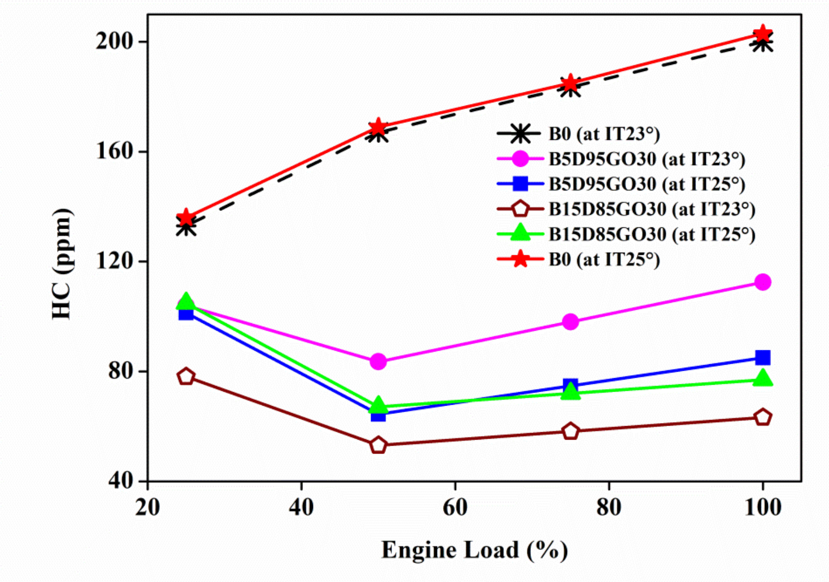


Fig. 11. HC emission as a function of engine load and injection timing

The HC emissions were lower for GO-BDBs as compared to diesel for all injection timings and loads due to the increase in gas temperature and higher oxygen content in GO-BDBs in comparison with conventional diesel. Nano-additives increases the rate of evaporation and cylinder temperature with improved mixing of air-fuel ratio leading to better oxidation and complete combustion process [66,67].

3.5.3. CO_2 emission

The CO_2 emission of the GO-BDBs at various engine loads and injection timing is shown in Fig. 12. Pure diesel emitted more CO_2 at both injection timings (IT23° and IT25°) as compared to GO-BDBS. In general, the CO_2 emission increased with the increase of engine load. The B15D85GO30 blend at IT23° gave the lowest CO_2 gas emission. Advancing the injection timing gave slightly lower CO_2 gas emissions for GO-BDBs (Fig. 12); this was happened due to the better premixing of air-fuel mixture providing sufficient time for the oxidation process to occur inside the cylinder [68,69].

3.5.4. Exhaust gas temperature (EGT)

Fig. 13 shows the EGT at various loads and injection timings. In general, the EGT was increased with the increase of engine loads. Pure diesel gave higher EGT as compared to GO-BDBs at both injection timings (Fig. 13). It was also observed that at any engine load and for all fuel blends, advancing the injection timings increased the EGT.

