

Article



Influence of Graphene Nano Particles and Antioxidants with Waste Cooking Oil Biodiesel and Diesel Blends on Engine Performance and Emissions

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Abstract: The main reason for the limited usage of biodiesel is it tends to oxidize when exposed to air. It is anticipated that the addition of an antioxidant along with graphene nano particle improves combustion of diesel-biodiesel blend. In the present research biodiesel made from the transesterification of waste cooking oil is used. Three synthetic antioxidants butylated hydroxytoluene (BHT), 2(3)-t-butyl-4-hydroxyanisole (BHA) and tert butylhydroquinone (TBHQ) along with 30 ppm of graphene nano particle were added at a volume fraction of 1000 ppm to diesel-biodiesel blends (B20). The performance and emission tests were performed at constant engine speed of 1500 rpm. Because of the inclusion of graphene nano particles, surface area to the volume ratio of the fuel is augmented enhancing the mixing ability and chemical responsiveness of the fuel during burning causing superior performance, combustion and emission aspects of compression ignition engine. The results revealed that there was a slight increase in brake power and brake thermal efficiency of about 0.29%, 0.585%, 0.58% and 6.22%, 3.11%, 3.31% for B20GrBHT1000, B20GrBHA1000 and B20GrTBHQ1000, respectively, compared to B20. Additionally, BSFC, HC and NO_x emissions were reduced to considerable levels for the reformed fuel.

Keywords: biodiesel; nano material; antioxidants; oxides of nitrogen (NO_x)

1. Introduction

The demand as well as cost of the petroleum fuel is increasing day by day. One of the foremost possible alternate fuel for compression ignition engine is biodiesel. Narrow reserves of petroleum-based fuel and environmental concern have set off researchers to find substitute fuel that replaces the petroleum-based fuel. Diesel consumption was at 81.1 million tons in 2017–2018 and 76 million tons in 2016–2017. Total auto fuel consumption during 2018–2019 was 4% higher, diesel consumption was 3% higher than 2017–2018 [1]. Heavy vehicles still depended on diesel as a main source of power. The main hindrance with diesel fuel at present is its exhaust tail pipe emission and the fear of depletion of petroleum fuel.

In this situation, energy from biofuels delivers a bright spot to compensate for the imports serving a good substitute for the fossil fuels [2]. Biodiesel is renewable, oxygen



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). rich, nontoxic, sulphur free clean burning fuel and contains no aromatic compounds. Conceivably there are quite a few drawbacks associated with biodiesel as a vehicular fuel, the major one is its inability to resist oxidation [3], since it degrades more when exposed to atmospheric oxygen and forms hydroperoxides which produce insoluble gums and sediment gums that chokes the injector and after oxidation viscosity of the fuel increases and results in poor atomization.

Based on research conducted earlier, it is learnt that the biodiesel blend as a fuel along with diesel, minimizes emissions such as carbon monoxide, hydrocarbon, sulphur oxides and particulate matter but there will be a rise in oxides of nitrogen [4]. The present research lies in addressing the oxides of nitrogen emission without compromising the power and efficiency of biodiesel blended diesel fuel. Oxides of nitrogen are one of the main forerunners of acid rain, which has serious physical and environmental effects [5]. The majority of the nitric oxide (NO) emission is anthropogenic. However, the major source of oxides of nitrogen emissions are through vehicles.

According to the Zeldovich equation [6], nitric oxide is the main preparator in the formation of oxides of nitrogen during combustion. The two main factors that contribute to the formation of oxides of nitrogen is oxygen content in the fuel and combustion temperature above 760 $^{\circ}$ C.

