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Research Article

Meysam Eshaghi Pireh, Mohammad Gholami Parashkoohi*, Davood Mohammad Zamani

Evaluation of combustion characteristics performances and emissions of a diesel engine using diesel and biodiesel fuel blends containing graphene oxide nanoparticles

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Abstract: In this study, the performance and emissions of a compression combustion diesel engine were investigated. The net diesel and the blends of diesel with waste cooking oil (WCO) biodiesel (5 and 20%) were considered as control fuel and were blended with graphene oxide nanoparticles (GONPs) (30, 60, and 90 ppm) and were evaluated. The engine was operated at full load at 1,500 rpm and the brake power (BP), brake thermal efficiency (BTE), and brake specific fuel consumption (BSFC) besides CO, CO2, and NO_x emissions appraised in the two sections of engine performance and emission, respectively, were evaluated. According to the results in the D₉₅B₅G₉₀ fuel blend, GONPs had a positive effect on BP. BTE also showed a significant improvement in $D_{95}B_5G_{60}$. GONPs increase NO_x and CO_2 emissions and decrease CO emissions. Overall, it can be concluded that GONPs can be introduced as a suitable alternative additive for diesel and WCOs biodiesel fuel blends.

Keywords: biodiesel, internal combustion engines, graphene oxide nanoparticles, emission analysis, engine performance

1 Introduction

The use of fossil fuels has increased dramatically due to increased quality of life, industrial revitalization in developing countries, and the rapid expansion of the world's

* Corresponding author: Mohammad Gholami Parashkoohi,
Department of Biosystems Engineering, Takestan Branch,
Islamic Azad University, Takestan, Iran,
e-mail: Gholamihassan@yahoo.com, m.gholami@tiau.ac.ir
Meysam Eshaghi Pireh, Davood Mohammad Zamani: Department of
Biosystems Engineering, Takestan Branch, Islamic Azad University,
Takestan, Iran

population. Inopportune use of fossil fuels causes depletion of non-renewable resources and exacerbate of environmental hazards simultaneously, which have negative impacts on human healthfulness and ecological systems [1]. Rising oil prices in the world market, along with declining sources of non-renewable fossil fuels, have raised concerns and created renewable energy as an alternative to fossil fuels. Moreover, as previously recognized, the use of fossil fuels generates a huge amount of greenhouse gas emissions, which eventually pollute the environment [2]. Thus, many researchers studied different renewable sources such as biomass [3–7] for attaining cleaner combustion and higher efficiency in recent years. Yet, in biodiesel production, so far there is a lack of environmental aspect of combustion and performance review.

The use of biodiesel as an alternative fuel has drawn global attention from fossil fuels to biofuels [8]. Biodiesel has attracted the attention of researchers because of its high potential as part of a renewable energy mix and as a sustainable energy source in the future [9]. Biodiesel has more useful combustion characteristics than diesel fossil fuels, such as lower CO, SO₂ and unburned HC emissions [10,11]. FAO [12] reported that global biodiesel production will reach 39.8 billion liters by 2030, which is equivalent to 9% increase compared to 2017. Figure 1 shows the estimation of global biodiesel production.

Sustainability is a pertinent issue in biodiesel industry. Hence, advanced techniques and criteria were employed on combustion systems and biodiesel production so as to attain the most economically, thermodynamically, and environmentally feasible solutions [13].

Bio-refineries are similar to current oil refineries, while biodiesel is produced from bio-oils and bio-fats instead of fossil oils. Despite the many advantages of biodiesel over diesel fuel, such as renewability, local availability, more cetane, less aromatic and sulfur content, higher efficiency, better safety characteristics, and better emission profile [14], biomass is considered as one

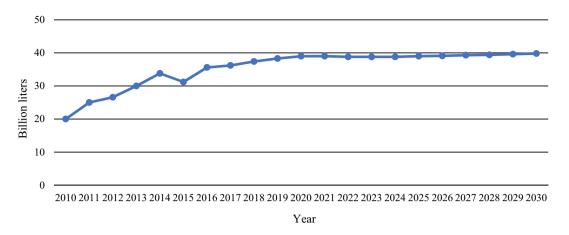


Figure 1: Estimation of global biodiesel production.

of the most promising renewable energy resources which accounted for 59% of the total renewable-based resources in 2015 in the European Union. The globally produced biomass energy equivalent was estimated to be eight times higher than the world total energy requirement [15]. The search for new alternative and cost-effective oil raw materials for biodiesel production like cheap waste cooking oils (WCOs) is essential, such a strategy can significantly improve biodiesel production in terms of sustainability [16].