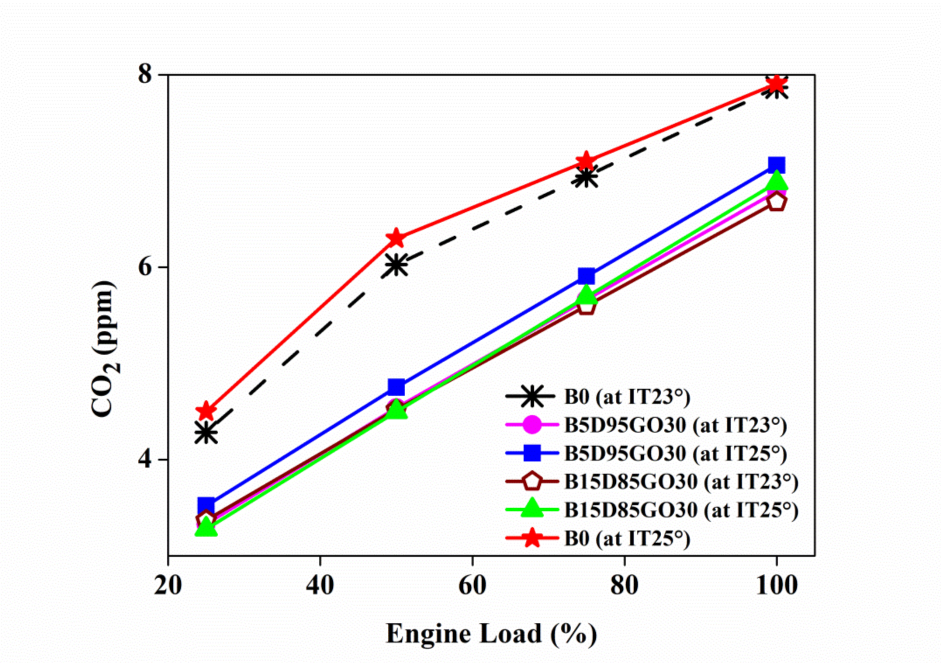


Fig. 12. CO_2 gas emission at various loads and injection timings

Furthermore, it was inferred that at full load and at IT23°, the EGT of B5D95GO30 and B15D85GO30 were 22.7ºC and 20.4ºC lower as compared to pure diesel. Whereas at IT25°, the EGT of B5D95GO30 and B15D85GO30 was 2.8ºC and 11.3ºC lower than pure diesel. At partial load conditions, the differences in the EGT of GO-BDBs were not significant. Overall, the EGT of B5D95GO30 and B15D85GO30 are 14-20ºC and 9.7-13ºC lower than pure diesel at both injection timings. This may be due to the reason that the cetane numbers of all GO-BDBs are lower as compared to fossil diesel (Table 6) and hence the ignition delays for all these blends are relatively higher as compared to pure diesel [70]. Summarily, GO-BDBs at IT25° gave lower EGT as compared to B0 fuel, the findings were supported by the literature [71,72].

3.5.5 CO gas emission

The CO emission of the nano-additive blends was found to dwindle as the engine load increased from 25% to 100% at both IT23° and IT25° (Fig. 14). At minimum loads, the CO emission of pure diesel was lower than nano-additive blends. At full load, the GO-BDBs emitted almost a similar amount of CO emissions. At partial loads, the CO emissions of the B5D95GO30 at IT23° were observed to be lower as compared to the CO emissions at IT25°. At IT23°, the B5D95GO30 and B15D85GO30 blends gave about 43% and 41.8% lower CO emissions as compared to pure diesel. On the other hand, at IT25°, compared to pure diesel the CO emission was reduced by 37% and 41.17% for B5D95GO30 and B15D85GO30 blends respectively. Similar findings were found in the literature [71,73].