 $N_2 + O \rightarrow NO + N$

 $N + O_2 \rightarrow NO + O$

 $\rm N + OH \rightarrow \rm NO + H$

It is known that: oxides of nitrogen formation happen in three prospects during combustion, i.e., thermal NO_x , fuel NO_x and prompt NO_x . Thermal NO_x is formed due to the amalgamation of nitrogen and oxygen that forms the main portion of the oxides of nitrogen development. Intensity of thermal NO_x formation rate becomes sharp with the increase in temperature above 1300 °C [7]. At this temperature the 'O' atom of the oxygen breaks the strong triple bond of the nitrogen, followed by O_2 and OH oxidizes the N atom [8], which leads to the formation of oxides of nitrogen. Fuel NO_x formed because of the contamination of nitrogen in the fuel, which contributes about 50% of oxides of nitrogen produced [7]. Nitrogen in the fuel undergoes thermal decomposition by O, H and OH leading to NH_i . NH_i molecules then undergo either oxidation to nitric oxide or reduction with NO to molecular nitrogen [9]. Prompt NO_x is the oxidation of the nitrogen in the air with the fuel, in a fuel rich condition. An important aspect of both prompt NO_x and fuel NO_x formation is the conversion of HCN (hydrogen cyanide) to NO [10].

 $\begin{array}{l} CH + N_2 \leftrightarrow HCN + N \\ HCN + O \leftrightarrow NCO + H \\ NCO + H \leftrightarrow NH + CO \\ NH + H \leftrightarrow N + H_2 \\ N + OH \leftrightarrow NO + H \end{array}$

Thermal NO_x is absolutely very low below 1300 $^{\circ}$ C, and rises sharply with temperature. Fuel NO_x does not vary with temperature. Prompt NO_x increases marginally with temperature.

Furthermore, the oxides of nitrogen formation also highly depend on the type of fuels, its physiochemical properties, injection parameters, inlet temperature and pressure and compression ratio of engine [11]. One of the methods for improved combustion and minimize perilous emission is through the fuel reformulation technique using fuel additive. Inclusion of nano particle possess large surface area to volume ratio of the fuel, which increases the catalytic reactivity thus improves combustion and curtail emissions.

Copious research has been done on the effect of metal-based additives, carbon-based additives, metallic oxides, oxygenated additives, etc. Graphene nanoparticles in the dosage of 50, 75 and 100 ppm on transesterified palm oil showed higher thermal efficiency of about 2.5% and reduction of unburnt hydrocarbon, carbon monoxide and a small rise in the emission of oxides of nitrogen of about 3.8% was observed. The presence of graphene reduced the ignition delay and improved the premixed combustion [4].

Graphene oxide added dairy scum oil methyl ester (DSOME) showed improved performance in terms of rise in thermal efficiency, drop in brake specific fuel consumption and significant reduction in unburnt hydrocarbon, carbon monoxide and smoke. Additionally, considerable decrement in duration of combustion and ignition delay period was observe [12].

By adding graphene nanoparticle in a suitable proportion to simarouba biodiesel blend could improve overall performance and emission of ci engine without engine alteration [13]. The use of GO nano particle to *Oenothera lamarckiana* biodiesel blend shows considerable reduction in carbon monoxide (5–22%), unburnt hydrocarbon (17–26%) and slight increase in carbon dioxide (7–11%) and oxides of nitrogen (4–9%) were observed in ci engine [14].

The result of alumina nanoparticle to mahua biodiesel bare subsequent reduction in the exhaust emissions such as carbon monoxide, hydrocarbon as well as smoke and slight improvement in the thermal efficiency was observed [6]. Better mixing and rate of reaction was found with the addition of alumina and cerium oxide nano particle of 30 ppm each with diesel-biodiesel blends [15]. Different monophyletic antioxidants like p-phenylenediamine, ethylenediamine, BHT and L-ascorbic acid showed substantial reduction in oxides of nitrogen for biodiesel [16].

Copious research has been done in improvising the oxidation stability of biodiesel and also to reduce the detrimental emission of the biodiesel diesel blend. The effect of addition of 2,6-di-tert-butyl-4-methylphenol and 2,2'-methylenebis antioxidants of 1% by volume to *Calophyllum inophyllum* based biodiesel showed good stability to resist the oxidation of the fuel. The outcome also showed the effectiveness of antioxidants in enhancing the start of combustion by shortening the ignition delay and improvement in power, efficiency and reduced specific fuel consumption. Additionally, both antioxidants considerably reduced oxides of nitrogen emission. Conversely, CO, HC and smoke opacity were slightly increased [17]. Two monophenolic antioxidants butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) at 1000 ppm and 1500 ppm concentration to B20 biodiesel blend derived from palm oil showed mean increase in brake specific fuel consumption, reduced brake thermal efficiency and reduced nitrogen oxide emission compared to B20 [3,18]. Addition of N-N'-diphenyl-1,4-phenylenediamine (DPPD) antioxidant to jatropha biodiesel reduced oxides of nitrogen, carbon monoxide, hydrocarbon emission with a trivial rise in terms of brake power and BSFC [19].