The use of fuel additives as a means of refining fuel is one of the most acceptable approaches that have been introduced to date [17–21]. The choice of additives for upgrading biodiesel properties depends on a number of parameters including toxicity, economic feasibility, fuel blending properties, solubility, impacts of viscosity of the fuel blend, impacts of flash point of fuel blend, etc.

The improving effects of nanoadditives can be explained by their high surface area-to-volume ratio, mass diffusivity, thermal conductivity, etc. [22,23]. Ceramic, metallic (e.g., cerium, titanium, aluminum, iron, etc.), carbonaceous, and polymeric materials can be used as fuel nanoadditives [20].

Despite the promising results obtained by the use of metal-based nanoparticles, the biosafety concerns associated with their applications are challenging [24–27]. Thus, most recent efforts have focused on the use of carbonaceous materials, which do not pose such hazards due to the combustible nature of carbon atoms.

Table 1 sums up the diversity of studies carried out in biodiesel production and assessment of environmental aspects of combustion of this biofuel in the engine with or without additives and studies on engine performance with different diesel/biodiesel/additive combinations.

Considering the studies done in this regard and the importance of this issue, the purpose of this study is to examine the impacts of graphene oxide nanoparticles (GONPs) application in diesel and biodiesel fuel blend on the performance, energy, and emission characteristics of a single-cylinder diesel engine. It is worth mentioning that the biodiesel is obtained from WCO through transesterification technique.

2 Materials and methods

2.1 Biodiesel feed stock provision

In the present study, WCO was elected as feed stock to produce biodiesel, WCO can be obtained from multiple sources, herein was collected from restaurants. The collected WCO contains a lot of impurities and high content of free fatty acids (FFAs). Hence, it is required to pretreat the WCO to eliminate any chunks of food particles and the amount of acid. It is achieved by filtration and deacidification of feedstock [43].

2.2 Biodiesel production

The transesterification of animal fats and vegetable oils is the most common way of producing biodiesel. Transesterification is a process wherein an alcohol from an ester is replaced by another in a process like hydrolysis, except that alcohol is utilized rather than water [44]. The current process is utilized to decrease triglyceride's viscosity. Transesterification reaction is demonstrated via the following equation:

$$\begin{array}{ccc}
RCOOR^{1} + R^{2}OH & \stackrel{Catalyst}{\longleftrightarrow} & RCOOR^{2} + & R^{1}OH \\
Ester & Alcohol & Ester & Alcohol
\end{array} (1)$$

Table 1: Summary of studies conducted on various diesel-biodiesel-additive fuel blends and engine combustion

Surveyed	Geographical scale Assessed fuels	Assessed fuels	Type of		Biodiesel production	uction	Reported re	Reported result content
, and				Feed stock	Without additive	With additive	Environmental impacts	Engine performance
[28]	Egypt	Diesel/biodiesel	1-cyl ^a , DI ^b , AC ^c , NA ^e	Jojoba oil	X	Multi-walled carbon nanotubes		
[29]	Spain	Biodiesel	×	WCO		×		X
[30]	Brazil	Biodiesel	X	WCO		X		X
[31]	India	Diesel/biodiesel	1-cyl, DI, AC, NA	WCO	×	Water and diethyl ether		
[32]	India	Diesel/biodiesel	1-cyl, DI, AC, NA	Juliflora oil		×		
[33]	Thailand	Diesel/biodiesel	1-cyl, DI, AC, NA	SVO	×	Ethanol		
[34]	Australia	Diesel/biodiesel	4-cyl, DI, WC ^d , NA	WCO and Macadamia oil		×		
[35]	Canada	Diesel/biodiesel	1-cyl, DI, AC, NA	SVO	×	Glycerin		
[36]	India	Diesel/biodiesel	1-cyl, DI, AC	Rapeseed oil	\S	×		
[37]	Turkey	Diesel/biodiesel	1-cyl, DI, AC, NA	Tea seed oil	×	Hydrogen		
[38]	India	Diesel/biodiesel	1-cyl, DI, WC, NA	Almond seed oil	×	Di-methyl-carbonate		
[39]	Hong Kong	Diesel/biodiesel	4-cyl, DI, WC, NA	WCO		×		
[40]	Australia	Diesel/biodiesel	6-cyl, DI, WC, TC ^f	WCO	×	Triacetin		
[41]	Iran	NG/diesel/ biodiesel	4-cyl, DI, WC, NA	WCO	X	Triacetate		
[42]	Romania	Diesel/glycerol derivatives	4-cyl, DI, WC, NA	X	×	×		
Present study	Iran	Diesel/biodiesel	1-cyl, DI, WC, NA	WCO	X	Graphene oxide nanoparticles	Zi	

