



EXPERIMENTAL INVESTIGATIONS ON THE EFFECTS OF CERIUM OXIDE NANOPARTICLE ADDITION IN DIESEL AND DIESEL-BIODIESEL BLENDS ON THE PERFORMANCE AND EMISSION CHARACTERISTICS OF A CI ENGINE

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Abstract

An experimental investigation is carried out to establish the performance and emission characteristics of a compression ignition engine while using cerium oxide nanoparticles as additive in neat diesel and diesel-biodiesel blends. In the first phase of the experiments, stability of neat diesel and diesel-biodiesel fuel blends with the addition of cerium oxide nanoparticles are analyzed. After series of experiments, it is found that the blends subjected to high speed blending followed by ultrasonic bath stabilization improves the stability. In the second phase, performance characteristics and emissions are studied using the stable fuel blends in a single cylinder four stroke engine coupled with an eddy current dynamometer and a data acquisition system. The cerium oxide acts as an oxygen donating catalyst and provides oxygen for the oxidation of CO. The activation energy of cerium oxide acts to burn off carbon deposits within the engine cylinder at the wall temperature on the emissions. The tests revealed that cerium oxide nanoparticles can be used as additive in diesel and diesel-biodiesel blends to improve complete combustion of the fuel and reduce the exhaust emissions significantly.

Keywords: diesel engine, emissions, nanoparticles, diesel-biodiesel blends.



Introduction

The compression ignition engines are widely used due to its reliable operation and economy. As the petroleum reserves are depleting at a faster rate due to the growth of population and the subsequent energy utilization, an urgent need for search for a renewable alternative fuel arise. Also the threat of global warming and the stringent government regulation made the engine manufacturers and the consumers to follow the emission norms to save the environment from pollution. Among the many alternative fuels, biodiesel (vegetable methyl esters) is considered as a most desirable fuel extender and fuel additive due to its high oxygen content and renewable in nature (Kwancharareon, 2007). Biodiesel is a renewable and eco-friendly alternative diesel fuel for diesel engine. Biodiesel has higher viscosity, density, pour point, flash point and cetane number than diesel fuel. Biodiesel is an oxygenated fuel which contains 10–15% oxygen by weight. Also it can be said a Sulfur free fuel. These facts lead biodiesel to total combustion and less exhaust emissions than diesel fuel (Mozhi et al, 2008). Furthermore also the energy content or net calorific value of biodiesel is about 12% less than that of diesel fuel on a mass basis. Using optimized blend of biodiesel and diesel can help reduce some significant percentage of the world's dependence on fossil fuels without modification of CI Engine, and it also has important environmental benefits. For example using optimized blend of biodiesel and diesel instead of the conventional diesel fuel significantly reduces the exhaust emissions particulate matter (PM), carbon monoxide (CO), sulfur oxides (SO_x), and unburned hydrocarbons (HC). Moreover additives are an essential part of today's fuels. Together with carefully formulated base fuel composition, they contribute to efficiency reliability and long life of an engine. They can have surprisingly large effects even when used in parts per million (PPM) range. With use of fuel additives in the blend of biodiesel and diesel fuelled in CI Engine which further more improve performance, combustion, and diminish emission characteristics and also improved fuel properties which enhance the combustion characteristics.

Among the various techniques available to reduce exhaust emissions, the use of fuel-borne catalyst is currently focused due to the advantage of increase in fuel efficiency while reducing harmful greenhouse gas emissions and the health-threatening chemicals such as NO_x and particulate matter. The influence of cerium oxide additive on ultrafine diesel particle emissions and kinetics of oxidation was studied by Jung *et al.* (Jung et al, 2005). They found that addition of cerium to diesel cause significant reduction in number weighted size distributions and light-off temperature and the oxidation rate was increased significantly. Escribano *et al.* studied the structural and morphological characterization of a Ce-Zr mixed oxide supported Mn oxide as well as on its catalytic activity in the oxidation of particulate matter arising from Diesel engines (Escribano et al, 2008). Mn-Ce-Zr catalyst shows high activity in the soot oxidation producing CO₂ and CO as a by-product in the range 425-725 K. Idriss studied the complexity of the ethanol reactions on the surfaces of noble metals/cerium oxide catalysts (Idriss, 2004). The hazard and risk assessment with the use of nanoparticle cerium oxide bases diesel fuel was studied by Barry Park *et al.* (Park et al, 2008). Auffan *et al.* studied the potential *in vitro* cyto- and genotoxicity of nano-sized CeO₂ on human dermal fibroblasts (Auffan et al, 2009). Ali Keskin et al. investigated the influences of Mg and Mo based fuel additives on diesel engine performance running with tall oil biodiesel. A single cylinder DI diesel engine was used in the tests. The authors found that the engine performance values did not change significantly with biodiesel fuels (Keskin et al, 2008). In the present work, waste oil methyl ester as additive is used with the diesel fuel and the emission reduction potential are investigated using cerium oxide nanoparticles as fuel borne additive with neat diesel and diesel-biodiesel blends on the compression ignition engine

2. Experimental Study

The experimental investigations were carried out in two phases. In the first phase, the various physicochemical properties of diesel – biodiesel blends were determined. The properties studied were the flash point, cloud and pour points and viscosity. Standard ASTM test procedures were used in the experiments. In the second phase, performance and emission tests were conducted on a single cylinder



compression ignition engine using the modified and base fuels, in order to evaluate the engine performance as well as the emission characteristics using an exhaust gas emission analyzer. The method of preparation of the fuels with the additive nanoparticles along with the experimental methods for obtaining the fuel properties and the details of the performance test facility are all presented below.

2.1. Preparation of Modified Fuels

Biodiesel used in this investigation was supplied from National Bioenergy Research Center (NBERC) of Tarbiat Modares University, Tehran, Iran. The biodiesel was produced by transesterification method from fried oil. The biodiesel would meet the requirements of international standard of ASTM D6751-09. Table 1 gives the different diesel-biodiesel fuel blends used in this study. Total of three fuel mixture samples with different percentages of two types of fuel was prepared and indicated by the acronym BxDy where B denotes biodiesel, x is biodiesel percentage in the sample, D is pure diesel, and y is the percentage of pure diesel in the fuel blend. Some of the major properties of biodiesel are shown in table (2).

Table (1): Diesel and biodiesel fuel blends used in this study.

