

## Study on the Emission Characteristics of a Biodiesel using Nano Additives

Vinod Kumari<sup>1\*</sup>, Archana Vishal Yewale<sup>2</sup>, Himakar, P.<sup>3</sup>, Mahesh Prakash Joshi<sup>4</sup>, Smriti<sup>5</sup> and Richa Khare<sup>6</sup>

<sup>1</sup>Department of Applied Science and Humanities, Panipat Institute of Engineering and Technology, Samalkha, Haryana 132102, India

<sup>2</sup>Department of First Year Engineering, Nutan Maharashtra Institute of Engineering and Technology, Talegaon Dabhade, Maharashtra 410507, India

<sup>3</sup>Department of Physics, P. R. Government College, Kakinada, Andhra Pradesh 533001, India

<sup>4</sup>School of Mechanical Engineering, MIT Academy of Engineering, Pune, Maharashtra 412105, India

<sup>5</sup>Amity School of Applied Sciences, Amity University, Lucknow, Uttar Pradesh 226010, India

<sup>6</sup>Amity School of Applied Sciences, Amity University, Lucknow, Uttar Pradesh 226010, India

\*Corresponding author (e-mail: dahiyavinod123@gmail.com)

The increasing environmental concerns and depletion of fossil fuel reserves have accelerated research into alternative and sustainable fuels. In this study, neem seed oil-based biodiesel was prepared and blended with pure diesel (PD) at a 15% concentration to create a biodiesel blend (PDNS). In order to enhance the combustion and emission characteristics, titania (TiO<sub>2</sub>) nanoparticles at varying concentrations (25 ppm, 50 ppm, and 75 ppm) were incorporated into the biodiesel blend (PDNS). The experimental investigation was conducted on a four-stroke, single-cylinder diesel engine under different engine loads. The performance parameters such as brake thermal efficiency (BTE), smoke opacity, carbon monoxide (CO), unburned hydrocarbons (HC), and nitrogen oxides (NO<sub>x</sub>) emissions were measured and compared. The results indicated that the addition of nano-TiO<sub>2</sub> significantly improved the BTE and reduced CO, HC, and smoke emissions, with the 50-ppm concentration exhibiting the most favorable performance. However, a slight increase in NO<sub>x</sub> emissions was observed due to enhanced combustion temperatures. The findings suggest that neem seed oil-based biodiesel doped with nano-TiO<sub>2</sub> could serve as a promising alternative fuel blend to improve the engine performance with reduced emissions.

**Keywords:** Biodiesel; neem seed oil; nano-TiO<sub>2</sub>; engine emission; brake thermal efficiency

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The increase in demand for fossil fuels is caused by the exponential growth of the transport and logistics sector across the globe. The transport vehicles play a significant role, both in personal and the commercial transportations. At present, the majority of the fuel demand has been fulfilled by the use of petroleum-based fuels. However, such fuels significantly contribute to the emission of hazardous contaminants and greenhouse gases into the air, which causes a substantial damage to the human health and the environment [1]. In this scenario, the alteration in the composition of the conventional fuel can be a better solution to address the present issues. It can aid to control the emission of the engine without compromising its performance. The alteration can be done by mixing a suitable biofuel within the conventional diesel in some suitable proportions, and these fuels are termed as biodiesel [2].

Biofuel is a non-conventional fuel resource produced by the transesterification process of feedstock oils. The use of pure biofuel significantly reduces the release of greenhouse gases and particulates. Nevertheless, the research of such alternative biofuel-

based energy sources for transportation vehicles remains immature and requires significant progress [3]. In contrast, biodiesels have been developed by the mixing of biomass oils with the conventional diesel fuel, in order to the improve efficacy of the internal combustion engines and reduce their greenhouse emissions [4, 5]. The characteristics of biodiesel have been ascribed to the quality and the proportions of the blended biofuel. Biodiesel has consistently garnered support from fuel experts as the most auspicious substitute for traditional fossil fuels. Constant endeavours have been undertaken to promote the increasing generation of environmentally friendly substitutive fuels through the enhanced utilization of various biofuel in biodiesel production [3, 5].