acyl – cylinder; DI – direct injection; AC – air cooled; WC – water cooled; NA – naturally aspirated; TC – turbocharged.

When methanol is utilized in this process, it is termed as methanolysis. Triglyceride methanolysis is demonstrated in the following equation:

Transesterification is a reversible reaction and goes on necessarily via blending the reactants, although the addition of a catalyst speeds up the conversion [45]. In general, transesterification is carried out by three procedures of catalyst utilization, which is summarized in Table 2.

Due to the advantages of NaOH such as high reaction speed and low cost, in this study, homogeneous procedure and NaOH alkaline catalyst were used. The transesterification reaction was conducted in a batch reactor with alkali catalyst and the WCO to methanol ratio was 1:6. In addition, the reaction temperature varied between 48 and 60C, and the reaction time was 3 h [56].

Table 3: Summary of surveyed fuel blends

		Diesel percentage	Biodiesel percentage	Graphene nanoparticles
Sample fuels	D ₁₀₀	100	0	0
Binary	$D_{100}G_{30}$	100	0	30
fuels	$D_{100}G_{60}$	100	0	60
	$D_{100}G_{90}$	100	0	90
	$D_{95}B_{5}$	95	5	0
	$D_{80}B_{20}$	80	20	0
Ternary	$D_{95}B_5G_{30}$	95	5	30
blends	$D_{95}B_5G_{60}$	95	5	60
	$D_{95}B_5G_{90}$	95	5	90
	$D_{80}B_{20}G_{30}$	80	20	30
	$D_{80}B_{20}G_{60}$	80	20	60
	$D_{80}B_{20}G_{90} \\$	80	20	90

2.3 Nanoadditive attributes

There are graphene particles in the specific surface area of $900\,\text{m}^2/\text{g}$ and average thickness is nearly 1.2 nm. In this study, GONPs were used as additive due to their unique characteristics like exceptional mechanical and

Table 2: Various procedures for biodiesel production from WCO through transesterification

Procedure	Catalyst instance	Advantage	Disadvantage	Reference
Homogenous	Acid	(1) Suitable for high FFA feed stock	(1) Slow reaction	[46,47]
catalyst	Concentrated H ₂ SO ₄ ,	(2) Yield is high	(2) Need extreme pressure	
	sulfonic acid		and temperature conditions	
			(3) Difficult to separate	
			(4) More corrosive	
	Alkali	(1) Fastest reaction	(1) Formation of soap	[46,48,49]
	NaOH	(2) Higher yield	(2) Difficult to separate it	
	KOH sodium methoxide	(3) Mild reaction condition	from the final product, water	
	Potassium methoxide	(4) Low cost	interferes with reaction	
Heterogeneous	Acid	(1) Less corrosive	(1) Low acid concentration	[46,50]
catalyst	ZnO/I_2 , $ZrO_2 = SO_2$,		(2) High cost	
	$Sr/ZrO_2TiO_2 = SO_2$	(2) Less toxicity	(3) Diffusion limitation	
		(3) Less environmental problem		
	Alkali	(1) Separation of catalyst from	(1) High methanol to oil ratio	[46,50-52]
	CaO , $CaTiO_3$, $CaZrO_3$,	product is easy	is required to reach the	
	CaO-CeO ₂ , CaMnO ₃ ,	(2) Formation of soap is avoided	highest possible conversion	
	$Ca_2Fe_2O_5$	(3) Less corrosive, less toxicity, less		
		environmental		
		problem		
Enzymatic	Candida antarctica fraction	(1) By product of process can be	(1) High reaction time	[46,53-55]
	B lipase, Rhizomucor miehei	easily removed	required	
	lipase, E. aerogenes lipase	(2) FFA can be completely converted	(2) Expansive, activity loss,	
		into methyl esters, regeneration and	agglomeration of enzyme	
		reuse of immobilized enzyme		
		catalyst are possible		