B0D100	B5D95	B20D80
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The fuel additive used in this investigation is cerium oxide, in the form of commercially available nanoparticles of size 10 to 30 nanometers and density of 7.13 g/mL. The dosing level of the cerium oxide nanoparticle samples (by weight) in the base fuel was varied from 5 to 25 ppm. The required quantity of the nanoparticle sample required for each dosing level was measured using a precision electronic balance and mixed with the fuel by means of an ultrasonic shaker, applying a constant agitation time of 30 minutes to produce a uniform suspension. The modified fuel was utilized immediately after preparation, in order to avoid any settling or for sedimentation to occur.

Table 2: Properties of biodiesel and diesel

Gasoline	Biodiesel	unit	Specifications
C16H34	C20H39O2		Chemical formula
57.5	62.1		Cetane number
42.57	41.3	J/kg	Heat value
3.09	6.482	cSt	Kinematic viscosity at 40 °C
0.839	0.878	gr/cm ³	Density at 25 °C
-----	10.5	%w	amount of oxygen

2.2. Determination of Fuel Properties

The viscosity, flash, pour and cloud points were measured using standard test methods. The viscosity was measured using the Redwood viscometer. One of the main characteristics of the fuel used in cold weather conditions is the cloud point. This point is a temperature which the first wax network is created in the cooling liquid to cloud. It is the lowest temperature that the fuel can be used. Using fuel in temperature lower than cloud point can cause fuel filter clogging. The cloud point is determined according to ASTM D5773 standard by observing the fuel transparency that is cold under the controlled conditions.

The pour point is the lowest temperature which the fuel can flow. Then the fuel becomes solid after this temperature and its not useable. This point is very important to transfer the fuels in cold temperatures. ASTM D97 is the standard to determine the point. A cleveland open cup flash and fire point apparatus was used for measuring the flash point.

2.3. Description of the Test Engine.



The experiments were carried out in thermodynamic laboratory, technical faculty, Islamic Azad University, Dezful Branch, Dezful, Iran. In order to study the effects of cerium oxide nanoparticle addition in different diesel and biodiesel fuel blends on small diesel engine performance parameters a test set up unit (Gunt model CT 159, Germany) was used in this study (Fig.1). The set up stand consists of three main components including a CT 159 for mounting of the engine and as a control unit, a universal drive and brake unit or dynamometer, (HM 365) as a load unit, and a four-stroke diesel engine (CT 151). The main function of CT 159 is to mount the engine, supply it with fuel and air and record and display relevant measurement data. The engine is mounted on a vibration-insulated base plate and connected by way of a belt drive to HM 365 dynamometer. Motor Scan analyzer is used to measure the exhaust gas constituents such as CO, CO₂, HC and NO_x. After the engine warmed up the dynamometer acts as a brake for applying resistant load to the engine. The lower section of the mobile frame contains fuel tank and a vessel for the intake air. A measuring tube for fuel consumption is also included in the test unit. The speed and torque are adjusted and displayed on the dynamometer. The measured values are transmitted directly to a personal computer via USB and the data acquisition software. The diesel engine brake power, torque and brake specific fuel consumption were measured at four engine speed levels (1500, 2000, 2400 and 2600 rpm) for the different fuel blends. A four stroke, single cylinder, air-cooled compression ignition engine was used to conduct the performance and emission studies. Engine is coupled to an eddy current dynamometer. A computerized data acquisition system is used to collect and store the data during the engine testing. Specifications of the engine used for the performance study are given in Table 3, and a schematic block diagram of the experimental test facility is illustrated in Figure 1.

Table 3: Engine specifications.

Hatz 1B20-6	Model
Gunt	Company
1	Number of Cylinder
mm 62	Stroke
69mm	Bore
approx. 1.5 kW	Rated output
21: 1	Compression ratio
Air cooled	Cooling System
DI	Type of fuel system
l×w×h 485 × 355 × 520 mm	Dimension
0.9 Lit	Oil Volume

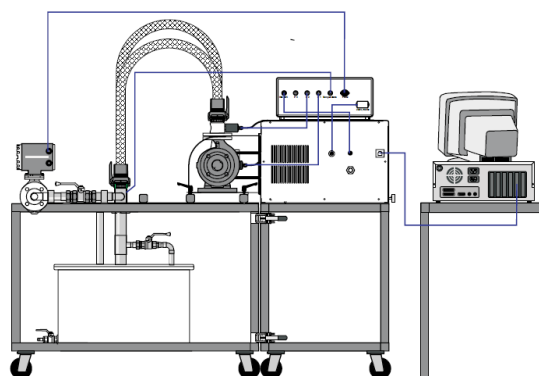


Figure 1: Schematic of the experimental set up.

3. Results and Discussion

The ASTM standard tests to determine various physicochemical properties of the base fuels (Bio diesel) as well as the modified fuels were carried out under identical laboratory condition so that the



results could be compared. The primary objectives of this investigation were to determine the variations in the properties of the fuels, due to the addition of the cerium oxide nanoparticles and to estimate the effect of the level of inclusion of the additives (dosing level) on these variations. performance tests were conducted on the diesel engine using the modified fuel samples and compared with those with the base fuels, to determine the engine performance enhancement and the reduction of emissions, due to the addition of the catalyst. Based on the experimental results, the variations in the physicochemical properties of the fuel, and the variations in the efficiency and emissions of the CI engine using the modified fuels were determined with various dosing levels as given below. Some indications on the existence of optimum additive nanoparticle dosing levels were also obtained as discussed in this section.

3.1. Fuel Properties

The flash point of the fuel gives an indication of the volatility of a fuel. The lower the volatility, the higher the flash and fire points. Figure 2 shows the variation of the flash point of the diesel-biodiesel blends as a function of the dosing level. As illustrated, the biodiesel shows an increasing trend for the flash point with the dosing level, which indicates a successive decrease in the volatility of the fuel with increases in the quantity of the fuel additive. As illustrated in Figure 2, this increase is nearly linear. Higher flash point temperatures are desirable for safe handling of the fuel. In this context, and because of its higher flash point temperature, the fuels modified with cerium oxide nanoparticles are inherently safer than the base fuels. The influence of the dosing level of the additive on the kinematic viscosity of diesel-biodiesel blends are illustrated in Figure 3, which indicates that the viscosity of the fuels decrease with an increase for all dosing levels. The change in the viscosity of the fuel affects the engine performance as well as the hydrocarbon emissions. Lower fuel viscosities may not provide sufficient lubrication of fuel injection pumps or injector plungers resulting in leakage or increased wear thus reducing the maximum fuel delivery. This imposes a limitation on the quantity of the fuel additive that can be used in enhancing the combustion performance of the fuel. The fuel atomization is affected by the fuel viscosity, and the fuel with higher viscosity tends to form larger droplets on injection, which can cause poor combustion and increased exhaust smoke and emissions. Thus, the selection of the dosing level of the catalyst should be based on a compromise between these two mutually contradicting effects on the performance of the engine.