However, certain investigations have demonstrated a slight increase in carbon monoxide and hydrocarbon releases at reduced load conditions, mostly caused by lack of atomization of fuel, that hinders adequate air-fuel blending [6, 7]. The increased viscosity of biofuel is a significant barrier when considering its direct application in engine. It may have a negative influence on fuel delivery, the atomization

process and efficiency of combustion [3, 8]. Furthermore, several investigations have found that diesel-powered engines operating on biofuels emit higher NO<sub>x</sub> levels. It may be attributed to variables such as the increased viscosity and enhanced levels of oxygen present in biofuels [9, 10]. The neem seed oil is one among the bio-oil, which can be extracted from the universally available neem trees at a very reasonable cost. The Indian states are home to perennial neem vegetation. The neem trees exhibit adaptability to soil composition. Massive quantities of triterpenoid compounds containing both unsaturated as well as saturated fatty acids make up the majority of neem. It is claimed that the fatty acids are crucial to the biofuel production process. A biodiesel-producing process is facilitated by the high free fatty acid content of neem seed-based oil [11].

Inclusion of nano-sized particles are being proposed as additives to the biofuel mixtures to enhance combustion efficiency and reduce emissions. Adding nanoparticles to the fuel enhances their thermo-physical characteristics, energy transfer level, stimulant reactions, and fuel-air mixture stability. Nano particles have unique qualities, such as enhanced chemical responsiveness, heat conductivity, and ability to transmit electricity in comparison to ordinary substances [12]. Nano particles possess distinctive both physical and chemical characteristics. Nano-additives improve combustion efficiency and reduce emissions by enhancing fuel-air blending. Furthermore, the inclusion of nanoparticles decreases fuel use and operating expenses while also lessening carbon pollutants. Nano additions enhance thermophysical diesel qualities such as surface area-to-volume proportion, heat transmission, and conductivity of heat. Adding these particles to fuels reduces their ignition lag and vaporization duration. Nanoparticle distribution enhances burning chemistry and thermo-physical characteristics of the fuels [4]. Nanoparticles have a significant influence on ignition as well as the burning process, prompting investigators to consider using them as possible enhancers. The nano-sized substances of metals and metal oxides, enhance vaporization rates and reactions. Nano-additives' nanometer size helps in an increased active burning zone [4, 13].

Purushothaman et al. [14] piloted an investigation to optimize the performance and engine exhaust characteristics of a diesel engine operating. The engine was operated on a biofuel blend made up of mixing diesel with the mahua oil emulsion along with the titanium oxide and alumina-based nano-additives. It was noted that the inclusion of nanoparticles significantly reduced the emission of nitrogen oxides and particulate matters. A study was carried out by Vellaiyan [15] in which a CI engine was powered with soybean oil blend-based biofuel along with the application of carbon nanotubes (CNTs) as nano-additives. The biofuel mixtures that were prepared exhibit enhanced efficacy, accompanied by a reduction

in the emission of nitrogen oxides and particulate matters, correspondingly.

The recent review articles highlighted effectiveness of incorporating different kind of nano-additives in biofuels to enhance its performance and to suppress the emissions of hazardous gases [16, 17]. Further, a few researchers have discovered that the utilization of titanium dioxide (TiO<sub>2</sub>) nanoparticles with biodiesel would significantly enhance the performance of the CI engines and mitigate the harmful emissions [18, 19]. As per the authors knowledge, the influence of TiO<sub>2</sub> nanoparticles on the emission performance of the neem seed oil-based biofuel was not properly dealt in any earlier literature. Hence, the objective of the present investigation is to determine the suitability of the TiO<sub>2</sub> nanoparticles in improving the emission characteristics of the biofuel which was prepared by blending diesel with the neem seed oil.

## MATERIALS AND METHODS

### Neem Seed Oil Preparation

Neem trees typically begin to bear fruit around their lifespans of three to five years and achieve peak output at around the age of ten years. This high level of cultivation may be sustained for a period of anywhere around 200 years. The seeds from the neem tree fruits have a high amount of oil, making as much as sixty percent of their dry weight. A matured neem tree may produce approximately 40 kg of pods each year [20, 21, 22]. The oil from neem seeds has a fatty acids proportion (saturated level to unsaturated level) that fluctuates around 0.54 [23, 24].