electronic properties, high thermal conductivity, outstanding mechanical strength, extraordinary electro-catalytic activities, excellent electrical conductivity, and high specific area.

2.4 Fuel blend proration

As summarized in Table 3, in this study, 12 different fuel combinations were evaluated and net diesel was considered as sample fuel. Biodiesel was combined with diesel in two levels (5 and 20%), and GONPs were added in three levels (30, 60, and 90 ppm) as additive. For additive stabilization, in the Renewable Energy Research Institute of the Faculty of Agriculture at Mohaghegh Ardabili University, it was combined using an ultrasonic cleaner for 30 min at a frequency of 28 MHz and then mixed with a homogenizer for 10 min to achieve fuel stability [57].

2.5 Engine setup

The engine tested in this study is a single-cylinder, fourstroke diesel engine with a compression ignition and watercooled, which is coupled with an 80 kW dynamometer. Experiments were carried out at full load at an engine speed of 1,500 rpm. The engine test time for each scenario was 5 min to stabilize all the parameters. A schematic presentation of the experimental setup is shown in Figure 2.

The specifications of the employed diesel engine, dynamometer, the measurement accuracies, and the computed parameter uncertainties are illustrated in Table 4.

2.6 Engine performance characteristics

Several indicators are used to compute the engine efficiency. These indicators help make an accurate decision and suggest appropriate strategies in future. Three major indicators of engine efficiency are given below.

2.6.1 Brake power (BP)

BP is the power output of the drive shaft of an engine in the absence of power loss due to gear, transition friction, etc. BP can be calculated from the following equation:

$$BP = \frac{2\pi TN}{60 \times 10^3},\tag{3}$$

where T is the torque (N m) and N is the speed (rpm) [58].

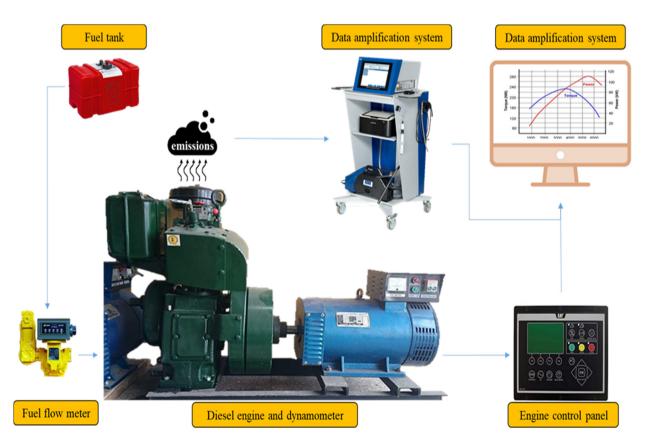


Figure 2: Experimental engine test setup.

Table 4: Specifications of the employed diesel engine, dynamometer, and the measuring instrument for engine parameters

Engine	Manufacturing factory	Kirloskar
	Number of cylinders	1
	Intake valves	2
	Bore and stroke	102 mm ×
		116 mm
	Displacement	948.1 cm ³
	Compression ratio	17.5:1
	Peak power	7.4 kW @
		1,500 rpm
	Max. speed	3,000 rpm
Dynamometer	Type	Dyno D400
	Max. power	80 kW
	Max. speed	10,000 rpm
	Max. torque	80 N.m
	Speed of max. torque	10,000 rpm
	Speed of max. power	3,030 rpm
	Speed calibration	±1 rpm
	accuracy	
	Torque calibration	$\pm 0.6\%$
	accuracy	
	Measuring	Accuracy
	instrument	
Fuel flow meter	PMID company	0.01 kg/h
Air flow meter	ABB Sensyflow P (Germany)	0.3 kg/h
Emissions (CO, CO ₂ , NO _x and O ₂)	AVL DITEST, model MDF418	0.01%

2.6.2 Brake specific fuel consumption (BSFC)

BSFC is a measurement criterion of an initial mover which burns fuel and generates rotatory or shaft power. For comparing the utility of internal combustion engines with a shaft output, this criterion is generally utilized. It is a measure for fuel utilization allocated via the generated power.