Figures 4 and 5 show the variation of the pour and cloud points of the diesel-biodiesel blends as a function of the dosing level. As illustrated, the fuels show a decreasing trend for the cloud and pour points with the dosing levels.

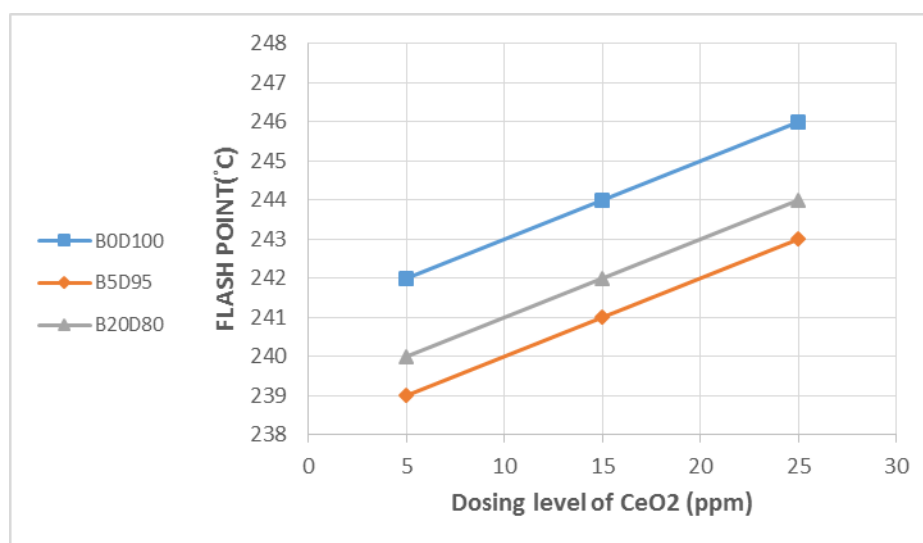


Figure 2: Variation of flash point with nanoparticle dosing level for diesel- biodiesel blends.

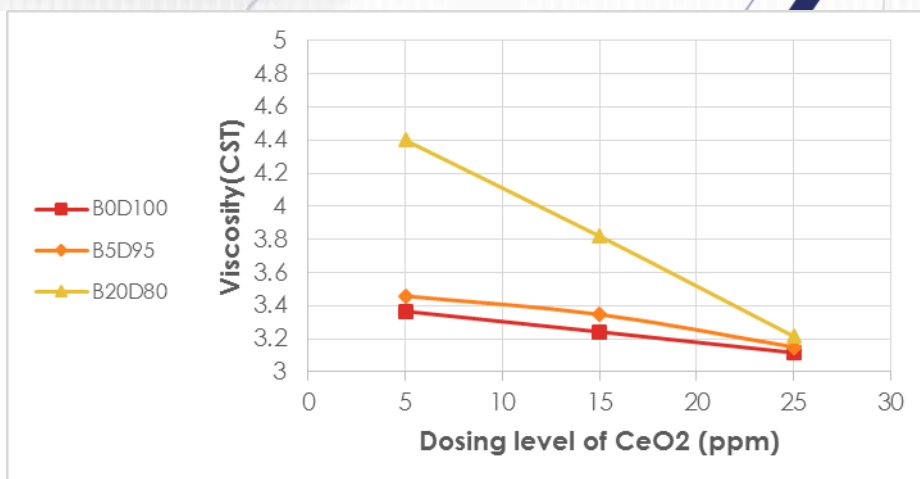


Figure 3: Variation of viscosity with nanoparticle dosing level for diesel- biodiesel blends.

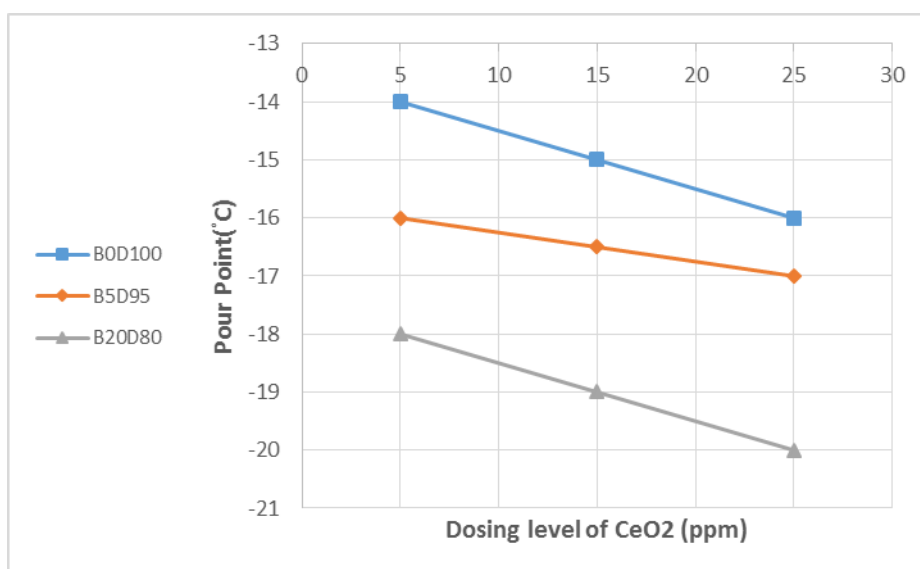


Figure 4: Variation of pour point with nanoparticle dosing level for diesel- biodiesel blends.