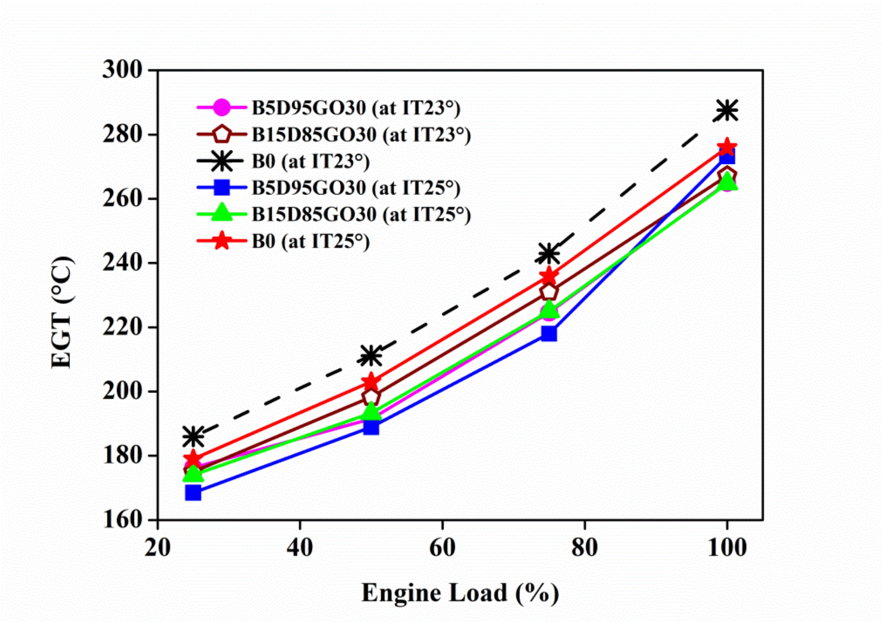


Fig. 13. EGT of tested fuels at various loads

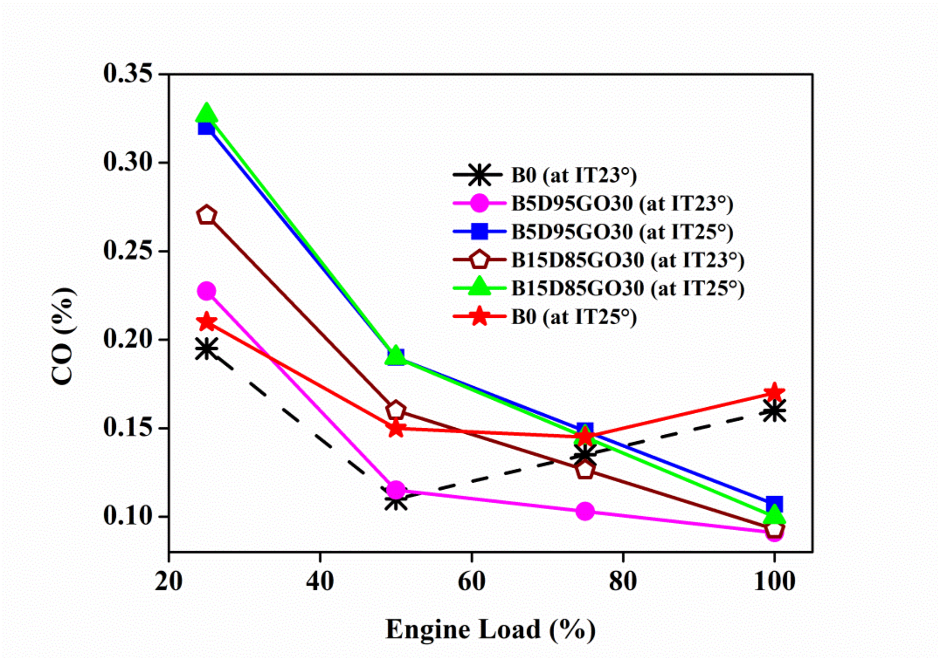


Fig. 14. CO gas emissions at various loads and injection timings

3.6. Potential application and recommendation for future work

Owing to the size and thermo-physical properties of nanoparticles, they are widely used in bioscience, medical and engineering applications including robotics, automobile, solar collectors and desalination. The nanocomposites improved the stability, combustion and performance characteristics, with reduced emissions when blended with virgin biodiesel. This extends its potential application in the transportation sector as a direct substitute for diesel fuel. The blending of renewable fuel with pure diesel has been commissioned in various countries including the UK and India. The NBDB can also be used in railways as a substitute for virgin fuels. In 2007, The British Royal Train was operated with 100% biodiesel fuel (biodiesel was supplied by Green Fuels Ltd, UK.).

In addition to this, biodiesel outspreads its application in the aviation industry. In 2011, United Airlines (Eco-skies Boeing 737-800) reported that their first aviation flight was operated on biofuel blend with 40% biofuel and 60% petroleum-derived jet fuels. So, when NBDB is implemented in these sectors, the performance and combustion characteristics of the engines increases further with the reduced emission paving a green environment [74–76].

In addition, nanoparticle enhanced biodiesel could be used as a heating fuel (heating oil + nano-biofuel) in boilers (oil-fired boilers). Furthermore, NBDB can also be used in diesel generators to reduce environmental pollution. The biodiesel has the potential of producing 78% less CO_2 emission as compared to fossil diesel [77,78] and this figure can further be reduced if NBDB is used. If traditional fuels are completely replaced with biodiesel and NBDBs, there will be a significant reduction in the emission of sulphur oxides, CO_2 and PM. Due to better buoyancy property, the NBDB fuels are used in shorelines to clean up the oil spills and to dissolve the crude oil through a single coating spraying process [75,79]. From the above applications, it is generally inferred that it is essential to bridge this outcome with other commercial end-users by integrating with various applications, thus reducing the reliance on petroleum products and to pave a better green environment for the future generation.

Future research can be focussed on (i) durability test of GO-biodiesel-diesel blends by conducting long hour engine operation and assessment of various engine components, (ii) implementing nano-additive blends for micro-algae species and immobilization of enzymes with the behavioural variations of a diesel engine, and (iii) in-depth characterisation of the blends based on size, range, distribution and clustering should be enabled with respect nanoparticles and various biodiesel blends.

4. Conclusions

Homogeneous graphene oxide - biodiesel - diesel blends (GO-BDB) were prepared and tested in a single-cylinder compression ignition engine. Macroscopic characterisations' were performed to confirm the presence of GO in the nano-additive blends. Fuel properties were measured. The injection timings and engine loads were varied. Engine performance, combustion and emission characteristics of the nano-additive blends were investigated and compared with pure diesel.

The findings of the study are summarized below:

(i) Compared to pure diesel, the flash point temperature, kinematic viscosity and density of the nano-additive blends were increased. On the other hand, the heating values and cetane number of the GO blends were reduced as compared to pure diesel.

(ii) At injection timing of 23°bTDC, brake specific fuel consumption, brake thermal efficiency, indicated mean effective pressure and indicated thermal efficiency of GO-BDBs were significantly improved as compared to pure diesel. At maximum load, the BSFC of the blend B5D95GO30 was found to be 13.5% and 11.5% lower than pure diesel at IT23° and IT25° respectively. The BTE and ITE of B15D95GO30 & B5D85GO30 blends were 7.62% & 5.8% and 6.8% & 4% higher than pure diesel at IT23° and at maximum load condition. However, better ITE was achieved at IT25° as compared to IT23°. At full load condition and at IT25°, the B15D85GO30 fuel gave lowest indicated mean effective pressure and was found to be 9.5% lower than pure diesel.

(iii) At maximum load, the heat release rates of nano-additive blends were found to be lower than the pure diesel at both injection timings of IT25° and IT23°. The peak in-cylinder pressures of B5D95GO30 at IT23° and B15D85GO30 at IT25° yielded minimum values as compared to pure diesel at maximum load conditions.

(iv) In general, the exhaust gas temperatures, CO_2, HC, and NO_X emissions of the nano-additive blends were decreased at all loads and at both injection timings. In addition, the HC, NO_x, CO_2 emissions were found to be significantly reduced for GO blends as compared to pure diesel at injection timing of 23° bTDC.

The study concluded that B15D85GO30 at IT23° gave optimum performance, combustion and emission characteristics when compared to other fuels considered for experimentation. Hence B15D85GO30 is suggested as a suitable blend for use in the diesel engine.

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