It may also be considered as power-specific fuel utilization. BSFC permits fuel performances of various engines to be straightly compared. The following equation is used for computing BSFC:

$$BSFC = \frac{\gamma}{\tau \omega}, \tag{4}$$

where y is in g/s, τ is in N m, and ω is in rad/s [58].

2.6.3 Brake thermal efficiency (BTE)

BTE is a technical scale of an engine's capability to turn fuel energy to mechanical work. The following equation is utilized to compute BTE in the current research:

Table 5: Thermophysical properties of fuel blends

	ASTM Units	Units							Fuel samples	SS				
			D ₁₀₀	$D_{100}G_{30}$	D ₁₀₀ D ₁₀₀ G ₃₀ D ₁₀₀ G ₆₀ D ₁₀₀ G ₉₀ D ₉₅ B ₅	$D_{100}G_{90}$	$D_{95}B_5$	$\mathbf{D_{80}B_{20}}$	$D_{95}B_5G_{30}$	$D_{95}B_5G_{60}$	$D_{95}B_5G_{90}$	$D_{80}B_{20} D_{95}B_5G_{30} D_{95}B_5G_{60} D_{80}B_{20}G_{30} D_{80}B_{20}G_{60} D_{80}B_{20}G_{90}$	$D_{80B_{20}G_{60}}$	$D_{80B_{20}G_{90}}$
Specific gravity at 15°C	ı	kg/L	0.8393	0.8391		0.8387	0.8413	0.8428	0.8413	0.841	0.841	0.8501	0.851	0.852
Kinematic viscosity at 40°C	D-445	mm ² /s	3.08	3.09	3.08	3.07	3.14	3.314	3.136	3.112	3.121	3.301	3.29	3.281
Calorific value	1	kJ/kg	42.57	42.56	45.52	45.5	42.304	41.506	42.3	42.29	42.292	41.509	41.5	41.496
Flash point	D-92	° د	88	88	88	89	91	86	91	92	92	86	86	66
Cloud point	D-2500	o,	-5	-5	-5	-5	7-	-2	-3	-5	4-	-2	-2	-1

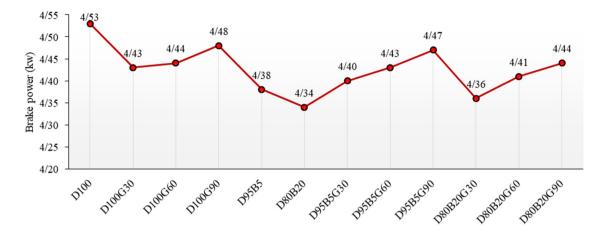


Figure 3: Variations in the BP for different fuel blends.

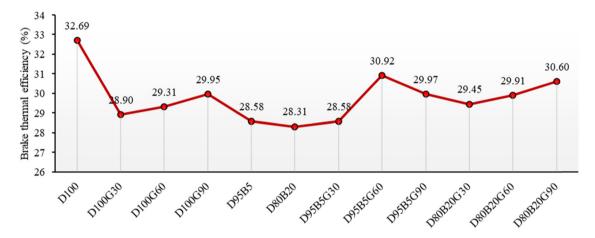


Figure 4: Variations in the BTE for different fuel blends.

$$\eta_{\rm bt} = \frac{\rm BP}{m_{\rm f} \times \rm CV},$$
(5)

where $\eta_{\rm bt}$ is the BTE, $m_{\rm f}$ is in kg/s, and CV is related to fuel in J/kg. As shown in equation (5), BTE has a straight relevance with BP [58].