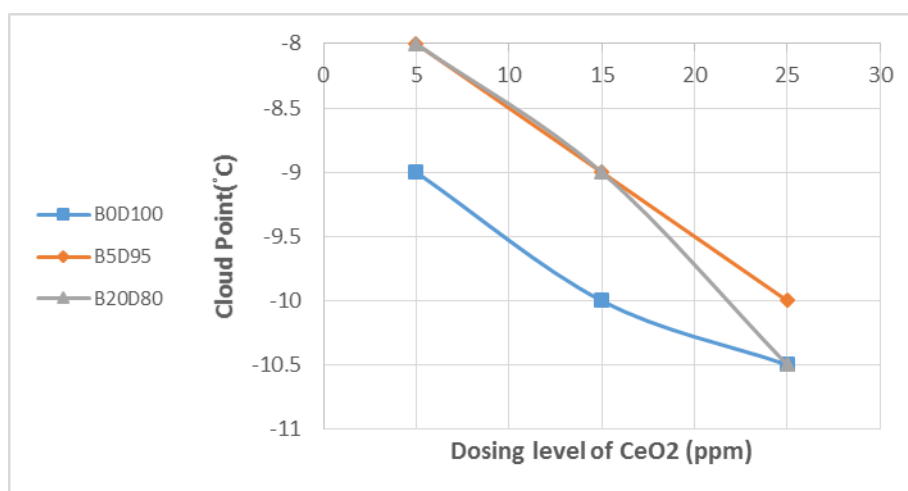


Figure 5: Variation of cloud point with nanoparticle dosing level for diesel- biodiesel blends.



3.2. Engine Performance

3.2.1. Engine Torque and power

Figure 6 illustrates the results of the power tests conducted on the diesel engine with different fuel blends. The results show that the brake power of the diesel engine is improved by the addition of cerium oxide in the fuel.

Diagrams related to power changes relative to engine revolution rate show that all fuel mixtures have the maximum power at 2400 rpm. Among these mixtures, B5D95-25 has greater maximum power and B0D100 has the lowest maximum power. In the general state, the power of mixtures increases gradually up to 2400 rpm speed. And in 2400 to 2600 rpm, the power of mixtures decreases or in some compounds increases slightly.

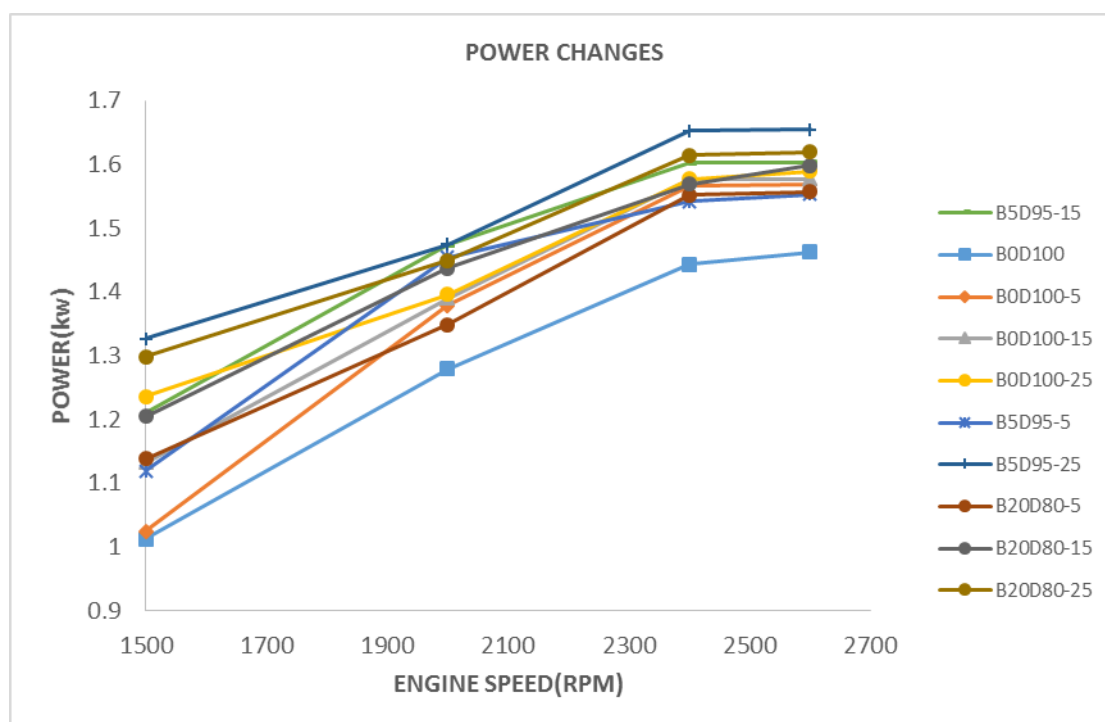


Figure 6. The relationship between engine power-speed in different diesel-biodiesel -nano particle fuel blends

In almost all speeds, power resulted from neat diesel fuel is less than the power of biodiesel-diesel compounds and nanoparticles, though in some references it has been stated that engine power in biodiesel fuel compounds should be less than neat diesel fuel due to the lower heating value of biodiesel fuel (Clark et al, 1997). Therefore, it seems that since biodiesel fuel and nanoparticles have oxygen, full combustion of the power resulted from diesel-biodiesel fuel compounds and nanoparticles increases.

Changes of engine torque under experiment relative to engine revolution rate using biodiesel-diesel fuel mixtures and nanoparticles are shown in Fig.7. As can be seen in Fig.7, by increasing engine speed, torque decreases gradually in all fuels. In these speed ranges, B5D95-25 mixture has the highest value and B0D100 fuel has the lowest value. By more increasing the speed, torque decreases and then remains constant in almost all mixtures. Generally, the cause of engine torque changes is well-filling of the cylinder in the breathing stage. In very high speeds, breathing time is lesser and consequently the cylinder is not filled fully. As a result, compaction pressure and combustion pressure become lesser, inertial forces of mobile parts of the engine increase, and finally the real torque of the engine decreases.