Numerous investigations analysing the composition of neem seed oil showed a total of around 14 forms of fatty acid groups, with 4 of them being considered the most abundant. Oleic acid, the main fatty acid, makes up to sixty percentage [5, 8] of the total fatty acids within the seeds. Palmitic as well as stearic acids constitute saturated fatty acids with the composition of around 16% and 20%, respectively, whereas linoleic acid (unsaturated) comprises around 14%. In the present investigation, the neem fruits were collected from near-by trees. The skin and the pulps were clearly removed from the seeds. They were sundried for two days and milled to extract the oil from them. The collected oil was in dark colour with a strong and bitter odour.

The production of neem seed biodiesel involves two processes: acid and alkaline esterification. The application of a catalyst made from acids in acid the esterification process reduces the amount of acids of raw neem seed oil to 3%. The second process is alkaline esterification. Subsequently, after the previous process, it undergoes transesterification to form monoesters of lipids using an alkaline stimulant, with a temperature of 60 °C sustained throughout the entire process. One litre of neem seed oil

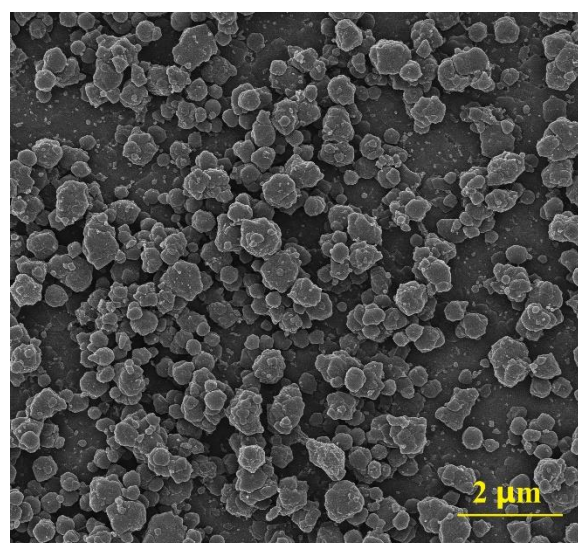
necessitates about 300 mL of methanol. The obtained neem seed oil was carefully transferred into the container and processed to around 55 °C. Methanol was incorporated into the pre-heated neem oil and agitated for about 10 minutes. Heating and agitating were maintained for 30 minutes. Upon completion of the reaction, the solution was transferred to a separation funnel to facilitate the removal of surplus alcohol. The collected neem oil would be used to mix with diesel for testing. Table 1 shows the characteristics of the neem seed oil.

### Preparation of Nano-TiO<sub>2</sub>/Biodiesel

The pure diesel fuel was labelled as PD. The biodiesel blends were prepared by mixing the PD with neem seed oil in the ratio of 85:15 and labelled as PDNS. The PDNS was thoroughly mixed using a magnetic stirrer for about 30 minutes for getting a homogeneous diesel fuel. The nano-TiO<sub>2</sub> particles with the average particle size of 30 nm had been procured from Nanoshel Inc. The FESEM image of the nano-TiO<sub>2</sub> is given in Figure 1.

**Table 1.** Characteristics of neem seed oil.

S. No.	Properties with unit	Neem seed oil
1.	Flash Point (°C)	145
2.	Pour Point (°C)	3
3.	Coefficient of Viscosity (mPa.s)	37.4
4.	Kinematic Viscosity (mm <sup>2</sup> /s)	24
5.	Calorific Value (MJ/kg)	40



**Figure 1.** FESEM of the nano-TiO<sub>2</sub>.

**Table 2.** Composition of nano/biodiesel.

Sample name	Composition of diesel (%)	Composition of Neem seed oil (%)	Composition of nano- TiO <sub>2</sub> particles (ppm)
PD	100	0	0
PDNS	85	15	0
PDNS25	85	15	25
PDNS50	85	15	50
PDNS75	85	15	75

The nanoparticles were taken separately and added with distilled water using a wetting agent. The measured quantity of the nano-TiO<sub>2</sub> solution was carefully transferred to the PDNS using the magnetic stirrer at three concentrations, 25 ppm, 50 ppm, and 75 ppm. Then, they were subjected to a high degree of stirring action to obtain the homogeneous nano/biodiesel fuels. The prepared samples are presented in Table 2.