3 Results and discussion

3.1 Fuel properties

Table 5 presents some thermophysical properties of all the prepared fuels measured on the basis of the ASTM standard guidelines. The density and viscosity of the WCO biodiesel were higher in comparison with those of neat diesel. The addition of GONPs did not have significant effect on the specific gravity and kinematic viscosity of the fuel blends.

The calorific value of the fuel blends was negatively correlated with biodiesel inclusion rates. This could be explained by the high oxygen content of the resultant blends.

3.2 Engine performance metrics and exhaust emissions

3.2.1 BP

In Figure 3, the effects of different fuel blends on the BP of the diesel engine are illustrated. As can be seen from the result, net diesel has produced the most BP. With the addition of biodiesel, power has decreased due to the reduction in the calorific value of the fuel also; the higher density and viscosity of biodiesel compared to net diesel have been effective in the reduction of power [59]. Furthermore, by adding GONPs the engine has shown better performance, especially at 90 ppm. This increase in engine

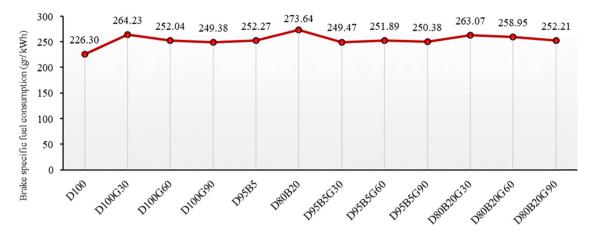


Figure 5: Variations in the BSFC for different fuel blends.

power can be due to the reduction in friction of engine components, because nanoparticles prevent the deposition of carbon and iron in the engine [60]. Also, nanoparticles increase the density of the fuel-air charge due to the increase of the heat of fuel evaporation. Likewise, adding GONPs decrease the combustion duration and the ignition delay that lead to faster heat release rate and higher cylinder pressure [61].

3.2.2 BTE

BTE is described as the ratio of power produced to the energy supplied from the fuel. Figure 4 demonstrates the effects of various fuel blends on the BTE. According to the results, it was found that by adding biodiesel to net diesel, BTE decreased. The lower BTE in the blends containing biodiesel compared to net diesel may result from the low calorific value and viscosity, as well as higher

density of biodiesel (Table 5). These results were in line with the results of other articles [62–64]. In the blends containing GONPs, BTE was somewhat lower compared to net diesel due to low calorific value and high viscosity of the blend. However, with increasing GONP content and reducing reaction time, some improved efficiency was observed and BTE increased [65].

3.2.3 BSFC

Figure 5 illustrates one of the considerable indicators to measure and compare the effects of different fuel blends on engine performance, and the ratio of fuel consumption to the power production which is known as BSFC. As the results show, adding biodiesel in both values increases the BSFC. Obviously, due to the low calorific value of biodiesel (Table 5), adding biodiesel to the fuel blends increases the BSFC [66]. As the results show, adding

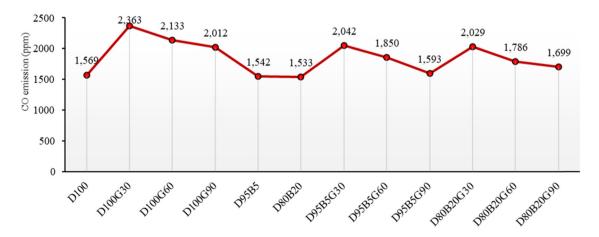


Figure 6: Variations of CO emission for different fuel blends.

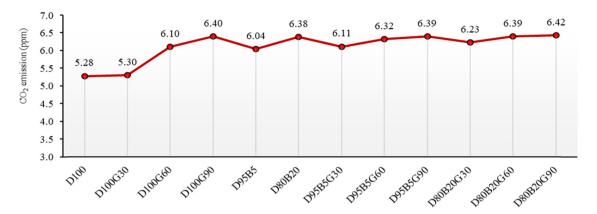


Figure 7: Variations of CO₂ emission for different fuel blends.

GONPs reduces BSFC. This is due to the improved combustion of fuel in the presence of GONPs, which has increased the power production and thus reduced fuel consumption in exchange for the power produced [61].