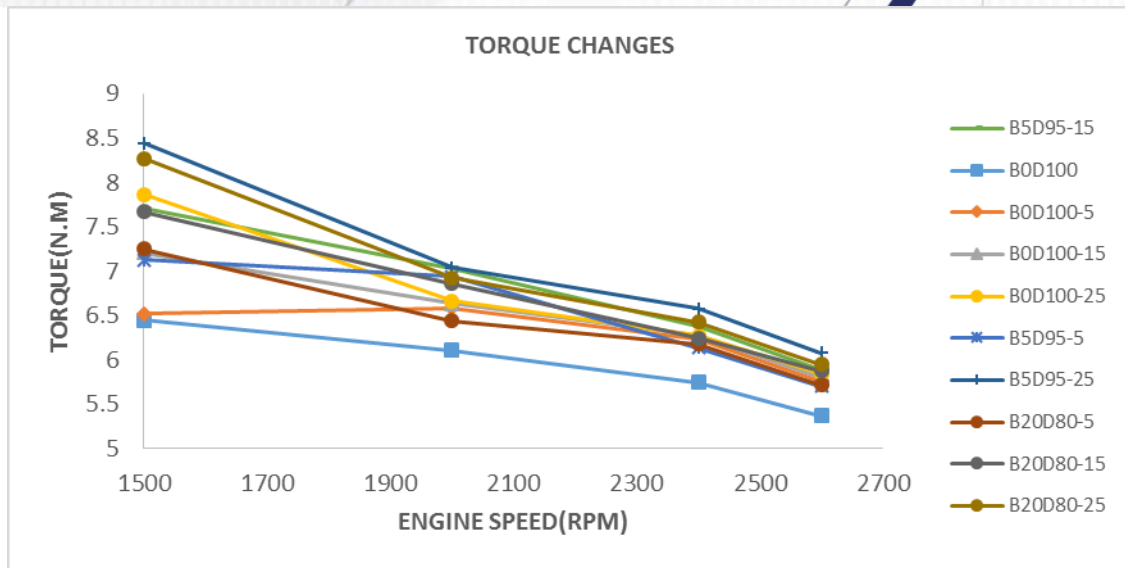


Figure 7. The relationship between engine torque-speed in different diesel-biodiesel-nano particle fuel blends

3.2.2. Engine fuel consumption and brake specific fuel consumption

It is observed in Fig.8 that fuel consumption amount of B20D80-5 blend in all speeds is less than other blends, and in contrast, B5D95-15 blend has the highest fuel consumption, which actually has an irregular behavior; up to 2000 rpm, fuel consumption is high, from 2000 to 2400 rpm, it decreases gradually, and from 2400 to 2600 rpm, it increases. It was expected that by increasing biodiesel amount in the blends, given the fact that biodiesel heating value is less than diesel fuel, more amounts of fuel be consumed for producing the same amount of power. However, it was not true. The reason can be the existence of the used nanoparticles. In all blends except B20D80-5 and B5D95-15, by increasing engine speed, no significant changes were observed. It is seen in Fig.9 that when B5D95-15 fuel compound is used, specific fuel consumption is more than that in other blends, and B20D80-5 compound has the lowest specific fuel consumption blend to other used fuel blends. Of course in all blends, no regular behavior is seen in speed changes.

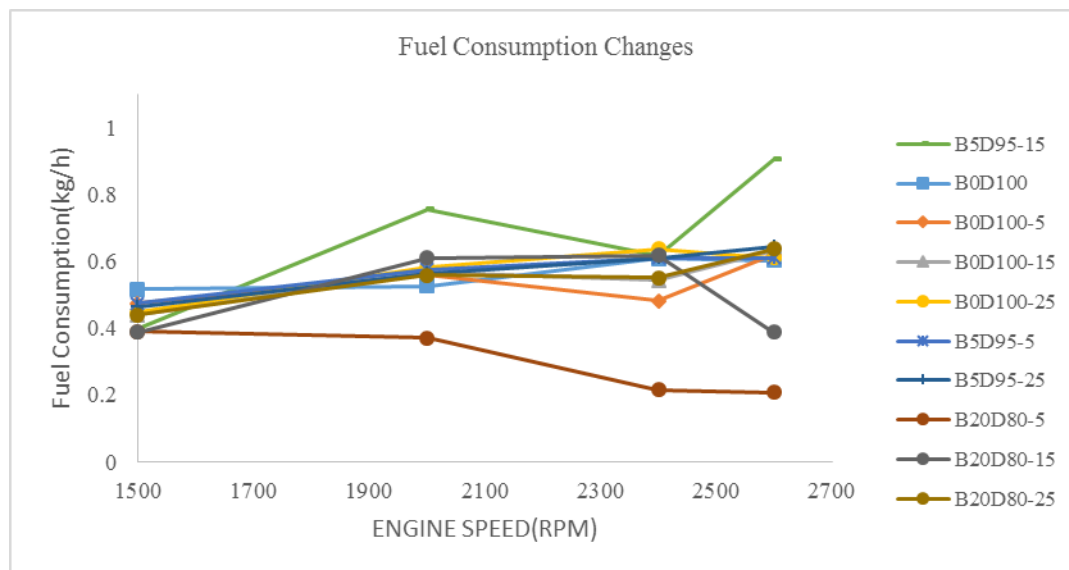


Figure 8. The relationship between engine fc-speed in different diesel-biodiesel-nano particle fuel blends