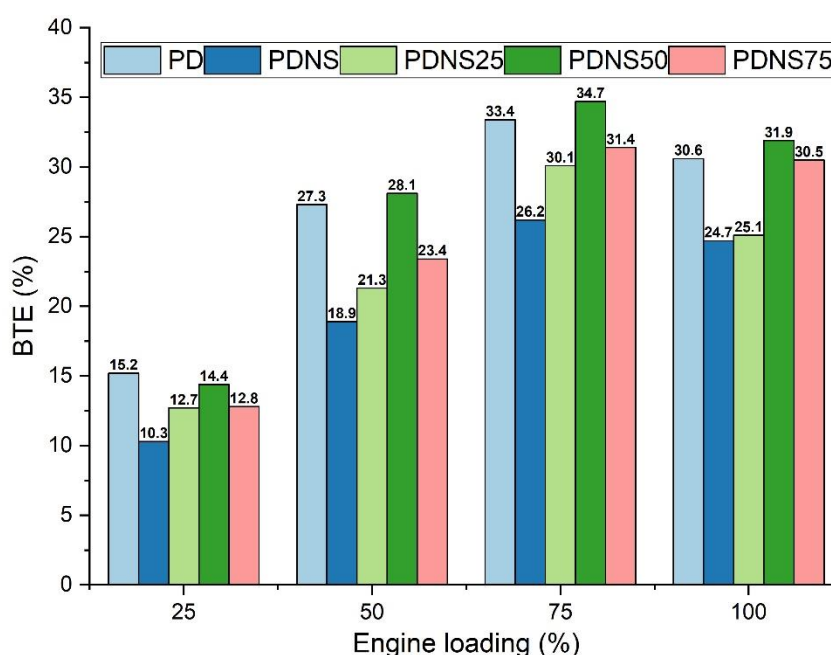
### Engine Test Rig

A four-stroke, single-cylinder diesel engine with a displacement of 553 CC was employed as the test rig for the experiments. The engine was water-cooled, with a power output of 5 HP operating at 1500 rpm. It operates with a compression ratio of 16.5:1. The test rig incorporates a data gathering system, consisting of several sensors for sending and collecting data from the engine throughout work. The test rig employs a number of standard sensors, including pressure transducers and thermostats. The signals denoting combustion characteristics are then transmitted to the

engine management module. The temperature of the flue gases released from the engine has been measured using thermostats. The flue gas tester was used to analyse the emissions released from the emission. The testing apparatus comprises a fuel container capable of holding gasoline, with the fuel flow rate controlled through a digital controller. Measurements are quantified based on the fuel consumption in ten cc across various loading conditions. The experiment was conducted under various loading conditions, alongside a constant crank rotational velocity of 1500 rpm. Investigations are being performed on the test rig using five different fuel samples under various loading conditions, including 25%, 50%, 75%, and 100% loading. The engine operated under steady circumstances, and five readings were recorded. The engine evaluation of brake thermal efficiency (BTE) and the emission parameters, namely hydrocarbons (HC), nitrogen oxides (NO<sub>x</sub>), smoke and carbon monoxide (CO) has been conducted and analyzed. The detailed specification of the engine is given in Table 3.