3.2.4 CO emissions

Generally, in the combustion reaction, deficiency of oxygen, shorter reaction time, and low reaction temperature are the main reasons for the formation of carbon monoxide. Figure 6 illustrates the effect of GONPs on diesel and biodiesel blend on the CO emission. As the results show, the addition of biodiesel increases the cetane number and the oxygen content of the fuel, and has a significant effect on reducing the emission of carbon monoxide [67], but on the other hand, addition of GONPs due to its large surface contact areas reduces the reaction time, and has caused to form more CO. Adding GONPs at the same time reduce the CO emissions due to the increase in the reaction temperature. Because the reaction time range is limited, the amount of CO emissions is reduced by increasing the amount of GONPs from 30 to 90 ppm [61].

3.2.5 CO₂ emissions

Figure 7 demonstrates the effect of GONPs on diesel and biodiesel blend on the CO_2 emissions. As can be seen from Figure 7, the addition of biodiesel increases the emission of CO_2 , and this is due to the higher amount of oxygen in the biodiesel, which causes the reaction to move toward the completion of the combustion process and the release of more CO_2 [68,69]. Also, adding GONPs improves the combustion process and increases the reaction temperature, which causes the reaction to move toward more CO_2 emissions [70].

3.2.6 NO_x emissions

 NO_x emission is highly dependent on the amount of oxygen concentration, the ignition timing, reaction time, and temperature of the contents inside the cylinder. Figure 8 shows the changes in NO_x emissions in engines with different fuel blends of diesel–biodiesel and GONPs as additive. The results show that the addition of biodiesel has increased the emission of NO_x and it is due to the unsaturated

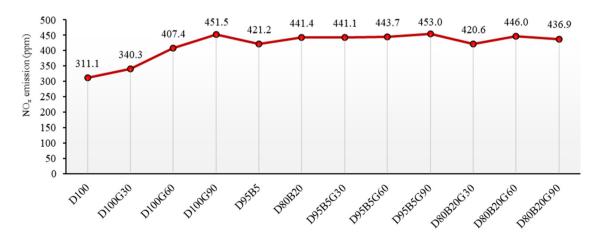


Figure 8: Variations of NO_x emission for different fuel blends.

compounds and higher oxygen content of biodiesel. Also, in addition to the biodiesel oxygen content, the high cetane number and the high temperature inside the cylinder in the biodiesel fuel also cause more NO_x emissions. Many studies have reported similar results for increased NO_x emissions due to the addition of biodiesel [71–77]. Regarding the effect of GONPs on NO_x emissions, the results show a direct relationship, because with the addition of GONPs, the pressure and temperature inside the cylinder increase and the high temperature is the main cause of NO_x formation and emission [70].

4 Conclusion

The principal aim of this study was to evaluate the combustion characteristics performances and emissions of a direct compression ignition diesel engine fueled with 12 different blends of diesel and WCO biodiesel containing GONPs. Based on the experimental results, the following conclusions are drawn:

- Adding biodiesel to fuel blends reduces BP. GONPs improve engine performance and increases BP, so that after pure diesel, more BP was obtained in the $B_{100}G_{90}$ blend.
- The highest amount of BSFC was observed in D₈₀B₂₀.
 GONPs had a subtle effect on reducing BSFC.
- BTE decreased significantly in the presence of biodiesel, while GONPs showed positive effects on increasing BTE followed by net diesel, the highest BTE was reported in DecGo.
- The highest CO emission was observed in D₁₀₀G₃₀ blend.
 The results showed that the amount of biodiesel and CO emission are inversely related.
- There was a direct relationship between CO₂ emissions and biodiesel. GONPs also had a negligible effect on increasing CO₂ emissions, so the highest CO₂ emissions were reported in B₈₀B₂₀G₉₀.
- GONPs were identified as the most important factor in increasing the NO_x emissions, so the effects of biodiesel are also covered to reduce NO_x emissions.

Given all these results, it can be concluded that GONPs are a useful additive to diesel and WCO biodiesel, can be a good alternative to improve combustion and engine performance and reduce some harmful engine emissions.

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Conflict of interest: The authors state no conflict of interest.

Data availability statement: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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