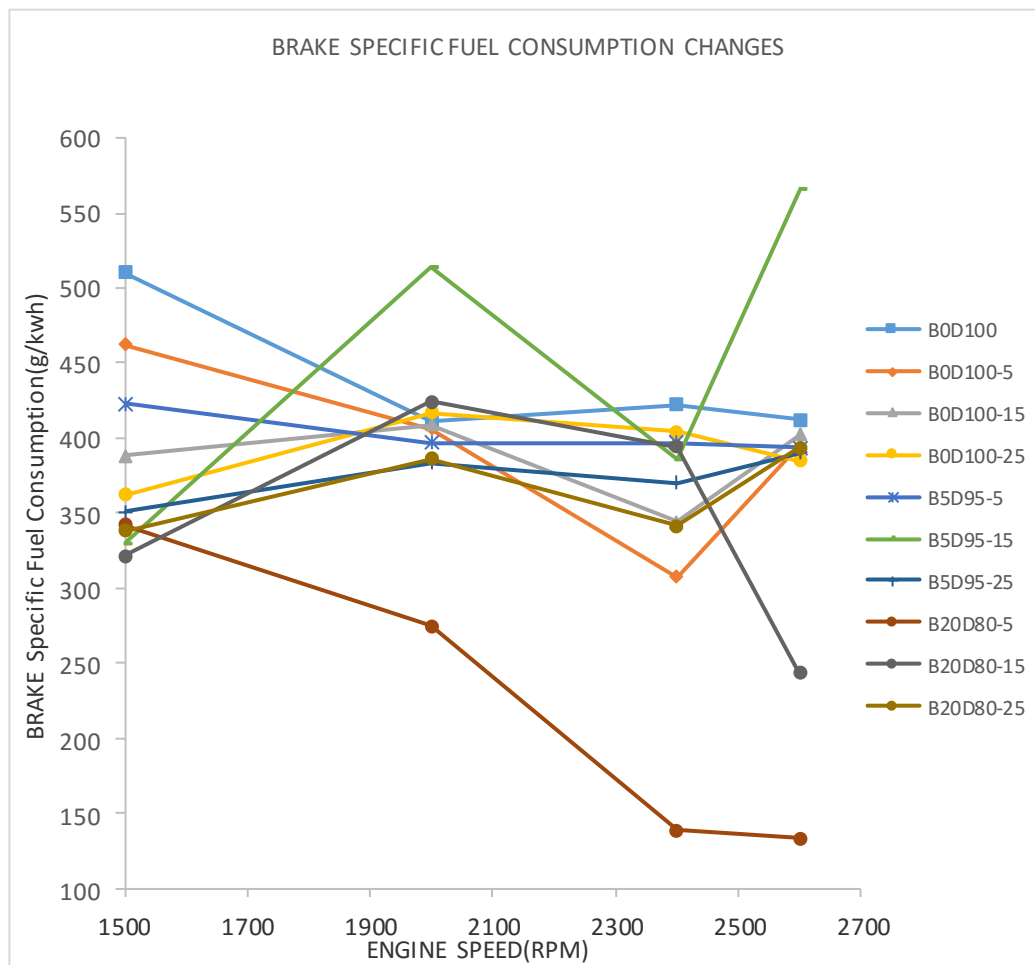
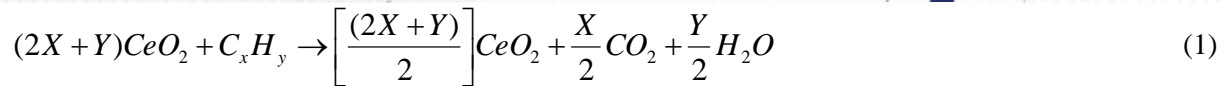


Figure 9. The relationship between engine bsfc-speed in different diesel-biodiesel-nano particle fuel blends.

3.3. Emissions.

The emissions have been measured by using an emission analyzer were manufactured by Motor Scan Italy. Figure 10 shows the variation of hydrocarbon emissions for different fuel blends. Among the causes of HC emissions can be non-stoichiometric air-fuel ratio point. HC emissions are strongly dependent on the amount of air-fuel ratio (AF). In a rich mixture, there is not enough oxygen to react with the carbon, leading to large amounts of HC and CO in the exhaust. According to Figure 10 it is clear that in most fuel blends, Hydrocarbon is reduced compared to neat diesel fuel. This could be due to the oxygen of the biodiesel and also cerium oxide nanoparticles (CeO₂). However, in some cases, despite sufficient oxygen, HC is more than Diesel fuel. The reason could be because of some positions in the combustion chamber, the mixture is so poor that do not burn properly and in other positions so rich that there is not enough oxygen to consume all the fuel. Among these blends, B5D95-25 has most reduction and B20D80-5 has the lowest reduction compared to neat diesel fuel. As mentioned above, this is because much oxygen in fuel mix, that there is more oxygen in the combustion chamber that complete combustion takes place, resulting in better combustion. Cerium oxide has the ability to undergo a transformation from the stoichiometric CeO₂ (+4) valance state to the Ce₂O₃ (+3) state via a relatively low-energy reaction. Cerium oxide supplies the oxygen for the reduction of the hydrocarbon as well as the soot and gets converted to cerous oxide (Ce₂O₃) as follows (Auckenthaler, 2005). Hydrocarbon combustion:



Soot burning:

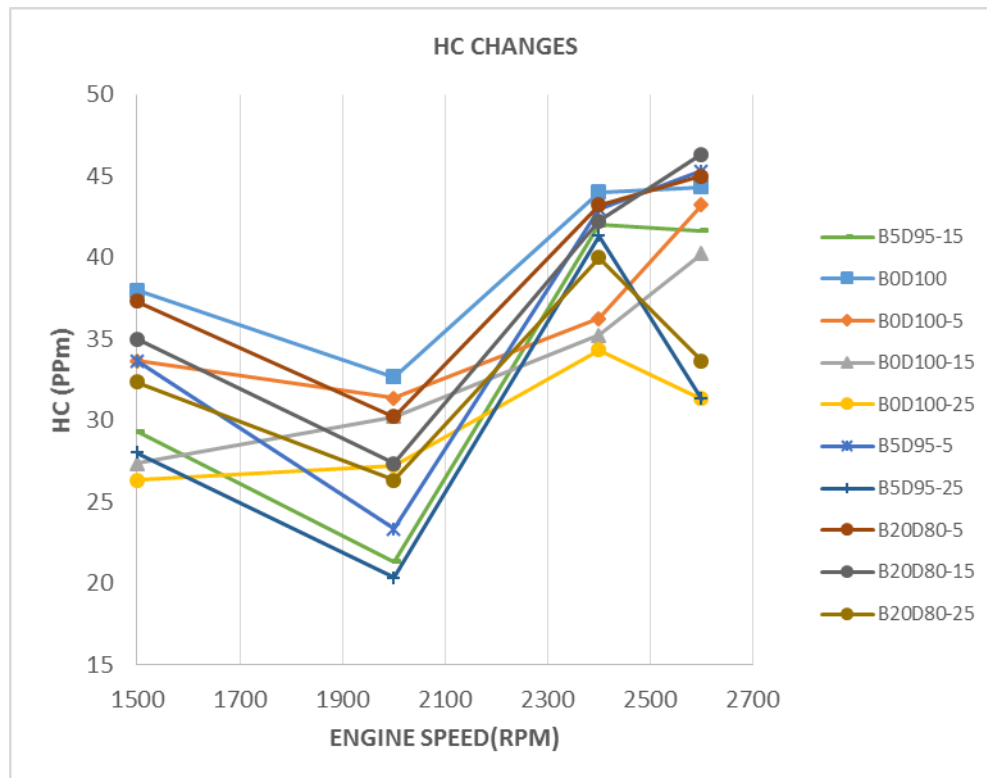


Figure 10: Variation of hydrocarbon emission with speed engine in different diesel-biodiesel-nano particle fuel blends.