**Table 3.** Specification of test rig.

Description	Specification
Model	Kisloskar
Stroke	110 mm
Bore	80 mm
Compression ratio	16.5:1
Engine capacity	553 CC
Peak power	5 HP at 1500 rpm



**Figure 2.** BTE of the fuel samples at varying engine loads.

## RESULTS AND DISCUSSION

This section provides a comprehensive examination of the performance and emission characteristics of neem seed oil-based biodiesel (NB15) mixed with different amounts of titanium dioxide ( $\text{TiO}_2$ ) nanoparticles. The evaluated fuels were pure diesel (PD), diesel with neem seed oil (PDNS), and PDNS with nano- $\text{TiO}_2$  additions at concentrations of 25 ppm (PDNS25), 50 ppm (PDNS50), and 75 ppm (PDNS75). The trials were performed at different load levels on a single-cylinder, four-stroke diesel engine. The data presented consist of brake thermal efficiency (BTE), smoke opacity, carbon monoxide (CO) emissions, unburned hydrocarbon (HC) emissions, and nitrogen oxides ( $\text{NO}_x$ ) emissions.

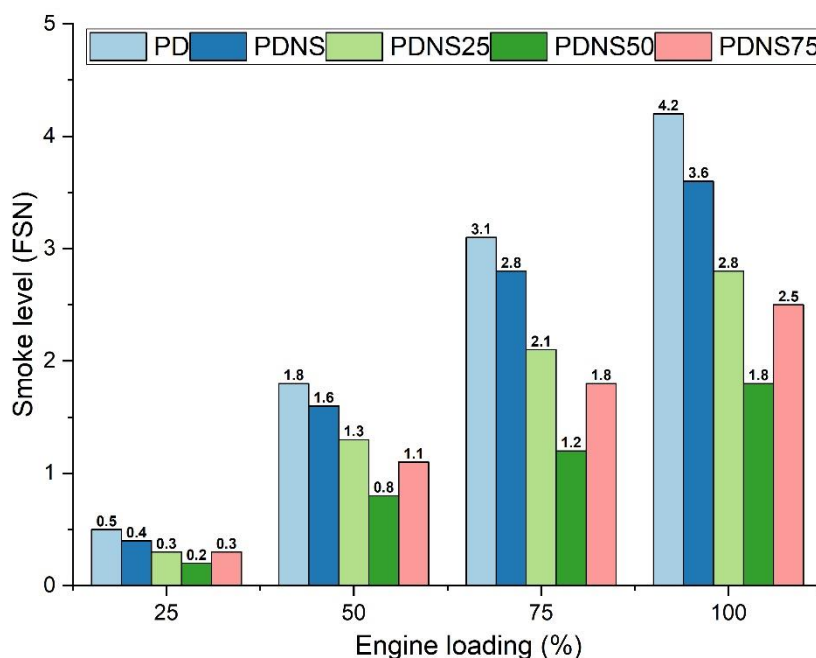
### Brake Thermal Efficiency (BTE)

The variation of brake thermal efficiency (BTE) with engine load for different test fuels is shown in Figure 2. In all cases, BTE was found to increase with increasing engine load. This behavior is primarily attributed to reduced heat losses and a better combustion process at higher loads, where the air-fuel mixture approaches stoichiometric conditions.

Among the various fuel samples tested, the PDNS50 blend demonstrated the highest BTE at all

loading conditions. At maximum engine load, PDNS50 achieved a BTE of 34.7%, which is superior to the BTE of pure diesel (33.4%) and all other blends. This improvement can be linked to the enhanced combustion characteristics facilitated by  $\text{TiO}_2$  nanoparticles. The nanoparticles, owing to their high surface area and catalytic properties, promote better atomization, quicker evaporation, and faster ignition of the fuel-air mixture. Consequently, the combustion becomes completer and more efficient, leading to higher thermal efficiency.

The PDNS25 blend showed moderate improvements over NB15 but did not outperform PDNS50. Meanwhile, PDNS75 exhibited a slight reduction in BTE compared to PDNS50. This suggests that while the addition of nanoparticles enhances combustion, an excess quantity could lead to nanoparticle agglomeration, resulting in uneven fuel dispersion and incomplete combustion. Therefore, an optimal concentration of nano- $\text{TiO}_2$  exists, around 50 ppm, beyond which performance benefits start to diminish. In comparison, the NB15 biodiesel blend without nanoparticles exhibited lower BTE compared to diesel due to its higher viscosity and lower calorific value. However, even for NB15, the addition of nanoparticles significantly improved performance, emphasizing the effectiveness of  $\text{TiO}_2$  as a combustion catalyst.