Profuse research findings have been done in observing the effect of carbon-based additive as well as antioxidants separately in overcoming the main limitation of biodiesel usage in engine. However, no report findings are available that elucidates both. In the present research, the influence of both graphene and antioxidants together is presented on performance and emission of diesel-biodiesel blend. From the previous literature it was observed that the addition of carbon-based nano particle as a fuel borne catalyst (graphene and carbon nano tube) could improve engine performance parameter and emission attributes in comparison with the pure diesel and biodiesel blend (B20). However, the majority of the researchers reported slight augmentation in oxides of nitrogen emission that needs to be addressed. On the other hand, from the previous studies it was also reported that use of antioxidants not only controls oxides of nitrogen emission but also causes poorer power development as well as a surge in specific fuel consumption. The innovative future of the present study aimed at experimental exploration with the unified effect of graphene nano particle with antioxidants in controlling the exhaust emission without compromising performance of the engine. For the present work, commercially available research grade graphene was purchased from Adnano Technology. Three monophenolic synthetic antioxidants butylated hydroxytoluene (BHT), 2(3)-t-butyl-4-hydroxyanisole (BHA) and tert butylhydroquinone (TBHQ) were purchased from Sigma-Aldrich.

2. Materials and Methods

2.1. Graphene Nano Material

Graphene is ultra-light weighed with less defected honey comb 2D carbon structuring and having minimum number stacking with high graphitized carbon. Technical specifications of graphene are given below in Table 1. Exactly 30 ppm of the graphene was considered for test fuel preparation.

Table 1. Technical specification of the graphene.

Purity	99%
Thickness (Z)	0.8–1.6 nm
Dimension (X and Y)	<1 µm
Number of Layers	1–5
Surface Area	$>200 \text{ m}^2/\text{g}$
Bulk Density	0.006 g/cm^3

2.2. Antioxidants

Antioxidants hinder the oxidation of the unsaturated fatty acids in the biodiesel and renders the formation of redundant yield. There are three basic types of antioxidants: phenolic, amines and thiophenols. Phenolic types of antioxidants are extensively used in the biodiesel industry because of their availability, low cost and feasibility.

2.3. Test Fuel Preparation

Biodiesel considered for the present study was derived from the transesterification of used cooking oil, which was collected from the Center for Renewable Energy and Sustainable Technology (CREST) at the National Institute of Engineering, Mysuru. The catalyst and alcohol used for the transesterification were potassium hydroxide and methanol, respectively. The waste cooking oil was heated to 65 °C after mixing with alcohol and catalyst for about 3 h with constant stirring. The formed glycerine was then removed and the pH value of 7 was maintained for methyl ester (formed biodiesel).

Biodiesel of 20% by volume (B20) was blended with diesel with the aid of magnetic stirrer for about 20 min at 1000 rpm. Exactly 30 ppm of graphene nano particle was weighed by precision electronic balance. Sodium dodecyl sulphate acts as an anionic surfactant for graphene nano particle. The role of anionic surfactant was considered to reduce the agglomeration tendency of graphene particle [20]. Graphene and surfactant were ultrasonicated for about 20 min for the equal dispersion of graphene in the fuel. Three antioxidants BHT, BHA and TBHQ of 1000 ppm concentration were considered separately with 30 ppm of graphene to prepare different test fuel samples. Each antioxidant was weighed and dissolved in ethanol. Then, they were added separately with the graphene nano particle. These mixtures were incorporated to the biodiesel blend and the improved dispersion was accomplished with ultrasonication followed by magnetic stirring.

2.4. Fuel Physical Property

Fuel physical properties of biodiesel were measured and compared with ASTM biodiesel standard as shown in the Table 2.