Cerium oxide as an oxidation catalyst also lowers the carbon combustion activation temperature and thus enhances hydrocarbon oxidation, promoting complete combustion. An average reduction of 3% to 24.8% in the hydrocarbon emissions was obtained for different diesel-biodiesel-nano particle fuel blends.

Figure 11 shows the variations of NOx emission with speed engine in ppm. As you can see, the amount of nitrogen oxides produced by the fuel blends increased relative to diesel fuel. The amount of NOx produced, depends on the position in the combustion chamber. In compression ignition Engine (CI), with divided combustion chamber and indirect fuel injection that generally have a greater compression ratios and higher temperatures and pressures tend to produce large amounts of NOx in these engines. The results show that B20D80-25 fuel blends have a further increase to other blends (%22.6953) in the production of nitrogen oxides compared with pure diesel fuel. B0D100-5 fuel blends has least increase in the production of NOx. Because of the increased Nox is Oxygen in fuel blends that due to the reaction with nitrogen and increases the combustion temperature, which provides the basis for the production of NOx.

In general, there is a increase in NOx emission due to the addition of cerium oxide. An average increase of 3.9% to 22.7% in the NOx emissions was obtained for different diesel-biodiesel-nano particle fuel blends.

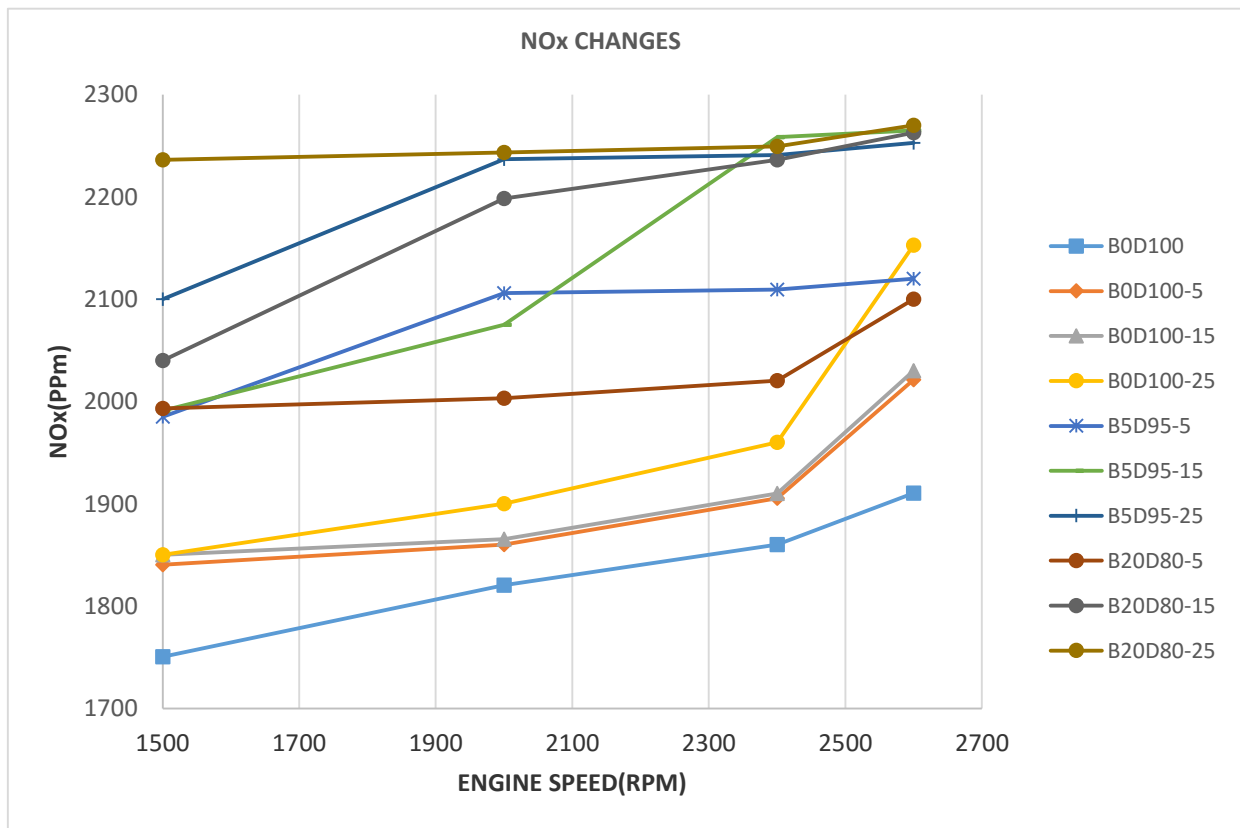


Figure 11: Variation of NOx emission with speed engine in different diesel-biodiesel-nano particle fuel blends.