**Figure 3.** Smoke emission of the fuel samples at varying engine loads.

## Smoke Emissions

Smoke emission is an important parameter reflecting the degree of incomplete combustion and particulate matter formation. Figure 3 illustrates the smoke opacity variations for the different fuel blends at various engine loads. As expected, smoke emissions increased with engine load for all the tested fuels due to higher fuel consumption and richer air-fuel mixtures. Pure diesel (PD) showed the highest smoke emissions at full load, recording 4.2 FSN (Filter Smoke Number). In contrast, the PDNS50 blend exhibited the lowest smoke emissions at all load conditions, reaching just 1.8 FSN at full load. The addition of nano-TiO<sub>2</sub> significantly suppressed smoke formation. This reduction is attributed to the catalytic effect of the nanoparticles, which facilitate complete oxidation of the hydrocarbons and soot precursors before they aggregate into visible particulates.

Furthermore, the oxygen buffering property of TiO<sub>2</sub> nanoparticles ensures localized availability of oxygen during combustion, thus accelerating oxidation reactions even in regions where the air-fuel mixture is rich. PDNS75 also demonstrated lower smoke emissions compared to PDNS25 and NB15, although slightly higher than PDNS50, supporting the notion that 50 ppm is the optimal nanoparticle concentration. Overall, these results confirm that TiO<sub>2</sub> nanoparticles are effective in minimizing particulate emissions and enhancing combustion cleanliness.

## Carbon Monoxide (CO) Emissions

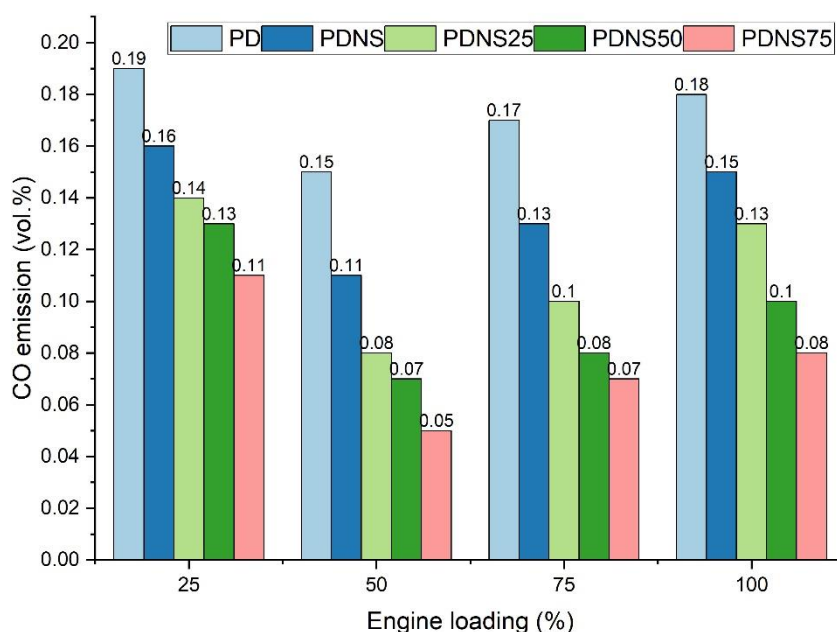
Figure 4 shows the variation of carbon monoxide (CO) emissions with engine load for the tested fuel blends. CO is a product of incomplete combustion, typically resulting from oxygen-deficient conditions

in the combustion chamber. The experimental results reveal that CO emissions increased with engine load for all fuels. However, the magnitude of emissions varied significantly depending on the fuel composition. Among the blends, PDNS50 achieved the lowest CO emissions across all engine loads. At full load, CO emissions for PDNS50 dropped to 0.08 vol.% compared to 0.18 vol.% for pure diesel. This substantial reduction is primarily due to the enhanced oxidation of CO into CO<sub>2</sub>, facilitated by the catalytic properties of TiO<sub>2</sub> nanoparticles.