Properties	Unit	ASTM D7467 Standard	Diesel	Biodiesel from Waste Cooking Oil (B20)	Waste Cooking Oil Biodiesel (B100)	BBD + GR- BHT1000 ppm	BBD + GR- BHA1000 ppm	BBD + GR- TBHQ1000 ppm
Flash point	°C	Min 52	65	71	160	79	79	79
Kinematic Viscosity, 40 °C	CST	1.9–4.1 (ASTM D93)	2 to 3.8	4.06	4.2	4.05	4.05	4.05
Calorific Value Density	kJ/kg kg/m ³	N/s N/s	42,600 820	41,320 880	36,848 920	40,750 880	40,090 880	40,090 880

Table 2. Fuel physical property in comparison with standard.

3. Engine Specification and Test Procedure

The experimental investigation was carried out in the engine lab, department of mechanical engineering at VVCE, Mysuru, India. Experimentation was performed on a research engine. Engine specification is shown in Table 3.

Product	1 Cylinder, 4 Strokes, Multifuel, VCR Research Engine		
Engine	Kirloskar made		
Type of cooling	water cooled		
Stroke, Bore, Cubic capacity	110 mm, 87.5 mm, 661 cc		
Rated Power	3.5 kW at 1500 rpm		
Dynamometer	Type eddy current, water cooled with loading unit		
Load sensor	Make VPG Sensotronics, Load cell, type strain gauge, range 0–50 Kg		
Overall dimensions	W 2000 \times D 2500 \times H 1500 mm		

Table 3. Engine specification.

Exhaust emission were measured in AVL DIGAS 444N, which was integrated to the engine. The experimental investigation involved a comparison study of combustion, performance and emission characteristics of diesel, biodiesel blend (B20) and graphene plus antioxidant added biodiesel blend. Blending of biodiesel was kept at 20% constant with diesel. Fuel blends are shown in Table 4.

Table 4. Fuel blends description.

B20	20% Biodiesel from Waste Cooking Oil + 80% Diesel
B20GrBHT1000	20% Biodiesel from waste cooking oil + 80% Diesel + 30 PPM of Graphene + 1000 ppm of BHT antioxidant
B20GrBHA1000	20% Biodiesel from waste cooking oil + 80% Diesel + 30 PPM of Graphene + 1000 ppm of BHA antioxidant
B20GrTBHQ1000	20% Biodiesel from waste cooking oil + 80% Diesel + 30 PPM of Graphene + 1000 ppm of TBHQ antioxidant

The layout of the research engine with dynamometer and exhaust gas analyser is shown in Figure 1a. Photographic view of the experimental set up is shown in the Figure 1b.



Figure 1. (a) Layout of experimental setup; (b) Photographic view of experimental setup.

4. Uncertainty Analysis of the Experimental Data

The accuracy of the engine parameter and uncertainties in the collected data from the test cell of the engine is given in Table 5. The error size was reduced by considering the mean of five readings.

Sl. No.	Parameter	Variables	Accuracy (\pm)	Uncertainty (%) (\pm)
1		Engine load (N)	0.05	-
2	Accuracy of the engine - _ parameter _	Engine speed (rpm)	2	-
3		Fuel flow rate, cc/min	0.1	-
4	Accuracy of the obtained emission value	Hydrocarbon emission	-	0.8
5		Carbon monoxide emission	-	1.3
6		Oxides of nitrogen	-	1.7
7	Determined a surger store	Brake Thermal Efficiency (%)	-	1
8	- Determined parameters	Heat release rate (J/oCA)	-	1.1

5. Results and Discussions

Experimentation was performed on a computerized, single cylinder, naturally aspirated diesel engine by keeping engine speed at 1500 rpm constant. Tests were performed by changing the engine load. Viscosity of the biodiesel was not changed too much since only 20% of the biodiesel was considered for the blending; hence, the experiments were performed for constant injection pressure of 650 bar, compression ratio of 18 and injection timing of 23° BTDC.

5.1. Brake Power

The effect of graphene nanoparticle and antioxidants at different loads on engine brake power for fuel samples such as diesel, B20 and B20 with graphene nano particle and three antioxidants BHT, BHA and TBHQ added fuel samples is shown in Figure 2.



Figure 2. Deviation of brake power with load.