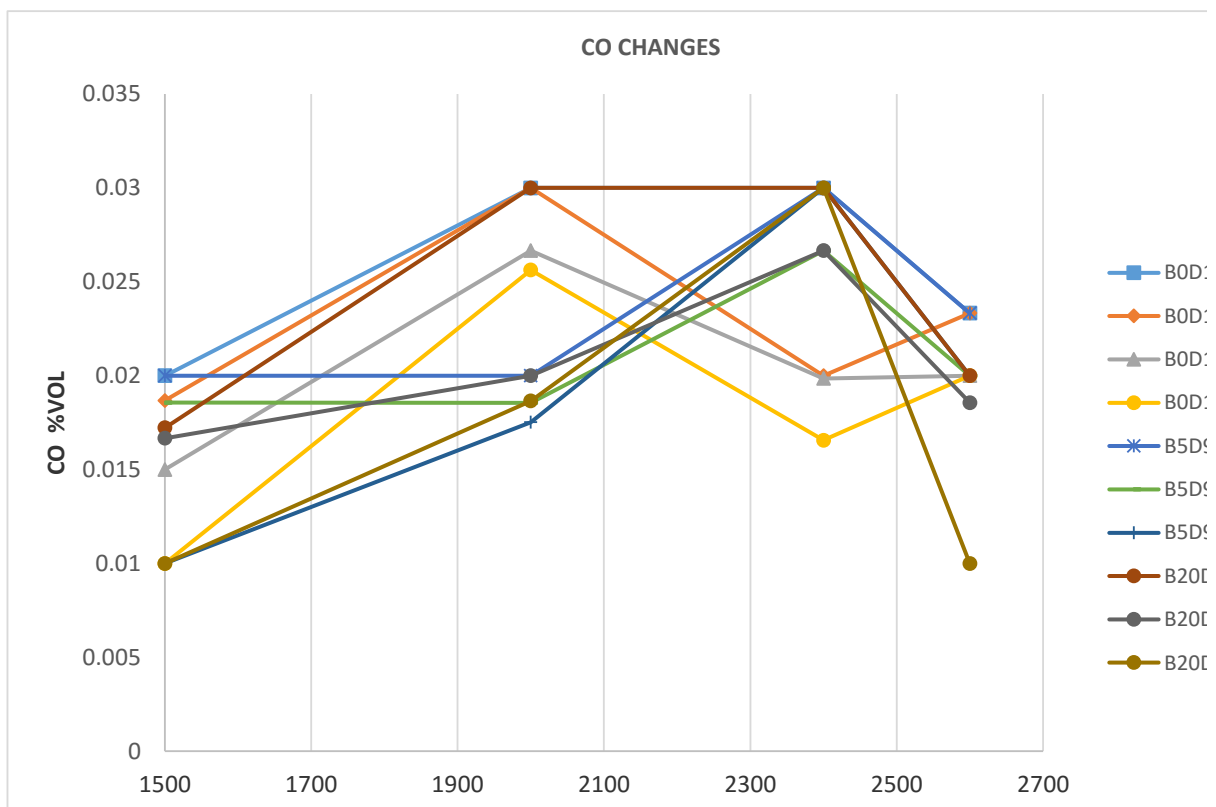


Figure 12: Variation of CO emission with speed engine in different diesel-biodiesel-nano particle fuel blends.



Figure 12 shows the variations of Carbon monoxide emission with speed engine. The CO emission were measured by volume percentage (V%) with emission analyzer. If the engine work with rich fuel equivalence ratio, carbon monoxide is produced. When there is not enough oxygen to convert all the carbon into CO₂, some of the fuel does not burn and much carbon remain as CO. The maximum amount of CO is produced when an engine work with a rich mixture, for example, start up the engine or accelerating under load, mixing the weak, the rich local areas and incomplete combustion will create CO. As can be seen in Figure 12, the amount of carbon monoxide produced by the diesel-biodiesel mixtures & nanoparticles is reduced compared to neat diesel fuel. An average reduction of 7% to 36.2% in the hydrocarbon emissions was obtained for different diesel-biodiesel-nano particle fuel blends.

4. Conclusions

One of the methods to vary the physicochemical properties and combustion characteristics of a hydrocarbon fuel is the use of additives, which are found to be especially effective in nanoparticle form, due to the enhancement of the surface area to volume ratio. ASTM standard tests for the fuel property measurements and engine performance tests were reported in this paper for bio diesel modified by the addition of cerium oxide nanoparticles. Experiments were carried out at different dosing levels of the nanoparticle additives, to investigate the influences on the physicochemical properties, engine performance. The major observations and inferences are listed below.

- The biodiesel showed an increasing trend for the flash point with the dosing level, which indicated a successive decrease in the volatility of the fuel with increases in the quantity of the fuel additive. In this context, and because of its higher flash point temperature, the fuels modified with cerium oxide nanoparticles are inherently safer than the base fuels.
- Viscosity of the fuels decreased with an increase for all dosing levels. The change in the viscosity of the fuel affects the engine performance as well as the hydrocarbon emissions. The fuel atomization is affected by the fuel viscosity, and the fuel with higher viscosity tends to form larger droplets on injection, which can cause poor combustion and increased exhaust smoke and emissions. Thus, the selection of the dosing level of the catalyst should be based on a compromise between these two mutually contradicting effects on the performance of the engine. Also the cloud and pour points with the dosing levels are reduced.
- In all fuel blends, by decreasing revolution rate and increasing engine load, the amount of the resulted power has increased compared to pure diesel fuel. In general, up to 2400 rpm speed range, the power of mixtures increases gradually. In 2400 to 2600 rpm range, the power of mixtures decreases or in some compounds increases slightly. The same behavior applies for torque. By increasing engine speed, torque decreases gradually in all fuels. In these speed ranges, B5D95-25 mixture has the highest value and B0D100 fuel has the lowest value. By more increasing the speed, torque decreases and then remains constant in almost all mixtures.
- B20D80-5 compound has the highest fuel consumption reduction compared to other compounds. B5D95-15 compound has the highest fuel consumption. Of course no specific trend is observed in increasing fuel consumption and increasing biodiesel compound and nanoparticles and it requires more study.
- It shows the amount of changes in specific fuel consumption of the engine in each of the compounds compared to the pure diesel fuel. It is observed that B20D80-5 compound has the highest specific fuel consumption reduction compared to other compounds. B5D95-15 compound has the lowest specific fuel consumption reduction. Specific fuel consumption is obtained by dividing fuel consumption rate by power.
- B5D95-25 compound has the highest amount of power and torque increase, while its specific fuel consumption increase is about 1.4% compared to pure diesel fuel. In higher percents of biodiesel and nanoparticles, B20D80-5 compound is a suitable compound due to having low fuel consumption and specific fuel consumption and relatively good power and torque.



- Cerium oxide as an oxidation catalyst also lowers the carbon combustion activation temperature and thus enhances hydrocarbon oxidation, promoting complete combustion. An average reduction of 3% to 24.8% in the hydrocarbon emissions was obtained for different diesel-biodiesel-nano particle fuel blends.
- B20D80-25 fuel blends have a further increase to other blends (%22.6953) in the production of nitrogen oxides compared with pure diesel fuel and B0D100-5 fuel blends had least increase in the production of NO_x.
- There is a increase in NO_x emission due to the addition of cerium oxide. An average increase of 3.9% to 22.7% in the NO_x emissions was obtained for different diesel-biodiesel-nano particle fuel blends.
- The amount of carbon monoxide produced by the diesel-biodiesel mixtures & nanoparticles is reduced compared to pure diesel fuel. An average reduction of 7% to 36.2% in the hydrocarbon emissions was obtained for different diesel-biodiesel-nano particle fuel blends.

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