The presence of TiO<sub>2</sub> promotes the breakdown of intermediate combustion species, improving the oxidation of CO even under richer air-fuel mixtures at higher loads. The CO emission trends for PDNS25 and PDNS75 also showed improvements over pure diesel and NB15, but PDNS50 consistently outperformed the others, affirming its effectiveness at optimal nanoparticle concentration. Thus, the incorporation of TiO<sub>2</sub> nanoparticles into biodiesel blends demonstrates a notable potential for reducing toxic carbon monoxide emissions in diesel engines.

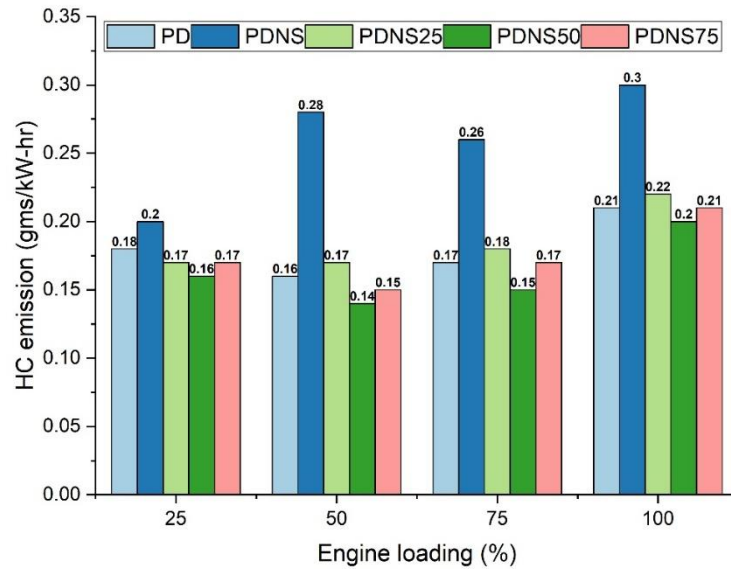
## Hydrocarbon (HC) Emissions

Unburned hydrocarbons (HC) are another critical emission parameter, indicating the fraction of fuel that escapes combustion. The variation of HC emissions with engine load for different fuels is depicted in Figure 5. As seen, HC emissions generally increased with engine load for all fuels, although the trends were not as steep as for CO or smoke emissions. Pure diesel exhibited higher HC emissions (0.21 g/kW-hr) compared to the nanoparticle-infused biodiesel blends. Among the blends, PDNS50 recorded the lowest HC emissions at 0.20 g/kW-hr at full load, indicating a 5% reduction compared to pure diesel.