It was observed that even though the calorific value and viscosity of the reformed fuel showed poor performance with reference to the diesel and B20, brake power of the engine for same reformed fuel showed a trivial surge in comparison with the diesel. The upturn in brake power was because of the secondary atomization and complete combustion with the inclusion of the graphene nano particle. Additionally, the inclusion of the graphene nano particle restricted the deposition of carbon and iron reducing the friction between the nano particle subsequently increasing power [14]. The performance of the biodiesel in terms of power and efficiency is always lower than diesel fuel due to shorter delay time and higher viscosity of the biodiesel [21]. Brake power of the engine increases with an increase in dosage level of graphene nano particle, which improves the thermal conductivity of the fuel and improves combustion [13] to simarouba biodiesel blend. There was a reduction in brake power of 3.9% for B20 compared to diesel and increase in brake power of 5.88%, 6.19% and 6.19% higher for B20GrBHT1000, B20GrBHA1000 and B20GrTBHQ1000, respectively, compared to B20.

5.2. Brake Thermal Efficiency

From Figure 3, it was observed that the thermal efficiency of B20 was marginally better than diesel at part load. Additionally, at the full load, the thermal efficiency falls below diesel. Thermal efficiency of graphene and antioxidants showed superior performance at almost all loads in comparable with diesel and B20. Thermal efficiency was increased by 6.22%, 3.11% and 3.315%, respectively for B20GrBHT1000, B20GrBHA1000 and B20GrTBHQ1000, respectively, higher than B20 at full load.



Figure 3. Deviation of brake thermal efficiency with brake power.

5.3. Specific Fuel Consumption

Engines with biodiesel blends consume more fuel for the same power with respect to diesel and thermal efficiency with the biodiesel blends will be lower than diesel [22] due to high density and lower heating value. From Figure 4, it was observed that diesel has obtained the lowest BSFC with 0.33 kg/kW-h at full load. The highest value of BSFC was found for B20 with 0.38 kg/kW-h with an increase of 15.15% compared to diesel. BSFC of B20GrBHT1000, B20GrBHA1000 and B20GrTBHQ1000 were found to be 0.34, 0.36 and 0.35 kg/kW-h, respectively. The increase in BSFC for biodiesel blend when compared to diesel was because of the increase in density of the fuel and inadequate atomization of the fuel. Further, BSFC of B20GrBHT1000, B20GrBHA1000 and B20GrTBHQ1000 were found to be 11.76%, 5.55% and 8.57% lower than that for B20. Even though the addition of graphene showed a slight dip in the heating value of the fuel, it promotes secondary atomization and accelerates combustion by increasing the power rendering slender drop in BSFC.



Figure 4. Deviation of brake specific fuel consumption with load.

5.4. Ignition Delay

The main factor while studying the combustion behaviour of any fuel is ignition delay. With the increase in engine loading, the ignition delay decreases for all the fuels. A good ci engine fuel should possess lower ignition delay value, which cutbacks the accumulation of the fuel and sudden burning of the fuel that results in excessive pressure rise rendering knocking. Ignition delay is calculated as the difference in terms of crank angle between start of injection and start of combustion. From Figure 5, it was clear that the ignition delay was lower for biodiesel blend fuels compared to diesel; this was due to the higher cetane rating of the biodiesel [5]. Delay period of the biodiesel blend tends to be lower compared to pure diesel because, of the high cetane number and higher oxygen content [21,23]. There was a decrease in the delay period of about 5.55%, 11.11% and 13.89% for B20GrBHT1000, B20GrBHA1000, and B20GrTBHQ1000, respectively, compared to B20. The decrease in the delay period with respect to reformed fuel was because of the better atomisation of the fuel and premixed phase.



Figure 5. Deviation of ignition delay with respect to loading.

5.5. Heat Release Rate

The inclusion of graphene nano particle promoted secondary atomisation of the fuel droplet that enhanced the combustion efficiency and improved heat release rate. This is because the addition of graphene nano particle in fuel samples increases higher carbon combustion activation and hence aids better combustion [13].

Additionally, the increase in heat transfer was due to the shorter in ignition delay occurs due to the micro explosion of the fuel with the influence of graphene nano particle [13]. From Figure 6, the net heat release rate was improved by 2.39%, 1.26% and 11.66% for B20GrBHT1000, B20GrBHA1000 and B20GrTBHQ1000, respectively, compared to B20. Net heat release rate for B20 dropped by 3.74% compared to B20.