**Figure 4.** CO emission of the fuel samples at varying engine loads.

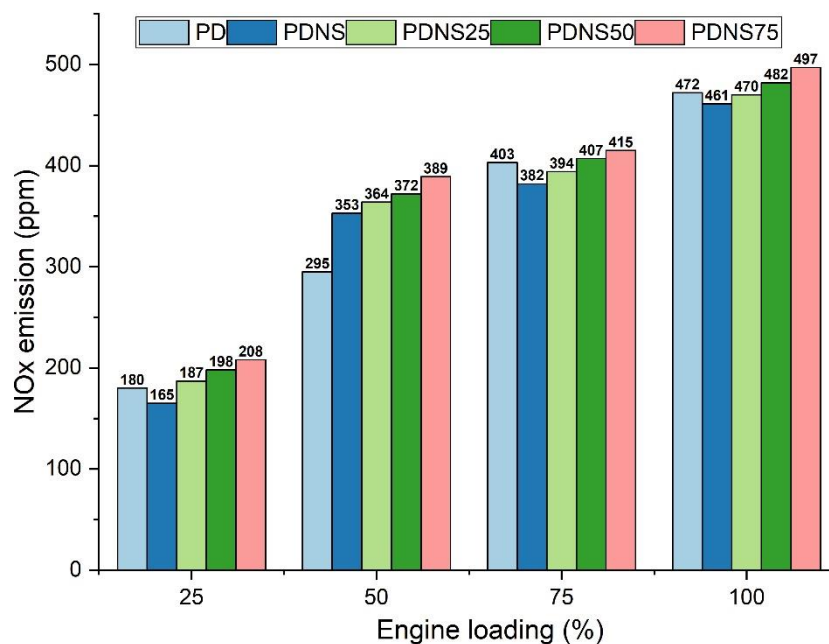




**Figure 5.** HC emission of the fuel samples at varying engine loads.

The reduction in HC emissions can be attributed to improved atomization and better air-fuel mixing provided by the nanoparticles. The catalytic properties of  $\text{TiO}_2$  promote more effective burning of hydrocarbons, even in regions of the combustion chamber where mixing is suboptimal. Interestingly, beyond 50 ppm concentration, the PDNS75 blend showed no further significant decrease in HC emissions. This observation might

be due to nanoparticle agglomeration at higher concentrations, which reduces their surface area and catalytic effectiveness. Therefore, while nanoparticles aid in reducing HC emissions, their concentration must be carefully optimized. Overall, the reduction of HC emissions with nano- $\text{TiO}_2$  addition aligns well with the trends observed for CO and smoke emissions, reinforcing the overall improvement in combustion efficiency.



**Figure 6.** NO<sub>x</sub> emission of the fuel samples at varying engine loads.

## Nitrogen Oxides (NOx) Emissions

Figure 6 presents the NOx emission characteristics for different fuel blends at varying loads. Nitrogen oxides are primarily formed at high combustion temperatures and pressures through the thermal fixation of atmospheric nitrogen. Unlike CO, HC, and smoke emissions, NOx emissions increased with the addition of TiO<sub>2</sub> nanoparticles. For example, NOx emissions at full load for PD were 472 ppm, while PDNS50 and PDNS75 showed slightly higher values of 490 ppm and 497 ppm, respectively. The increase in NOx emissions with the use of nanoparticles is linked to the higher combustion temperatures achieved due to enhanced burning rates and improved thermal efficiency.

While higher combustion efficiency leads to a cleaner burn with reduced particulate and CO emissions, it also promotes NOx formation due to elevated in-cylinder peak temperatures. Although the increase in NOx is relatively modest compared to the reductions in other emissions, it remains an important consideration for emission control.

This finding highlights the classic trade-off in combustion improvement strategies: while measures to enhance combustion efficiency reduce soot and CO, they can inadvertently elevate NOx emissions. Therefore, further after-treatment technologies, such as exhaust gas recirculation (EGR) or selective catalytic reduction (SCR) systems, may be necessary to control NOx when using nano-additive biodiesel blends.

## CONCLUSION

The biodiesel blend containing 85% pure diesel and 15% neem seed oil had been prepared and the influence of mixing nano-TiO<sub>2</sub> at different concentrations (25 ppm, 50 ppm and 75 ppm) in biodiesel on the combustion and emission performance of the biodiesel was assessed.

- The experimental investigation demonstrated the potential of TiO<sub>2</sub> nanoparticles as an effective additive for neem seed oil-based biodiesel blends in diesel engine applications.
- The incorporation of nano-TiO<sub>2</sub> at different concentrations notably influenced the combustion and emission characteristics of the engine.
- Among the tested samples, the PDNS blend supplemented with 50 ppm of nano-TiO<sub>2</sub> (PDNS50) consistently delivered superior results. It achieved the highest brake thermal efficiency while simultaneously lowering the emissions of carbon monoxide, unburned hydrocarbons, and smoke compared to both

pure diesel and the biodiesel blend without nanoparticles.

- Nonetheless, a marginal increase in NOx emissions was observed, attributed to the higher combustion temperatures resulting from improved oxidation processes. This observation indicates the need for supplementary NOx control strategies, when adopting nanoparticle-infused biodiesel blends.

The study confirms that nano-TiO<sub>2</sub> additives significantly enhance the performance and environmental viability of biodiesel derived from neem seed oil. With further optimization, such nano-enhanced biofuels could represent a feasible and sustainable alternative to conventional fossil fuels, supporting cleaner transportation solutions without sacrificing engine performance.

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