5.6. Pressure Rise Rate

Figures 7 and 8 show the rate of pressure rises with respect to crank angle and loading, respectively. The rate of pressure rise was highest for B20GrTBHQ1000 for all loading. The pressure rise rate increases with increase in loading. The rate of pressure rise should be less than 9 bar/° CA for a stationary engine. It was observed that for the reformed fuel (graphene+antioxidants added fuel) a small increase in the rate of pressure rise was observed. There was an increase in rate of pressure rise of about 4.41% that was observed for B20GrTBHQ1000 compared to diesel. Additionally, the pressure rise rate of about 0.5% and 1.528% was observed for B20GrBHT1000 and B20GrBHA1000, respectively. Higher ignition delay could be the possible reason for the surge in the maximum rate of pressure rise, which causes more entrainment of mixture and results in higher premixed combustion energy [13].



Figure 6. Deviation of heat release rate with crank angle.



Figure 7. Deviation of pressure rise rate with crank angle.



Figure 8. Deviation of pressure rise rate with loading.

5.7. CO Emission

Figure 9 shows deviation of carbon monoxide emission with loading for diesel, B20 and graphene plus antioxidant added fuel samples. Carbon monoxide emission increases with an increase in loading. The foremost cause for the same was that the fuel becomes comparatively richer at higher loads with a richer mixture of carbon content as the fuel increases. From the graph it was learnt that diesel has more CO emission at all loads compared to B20 and reformed fuel. The decline in CO emission for biodiesel blend was owing to higher oxygen concentration in the biodiesel, which ensures complete combustion of the fuel leaving behind the small traces of the CO emission in comparable with the diesel fuel. There was a reduction of 26.68%, 18.53%, 14.46% and 22.6% for B20, B20GrBHT1000, B20GrBHA1000 and B20GrTBHQ1000, respectively, in comparison with the diesel fuel. It was also evident that with the presence of graphene nano particle which increases the chemical reactivity and promotes good combustion by oxidizing CO to CO_2 [14]. Correspondingly, the manifestation of antioxidants proved to be a trivial upturn in CO emission. The inclusion of antioxidants increases the CO emission by 14.2%, by lowering the conversion efficiency of CO to CO_2 [21].



Figure 9. Deviation of carbon monoxide emission with loading.

The formation of hydroxyl radicals because of the oxidation of the peroxyl and hydrogen peroxide decreases the conversion efficiency of CO to CO_2 [24,25]. From the present experiments there was an increase of 11.11%, 22.22% and 16.66% of CO for B20GrBHT1000, B20GrBHA1000 and B20GrTBHQ1000, respectively, compared to B20. The main reason for CO emission upturn can be explained that the addition of BHA, BHT and TBHQ antioxidants lower the peroxyl and hydrogen peroxide radicals, which have a negative impact on the formation of OH radical as well as oxidation of CO [26].

5.8. HC Emission

Hydrocarbon emission for different fuel samples is shown in Figure 10. The main reason for the hydrocarbon emission is the incomplete combustion of the fuel. From the graph, it was evident that diesel has a higher HC emission at all loads compared to B20 and graphene plus antioxidant added biodiesel blend. Owing to the large surface area to the volume ratio of the fuel with the presence of nano particle, which accelerates the combustion rendering ample improvement in combustion of the fuel and minimizing unburnt hydrocarbon emission. There was a reduction in HC of 42.85%, 64.28% and 71.42% for B20GrBHT1000, B20GrBHA1000 and B20GrTBHQ1000, respectively, compared to B20. Additionally, the combined effect of graphene and antioxidants promotes complete combustion with minimum hydrocarbon emission.



Figure 10. Deviation of hydrocarbon emission with loading.

5.9. NO_X Emission

High combustion temperature is the main culprit for the development of oxides of nitrogen in exhaust emissions. About 95% of the oxides of nitrogen produced in the high temperature burning process are in the form of nitric oxide [27]. This is because the high temperature inside the cylinder splits the triple bond of the nitrogen molecule and makes less reactive atomic nitrogen. This nitrogen again combines with oxygen and forms thermal NO_x . Biodiesel blends as a fuel increases both oxygen content in the fuel as well as the combustion temperature. Increased formation of CH radicals during biodiesel combustion leads to surge in oxides of nitrogen emission [11].

Biodiesel has a higher amount of oxygen and lower ignition delay than diesel; this increases the oxides of nitrogen emission compared to diesel. Inclusion of 1000 ppm of BHT antioxidants showed a positive impact in reducing the exhaust gas temperature and rendered a reduction in oxides of nitrogen emission to 9.45% [28]. We learned from the majority of the previous studies that the oxides of nitrogen emission keep increasing even with nano additives because of the better combustion and higher adiabatic flame temperature [29]. From the various studies [16,21,24,25,28], it was stated that the reaction between nitrogen molecule and hydrocarbon free radicals are the main culprit in the process of formation of oxides of nitrogen. The presence of antioxidants minimizes these reactions and consequently lowers oxides of nitrogen emission.

Figure 11 shows variation of oxides of nitrogen emission with respect to loading. From the figure it was clear that for B20, oxides of nitrogen emission were higher at all loads. With the increase in loading, the combustion temperature becomes higher and results in higher ppm of oxides of nitrogen. There was a reduction of 18.73%, 24.81% and 27.91% lesser oxides of nitrogen emission for B20GrBHT1000, B20GrBHA1000 and B20GrTBHQ1000, respectively, compared to B20. Antioxidant inclusion has shown a positive impact on reducing oxides of nitrogen emission.



Figure 11. NO $_X$ emission with loading.

6. Conclusions

The motive of the present research is to improve the performance and to reduce emission of biodiesel operated fuel in compression ignition engine. From the extensive survey of the previous literature, it has been noted that the addition of graphene improves performance and emissions, but also there was a slight surge in the oxides of nitrogen emission; the addition of antioxidants lowers the oxides of nitrogen emission. Simultaneously, CO emissions surge slightly and performance parameters are decreased. The outcome of the combined effect of graphene and antioxidants studied in the present study are in line with what most of the studies reported in terms of performance and emission.

Based on the experimental test, which was carried out on a single cylinder 4 stroke compression ignition engine, for fuel samples of diesel, B20 and three different monophyletic antioxidants BHT, BHA and TBHQ with graphene nano particle, the following conclusion can be drawn:

- A 20% blending of biodiesel derived from waste cooking oil met ASTM specification for diesel-biodiesel blend and can be used without any modification to the engine.
- The addition of graphene nanoparticle and BHT, BHA and TBHQ antioxidants yielded a diminutive reduction in calorific value of the fuel samples without altering kinematic viscosity and density compared to B20.
- There was an increase in brake thermal efficiency of 6.22%, 3.11% and 3.315%, respectively, for B20GrBHT1000, B20GrBHA1000 and B20GrTBHQ1000, respectively; this is higher than B20 at full load. The graphene nano particle played a tremendous role here for boosting the efficiency, even though the addition of antioxidants might not yield a good result in terms of performance of the engine is considered.
- BSFC of the reformed fuel showed lower specific fuel consumption compared to B20. BSFC of B20GrBHT1000, B20GrBHA1000 and B20GrTBHQ1000 were found to be 11.76%, 5.55% and 8.57% lower than that for B20. Even though the addition of graphene showed a slight dip in the calorific value of the fuel, it promotes the

secondary atomization and accelerates combustion by increasing the power rendering slender drop in BSFC.

- There was a reduction in HC of 42.85%, 64.28% and 71.42% and oxides of nitrogen by 18.73%, 24.81% and 27.91% for B20GrBHT1000, B20GrBHA1000 and B20GrTBHQ1000, respectively, compare to B20.
- There was a slight increase in CO of about 11.11%, 22.22% and 16.66% for B20GrBHT1000, B20GrBHA1000 and B20GrTBHQ1000, respectively, compared to B20. The inclusion of antioxidants lowers the peroxyl and hydrogen peroxide radicals, which has a negative impact on the formation of OH radical as well as oxidation of CO.
- There was a reduction of 18.73%, 24.81% and 27.91% lesser oxides of nitrogen emission for B20GrBHT1000, B20GrBHA1000 and B20GrTBHQ1000, respectively, compared to B20. Antioxidant inclusion showed a positive impact on reducing oxides of nitrogen emission.
- B20GrTBHQ1000 has yielded the best result in terms of power, efficiency and emission.

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